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TP 96-01  
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**Sandia National Laboratories  
Waste Isolation Pilot Plant  
Test Plan TP 96-01**

**Test Plan for Evaluation of Colloid-Facilitated Actinide Transport  
at the Waste Isolation Pilot Plant**

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Effective Date: 16 January 1996

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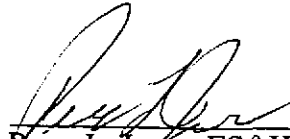
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## Definition of Abbreviations

An	generic actinide element
ANL	Argonne National Laboratory
ASTP	Actinide Source Term Program
BNL	Brookhaven National Laboratory
c.c.c.	critical coagulation concentration
c.m.c.	critical micellization concentration
CAO	U.S. Department of Energy, Carlsbad Area Office, Carlsbad, New Mexico
CFR	Code of Federal Regulations
CH-TRU	contact-handled transuranic
DLVO	theory of lyophobic sols by Derjugin, Landau, Verwey, and Overbeek
DOE	U.S. Department of Energy
DQO	Data Quality Objective
E1	single-borehole intrusion scenario, penetrating the Castile Formation
E1E2	double-borehole intrusion scenario, combination of E1 and E2 scenarios
E2	single-borehole intrusion scenario, penetrating the Salado Formation
EEG	New Mexico Environmental Evaluation Group
EPA	U.S. Environmental Protection Agency
ES&H	Environmental Safety and Health
FSU	Florida State University
INEL	Idaho National Engineering Laboratory
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
Me	generic metal cation
NAS	National Academy of Sciences, Waste Isolation Pilot Plant Panel
NIST	National Institute of Standards and Technology
NRC	National Research Council, Waste Isolation Pilot Plant Panel
PA	Performance Assessment
PDI	potential-determining ion
pH <sub>zpc</sub>	pH at zero-point-of-charge
PNL	Pacific Northwest Laboratory
QA	Quality Assurance
QAP	Quality Assurance Procedure
QAPP	Quality Assurance Program Plan (same as Quality Assurance Program Description)
RH-TRU	remote-handled transuranic
SECO-TP	advection-dispersion transport code
SNL	Sandia National Laboratories
SOP	Standard Operating Procedure
SPM	Systems Prioritization Methodology
STTP	Source-Term Test Program
TOP	Technical Operating Procedure
TRU	transuranic
WBS	Work Breakdown Structure
WIPP	Waste Isolation Pilot Plant
WTAC	WIPP Technical Advisory Consultants

## 1.0 Introduction

Under the authorization of Public Law 96-164 (1979), the U.S. Department of Energy (DOE) has been developing a nuclear waste disposal facility, the Waste Isolation Pilot Plant (WIPP), located approximately 42 km east of Carlsbad, New Mexico. The WIPP is being designed to demonstrate the safe disposal of transuranic wastes produced by the defense nuclear-weapons program. Transuranic waste, defined as waste contaminated with radionuclides having an atomic number greater than 92, a half-life greater than 20 years, and a concentration greater than 100 nCi/g (US EPA, 1985), is regulated by U.S. Environmental Protection Agency regulations in Subpart B of 40 Code of Federal Regulations (CFR) Part 191 (US EPA, 1985) and Subpart B of 40 CFR Part 194 (US EPA, 1995; not yet promulgated). These regulations place limits on cumulative radioactive release to the accessible environment over 10,000 years, and require that performance assessment analyses be performed to demonstrate the WIPP facility compliance with the regulatory standards before the WIPP could be opened for permanent disposal of nuclear waste (WIPP PA Division, 1991a; WIPP PA Department, 1992a). Hazardous waste constituents, such as hazardous organic compounds, are addressed in Resource Conservation and Recovery Act (RCRA) regulations (US DOE, 1990).

The task of quantifying the performance of the WIPP over the 10,000 year period is the responsibility of the Sandia National Laboratories (SNL) WIPP Performance Assessment (PA) Department. Performance assessments use various mathematical and numerical models with their associated model parameters values to calculate cumulative releases of radioactivity to the accessible environment (Figure 1<sup>1</sup>). The calculated releases are compared with limits in Subpart B of 40 CFR Part 191, the standard for evaluating WIPP compliance (WIPP PA Division, 1991a-c; Helton et al., 1992; Sandia WIPP Project, 1992; WIPP PA Department, 1992a,b; WIPP PA Department, 1993a,b). Isotope ratios in the initial repository inventory and decay rates are considered in calculating the releases of individual radioactive isotopes of each element. The release of each isotope is weighted by its specific activity.

The only credible potential mechanism for escape of radioelements to the accessible environment involves a breach of the repository by drilling, or "human intrusion" (WIPP PA Division, 1991a; WIPP PA Department, 1992a). In human intrusion scenarios, the repository is pierced by boreholes during prospecting for natural resources. The brines present in the repository together with introduced drilling muds are transported up the intrusion boreholes under the driving force of pressurized fluids in the disposal area. Some of the radioactive isotopes could reach the surface, while others could move laterally toward the WIPP Site boundary, principally through the Culebra Dolomite Member of the Rustler Formation (Culebra). Performance assessment calculations (WIPP PA Division, 1991a,b) showed that releases of radioactive isotopes of the actinide elements

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<sup>1</sup>Figures are included in Appendix B.



Th, U, Np, Pu, and Am would contribute the most to the total release of radioactivity, with Pu and U being the largest contributors (see also Lucero et al., 1995, Appendix A).

Three types of human intrusion scenarios are recognized (Figure 2; WIPP PA Department, 1992a). In E1 or E2 intrusion scenarios, a single borehole penetrates the repository. In the E1 scenario, hydraulic communication occurs between the Castile Formation, which may contain pockets of brine with greater than hydrostatic pressures, the repository, and the Culebra. In the E2 scenario, hydraulic communication occurs between the repository and the Culebra. The E1E2 scenario involves two boreholes that allow hydraulic communication between the Castile Formation, the repository, and the Culebra. In the E2 scenario, only Salado Formation brines will have interacted with the waste. In the E1 and E1E2 scenarios, Castile Formation brines, as well as Salado Formation brines, will have interacted with the waste.

Colloidal particles, which are generally defined as particles with sizes between 1 nm and 1  $\mu\text{m}$  in a liquid dispersant, will be generated in the repository environment as a result of microbial degradation of cellulose, corrosion of steel waste containers and waste constituents, by the hydrodynamic entrainment of colloidal-sized mineral fragments, and several other mechanisms. Those colloidal particles may sorb dissolved actinides or the dissolved actinides themselves may form colloidal-sized particles. In a breach scenario, actinide-bearing colloidal particles, together with dissolved actinides, may be transported to the Culebra by Castile or Salado Formation brines that are present in the repository. Additional colloidal particles may be present in natural Culebra groundwater and could form additional actinide-bearing colloidal particles. After introduction to the Culebra, the dissolved actinides and actinide-bearing colloidal particles are transported by Culebra groundwaters. Both types of actinides will interact with the rock, possibly resulting in chemical and physical retardation.

Several sets of preliminary WIPP performance assessment calculations and sensitivity analyses have been performed (Lappin et al., 1989, 1990; Rechard et al., 1990; WIPP PA Division, 1991a-c; Helton et al., 1992, 1993; Sandia WIPP Project, 1992; WIPP PA Department, 1992a,b; WIPP PA Department, 1993a,b) using the most current data and models available at the time. Colloid-facilitated transport of actinides has not been included in past Performance Assessment calculations because of the lack of adequate information to model this phenomenon and to demonstrate its impact on compliance (see, e.g., WIPP PA Department, 1992a, p. 4-12, line 29). Transport of actinides by colloidal particles has been recognized only relatively recently as a phenomenon of critical importance to the performance of nuclear waste repositories (Jacquier, 1991; Avagadro and de Marsily, 1983).

## 1.1 Objective of the WIPP Colloid Research Program

The objective of the WIPP colloid research program is to provide the WIPP PA Department with sufficient information to quantify the concentration of colloidal actinides that reaches the accessible environment. Tasks required to meet that objective include two main components: (1) the quantification of the mobile actinide-bearing colloid component of the actinide source term, and (2) the quantification of colloid-facilitated transport of actinides in the overlying Culebra, in the event of a repository breach. The laboratory experimental program focuses on radioactive isotopes of the actinide elements Th, U, Np, Pu, and Am, which have been identified as the greatest contributors to the total release of radioactivity. The laboratory and field experiments described herein cover the range of colloid types that conceivably could be involved in transport of actinides.

The colloid research program makes use of existing information to the maximum extent possible. The experimental program is designed to utilize screening experiments to allow quick focus on work that requires additional resources, or to demonstrate that a particular aspect does not have a potential impact on the performance of the repository. However, experiments are also included to challenge the conceptual models on which the screening experiments are based.

## 1.2 Test Plan Organization

The SNL Quality Assurance Procedure QAP 20-1 (Preparing, Reviewing, and Approving Test Plans), prepared to augment the WIPP Quality Assurance Program Description (QAPD, Revision R), states specifically, that "Test plans are approved for each WIPP test or experiment prior to initiation of work activities and describe the test or experiment in sufficient detail that the test or experiment may be conducted." In accordance with that request, this Test Plan has been written to document the plan for laboratory and field experiments to evaluate colloid formation in the WIPP repository environment and the Culebra and colloid-facilitated transport of actinides in the Culebra.

The specific interests and technical expertise of the anticipated audience for this Test Plan are diverse. The primary motivations for preparing this document are the following: (1) to clearly convey the full scope of the WIPP colloid research program to the organizations directly participating in the colloid research program; (2) to clearly convey the full scope of the WIPP colloid research program to individuals who will potentially benefit from the results of the colloid research program; (3) to provide a basis for independent review of the WIPP colloid research program, as stipulated in US EPA 40 CFR 194 (US EPA, 1995); and (4) to focus the direction of the WIPP colloid research program to maximize the efficiency of acquiring technically high quality information necessary for the WIPP Program.

The anticipated audience of this Test Plan is broad and will include readers with a range of specific interests and various levels of technical knowledge and WIPP-specific knowledge. Readers are likely to include individuals from the following groups:

- National Academy of Sciences-WIPP Panel (NAS);
- State of New Mexico Environmental Evaluation Group (EEG);
- State of New Mexico Office of the Attorney General and Environmental Department;
- U.S. Environmental Protection Agency (EPA) and their consultants;
- WIPP Technical Advisory Consultants (WTAC), who function as independent consultants to the U.S. Department of Energy (DOE) Carlsbad Area Office (CAO);
- DOE/CAO staff members;
- staff members of the SNL PA Department;
- staff members of external contract laboratories such as Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), and Brookhaven National Laboratory (BNL);
- technical staff members (Principal Investigators and Project Scientists) at SNL conducting colloid research;
- technical staff members at SNL conducting related research;
- staff members at LANL implementing the Source Term Test Program (STTP) portion of the Actinide Source Term Program (ASTP);
- SNL WIPP Quality Assurance Department staff.

This Test Plan includes significant detail covering the range of the interests of the anticipated audience.

The content of this Test Plan includes the required Test Plan contents described in QAP 20-1 (Preparing, Reviewing, and Approving Test Plans). Because of the specific interests of the anticipated audience, we have intentionally deviated from the outline suggested in QAP 20-1, although the required information is included.

The strategy for the experimental program described in this Test Plan is based heavily on the outline for design of the experimental programs described in the "Guidance for the Data Quality Objectives Process" (US EPA, 1994). That document presents in a concise form, the thought process required to develop a logical, as well as reasonable and efficient, experimental program. Section 4 of this Test Plan focuses on developing high-level Data Quality Objectives (DQOs) that are used in following sections to develop the experimental program, using the seven steps described in US EPA (1994): Step 1: State the Problem; Step 2: Identify the Decision; Step 3: Identify the Inputs to the Decision; Step 4: Define the Study Boundaries; Step 5: Develop a Decision Rule; Step 6: Specify Tolerable Limits on Decision Errors; and Step 7: Optimize the

Design. The results of the Systems Prioritization Methodology (SPM) calculations, a series of computations designed to assist the WIPP management in focusing resources on critical research areas (Prindle et al., 1996a,b), provides a means to develop action levels.

To set the stage for discussion of DQOs, the experimental program, and specific discussion on quality assurance, necessary background information is discussed in the following subsections, and a review of current knowledge is provided in Section 2. Because of the interaction with other groups, particularly the STTP at LANL and the WIPP PA Department, separate sections are included that include specific discussion on the role of the STTP (Section 6) and the interface with PA (Section 7).

### 1.3 Test Plan Revision History

Experimental work to date has been conducted under plans described in several documents: the "Experimental Program Plan for the Waste Isolation Pilot Plant" (US DOE, 1994b); the "Department of Energy Five-Year Plan, Activity Description System" (US DOE, 1994a); and draft precursors to this Test Plan. The guidance presented herein supersedes all previous plans.

A draft precursor to the WIPP Colloid Test Plan, the "Actinide Source Term Model Development Plan," written by Hans W. Papenguth, Craig F. Novak, and E. James Nowak, was distributed for review by technical experts in the radiochemistry, geochemistry, colloid chemistry, and geochemical modeling communities, as well as the DOE (the WIPP Project Integration Office, formerly located in Albuquerque, New Mexico). The reviewers included Carol Bruton (LLNL), Gregory R. Choppin (Florida State University), Andrew R. Felmy (PNL), Bruce Honeyman (Colorado School of Mines), Kenneth Jackson (LLNL), Robert E. Mesmer (ORNL), Frank Millero (University of Miami), James J. Morgan (California Institute of Technology), Heino Nitsche (then at LBL), Cynthia E. A. Palmer (LLNL), Dhanpat Rai (PNL), Robert J. Silva (LLNL), and Thomas Wolery (LLNL). (Refer to page 6 for explanation of abbreviations). The comments from the reviewers helped refine portions of the program which are documented herein. That original "Model Development Plan" has evolved into this Test Plan and the Test Plan for the dissolved actinide laboratory and analysis program for the WIPP System (Novak, in review). The descriptions of the colloidal actinide source term for the WIPP repository environment presented herein incorporates the input received during the review process.

### 1.4 Research Components

The two primary research initiatives required to evaluate colloid-facilitated transport are: (1) quantification of the mobile colloidal source term, including mobile actinide-bearing colloidal

particles generated in the repository environment and in the Culebra; and (2) quantification of colloid-facilitated actinide transport in the Culebra. Both the characterization and the transport initiatives are included in the following:

WBS 1.1.5.1.6 (Initiative 127) "Colloid Characterization and Transport"

The terms "Work Breakdown Structure" (WBS) and "Initiative" correspond to project tracking methodologies used by SNL and the DOE/CAO, respectively. The mobile source term includes both the repository environment and the Culebra. Because of the variability in behaviors of different types of colloidal particles, it is mandatory to know what types of colloids potentially will be available for transport of actinides. Consequently, the colloid characterization component must be done concurrently with or prior to the transport component.

## 1.5 Relationship to other WIPP Programs

Several other WIPP research initiatives are underway that produce information that is useful to the colloid characterization and transport activity. Conversely, several research initiatives may benefit from the results of the colloid research activity. The WIPP PA Department, of course, is the ultimate recipient of the output of the colloid program.

### 1.5.1 Actinide Source Term Program

The actinide source term program (ASTP) consists of three subprograms: the dissolved actinide species program; the mobile colloidal-actinide program (described herein); and the source term test program (STTP). The first two subprograms are laboratory research activities designed to investigate the impact of the full range of chemical parameters that may be important at the WIPP Site. The final products from those two research subprograms will be conceptual models, mathematical models, and/or numerical models that provide the total mobile actinide concentrations for each of the five actinides of interest (see Section 1.5.3 for discussion of various types of "models"). The third subprogram consists of a series of experiments with actual transuranic (TRU) waste from one of the generator sites, Los Alamos National Laboratory. Because of the limited range of chemical conditions and the complexity of the experiments, the results of the STTP experiments are intended to test the predictive capability of the conceptual models, mathematical models, and numerical models, as appropriate, that are produced from the first two subprograms, the dissolved actinide species subprogram, and the mobile colloidal-actinide subprogram.

Prediction of total dissolved actinide concentrations and total mobile actinide colloid concentrations in the repository have intentionally been decoupled, to simplify the experimental programs and the

development of mathematical and numerical models. Decoupling the programs cannot result in underestimation of the total mobile actinide concentration as described in the following conceptual model. In a closed-system environment (e.g., the repository in an undisturbed case), the concentration of a dissolved actinide is limited by dissolution-precipitation reactions with one or more solubility limiting, crystalline or amorphous, solid phases. The concentration is ultimately limited by the inventory of that actinide in the waste. That balance between dissolution and precipitation of the actinide-bearing solid phase is dictated by an equilibrium constant (i.e., the solubility product,  $k_{sp}$ , or more generally, the ion activity product, IAP). If mobile or immobile colloidal particles, or fixed substrates (e.g., steel waste containers) are introduced to the system, a new equilibrium will develop between the three components: the solubility limiting solid phase, the dissolved actinides, and actinides sorbed onto colloidal or fixed substrates. In simple cases, sorption of actinides may also be described by an equilibrium (distribution) constant ( $K_d$ ). Quantifying the interaction in such a multiple component system is currently beyond the scope of our abilities. Regardless of whether actinide sorption is high or low or whether sorption is reversible or irreversible, interaction of dissolved actinides with a substrate cannot increase the total concentration of dissolved actinides. (To do so would require that the substrate-actinide pair become the solubility-limiting solid with a greater solubility than the initial amorphous or crystalline solid. That phenomenon is not consistent with thermodynamics because it would involve a net increase in system free energy.) The net impact of disregarding the coupling, therefore, is that the apparent solubility of actinides will be greater than the actual solubility.

#### 1.5.1.1 Dissolved Actinide Species Sub-Program

The activities being conducted in support of the dissolved actinide species subprogram of the actinide source term program include the following:

- WBS 1.1.1.1.4 (Initiative 071): "ASTP Laboratory Studies"
- WBS 1.1.1.2.6 (Initiative 076): "Source-Term Model"
- WBS 1.1.5.2.2 (Initiative 129): "Non-Salado Model Development"

The colloid experimental program requires information from the laboratory component of the dissolved actinide experimental program and the development of conceptual models for that program (refer to the Test Plan for that program, Novak, in review, and references cited therein). General information on actinide speciation under various geochemical conditions and the nature of the solubility limiting solid phases is useful although not mandatory. That information is used to improve the understanding of the formation of one particular type of colloidal particle, the actinide intrinsic colloid. Information on dissolved actinide interaction with organic complexants is especially useful because of the similarities with the formation and behavior of humic substances.

Conversely, results of the WIPP colloid research program are anticipated to produce information that is highly useful for the dissolved actinide species program described in Novak (in review). Several of the colloidal particle types (especially humic substances and actinide polyelectrolytes; refer to Sections 2.5.2 and 2.5.3), are dissolved species themselves, and have many similar characteristics to dissolved ionic forms studied by Novak (in review). Some of the laboratory programs conducted for colloidal-actinide source term information will provide Novak (in review) with solubility information, albeit qualitative. Further, humic substances are expected to have complexation behaviors similar to that of some of the organic complexants being investigated as part of the dissolved actinide solubility program (Novak, in review).

### 1.5.1.2 Real-Waste Test Sub-Program

The source term test program (STTP) subprogram of the actinide source term program is not under direct SNL control but is funded directly by the DOE/CAO. The STTP does not fit in the SNL WBS structure format, but is related to:

WBS 1.1.1.1.4 (Initiative 071): "Radionuclide Disposal Room Chemistry"

The STTP component of the ASTP is described in the Technical Requirements for the Source-Term Test Program (Phillips and Molecke, 1993) and in the Test Plan for the STTP portion of the ASTP (Villarreal and Phillips, 1993). The purpose of the STTP is to provide a means to test the predictive capability of conceptual models, mathematical models, and numerical models produced with information acquired from the laboratory research programs. A description of the relationship between the STTP and the mobile colloidal-actinide subprogram is included in Section 6.

### 1.5.2 Chemical Retardation Program

From a transport perspective, the colloid transport program benefits from the chemical retardation program through the development of conceptual models of fluid flow through the Culebra, from the knowledge base and numerical tools that are being developed to interpret elution curves, and through the use of equipment and procedures developed to evaluate retardation of dissolved actinides. The specific activities being conducted to evaluate chemically retarded transport in the Culebra are described in the Test Plans listed below. The chemical retardation program consists of two activities designed to acquire the required number of retardation factors over the range of chemical conditions expected in the Culebra. That work is being conducted under the following WBS number:

WBS 1.1.5.1.1 (Initiative 122): "Mechanistic Adsorption Tests"

WBS 1.1.5.1.4 (Initiative 300): "Empirical Sorption Tests"

The mechanistic adsorption tests and the empirical sorption tests are described in a separate Test Plan (Papenguth and Behl, in review; that Test Plan also includes discussion on the relationship of the brine mixing calculations and the field sorbing tracer tests). The conceptual model for fluid flow through the Culebra is being done as part of the former activity.

Information on the geochemical environment of chemical retardation in the Culebra will come from the following activity:

WBS 1.1.5.1.3 (Initiative 124): "Brine Mixing Calculations"

An evaluation of the effects of coupled processes under flow conditions is necessary to demonstrate that the static sorption and adsorption measurements provide information that is relevant to a more realistic system. The following laboratory activity is designed to provide that information:

WBS 1.1.5.1.5 (Initiative 126): "Core Column-Flow Tests"

The core column flow experiments are described in a separate Test Plan (Lucero et al., 1995). In addition to providing information on coupled processes, computer-aided tomography measurements of the actinide plume made during the core column-flow tests provide an image of the retardation front and also provide information on physical retardation of solutes due to matrix diffusion.

An investigation of flow properties of the Culebra is being investigated with a non-sorbing field tracer test, which is being conducted under the following WBS numbers:

WBS 1.1.5.3.4 (Initiative 137): "Non-sorbing Field Tracer Test"

WBS 1.1.5.2.3 (Initiative 130): "Field Test Design and Interpretation"

In addition to the activities listed above, the colloid transport program benefits from information gained from hydrogeologic investigations, particularly the following:

WBS 1.1.5.2.1 (Initiative 128): "Regional Flow and Transport Sensitivity Studies"

### 1.5.3 Performance Assessment Program

The ultimate recipients of the results of the WIPP Colloid Research Program are members of the



SNL WIPP PA Department, and the focus of the experimental program described herein is to provide the PA Department with the conceptual, mathematical, and, where appropriate, numerical models to implement the results<sup>2</sup>. Consequently, it is imperative to maintain close interaction with representatives of the SNL WIPP PA Department throughout the implementation of the work proposed herein. More detailed discussion of deliverables to the SNL WIPP PA Department is included in Section 7.

#### 1.5.4 Other Programs

A intensive research program has been conducted over the past decade to quantify the amount of gases produced by microbial degradation of wastes and by corrosion of wastes and the waste containers. Both the microbial degradation and corrosion studies provide useful information to the WIPP colloid research program. The gas generation research program is described in a detailed Test Plan (Brush, 1990) and in program reviews (Telander and Westerman, 1993; Francis and Gillow, 1994).

The plausibility of emplacing additives with the waste has been considered at SNL and at DOE/CAO (see e.g., Butcher et al., 1991). Engineered alternatives which have been considered include clay mineral and salt backfill additives to reduce permeability or to sorb actinides, chemical additives to buffer pH to reduce the solubility of actinides, and chemical additives to reduce pCO<sub>2</sub>. The current plan for waste disposal does not include engineering alternatives. For completeness in this Test Plan, however, we will consider the potential effects of some potential engineered alternatives on the formation of mobile actinide-bearing colloidal particles and their behaviors.

#### 1.6 High-Level Milestones and Schedules

The highest level schedule driving this work is the Revised WIPP Disposal Decision Plan (US DOE, 1995), a planning document prepared by the DOE/CAO (Figure 3) to begin disposal operations by April 1998. To meet that schedule, which states that a complete compliance application package be provided to the EPA by October 1996, three high-level milestones relate directly to the experimental programs.

First, by 30 September 1995, requests and recommendations for modification or additions to the WIPP performance assessment numerical codes used for compliance calculations must be provided

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<sup>2</sup>We recognize the following types of "models:" (1) a conceptual model is a non-mathematical qualitative description of a process or groups of processes; (2) a mathematical model is an equation or set of equations that quantitatively describes a process or groups of processes; and (3) a numerical model is a computational code designed to arrive at a solution that simulates the conceptual models using mathematical models.

to the SNL WIPP PA Department.

Second, by 31 March 1996, parameter values supporting the performance assessment numerical codes must be provided to the SNL WIPP PA Department. Whereas critical experiments must be completed by 31 March 1996 to support performance assessment calculations, additional experiments may be conducted after that date to confirm assumptions.

Third, by 30 June 1996, documentation for all conceptual, mathematical, and numerical models and parameter values must be prepared. Between 31 March 1996 and 30 June 1996, however, additional experimental work may be conducted to verify assumptions made in the design or interpretation of the experiments, but the potential impact on Performance Assessment calculations should not be significant.

It is not anticipated that those time constraints will change. Interim deliverables and lower-level milestones, along with their associated schedules, are presented in Section 5.4.

## 2.0 Review of Current Knowledge

Over the past several decades, geochemists, hydrogeologists, and environmental engineers have recognized that colloidal particles can have an impact on transport of contaminants in the subsurface. In general, the understanding of colloid-facilitated transport of contaminants is less mature than the understanding of transport of dissolved contaminants, because of the added complexities of colloidal particle behavior and interaction with the host rock. That is particularly true for the deep subsurface environments, which are more challenging to test than shallow soil environments. Because of the uncertainties in the behaviors of colloidal particles in the deep subsurface and uncertainties in the potential impact of colloid-facilitated transport of actinides at the WIPP, it is imperative to consider the effect of colloidal particles on the long-term performance of the WIPP system.

The objective of this Section is to provide a review of the current knowledge of colloid geochemistry, with an emphasis on the behavior of colloidal particles in the WIPP system.

### 2.1 Colloidal Particles

Colloidal particles may be categorized according to several schemes, based on their physical and chemical properties. The phenomena which must be considered when evaluating the impact of a colloidal particle on actinide transport are the following:

- (1) formation;
- (2) interaction with radionuclides;
- (3) physical structure;
- (4) physicochemical behavior in the dispersant; and
- (5) transport properties.

In the remainder of this section we discuss the five categories of phenomena. In this Test Plan, we use the term "radiocolloid" to describe any colloidal sized particle that has an actinide element associated with it.

Colloidal particles are generally defined as particles with at least one dimension between 1 nm and 1  $\mu\text{m}$ , suspended in a liquid, and maintained in suspension for very long periods of time by Brownian (random thermal) motion (Hiemenz, 1986; Buddemeier and Hunt, 1988; Stumm, 1992, 1993). Those size boundaries are approximately defined on the basis of physical phenomena. Particles larger than about 1  $\mu\text{m}$  are too large for Brownian motion to overcome gravitational forces, and the particles will rather quickly settle by gravity. An exception is the case of microbes, however, which are considered to be colloidal, but may exceed 1  $\mu\text{m}$ . The specific gravities of

microbes are typically quite close to that of the dispersant, and so they may not settle by gravitational forces. Generally, particles smaller than approximately 1 nm behave like dissolved ionic species. Cases in which dissolved non-colloidal species exceed 1 nm do exist however. Uranium citrate, for example, is larger than 1 nm because of the relatively large size of the citrate ion, but is a dissolved non-colloidal ion.

### 2.1.1 Distinguishing Characteristics

Inorganic colloidal particles have been reported to form by a number of different processes. Colloidal particles may form by condensation or homogenous nucleation from dissolved species when a mineral phase is supersaturated or as hydrolyzed precipitates of mixed metal ions (Kim, 1992). Colloidal particles may also form by release of particles from bulk material due to disruption of fragile aggregates by changes in ionic strength or hydrodynamic forces, dissolution of a more soluble surrounding matrix (Buddemeier and Hunt, 1988; Kim, 1991), mechanical grinding of mineral surfaces, or mechanical disruption of secondary minerals present at mineral surfaces (McCarthy and Zachara, 1989; McCarthy, 1990).

Organic colloidal particles may form from microbial degradation of materials, condensation reactions of organic molecules to form humic substances, or microbe activity. A variety of naturally occurring organic materials, such as viruses, microbes, and pollen, are colloidal-sized particles (Figure 4; see also McCarthy and Zachara, 1989; McCarthy, 1990; Stumm, 1992).

Colloidal particles may interact with actinides to form radiocolloids in two ways (see, e.g., Lieser et al., 1986a,b, 1990; Kim et al., 1984a,b; Buddemeier and Hunt, 1988; Kim, 1992, 1994). First, radiocolloids may form as a result of chemical reactions involving dissolved polyvalent actinide ions. Hydrolysis and condensation reactions have been shown to form actinide macromolecules in which the actinide ions are bridged with hydroxyl ions to form polymers. Those radiocolloids are termed "actinide intrinsic colloids," "true colloids," "real colloids," "Eigenkolloide," or "type I colloids."

A second means to form radiocolloids is by sorption of actinides by ordinarily non-radioactive colloidal particles. In the actinide environmental geochemistry literature, the non-radioactive colloidal particle has been called a "ground-water colloid." Once actinide sorption has occurred, the resulting radiocolloids may be called "pseudo-colloids," "carrier colloids," "Fremdkolloide," or "type II colloids." Hobart (1990) proposed the name "association colloid" to describe a radiocolloid type synonymous with pseudo-colloid. We advise against using that term for pseudo-colloids because it has a very specific meaning in colloid chemistry, describing a colloidal particle on which a polyelectrolyte is attached. The colloidal substrate for sorption may be a mineral fragment, a microbial cell, or a humic substance. Bates et al. (1992) recently described

radiocolloids, which they called "primary colloids," forming in situ at the surfaces of vitrified radioactive waste as it reacts chemically with water. Considering that coprecipitation is a continuum with adsorption (see, e.g., Comans and Middleburg, 1987; Stumm, 1992), the "primary colloid" can be included in the carrier colloid category. A similar sort of colloid would form by isomorphous lattice substitution of actinide ions during mineral precipitation (i.e., coprecipitation) or precipitation of actinide minerals. As will be shown below, "primary colloids" are mineral fragment type colloidal particles.

In the traditional colloid chemistry literature, two types of colloidal particles are defined on the basis of how they interact with the dispersant (see, e.g., Alexander and Johnson, 1949; Vold and Vold, 1983; Hirtzel and Rajagopalan, 1985; Hiemenz, 1986; Ross and Morrison, 1988; Hunter, 1991). Hydrophobic colloids are stabilized by electrostatic forces, whereas hydrophilic colloids are stabilized by solvation forces. In light of increased knowledge of aqueous surface chemistry gained over the past two decades, the terms hydrophilic and hydrophobic must be used cautiously, because even hydrophobic surfaces have hydrophilic surface functional groups (Stumm, 1992). It is important, however, to make the distinction between how those two types of colloidal particles behave, because they exhibit different kinetic stability behaviors in electrolytes.

A distinction is made here between kinetic stability and thermodynamic stability. Thermodynamic stability refers to the chemical equilibrium between the colloidal particles and the dispersant, whereas kinetic stability refers to the rate at which colloidal particles in a colloidal dispersion are removed from suspension due to agglomeration followed by gravitational settling. Thermodynamic stability is perhaps most important for actinide intrinsic colloids, because that type of colloid forms directly from solution by chemical reactions. Kinetic stability is inversely related to the rate of particle aggregation, which is dependent on the frequency and efficiency (the fraction resulting in permanent joining) of collisions between colloidal particles. As will be discussed in detail in subsequent sections, the behavior of colloidal particle types as a function of ionic strength is probably the single most important phenomenon affecting the importance of colloid-facilitated actinide transport at the WIPP.

Hydrophobic colloidal particles are kinetically stabilized and destabilized by electrostatic forces. In an aqueous dispersant, hydrophobic colloidal particles are attracted to one another by van der Waals forces. That electrostatic attraction is countered by repulsive forces generated by a cloud of counterions surrounding each particle (Lyklema, 1978; Hiemenz, 1986). In a kinetically stable colloidal dispersion colloidal particles are usually repelled from one another before they get close enough to become agglomerated. However, as the ionic strength of the dispersion is increased, the thickness of the cloud of counterions is compressed, allowing closer particle-particle interaction. The net effect is that as colloidal particles come into proximity with one another in the dispersion, a greater chance for sticking exists, and so the rate of agglomeration increases. That phenomenon is very effective at removing colloidal particles from suspension even at fairly low ionic strengths

over periods of hours to days. Mineral fragments, which are a hydrophobic colloid type, are affected by ionic strength in this way.

Hydrophilic colloidal particles are stabilized by solvation forces, which are largely independent of the ionic strength of the dispersant (Alexander and Johnson, 1949). This type of colloidal particle is essentially a dissolved macromolecule. Humic materials are an example of the traditional hydrophilic colloid type. Two major categories of hydrophilic colloidal particles are recognized. Micelles are aggregates of dissolved monomers, that are in thermodynamic equilibrium with those monomers. Polyelectrolytes are charged polymers which are not in thermodynamic equilibrium with a monomeric species (examples of polyelectrolytes include gum arabic, gelatin, pectin, and proteins). An important distinction, therefore, is that micelles require a minimum threshold concentration of monomers (the critical micellization concentration, or c.m.c.) to form. In contrast, the formation of polyelectrolytes is not dependent on monomer concentration. Polyelectrolytes may act as an association colloid by adsorbing on hydrophobic colloidal particles. The resulting dispersions may be extremely kinetically stable (Vold and Vold, 1983; Hiemenz, 1986, p. 659).

The kinetic stability of hydrophobic colloidal particles may be modified by coatings of steric stabilizing compounds, which themselves are essentially hydrophilic materials (also referred to as protective or association colloids) which modify the surface behavior to inhibit close interaction of particles. Such colloidal systems are rendered kinetically stable. Particles stabilized by organic compounds in seawater are an example of a sterically stabilized colloidal system. Microbes can be considered as stabilized in a similar manner, except that the stability is imparted by molecules (e.g., polysaccharides), attached to the surface of the microbe, which have hydrophilic parts extending into the dispersant.

Colloidal particles may have rigid or flexible structures, which may affect the way in which they interact with the host rock during transport. "Hard-sphere" colloidal particles, such as mineral fragments, have discrete well-defined boundaries at the particle-water interface, and are rigid. "Soft-sphere" colloidal particles, such as humic substances, have less distinct boundaries at the particle-water interface, are flexible and may undergo conformational changes in response to environmental variations. "Soft-sphere" colloids are essentially dissolved macromolecules and are closest in form and behavior to particles referred to as hydrophilic colloids in the traditional colloid chemistry literature (Lyklema, 1978; Hiemenz, 1986).

A final consideration is transport and retardation of colloidal particles in the subsurface. Mobile colloidal particles are those particles that are entrained in groundwater and are readily transportable. Immobile colloidal particles are those that have been chemically or physically sequestered by fixed substrates (e.g., the host rock, backfill materials, etc.) or have agglomerated and cannot be hydraulically entrained. In the absence of retardation mechanisms, the velocity of mobile colloidal

particles can actually exceed that of non-sorbed dissolved solutes, because of surface charge and the non-negligible size of colloidal particles. A variety of retardation mechanisms counter that phenomenon, including destabilization due to ionic strength effects, electrostatic and chemical interaction with the host rock, and particle sieving. Key parameters controlling colloid-facilitated actinide transport include the surface chemistry, size, density, population, morphology, density, and physical structure of the colloidal particles, the physical and chemical characteristics of the host rock, and the hydrogeologic system.

### 2.1.2 Definitions of Types

On the basis of those phenomena described in the previous Section, several classification schemes have been proposed by various workers, and a surprising number of descriptive terms have evolved and propagated in the literature. For actinide environmental geochemistry, most of the classification schemes are based on how the colloidal particle interacts with radionuclides. During discussions with co-workers over the past several years, we have found that communication is simplified by dismissing the previous classification schemes and, instead, adopting a classification based on the formation of the colloidal particle (i.e., a genetic classification). We classify colloidal particles into the following four types for evaluation of colloid-facilitated actinide transport at the WIPP Site:

- (1) Mineral fragments are hydrophobic, hard-sphere particles, that are kinetically stabilized or destabilized by electrostatic forces, and may consist of crystalline or amorphous solids. Mineral fragments may be made kinetically stable by coatings with steric stabilizers that prevent close contact. Mineral fragments may act as substrates for sorption of actinides or they may consist of precipitated or coprecipitated actinide solids.
- (2) Actinide intrinsic colloids are macromolecules of actinides that, at least in some cases, may mature into a mineral fragment type colloidal particle. When immature, they are hydrophilic; when mature, they become hydrophobic.
- (3) Humic substances are hydrophilic, soft-sphere particles, that are stabilized by solvation forces. They are powerful substrates for uptake of metal cations and are relatively small (less than 100,000 atomic mass units).
- (4) Microbes are relatively large colloidal particles that are stabilized by hydrophilic coatings on their surfaces, which behave as steric stabilizing compounds. They may act as substrates for extracellular actinide sorption or they may actively bioaccumulate actinides intracellularly.

## 2.2 Sources of Colloidal Particles at WIPP

Colloidal particles may be present in natural groundwaters at the WIPP including the Castile Formation, the Salado Formation, and the Culebra. They may be generated from interaction between those groundwaters and the waste, including microbially assisted reactions. Information is available on the nature of the waste from the Baseline Inventory Report (US DOE, 1994c). Information on groundwaters and the host rock is available from a variety of Site Characterization reports cited below. Information on interactions between the waste and groundwater is available from the gas generation program, from both a corrosion perspective and a microbial perspective. Information on interaction between actinides, potential backfill materials such as bentonite and concrete, and WIPP brines, is described in several reports (see, e.g., Butcher et al., 1991; Krumhansl et al., 1991b; Lambert et al., 1992; Nowak et al., 1992). Sorption of actinides by backfill will not be described herein. To describe the potential sources of colloidal particles, we separate the WIPP System into the repository environment and the Culebra environment.

### 2.2.1 Natural Geologic Media

Mineral fragment type colloidal particles may be present in naturally occurring groundwaters, and they may be released from the host rock due to disruption of fragile aggregates by changes in ionic strength or hydrodynamic forces, dissolution of a more soluble surrounding matrix (Buddemeier and Hunt, 1988; Kim, 1992), mechanical grinding of mineral surfaces, or mechanical disruption of secondary minerals present at mineral surfaces (McCarthy and Zachara, 1989). The Salado Formation at the WIPP repository horizon consists of bedded halite with intercalated argillaceous lenses ("marker beds") containing anhydrite, polyhalite, glauberite and several clay minerals (WIPP PA Department, 1992b, p. 2-11; Krumhansl et al., 1990; Lambert, 1991). The less soluble halide salts, carbonate minerals, and clay minerals present in the "marker beds" could form mineral fragment type colloidal particles. The underlying Castile Formation, which, in an intrusion scenario could be penetrated allowing Castile Formation groundwater to flow into the repository, consists of anhydrite and intercalated limestone and halite (WIPP PA Department, 1992b, p. 2-11). It is possible that fragments of those minerals could be mobilized as colloidal particles also. Mixing of Castile and Salado Formation groundwaters in the repository may result in precipitation of mineral fragments. If minerals were to precipitate, they might consist of carbonate or sulfate minerals.

Naturally occurring halophilic and halotolerant microbes have been identified in Salado Formation brine seeps in the WIPP repository environment (Francis and Gillow, 1994). The concentrations of those microbes are anticipated to become enhanced in the presence of the waste material. No



information exists about total organic carbon concentrations in Salado or Castile Formation groundwaters, which would provide bounds on the possible concentrations of humic substances. Considering the depth and composition of those Formations, the concentrations of humic materials is likely to be small because of the time available for oxidation and incorporation of humic substances into the host rock. The concentrations of humic substances contained in components of the waste is expected to be far greater than naturally occurring indigenous humic substances.

The Culebra consists primarily of dolomite, gypsum, an ordered mixed-layer chlorite-saponite clay mineral identified as corrensite, minor calcite and quartz, and trace quantities of pyrite, and goethite (Sewards et al., 1992). Under certain conditions, such as extreme changes in ionic strength of the groundwater or by physical disruption due to natural or human-induced events, mineral fragment type colloidal particles could be produced from the Culebra. In an intrusion scenario at the WIPP, mixing of repository brines with Culebra brines is likely to result in mineral precipitation which may include coprecipitation of actinide-bearing minerals, or dissolution of existing Culebra minerals. Precipitation may result in the formation of relatively large crystals in the rock matrix, or it may result in the formation of mineral fragment type colloidal particles.

The total organic carbon concentration in Culebra groundwaters ranges from less than 1 mg/L (the minimum analytical detection limit of analyses described in Myers et al., 1991, was probably 1 mg/L) to 6 mg/L, with a median of about 1 mg/L or lower (Figure 6; Myers et al., 1991). Deep Palo Duro Basin brines, which are likely to have ages and compositions similar to some WIPP brines, consist largely of short-chain aliphatic acids (Fisher, 1987; Means and Hubbard, 1987). It is unlikely that the organic carbon concentration measured in Culebra brines consists of colloidal natural organic matter such as humic acid, for example, because of the high probability for oxidation of organic compounds in such relatively old brines. Thurman (1985) summarized the general concentration trend of naturally occurring organic matter in groundwaters. In order of decreasing importance, Thurman listed humic substances (humic and fulvic acids) last: hydrophilic acids (e.g., fatty, hydroxy, and complex polyelectrolytic acids with many hydroxyl and carboxyl functional groups) and identifiable compounds (carboxylic acids, amino acids, carbohydrates, volatile hydrocarbons, and other simple compounds), humic and fulvic acids.

### **2.2.2 Repository Environment**

The most likely source of potential colloidal particles is from the waste itself or from interactions between the waste and groundwaters. The most current information on the nature of the waste destined for the WIPP Site is contained in the Baseline Inventory Report (US DOE, 1994c). For that document, the generator sites have participated in providing their best available information on the nature of the wastes, and have grouped their contact-handled (CH) and remote-handled (RH) transuranic (TRU) wastes into thirteen Waste Matrix Code Groups (WMCGs).

The following waste parameter information is taken with little modification from the Baseline Inventory Report (US DOE, 1994c):

1. Inorganics.
  - A. Iron-based metals/alloys. Includes iron and steel alloys in the waste and does not include the waste container materials.
  - B. Aluminum-based metals/alloys.
  - C. Other metals. Includes all other metals found in the waste materials (e.g., copper, lead, zirconium, tantalum, etc.). The lead portion of lead rubber gloves/aprons is also included in this category.
  - D. Other inorganic materials. Includes inorganic non-metal waste materials such as concrete, glass, firebrick, ceramics, sand, and inorganic sorbents.
2. Organics.
  - A. Cellulosic. Includes those materials, generally derived from high polymer plant carbohydrates. Examples are paper, cardboard, Kimwipes, wood, cellophane, cloth, etc.
  - B. Rubber. Includes natural or manmade elastic latex materials. Examples are Hypalon, Neoprene, surgeons' gloves, leaded-rubber gloves (rubber part only), etc.
  - C. Plastic. Includes generally manmade materials, often derived from petroleum feedstock. Examples are polyethylene, polyvinylchloride, Lucite, Teflon, etc.
3. Solidified materials.
  - A. Inorganic matrix. Includes any homogeneous materials consisting of sludge or aqueous-based liquids that are solidified with cement, Envirostone, or other solidification agents. Examples are wastewater treatment sludge, cemented aqueous liquids, and inorganic particulates, etc.
  - B. Organic matrix. Includes cemented organic resins, solidified organic liquids, and sludges.
4. Soils.
  - A. Generally consists of naturally occurring soils that have been contaminated with inorganic waste materials.
5. Packaging materials.
  - A. Steel. Currently, CH-TRU waste is assumed to be packaged in 55-gallon drums and RH-TRU waste is assumed to be packaged in RH-TRU shipping containers designed for disposal at the WIPP. As additional data on other packaging configurations are specified by the TRU-waste generator and storage sites, this may be modified.
  - B. Plastic. Currently, all CH-TRU waste is assumed to be packaged in ca. 80-

mil high-density polyethylene liners with several layers of plastic bags inside.

- C. **Lead.** The RH-TRU canister contains lead as well as steel.

The total masses of the CH-TRU and RH-TRU waste material inventories are summed in Table 1<sup>3</sup> based on the "...final rollups of the WIPP waste profiles..." from the Baseline Inventory Report (US DOE, 1994c). In terms of total mass, cellulosic organics and iron in the form of steel packaging materials and inorganic iron-based metals/alloys account for about 65 wt% of the waste. Plastic organics, other inorganic materials, and plastic packaging materials account for about 25 weight percent of the waste. The remainder consists of solidified material-inorganic matrix, rubber organics, other inorganic materials, solidified material-organic matrix, lead packaging materials, soils, and inorganic aluminum-based metals/alloys. Note that only about one-half weight percent of the anticipated waste is soil.

Once waste is emplaced and the repository is sealed, it is anticipated that within a relatively short time compared to the 10,000-year performance period, reducing conditions will be established in the repository. Brush (1990) has qualitatively defined the extremes in pH-Eh space (Figure 5). In the absence of any pH-Eh buffering backfill materials, pH may range from approximately 3.5 to 11.5, or perhaps even higher in the presence of some cementitious materials. The stability field of water limits Eh to a range of about -0.7 to 1.0 V in that pH range. The ranges in pH-Eh conditions in the repository are being refined as part of the gas generation program (see Section 1.5.4; Brush, 1990).

Under those conditions, metals, particularly iron-bearing waste and the steel packaging materials, will corrode, producing mineral fragment type colloidal particles. In addition, the solidification matrix, particularly the Portland cement (and perhaps Envirostone, which is calcium sulfate mixed with melamine formaldehyde) based matrixes will be attacked and will produce mineral fragment type colloidal particles. Bentonite, which is frequently a constituent of drilling mud, and in the past had been considered as a backfill material, is itself a potential source of mineral fragment type colloidal material that should be considered for actinide transport. In scenarios which involve human intrusion, drilling mud may be introduced into the repository and mix with the repository brine and waste.

If the repository conditions become anoxic as anticipated, it is likely that the primary corrosion product will be ferrous iron hydroxide, Fe(II)(OH)<sub>2</sub> (Table 2; Brush, 1990; Telander and Westerman, 1993). Common corrosion products of iron forming in oxic environments provide mineral fragment type colloidal particles similar to ferrous iron hydroxide. Oxic corrosion products potentially include: goethite ( $\alpha$ -FeO·OH), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), lepidocrocite ( $\gamma$ -

<sup>3</sup>Tables are included in Appendix C.

FeO·OH), and limonite (FeO·OH· $n$ H<sub>2</sub>O; cryptocrystalline goethite or lepidocrocite with adsorbed water). Under certain conditions, the pH of the repository may be driven to fairly basic pH values. At a pH value of approximately 8.5 brucite [Mg(OH)<sub>2</sub>] is likely to begin precipitating. At higher pH values, brucite is not thermodynamically stable and other magnesium-bearing solids, such as hydrotalcite, may be important. The Salado Formation brines contain a large concentration of Mg, and so the mass of brucite that could be produced is quite large. As a mineral fragment type colloidal particle, however, brucite will be destabilized by the high ionic strength of the brine.

Microbes, which are colloidal particles themselves, will interact with nutrients and cellulosic components (polysaccharides consisting of linked glucose molecules) of the waste and may produce colloidal-sized degradation products, such as cellulose itself, as well as saccharic acid and gulconic acid. Potential steric stabilizers such as alcohols and carboxylic acids are produced as by-products of microbial degradation of the waste (Francis and Gillow, 1994), in addition to the anthropogenic organic complexants contained in the waste (Table 3). It is not likely that condensation of alcohol and carboxylic acid by-products could result in production of humic substances.

The soil component of the waste is likely to contain organic matter that will contain humin, humic, and fulvic substances. Interaction with groundwater in the repository may mobilize some of that material. It is not likely that by-products from microbial degradation of wastes will condense to form humic substances. Work by Francis and Gillow (1994) have shown that only simple organic compounds are produced. Paine and Dosch (1992) conducted experiments on degradation of anticipated waste constituents and found that lignin was difficult to degrade.

A variety of anthropogenic organic ligands are expected to be included in the waste (Table 3). Many of those ligands are not soluble in aqueous systems and do not need to be considered further. Approximately ten organic complexants were identified as occurring in significant concentrations in existing defense-related transuranic wastes (refer to Brush, 1990, for summary). The effects of those organic complexants on actinide solubility is being investigated as part of the actinide source term solubility program. The five organic ligands which may be important at the WIPP (acetate, citrate, EDTA, lactate, and oxalate) are currently being investigated for complexation behavior (Novak, 1995).

Other organic compounds will be present in the waste, and may include the following volatile organic compounds (Brush, 1990): 1,1,1-trichloroethane (1,1,1-TCA; CH<sub>3</sub>CCl<sub>3</sub>), carbon tetrachloride (CCl<sub>4</sub>), Freon, methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), trichloroethylene (TCE, CHCl:CCl<sub>2</sub>), and 1,2-dichloroethane (1,2-DCA; ClCH<sub>2</sub>CH<sub>2</sub>Cl). Other organic compounds that may be present include: alcohols and glycols, aldehydes, aromatic hydrocarbons, aliphatic hydrocarbons, halogenated organics, ketones, phenols, and cresols (Brush, 1990).

In Table 4, the anticipated concentrations of actinide isotopes contained in wastes destined for the WIPP are summarized. As is discussed in detail in Section 2.5.3, actinide intrinsic colloids are most likely to form in environments of high actinide concentrations and high pH values. Consequently, if they form, they are most likely to form in the repository environment rather than in the Culebra where actinide concentrations have been reduced by dispersion and sorption on the host rock. In addition, the concentration of humic materials in repository brines is likely to exceed the concentration of humic materials in Castile or Salado Formation groundwaters as well as Culebra groundwaters. Likewise, because of the nutrients provided by organic components of the waste, the concentrations of microbes in the repository environment will exceed the concentration of microbes occurring naturally in the groundwaters.

### 2.3 Compositions of Groundwaters Associated with the WIPP

The WIPP Site is unique among proposed nuclear waste repositories in that groundwaters in both the near-field (i.e., the repository) and the far-field (i.e., the Culebra) environments consist of high ionic strength brines. Electrolytes have a strong influence on the behaviors of colloidal particles, and a discussion of groundwater compositions is useful background.

Two hydrochemical facies have been identified in the Culebra within the WIPP Land Withdrawal Boundary by Siegel and Lambert (1991) and Siegel et al. (1991). Hydrochemical facies C consists of brines similar in composition to present-day seawater, in which the ionic strength is about 0.8 molal and the primary constituents are  $K^+$ ,  $Na^+$ ,  $Cl^-$ , and  $SO_4^{2-}$ . A representative example of hydrochemical facies C brine is the brine collected from seeps and boreholes within the air intake shaft (Table 5). Hydrochemical facies A, which is found in the Culebra in roughly the western half of the Land Withdrawal Boundary, consists of brines with ionic strengths of about 3.0 molal, and is primarily a NaCl brine with some  $SO_4^{2-}$  (note that hydrochemical facies B and D do not occur within the Land Withdrawal Boundary). Samples collected from borehole H-17 provide representative hydrochemical facies A brine compositions (Table 5).

The pH values in Culebra brines range from about 6.0 to 8.0 (Siegel et al., 1991, Figure 2-44, Table 2-2). Those pH values were measured with traditional solution techniques (e.g., with Orion Ross combination electrodes) and are likely to be somewhat inaccurate because of liquid-junction potential effects (refer to Novak, in review and Rai et al., 1995, for a discussion of pH measurements in brines). Carbon dioxide partial pressures ( $pCO_2$ ) ranging from that of the ambient atmosphere ( $10^{-3.5}$  atm) to about 100 times that concentration ( $10^{-1.5}$  atm) have been calculated by Siegel et al. (1991, Figure 2-46) based on pH and brine compositions. Values close to atmospheric  $pCO_2$  could represent contamination due to equilibration of the sampled brines with air.

Investigations of the current dominant flow path above the repository suggest that flow will be approximately southward (LaVenue et al., 1990). In the event of an intrusion at the WIPP, the initial groundwater encountered in the Culebra is expected to be hydrochemical facies C. As a carbonate rock system, the Culebra has a tremendous acid-base (and therefore carbon dioxide) buffering capacity. Consequently, in an intrusion scenario, acidic or basic repository groundwaters will quickly be neutralized to ambient Culebra conditions.

Reviews of the chemistry of intergranular brines in the Salado Formation are found in Stein and Krumhansl (1986, 1988), Deal and Case (1987), Deal et al. (1987), Lappin et al. (1989, pages 3-14 to 3-23), Brush (1990, pages 17-21), Deal and Roggenthen (1991), Krumhansl et al. (1991a), and references cited in those publications. Representative Salado Formation brine chemistries are difficult to define because the low permeability of the rock makes it difficult to collect sizable samples, and the high total dissolved solids of the brine makes precipitation likely even with small amounts of evaporation. Krumhansl et al. (1991a) sampled and characterized samples collected from several dozen weeps in the WIPP repository. They found small but significant differences in compositions that exceeded expected deviations due to evaporation and concluded that discrete brine reservoirs are present in the Salado Formation in proximity to the repository. In Table 5, the composition of a repository weep (i.e., G-seep) and the composition of brine collected from a borehole drilled from the repository into adjacent rock (i.e., drill hole DH-36) are listed.

Reviews of the compositions of Castile Formation brines are presented in Popielak et al. (1983), Brush (1990, pages 21-22), and references cited in those publication. Representative compositions come from groundwater samples collected and analyzed from the ERDA-6 well and the Union well (Table 5).

## **2.4 Transport and Retardation of Colloidal Particles**

The potential importance of *colloid-facilitated radionuclide transport* has only been recognized for about a decade (see, e.g., Avogadro and de Marsily, 1984). More recently, the importance of colloidal particles in transport of low solubility actinides has been demonstrated (see, e.g., Honeyman, 1991; Honeyman and Santschi, 1992; Read et al., 1994).

Many examples have been cited in the literature where highly adsorbing actinides or metals have traveled greater distances than expected (e.g., McCarthy and Zachara, 1989). In many of those cases, the presence of colloidal particles has been implicated for the unexpected behavior, although often on the basis of speculation rather than direct evidence. Few, if any, conclusive demonstrations have been made for colloid-facilitated metal transport in the deep subsurface. Most of the examples cited are for shallow subsurface environments which are rich in organic

constituents (e.g., humic substances). Current information on colloid-facilitated metal transport indicates that there are several viable mechanisms that have the potential to retard colloidal actinide transport. In this section, we discuss the mechanisms for transport and retardation of actinides due to the presence of colloidal particles.

To put this discussion into the context of the WIPP Site, we briefly discuss the hydrogeologic properties of the Culebra. Details of how we plan to implement a colloid transport model to help evaluate the performance of the WIPP are discussed in detail in Section 7.2.

#### 2.4.1 Hydrogeologic Properties of the Culebra

Detailed conceptual models of the hydrogeologic properties of the Culebra are developed and discussed in Papenguth and Behl (in review). In this Section we summarize some key points.

The Culebra is an approximately 8-meter thick fractured microcrystalline dolomite, and has been identified as the most hydraulically transmissive rock unit overlying the repository. On the basis of information from a large number of cores obtained from the Culebra and field tracer tests conducted in the Culebra, it is clear that the Culebra contains several different scales of porosity, including fracture porosity and intercrystalline porosity. The mean grain size is approximately 2  $\mu\text{m}$ , and the intercrystalline pore throats range in size from 0.15 to 1.6  $\mu\text{m}$ , with an arithmetic mean of 0.63  $\mu\text{m}$  (Kelley and Saulnier, 1990, p. 4-10). Hydrogeologic flow through the Culebra may be affected by the double porosity system established by permeability variations resulting from the presence of the two dominant porosity types (e.g., fracture and intercrystalline, or matrix, porosity). Flow may occur primarily by advective flow in the relatively high permeability fractures, accompanied by diffusive flow into the lower permeability intercrystalline porosity such that the bulk rock provides storage (computationally, diffusion is in a direction approximately normal to the main advective flow direction) (Reeves et al., 1987; Beauheim and Holt, 1990; LaVenue et al., 1990; Corbet and Wallace, 1993; and references cited in those publications). The fracture apertures, spacing, and distribution in the Culebra have not been conclusively determined.

Several of the proposed nuclear waste repositories are situated in rocks having a double porosity characteristics, and much of the discussion of colloid-facilitated radionuclide transport in published nuclear waste management literature is focused on describing flow in those double porosity type rocks. Examples include the the Yucca Mountain Site in Nevada, Grimsel Test Site in Switzerland, and the Whiteshell Site in the Canadian Shield (see, e.g., Hwang et al., 1989; Grindrod and Worth, 1990; Light et al., 1990; Smith and Delgueldre, 1993; Harmand and Sardin, 1994). It is imperative to note, however, that nearly all of those discussions are for crystalline (intrusive igneous) basement rocks (i.e., "granites"), which have substantially narrower fracture apertures and smaller intercrystalline pore throats than the Culebra. It is also important to

distinguish between transport in the shallow subsurface, where many studies have been made that conclusively demonstrate the importance of colloid-facilitated contaminant transport. Shallow and deep subsurface environments are substantially different, however. Typically, the geologic media in the shallow subsurface consists of soils and other sediments which are unconsolidated, or only loosely consolidated, with minimal compaction. The net result is that pores are large and interconnected, providing high permeabilities and reduced filtration effects.

Understanding the nature of the porosity in the Culebra is important in transport because of size exclusion effects. Colloidal particles which are large relative to the pore throat diameters will not be transported into the matrix by advection or diffusion, whereas relatively small colloidal particles may be physically retarded by advection or diffusion into the rock matrix.

A further consideration is the presence of mineral substrates in the Culebra which may participate in chemical (i.e., surface interaction) with colloidal particles. The dominant substrates available for interaction are an ordered mixed layer chlorite-saponite clay mineral identified as corrensite, and, of course, dolomite.

#### **2.4.2 Mechanisms of Transport Enhancement**

Mechanisms that enhance colloidal transport of actinides (relative to an ideal non-sorbing solute) result from physical or chemical exclusion effects that force the colloidal particle to move in higher velocity flow paths in the host rock. Three potentially important mechanisms must be considered. The first two enhancement mechanisms relate to enhancement of colloid transport. The third relates to enhancement of actinide transport by colloidal particles.

First, in some situations, the surface charge of the colloidal particle and the host rock have the same sign, and the colloidal particles are repelled from the host rock. It is believed that this phenomenon occurs frequently, and especially for mineral fragment type colloidal particles, because the mineralogies of the host rock and the colloidal particle are similar. The result is that colloidal particles are forced to move in the higher velocity zone in the central region of the flow channel. A complementary effect results from the large size of colloidal particles relative to the sizes of dissolved solute and other ions, which precludes the colloidal particle from moving within the slow velocity region immediately adjacent to the wall of the channel.

The distribution of flow velocities within a flow channel such as fracture is parabolic with the maximum velocity near the center of the fracture. Current estimates are that colloid velocities due to this phenomena, referred to by some as hydrodynamic chromatography, can be as great as about twice the average flow rate for a cylindrical channel and one-and-one-half the average flow rate for a planar fracture. For colloidal particles moving through channels by laminar flow, the parabolic



velocity profile is described by (Vennard and Street, 1982):

$$v = v_{\max} \left( 1 - \frac{y^2}{R^2} \right) \quad (1)$$

where

- v velocity in channel at distance y from center of channel
- $v_{\max}$  maximum velocity, at center of channel
- y distance from center of a channel
- R half-width (radius) of channel aperture

The average velocity (V) across the width of a cylindrical channel is:

$$V = \frac{1}{\pi R^2} \int_0^R v_{\max} \left( 1 - \frac{r^2}{R^2} \right) 2\pi r dr \quad (2)$$

which reduces to:

$$v_{\max} = 2V \quad (3)$$

For planar fractures:

$$v_{\max} = 1.5V \quad (4)$$

A second important phenomenon that could result in actinide transport enhancement, is the size exclusion effect (Fetter, 1993, p. 150). Depending on the porosity types, porosity distribution, pore throat diameters, and fracture apertures in a sediment or rock, relatively large colloidal particles may be physically excluded from advective or diffusive transport into portions of the rock normal to the net flow direction, and limited to movement in higher velocity interconnected pores, channels, or fractures. Enhanced transport along such preferential pathways has been observed by several investigators (see, e.g., Enfield and Bengtsson, 1988; Toran and Palumbo, 1992; and references cited in those publications), and results in a retardation factor of less than one relative to the unimpeded movement of an ideal non-sorbing aqueous solute.

Third, if mobile colloidal particles compete with the host rock as a sorbent, transport of dissolved solutes may be enhanced due to sorption on the mobile colloidal particle. For example, consider a case in which dissolved solutes are introduced to a rock unit rich with mobile mineral fragment type colloidal particles. Instead of being sorbed by the host rock, which would result in retardation, the dissolved solutes are sorbed by the mineral fragment type colloidal particles, which

then may enhance the transport of the solutes because of hydrodynamic chromatography and size exclusion effects. In the laboratory, Read et al. (1994) recently demonstrated that thorium associated with colloidal particles was retarded by a factor of six relative to a non-sorbing dissolved-solute tracer in a crushed-rock column flow experiment. Dissolved thorium, however, was retarded by several orders of magnitude more. For that sort of competitive phenomenon to have a negative impact on compliance at the WIPP Site, however, requires that colloidal particles are present in the far field which can act as mobile substrates for sorption of actinides. At the WIPP, the source of colloidal particles will be from the disposal room and the concentration of mobile colloidal particles that could sorb dissolved actinides in the far field (i.e., the Culebra) is anticipated to be comparatively small (refer to Section 2.2).

### 2.4.3 Mechanisms of Retardation

Retardation of colloid-facilitated actinide transport can occur as a result of agglomeration and gravitational settling of actinide-bearing colloidal particles, by electrostatic attraction of actinide-bearing colloidal particles to rock surfaces (surface filtration), by entrapment of actinide-bearing colloidal particles by small pores within the rock matrix (physical filtration, or sieving), and by diffusion into intercrystalline porosity. Cosorption, in which contaminant-bearing colloidal particles are sequestered by the host rock, is a commonly observed phenomenon which results in retardation of the contaminant.

Kinetic destabilization of colloidal particles may contribute significantly to the retention of radioactive material in subsurface geologic media. Some colloidal particles may be destabilized and immobilized within hours or days (refer to Section 2.5.1; see also Apps et al., 1983). Kinetically destabilized colloidal particles with sorbed radionuclides act as immobile sinks for those radionuclides. Destabilization of colloidal particles may result from chemical coagulants, which affect electrostatic behaviors, or by flocculants, which modify the chemical nature of colloidal particle surfaces. In dilute groundwaters, colloidal particles that have been destabilized may be peptized by changing the concentrations of coagulants or flocculants. The impact of kinetic destabilization of colloidal particles at the WIPP is discussed in detail in Section 2.5.

Filtration of colloidal particles due to chemical interaction between the particle and the host rock has been shown to be important with many rock and colloidal particle types. In most cases, the surface charge of minerals in natural groundwaters is negative. As is discussed in Section 2.5 in detail, some of the potentially important colloidal particle types at the WIPP may have positive charges and will be chemically sequestered by the Culebra.

Physical filtration of colloidal particles occurs by sieving effects. Colloidal particles may be sequestered at the surface of fractures in porous materials, such as the Culebra. If matrix advection

occurs in the Culebra (refer to Axness et al., 1995), physical filtration of relatively large colloidal particles is likely to have a substantial effect on actinide retardation. A compounding effect on retardation by physical filtration, as well as chemical filtration, results from permeability reduction of the porous medium by clogging pores. In fact, clogging is a major reason for the effectiveness of engineered clay barriers, which are routinely used for waste isolation (McDowell-Boyer et al., 1986, 1987). Those authors attribute the observed orders-of-magnitude reduction in the permeability of clay liners to pore clogging effects.

Colloidal particles may actually be slightly smaller than pore throats and yet still be excluded solely by physical effects. Using the criteria of Vilks (1994) with a mean Culebra grain size of 2  $\mu\text{m}$ , cake filtration may occur with colloidal particles as small as 0.2  $\mu\text{m}$ , and straining filtration may occur with particles in the 0.1 to 0.2  $\mu\text{m}$  size range. Physical retardation would not be expected to occur for colloidal particles with mean diameters less than 0.1  $\mu\text{m}$ . The guidelines proposed by Vilks are highly idealized, however, and apply rigorously only to very uniform filtration systems. Exclusion from pores is also dependent on the physical structure of colloidal particles. It is conceivable although probably unlikely that "soft-sphere" colloidal particles of the same general size of "hard-sphere" colloidal particles could undergo deformation and enter pores in which the latter particles were excluded.

Colloidal particles, together with any associated actinides, that are sufficiently small may diffuse into intercrystalline porosity in the Culebra and will be physically retarded. Physical retardation of dissolved actinides is best evaluated using Fick's Law, in which the mass diffusion constant ( $D$ ; also referred to as diffusivity or the free-water diffusion constant) is a critical parameter. At a fundamental level, diffusivity is related to the physical characteristics of the diffusing molecule and the molecules of the host medium and the intermolecular forces acting between them. For example, the diffusivity of a gas molecule in another gas (the host gas) at low density is inversely proportional to the square root of the reduced mass of the diffusing and host gas molecules and the collision diameter. Whereas a rigorous theory of solute diffusion in liquids is apparently not available, order of magnitude estimates may be made on the basis of hydrodynamical theory. With that theory, the diffusivity of a solute in a liquid is inversely proportional to the radius of the diffusing particles (Bird et al., 1960, p. 513). Free water diffusivities of dissolved actinides are compiled in Reeves et al. (1991, Table 2.7). Rates of diffusion of colloidal particles can be estimated by scaling those experimentally determined free water diffusion constants for dissolved actinides to dissolved colloidal materials on the basis of size (Stokes-Einstein relationship) as follows:

$$D_{\text{coll}} = D_{\text{ion}} \left( \frac{r_{\text{ion}}}{r_{\text{coll}}} \right) \quad (6)$$

where:

- $D_{\text{coll}}$  diffusion constant for a colloidal actinide of radius  $r_{\text{coll}}$
- $D_{\text{ion}}$  diffusion constant for a dissolved actinide of radius  $r_{\text{ion}}$
- $r_{\text{coll}}$  radius of the colloidal actinide
- $r_{\text{ion}}$  radius of the dissolved actinide

For example, given an ionic radius and a colloidal particle radius of 1 Å and 10 nm, respectively, the free-water diffusion constant for the colloidal particle would be that of the dissolved actinide reduced by a factor of 100. That approach is consistent with discussions in Hiemenz (1986, p. 81).

Several other colloidal transport mechanisms have been proposed. Colloidal "relaying" of actinides has been proposed as transport mechanism in the subsurface by some workers. That phenomenon occurs when actinides repeatedly sorb and desorb onto colloidal particles as those colloidal particles repeatedly become mobilized and immobilized as the result of interaction (either chemically or physically) with the host rock. Transport rates of colloidal particles with rough surfaces may be less than rates for smooth, uniformly spherical particles because of turbulence. Those phenomena would be exceedingly difficult to model numerically and parameterize. Disregarding those phenomena is conservative in that calculated releases to the accessible environment are over-estimated.

Apps et al. (1983) have shown that for uncharged particles gravitational settling may eliminate particles with sizes on the order of 0.1 µm or larger on the time frame of weeks (note that in high ionic strength electrolytes, the assumption of uncharged particles may not be far off). That conclusion suggests that the generally accepted size range for colloidal particles (1 nm to 1 µm) may be reduced for environmental transport considerations. The size cut-off above which colloids settle due to gravity would depend on the characteristic time scales of interest and the nature of the particle-surface forces, which were not included in the calculations of Apps et al. For the colloids in the size range of ångströms (atomic scales), no settling is expected because the colloids will essentially behave like other molecules and ions in the solution.

## 2.5 Geochemical Behavior of Colloidal Particle Types

In this section, the four categories of colloidal particles are described, their anticipated sources are summarized, and implications for the performance of the WIPP are described.

### 2.5.1 Mineral Fragments

Ions in a dispersant interact with mineral surfaces, including mineral fragment type colloidal particles, in two ways. First, "non-specific interaction" refers to electrostatic effects that do not involve specific chemical reactions with moieties present at mineral surfaces in aqueous environments. In other words, surface complexes do not form. Electrolytes that interact with mineral surfaces in such a way are referred to as "inert" or "indifferent" electrolytes. The interactions between ions in high ionic strength brine and a mineral fragment that result in kinetic destabilization are non-specific interactions. This interaction is referred to as an "outer-sphere" phenomenon, meaning that the dissolved ions are interacting with the mineral surface at some distance away from the actual surface.

In contrast, "specific interaction" involves chemical reactions, as well as a component of electrostatic interaction, between surface moieties and dissolved ions, to form surface complexes. This phenomenon is also referred to as chemi-sorption, and is responsible for adsorption of dissolved ions onto a substrate. It is this specific interaction that can result in the reversal of charge at mineral surface. In other words, the ions in the electrolyte that interact specifically with the surface, are considered to be "non-indifferent" ions.

#### 2.5.1.1 Non-Specific Interaction with Electrolytes

This section provides the theoretical basis for explaining why mineral fragments are not expected to be kinetically stable in high ionic strength electrolytes. The effect of electrolytes on the kinetic stability of some colloidal particles (including mineral fragment type colloidal particles) has been formally recognized since the work by the founder of modern colloid chemistry, Thomas Graham, in the middle 19th century. It was not until the about one-hundred years later, however, that a conceptual model and a semi-quantitative mathematical implementation, the DLVO theory, was developed. In the following paragraphs, we describe that model.

In an aqueous environment, mineral surfaces develop a surface charge because of broken bonds and isomorphous lattice substitutions involving ions with different valences. Charge at the surface that has developed due to isomorphous lattice substitutions is fixed, and does not change as a function of solution conditions. However, most of the charge at mineral surfaces is not fixed, and changes as a function of the concentration of potential-determining ions (PDIs) in solution. For most oxides and many silicates, the PDI is the hydrogen ion. For other minerals, such as carbonates, the PDIs may be an ion not directly linked to pH, such as calcium or magnesium (Brady et al., in review).

To counteract the surface charge, layers consisting of ions of the opposite charge (i.e., counterions) develop at the surface. The electric double layer is a conceptual model describing two layers of counterions (Figure 7). The Stern layer is a fairly dense layer of counterions that forms immediately adjacent to the mineral surface. The diffuse layer is a less dense layer of ions that forms adjacent to the Stern layer. The Schulze-Hardy rule, formulated on the basis of empirical observations nearly one century ago (e.g., Hardy, 1900), states that the kinetic stability of a colloidal suspension is dependent on the concentration of the dissolved ions with charge opposite to that of the colloid surface, and the valence of those dissolved ions (Matijević, 1973; Overbeek, 1980, 1982b; Miller and Neogi, 1985). At near neutral pH values, most colloid particles in natural groundwaters are negatively charged, so their kinetic stability will generally be dependent on the concentration of dissolved cations.

The theoretical explanation for the Schulze-Hardy rule was provided by DLVO theory. That theoretical explanation, named the DLVO theory after the four authors (Derjaguin and Landau, 1941; Verwey et al., 1948), was a landmark in demonstrating the understanding of surface phenomena of hydrophobic (or more generally, lyophobic) colloidal particles. The DLVO theory describes kinetic stability of hydrophobic colloidal particles in terms of attractive forces and repulsive forces. The total free energy of interaction between two like colloidal particles is simply the sum of those forces. For two equal-sized spheres, the electrostatic repulsion term ( $\Delta G_R$ ) describing repulsive interaction energy is:

$$\Delta G_R = \frac{64n_0\pi akT\gamma^2}{\kappa^2} \exp(-\kappa H_0) \quad (6)$$

with

$$\kappa^2 = \frac{e^2}{\epsilon_r \epsilon_0 kT} \sum n_{i0} z_i^2 \quad (7)$$

and

$$\gamma = \tanh \frac{ze\phi_0}{4kT} \quad (8)$$

where:

- $n_0$  number of dissolved ions or molecules or paired ions per volume
- $a$  colloidal particle radius
- $k$  Boltzmann constant
- $\kappa$  inverse Debye length, roughly equivalent to the reciprocal double layer thickness
- $T$  temperature in Kelvin

$H_0$	shortest interaction distance between two colloidal particles
$N_A$	Avogadro constant
$z$	valence of ion including the sign of the charge
$e$	elementary charge
$\epsilon_0$	Permittivity of free space
$\epsilon_r$	static dielectric constant of the solvent
$\phi_0$	electrical potential at the colloidal particle surface

The dispersion force attraction term ( $\Delta G_A$ ) describing van der Waals attraction energy for very short distances is:

$$\Delta G_A = - \frac{A_{121}a}{12H_0} \quad (9)$$

where:

$A_{121}$  Hamaker constant, describing energy of interaction between two spheres of material 1 separated by material 2

Summing the electrostatic repulsion and the dispersion force attraction terms provides the total electrostatic stabilization term ( $\Delta G_T$ ):

$$\Delta G_T = \Delta G_R + \Delta G_A = \left( \frac{64n_0\pi akT\gamma^2}{\kappa^2} \exp(-\kappa H_0) \right) - \left( \frac{A_{121}a}{12H_0} \right) \quad (10)$$

Note that the attraction term,  $\Delta G_A$ , is only dependent on the distance between two colloidal particles and is not affected by ionic strength of the dispersant. The value of the Hamaker constant varies only slightly for different mineral fragments anticipated to be present in the WIPP environment (refer to compilation in Ross and Morrison, 1988, Table A.6). In contrast, the repulsion term,  $\Delta G_R$ , is related to ionic strength through the inverse Debye length ( $\kappa$ ), which is roughly related to the reciprocal of the thickness of the electric double layer, in the exponential term. The effects of these relationships can be observed in Figures 8a-c, which qualitatively show the magnitude of the attraction and repulsion forces, and the total force, as a function of interparticle distance. When the ionic strength of the electrolyte results in a reduction in the magnitude of the repulsion term so that it is slightly less than the attraction term, the colloidal dispersion rapidly forms agglomerates large enough to settle by gravitational forces. That electrolyte concentration is termed the critical coagulation concentration (c.c.c.), and is usually expressed in molarity. Experimentally, the effects of reaching the c.c.c. are quite striking, in that only a very small addition of salt to a kinetically stable dispersion at the c.c.c. will result in destabilization and settling on the order of only a few hours.

By equating the  $\Delta G_R$  and  $\Delta G_A$  expressions and solving, a relationship between the ionic strength (and valence of symmetrical electrolytes) and the c.c.c. can be established (Ross and Morrison, 1988):

$$\text{c.c.c. (moles/L)} = \frac{8.78 \times 10^{-39} \gamma^4}{z^6 (A_{121})^2} \quad (11)$$

Although the c.c.c. relationship in equation (11) is related to the sixth power of ionic strength, in practice c.c.c. is more closely related to the square of ionic strength because of the surface potentials of colloidal particles are reduced as the c.c.c. is approached (Stumm, 1992, p. 266).

The Hoffmeister, or lyotropic, series describes empirical observations that, at a given valence, certain ions are more effective at kinetically destabilizing hydrophobic colloidal particles. For monovalent anions and cations, the following series are observed (Hunter, 1991):



These series are explained on the basis of ionic radii and polarizability, the same features that are used to explain tendencies for complexation of ions. The interaction between surfaces and counterions of an indifferent electrolyte are often not absolutely ideal (see, e.g., Liang and Morgan, 1990a,b) due, for example, to solvation, hydration, and capillary effects (Stumm, 1992, p. 266), and the predictive accuracy of the DLVO approach is reduced.

In his treatise on clay colloidal dispersions, van Olphen (1991, p. 24) summarized empirically determined c.c.c. values as follows:

<u>counterion valence</u>	<u>c.c.c. (M)</u>
+1	0.025 to 0.150
+2	0.0005 to 0.002
+3	0.00001 to 0.0001

For example, on the basis of the c.c.c. values above, consider the destabilization effects of some common groundwater cations:

<u>counterion</u>	<u>c.c.c. (mg/L)</u>
Na <sup>+</sup>	600 to 3,500



Ca <sup>2+</sup>	20 to 80
Al <sup>3+</sup>	0.3 to 3

Values for c.c.c. provided by Gregory (1978, p. 93) are within the ranges provided by van Olphen (1991).

Since the publication of the DLVO theory, there have been many demonstrations that the mathematical model is applicable at best only under highly idealized conditions. Nevertheless, the DLVO model provide a useful framework to envision the behaviors of colloidal particles such as mineral fragments as a function of the ionic strength of the dispersant (see, e.g., Hunter, 1991, p. 446).

### 2.5.1.2 Agglomeration Kinetics

Conceptual models describing the agglomeration kinetics of colloidal particles are discussed briefly in this Section (refer to O'Melia and Tiller, 1992, and references cited therein, for a more thorough review). Aggregation kinetics for the rate of formation of two-particle clusters of colloidal particles (Hiemenz, 1986) is described by the following relationship:

$$-\frac{dn}{dt} = k_2 n^2 \quad (14)$$

where:

- n      colloidal particle concentration (number of particles per unit volume) at time t
- t      time
- k<sub>2</sub>    second order rate constant

The solution to equation (14) shown above is:

$$\frac{1}{n} = \frac{1}{n_0} + k_2 t \quad (15)$$

where:

- n<sub>0</sub>    initial colloidal particle concentration (number of particles per unit volume)

By rearranging the equation above, one can solve for colloid half-life (t<sub>0.5</sub>), which is the time required for concentration of colloids to be reduced to one-half of the initial concentration, t<sub>0.5</sub>, a value that quantitatively describes colloid stability:

$$t_{0.5} = \frac{1}{k_2 n_0} \quad (16)$$

Inspection of equations 14-16 shows that the rate of agglomeration of colloidal particles decreases as the concentration of particles decrease, because of the reduced likelihood of particle-particle collisions. Related to that concept is the fact that under the same initial conditions, agitating a colloidal dispersion by advective flow, stirring, sedimentation, etc., will result in faster agglomeration kinetics because particle-particle collisions are increased. In other words, orthokinetic coagulation rates are faster than perikinetic coagulation rates under the same initial conditions.

Because of the complexities introduced in quantifying agglomeration kinetics of heterodisperse populations of colloidal particles of different compositions even under static conditions, we do not believe that it will be feasible to quantify agglomeration kinetics for the WIPP system.

Under conditions in which colloidal particles are kinetically destabilized and have agglomerated, settling occurs due to gravitational forces. Stokes Law describes the time required for settling (Jackson, 1974):

$$t = \frac{18\mu h}{g(s_p - s_1)} D^2 \quad (17)$$

where:

t	settling time (sec)
$\mu$	viscosity (cp)
h	settling distance (cm)
g	gravitational constant
D	spherical particle diameter (cm)
$s_p$	specific gravity of particle
$s_1$	specific gravity of dispersant

As kinetic destabilization occurs to make multi-particle agglomerates, the time required for gravitational settling decreases proportionally to the square of the agglomerate diameter. For mineral fragment type colloidal particles (specific gravity for many minerals is about 2.5, ranging from about 1.5 to 3.0) in Salado Formation brines (viscosity 2.15 centipoise; specific gravity 1.201; Yeh, 1993a-c), the Stokes Law settling velocities for 1  $\mu$ m particle agglomerates are on the order of about 10 to 40 hours per centimeter. The settling rate is slightly faster in less dense Culebra brines (Figure 9).

### 2.5.1.3 Stabilization of Mineral Fragments

The discussion above on the impact of non-specific interaction of counterions on an aqueous surface is rather idealized, because most so-called inert counterions have at least some chemical interaction with the surface. That specific interaction can result in a range of behaviors from very loosely bound ions, as is the case with many of the monovalent and divalent cations (e.g.,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Cl}^-$ ), to very strongly bound ions, such as  $\text{Am}^{3+}$ . The latter example is considered adsorption, which is discussed in a later section. In the present section, we consider the effects of specific interaction on the kinetic stability of mineral fragment type colloidal particles. We focus on two effects, surface charge reversal, and steric stabilization.

Charge reversal occurs when a sufficient number of ions chemically interact with an aqueous surface to modify or replace the moieties at the surface. At the WIPP, the vast majority of anions and cations in the brine are fairly indifferent and will not have a profound effect on surface charge. The anions and cations that could alter surface charge, mainly the strongly adsorbing ions such as the actinides, are not likely to be present in sufficient abundance to have much of an effect. Regardless of surface charge reversal, however, mineral fragment colloidal particles will be kinetically destabilized by the electrostatic effects of the enormous concentration of counterions present in the brine. The only potential impact of charge reversal, if it were to occur, would be in changing the sorption properties of affected colloidal particles on fixed substrates (e.g., steel waste containers, backfill material, the host rock; which, incidentally are also susceptible to charge reversal by specific interaction). The total concentration of strongly sorbing solutes compared to the concentration of potential adsorption sites on fixed substrates is virtually negligible. We conclude for mineral fragments that surface charge reversal is not an important phenomenon at the WIPP Site.

Steric stabilizers are typically organic molecules that attach to a hydrophobic surface and inhibit close interaction with other particles (the term "steric" in colloid chemistry refers to the arrangement of molecules in space, but more specifically how the molecules are arranged on the surface of a colloidal particle). A sterically stabilized mineral fragment type colloidal particle is essentially protected from becoming part of an agglomerate because it cannot get close enough for van der Waals attractive forces to overcome the electrostatic repulsive forces. In dispersants with low to intermediate ionic strengths, the steric macromolecule extends effectively into the dispersant away from the particle surface, thereby protecting it from close encounters with neighboring particles. As ionic strength is increased, however, the conformation of macromolecules in electrolytes become compressed (O'Melia and Tiller, 1992, p. 373; Stumm, 1993). In the case of colloidal particles coated with steric macromolecules, the loops and tails of the macromolecules extending from the surface of colloidal particles become compressed, and steric stabilization is no longer effective in preventing agglomeration.

The most effective steric stabilizers are organic macromolecules, which are used in industry for waste water treatment, drilling mud stabilization, etc. (see, e.g., Theng, 1979; Sato and Ruch, 1980). Typically, the concentration of steric stabilizers must be carefully optimized to produce stabilization. If the concentration is not great enough, the van der Waals attractive forces of adjacent particles cannot be overcome. Conversely, if the concentration is too great, the steric compound can act as a flocculant to accelerate aggregation by chemical means, rather than by electrostatic forces (i.e., coagulation).

In the WIPP environment, industrial steric stabilizers will not be present as a waste constituent. Very low concentrations of simple monofunctional carboxylic acid anions such as formate and acetate be present in the natural groundwater, organic solvents are waste constituents, and alcohols and carboxylic acids are produced by microbial degradation of the cellulosic waste. There are instances where relatively low concentrations of similar compounds resulted in steric stabilization (Stumm, 1992). For example, Liang and Morgan (1990a,b) demonstrated that carboxylic acids, e.g., octanoic acid [ $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ ], capric acid [ $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ ], and lauric acid [ $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ ], destabilized hematite particles at low concentrations, but stabilized them at slightly higher concentrations. The background "inert" electrolyte concentrations in those experiments, however, was very low.

Considering the extremely high ionic strength of WIPP repository brines, coupled with the very low concentrations of potential steric stabilizing compounds, steric stabilization of mineral fragment type colloidal particles is unlikely.

#### 2.5.1.4 Interaction with Actinides

The discussion above suggests that mineral fragment type colloidal particles will be kinetically destabilized by brines associated with the WIPP, and will not mobilize actinides. As immobilized colloidal particles, however, they are likely to sequester actinides. Currently, the WIPP Project is not conducting the required research to quantify that phenomenon, but instead are using it as a mechanism for "secondary containment" to increase public confidence that, if compliance of the WIPP is demonstrated, that additional safety factors are included. In this Section we discuss the interaction of minerals with adsorbates.

Sorption includes all mechanisms which reduce the concentration of sorbates in a solution as a result of physicochemical interactions between a minerals and the sorbate. Sorption may be a reversible (equilibrium) or irreversible process. One of the assumptions of the linear isotherm ( $K_d$ ) model is that sorption is reversible. Mechanisms included are adsorption, ion exchange, and absorption. Absorption is physical containment or entrapment of a solute in the solid substrate, and involves no chemical bonding. Adsorption is not considered to be significant at the WIPP.

Adsorption involves a chemical interaction (electron transfer, or more precisely, electron cloud sharing) that occurs between an actinide ion and ligands at the surface of the mineral adsorbent (see, e.g., Kent et al., 1988; Weber et al., 1991; Mariner and Jackson, 1993). Adsorption may occur as an inner sphere phenomenon, which results in relatively higher  $K_d$  values, or as an outer sphere phenomenon, which results in relatively lower  $K_d$  values because of the weaker chemical bonding. Ion exchange describes the exchange of a very weakly held ion, typically a cation, with a similar size ion. Ion exchange most commonly occurs in zeolites and layered aluminosilicate (phyllosilicate) minerals such as clays, and as defined above, will not occur with carbonate minerals. Ion exchange is not likely to be affected by ionic strength of the solution, unless the ion defining ionic strength participates significantly in ion exchange (e.g.,  $\text{Na}^+$  with Ca-bentonite in a NaCl brine).

Chemical retardation factors are calculated using the following equation (Freeze and Cherry, 1979):

$$R = 1 + \frac{\rho_b K_d}{\phi} \quad (18)$$

where:

- R      chemical retardation factor
- $K_d$     distribution coefficient
- $\rho_b$     bulk density of the adsorbent
- $\phi$       porosity

This equation can be derived from the advection-dispersion equation assuming local equilibrium for adsorption. The linear isotherm model relationship is defined as follows:

$$S = K_d C \quad (19)$$

where:

- S      amount of a solute adsorbed on a unit mass of solid
- C      concentration of the adsorbing solute

The amount of solute adsorbed on a solid can also be defined on the basis of area as follows:

$$S = K_a C \quad (20)$$

where:

- $K_a$     distribution coefficient

In addition to the linear isotherm model (the " $K_d$  model"), there are isotherms that show adsorbate saturation effects at higher solute concentrations (Fetter, 1993). In some cases, as the solute concentration is further increased, adsorption increases rapidly due to additional processes such as surface precipitation (as monolayers on surfaces) coming into play, and the isotherm takes on an S-shape. Single-point isotherms may be misrepresentative because one could connect the zero-point and the measured non-zero point of an isotherm using an infinite number of possible curves, instead of a straight line as required by the linear isotherm model.

Local chemical equilibrium may not always exist between solutes and solid phases, a phenomenon that is quite common for many organic solutes (Brusseau et al., 1989, and references cited therein). Since the equilibration times for relevant actinides are not known, it is not possible to assess the impact of the assumption of local chemical equilibrium on radionuclide release.

The relative tendency for actinides to undergo complexation or sorption reactions is the following (Choppin, 1983):



### 2.5.1.5 Actinide Transport Capacity

In evaluating the potential impact of colloidal particles that may act as substrates for actinide sorption, a critical factor to examine is the amount of surface area available for adsorption.

Concentrations of actinides attached to the surfaces of carrier colloids can be estimated using simple geometry by assuming that the actinides are present as metallic actinide monolayers or by using ranges of values for adsorption site densities taken from surface complexation modeling research. The latter approach is more realistic.

The actinide concentration sorbed to a single mineral fragment type colloidal particle can be calculated by considering the geometrical surface area of a spherical particle:

$$[\text{An}]_p = \left( \frac{\pi \Phi^2 N_S}{N_A} \right) \quad (22)$$

where:

- $[\text{An}]_p$  concentration of an adsorbed actinide element (moles/particle)
- $\Phi$  spherical colloidal particle diameter (nm)
- $N_S$  adsorption site density (sites/nm<sup>2</sup>)

$N_A$  Avogadro constant

The upper bound for adsorption site density is generally limited by atomic-level spatial constraints at the surface of a mineral. Oxide adsorbents (e.g., goethite,  $\alpha$ -FeOOH), which tend to be quite powerful, have site densities between about 2 and 20 sites/nm<sup>2</sup> (Kent et al., 1988, Table 3-1). However, ternary adsorption systems, in which an intermediate material adsorbs onto a substrate and then acts as a substrate itself (i.e., a cosorbent), may increase the apparent site density by several orders of magnitude. For example, Righetto et al. (1991) demonstrated that complex organic molecules, such as humic acid, act as cosorbents in low-ionic strength dispersions of amorphous silica and alumina colloids and further increased transport of Am(III), Th(IV), and Np(V).

Using a reasonably large adsorption site density of 10 sites/nm<sup>2</sup> in equation (22) above, shows that 10 nm and 1  $\mu$ m diameter particles contain about 10<sup>-21</sup> and 10<sup>-17</sup> moles actinide per particle, respectively (Figure 10). Despite the four order-of-magnitude increase in actinide mass that can be carried by larger colloids, it is the very large number of smaller colloids that provide the bulk of the mobile surface area in many natural groundwaters. It is clear that a large colloidal particle population is required to have a significant impact on actinide transport. Stumm (1992, p. 246) stated that colloidal particles in natural groundwaters are "ubiquitous" and cited a typical concentrations from 10<sup>7</sup> to 10<sup>8</sup> particles/L. Based on that concentration range, the concentration of actinides associated with those colloids is on the order of 10<sup>-10</sup> moles/L, which is quite low compared to anticipated concentrations of dissolved actinides. For typical natural groundwaters, however, the estimate reported by Stumm is probably low. Additional discussion of populations of colloidal particles in natural waters is presented in Section 2.6.

#### 2.5.1.6 Potential Impact of Mineral Fragments at the WIPP

Considering the strong impact of ionic strength on kinetic destabilization of mineral fragment type colloidal particles and the high ionic strengths of the groundwaters associated with the WIPP, it is likely that mineral fragment type colloidal particles can be eliminated from further consideration as having a major potential impact on performance of the WIPP. This group of colloids includes many of the colloidal particles identified at other sites (see e.g., McCarthy and Degueldre, 1992, Table 6) and includes iron(III)-(hydr)oxides, clay minerals such as montmorillonite, and mineral constituents of the host rock. Colloidal particles produced from drilling (i.e., cuttings) and mineral precipitates formed from brine mixing are also included in this group.

In addition to laboratory confirmation of kinetic destabilization of mineral fragment type colloidal particles under WIPP-like conditions, several additional factors must be considered. First, the rate

of aggregation of colloidal particles is directly proportional to the number of colloidal particles present. At very low populations of colloidal particles, aggregation may occur rather slowly. The potential impact of that very low population of colloidal particles should be addressed. Second, in an intrusion scenario, entrainment of agglomerated colloidal particles should be addressed. Those questions, and particularly the first question, can be addressed in part with bounding calculations described in Section 2.6.1 and with proposed experiments described in Section 5.1.1.

## 2.5.2 Humic Substances

Humic substances are high-molecular-weight organic polymers that form from degradation of plant components in terrestrial and marine environments to form highly variable poorly-defined structures with complicated three-dimensional conformations (Figure 11). Humic substances are subdivided into several categories on the basis of solubility. Humin is the alkali insoluble fraction; humic acid is the alkali-soluble, acid insoluble fraction; and fulvic acid is soluble in both alkali and acid. Humic acids are refractory materials resistant to oxidation, and are eliminated by incorporation into sediments rather than by degradation. Humic substances are of particular concern in evaluating the performance of the WIPP because of their well-known capability of complexing with metal cations, including actinides (see, e.g., Choppin, 1988, Dearlove et al., 1990; Vlassopoulos et al., 1990; Tiller and O'Melia, 1993; Tipping, 1993; van der Lee et al., 1993, 1994).

### 2.5.2.1 Formation

High-molecular weight organic matter, which consists primarily of humic and fulvic materials, are generated by degradation of naturally occurring organic matter. High-molecular weight organic matter is typically found in soils, surface-waters, seawater, and in groundwaters present in shallow subsurface environments. Humic substances that form in marshes and swamps tend to have more condensed aromatic structures derived from lignin (a polyphenol), compared to humic substances that form in a marine environment from algae that have no lignin. Terrigenous humic substances form from soil-mediated microbial degradation of plant cell and wall material such as woody and herbaceous materials, which are composed primarily of lignin, cellulose, and tannins. Marine humic substances form by condensation, polymerization, and partial oxidation of smaller molecules such as triglycerides, sugars, and amino acids (Morel and Hering, 1993).

### 2.5.2.2 Surface Chemistry

Humic substances contain a large number of simple functional groups for complexation at the



surface of the molecules: phenolic OH, alcoholic OH, and carboxylic groups; most are carboxyl, the remainder are often assumed to be phenolic. In addition, amines, amino acids, thiols, disulfides, and polysulfides have been reported (Vlassopoulos et al., 1990). The reactivity of the functional groups is dependent on pH. Phenolic OH is not important as a reactive ligand until pH values become greater than about 8 (Sposito, 1984). There are steric effects (steric in the traditional organic chemistry sense) and complex interactions between the functional groups. Natural organic matter can also act as a cosorbent, increasing the amount of adsorption on minerals by several orders of magnitude. In systems with high concentrations of humic substances, the humic substances may coat the mineral surfaces so that humic substances become the dominant sorbent.

The behaviors of the functional groups can be simulated to a degree by model compounds (Morel and Hering, 1993, p. 377). The carboxylic groups can be investigated by examining acetate (an aliphatic monocarboxylic acid anion), malonate (an aliphatic dicarboxylic acid anion), and phthalate (an aromatic dicarboxylic acid anion). Phenolic groups can be investigated by evaluating catechol (a quinone, a dihydroxy phenolic acid anion). Also important is salicylate which has both a phenolic OH and a carboxyl functional group.

Two sets of experiments are generally required to quantify the behavior of ligands and trace metals. First, acid-base titrations are conducted to determine the protonation constant(s) for the ligand to provide information on the total concentration of deprotonated sites available for complexation. Second, metal-coordination experiments are conducted to determine the amount of metal that can be sequestered by the ligand under various chemical conditions. Those techniques generally work well for anthropogenic organic ligands such as EDTA, ascorbate, citrate, etc. For humic substances, however, the titration curve defining the acid-base character is "smeared" and does not have distinct inflection points to define the  $pK_a$ 's for the following reasons (Morel and Hering, 1993, pp. 379-380): (1) coordination sites may have a continuous range of affinities for metal ions and protons because of chemical and steric differences in neighboring functional groups; (2) the coordination properties of the molecule are dependent on the extent of cation binding and the ionic strength of the solution because of conformational changes from electrostatic interactions among the functional groups on the molecule; and (3) the metal complexation constant is dependent on the extent of cation complexation of the ligand because electrostatic attraction and repulsion from other ionized groups may affect the metal affinity.

Typically there are 10 to 20 milliequivalents per gram carbon (meq/gC) of titratable acid groups, and typically humic acid is 50 wt% carbon (Morel and Hering, 1993). For a humic substance concentration of 1 mg/L (consisting of 50 wt% C) in groundwater, a titratable acid group concentration of 20 meq/gC corresponds to  $10^{-5}$  moles/L of binding sites.

### 2.5.2.3 Specific Interaction with Electrolytes

Divalent cations, such as calcium and magnesium, diminish the tendency of humic acids to complex trace metals by shielding the electrostatic (coulombic) attraction of neighboring ionized functional groups (i.e., the oligoelectrolyte effect) and by decreasing the affinity of the ligand for the actinide (Morel and Hering, 1993). Trace metals do not compete effectively with each other for the same ligand as long as the total concentration of ligands is much greater than the total concentration of metals (i.e.,  $L_T > Me_T$ , where T indicates "total"; Morel and Hering, 1993, p. 375). An additional effect of electrolytes, is that the conformation of macromolecules become compressed (O'Melia and Tiller, 1993, p. 373; Stumm, 1993), slowing further complexation kinetics and decreasing solubility of the humics.

Approaches for modeling the complexation of inorganic ions with humic substances fall into three categories: 1) discreet ligand non-electrostatic models, 2) continuous distribution models, and 3) discrete ligand electrostatic models. Discrete ligand non-electrostatic models are based on approximating large humic molecules as a number of sites and site types. Each site type is defined in terms of a highly conditional stability constant and the effects of non-specific binding and ionic strength are neglected (Sposito and Mattigod, 1980; Alberts and Geisy, 1983). Continuous distribution models consider data for organic binding in terms of a statistical distribution function which simulates the polyfunctionality of the organic molecule and implicitly accounts for interference between sites and non-specific binding. Discrete ligand electrostatic models treat binding constants as comprised of an intrinsic component related to the thermodynamics of the reaction and an electrostatic component which varies and takes into account ionic strength effects and the total surface charge of the humic molecule (Crawford, 1993). One well-accepted model of this type has been proposed by Tipping (1993).

### 2.5.2.4 Potential Impact of Humic Materials at the WIPP

At the WIPP, humic materials may be introduced in three ways: (1) humic materials introduced along with the organic constituents of soil wastes; (2) in situ microbial degradation of cellulosic materials followed by condensation reactions to form humic materials; and (3) humic components of the naturally occurring organic matter present in Culebra brines. The dominant source of humic substances is from soil wastes.

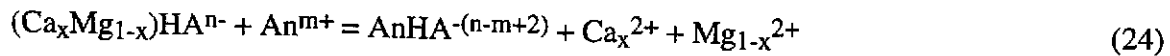
In WIPP brines, the concentrations of magnesium and calcium are on the order of 0.02 to 0.8 and 0.008 to 0.04 moles/L, respectively (Table 5). The total concentration of humic materials may be on the order of  $4 \times 10^{-4}$  moles/L (moles binding sites/L) on the basis of the bounding calculations conducted below. The actinide concentration is likely to be less, perhaps in the micromolar range. Summarizing, at the WIPP:

$$[\text{Mg}_T] \geq [\text{Ca}_T] \gg [\text{HA}_T] \gg [\text{An}_T] \quad (23)$$

where:

- $[\text{An}]_T$  total concentration of dissolved actinide-bearing ions (non-colloidal)
- $[\text{Mg}]_T$  total concentration of non-complexed magnesium (non-colloidal)
- $[\text{Ca}]_T$  total concentration of non-complexed calcium (non-colloidal)
- $[\text{HA}]_T$  total concentration of humic substances

Consequently, the capacity of humic acid for an actinide is decreased (Morel and Hering, 1993, p. 368) because of competition for humic sites by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ :



High calcium and magnesium concentrations will push the reaction to the left, reducing the amount of actinide (An) that is complexed with humic acid.

Humic substances are sufficiently small to enter the intercrystalline pore throats in the Culebra, and so would be retarded by diffusion into intercrystalline (i.e., matrix) pores. Parameters used to quantify the extent of physical diffusion of solutes are the free water diffusion constants, porosity, and tortuosity. The effective diffusion constant is then calculated from those parameters and is used in performance assessment calculations. For colloidal particles, effective diffusion constants can be estimated by modifying the free-water diffusion constant for dissolved actinides on the basis of sizes of dissolved actinides and colloidal particles, because the diffusion constant is inversely proportional to the radius of spherical particles (Hiemenz, 1986, p. 81). Humic materials are on the order of 10 nm or less in size, and will exist as compressed forms rather than elongated chains in a high ionic strength dispersant (Stumm, 1992, Figure 4-17). Dissolved actinides are on the order of 1 Å or greater in diameter. Consequently, the diffusion constant for humic substances can be estimated by reducing that for the dissolved actinides by at least a factor of 100 (see Section 2.4.3).

The free-water diffusion constants for the five actinide elements of particular importance to the WIPP are approximately the same, and range from  $1.0 \times 10^{-6} \text{ cm}^2/\text{s}$  for thorium to  $2.7 \times 10^{-6} \text{ cm}^2/\text{s}$  for uranium (mean =  $1.8 \times 10^{-6} \pm 0.6 \times 10^{-6} \text{ cm}^2/\text{s}$ , Reeves et al., 1991, Table 2.7; see also Sandia WIPP Project, 1992, Table 3.3-4). Using the diffusion constant reduction factor of 100, a mean value of about  $2 \times 10^{-8} \text{ cm}^2/\text{s}$  is a reasonable value for the free-water diffusion constant for humic substances. The modified free-water diffusion constant can then be used to determine the effective diffusion constant for the colloidal particle.

The total amount of soil that is expected to be buried in the repository has been estimated in the most current revision of the Baseline Inventory Report (US DOE, 1994c). Wastes primarily consisting of soil (Waste Matrix Codes 4000, 4100, 4200, and 4900) are generated by the Idaho National Engineering Laboratory (INEL) and the Hanford (Richland, Washington) Site (US DOE, 1994c, Tables 1-2, 5-2; Figure 5-8). Much of that Waste Matrix Code Group consists of non-soil materials (US DOE, 1994c, Figure 5-8).

The average concentration of soil in all waste streams scheduled to be buried at the WIPP is  $5.3 \text{ kg/m}^3$  (US DOE, 1994c, Table 6-2). Multiplying that estimated concentration by the total volume of the repository ( $1.756 \times 10^5 \text{ m}^3$ ) provides an estimate of the total average inventory of soil at the WIPP. The maximum concentration of actinides sorbed to humic substances in the WIPP soil wastes with bounding calculations using the following assumptions: (1) the soil contains 1 wt% organic material; (2) the organic material contains 20 wt% humic substances that is kinetically stable in WIPP brines; (3) the concentration of binding sites on the humic substances (titratable acid groups such as carboxyl, alcoholic hydroxyl, phenolic hydroxyl groups, etc.) is  $20 \text{ meq/gC}$  (Morel and Hering, 1993); (4) the humic substance consists of 50 wt% carbon; and (5) the volume of the repository filled with brine is  $5 \times 10^4 \text{ m}^3$ . The experimental program described below is anticipated to demonstrate that values for assumptions (2) and (3) are much too large. The maximum complexation capacity of the humic substances is:

$$[\text{An}] = \frac{(5.3 \frac{\text{kg}}{\text{m}^3})(1.756 \times 10^5 \text{ m}^3)(0.2 \text{ wt\% humics})(20 \frac{\text{eq}}{\text{kgC}})(50 \text{ wt\% C})}{(5 \times 10^4 \text{ m}^3)(10^3 \frac{\text{L}}{\text{m}^3})} \quad (25)$$

which amounts to  $4 \times 10^{-4} \text{ eq/L}$  (or  $40 \text{ mg/L}$  humic substances). Using that value, the maximum concentration of an actinide element potentially mobilized by humic substances ranges from  $1 \times 10^{-4} \text{ moles/L}$  to  $4 \times 10^{-4} \text{ moles/L}$ , corresponding to tetravalent (e.g.,  $\text{Th}^{4+}$ ) and univalent [e.g.,  $\text{Pu(V)O}_2^+$ ] ions.

### 2.5.3 Actinide Intrinsic Colloids

Actinide intrinsic colloids (also known as true colloids, real colloids, type I colloids, and Eigenkolloide) form by condensation reactions of hydrolyzed actinide ions and consist solely of actinide cations linked by anions. As discussed below in detail, there are several stages in the development of actinide intrinsic colloids at which they have significantly different behaviors. Depending on their stage of maturation, actinide intrinsic colloids display physicochemical properties that are similar to mineral-fragment type colloidal particles and humic substances.

### 2.5.3.1 Intrinsic Colloids of Plutonium

The most well-known and well-studied actinide intrinsic colloid is the Pu(IV) intrinsic colloid, which has been used as a basis of comparison for investigating intrinsic colloids of other actinides. Most of the knowledge about the Pu(IV) intrinsic colloid comes from research at high Pu concentrations in highly acidic solutions, which was conducted to help improve the efficiency of processing techniques (see, e.g., Kraus, 1956; Ockenden and Welch, 1956; Costanzo et al., 1973; Bell et al., 1973a,b; Johnson and Toth, 1978; Lloyd and Haire, 1978; Cleveland, 1979a; Toth et al., 1981). The Pu(IV) intrinsic colloid is notorious in its propensity to polymerize to form a gel-like material, which can even plug process lines (Katz et al., 1986). Evaluation of transport in most natural waters, of course, involves near neutral pH values (usually 6 to 9), and low concentrations of actinides. Reviews and investigations focusing on chemical conditions relevant to environmental concerns have been conducted more recently (Cleveland, 1979b; Rai and Swanson, 1981; Kim et al., 1984a, Kim, 1992; Nitsche et al., 1992, 1994).

A conclusive demonstration of the mechanisms of formation of the Pu(IV) intrinsic colloid has not yet been made, but there is a preponderance of evidence that suggests that polymerization is strongly linked to hydrolysis, and that the initial polymerization, or condensation, produces a macromolecule that becomes progressively more crystalline with time (Figure 12). The polymer is generally recognized as having a stoichiometry of  $n\text{Pu}(\text{OH})_2^{2n+}$  (aq), although the charge on each nucleus is not divalent, but is closer to +0.4 to +0.8. The final mature colloid has a composition between  $\text{Pu}(\text{OH})_4$  (am) and  $\text{PuO}_2$  (c), although the latter compound may be only partly crystalline and both may include interstitial water molecules.

A complicating factor in interpreting published literature describing the past four decades of research on the Pu(IV) intrinsic colloid is the inconsistent use of terminology describing behaviors related to chemical equilibria and colloid chemistry. To be more precise in further discussion, we define the following terms:

- (1) Pu(IV) intrinsic colloid is used as a general term for all stages of development of the Pu(IV) colloidal particle.
- (2) Pu(IV) polyelectrolyte is a dissolved macromolecular colloidal particle with an ionic charge. The Pu(IV) polyelectrolyte is synonymous (when used precisely) with the "fresh" Pu(IV)-polymer or the "fresh" Pu(IV) colloid as used in the literature. As a dissolved macromolecule, the Pu(IV) polyelectrolyte is similar to humic substances described in Section 2.5.2 (in traditional terms, a hydrophilic colloid). Kraus (1956, p. 248) made a similar observation by comparing actinide polymers to

organic polyelectrolytes.

- (3) Pu(IV) mineral fragment type colloidal particle is an amorphous or crystalline solid colloidal particle that behaves like the mineral fragment type colloidal particle described in Section 2.5.1 (in traditional terms, a hydrophobic colloid). The Pu(IV) mineral fragment colloid is synonymous (when used precisely) with the "aged" Pu(IV) polymer or "aged" Pu(IV) colloid as used in the literature.
- (4) For actinide intrinsic colloids (as well as other systems), we use the term precipitation to mean chemical precipitation due to exceeding a solubility product according to chemical equilibria, and the term coagulation to mean kinetic destabilization by electrostatic phenomena to form an agglomerate of particles.

Recognizing the distinction between polyelectrolyte and mineral fragment type colloidal particles is particularly important for evaluating the impact of actinide intrinsic colloids on the performance of the WIPP Site, because of the different kinetic stability behaviors of those colloidal particles in electrolytes. In Section 2.5.1.3, we suggest that mineral fragments are not kinetically stable in WIPP brines. Actinides adsorbed on those colloidal particles are not mobile. In contrast, the kinetic stability behavior of polyelectrolytes, including humic substances and Pu(IV) polyelectrolyte, in WIPP brines is not as straight forward.

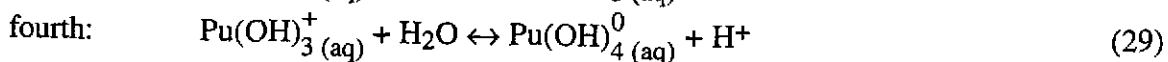
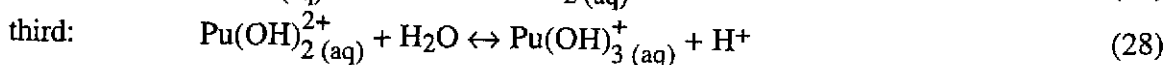
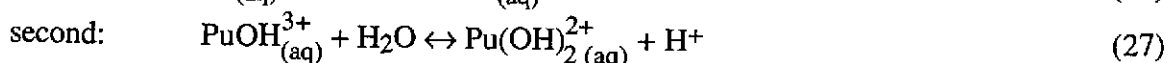
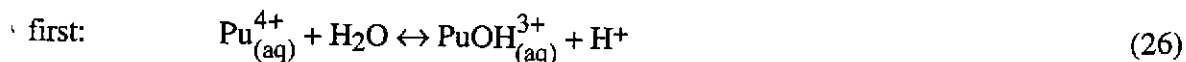
Because of the propensity for the Pu(IV) aquo ion to polymerize immediately after hydrolysis, most of the experiments on the formation of Pu(IV) intrinsic colloids begin with an extremely acidic stock solution (e.g., concentrated HNO<sub>3</sub>). As the pH of the acidic Pu(IV) aquo ion stock solution is increased by the addition of water or base, the first hydrolysis reaction is instantaneous, and polymerization to form the Pu(IV) polyelectrolyte occurs nearly instantaneously thereafter, which results in a bright apple-green-colored dispersion. The tendency for polymerization is so strong that determination of acceptable thermodynamic constants for the second, third, and fourth hydrolysis reactions have not been particularly successful.

The mechanisms for the subsequent condensation and maturation steps are less clear. The mature Pu(IV) mineral fragment type colloidal particle produced at temperatures near 25°C appears to be an amorphous to partly crystalline plutonium dioxide or hydroxide with *d*-spacings suggestive of PuO<sub>2</sub>. On the basis of density measurements, Rundberg et al. (1988) suggested that it may be PuO<sub>2</sub> with waters of hydration. The maturation steps are accelerated as temperature is increased. At 100°C, for example, a crystalline PuO<sub>2</sub> Pu(IV) mineral fragment type colloidal particle is produced.

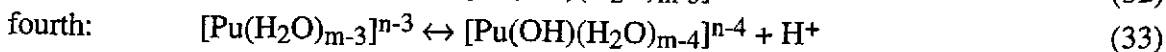
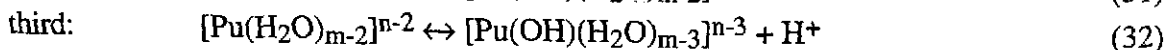
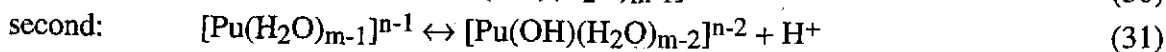
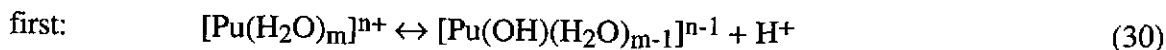
The most convincing and consistent explanation for the chemistry of the Pu(IV) intrinsic colloid is presented by Johnson and Toth (1978) of Oak Ridge National Laboratory. Those authors

developed a conceptual model to explain the solution chemistry of a variety of metal cations and a variety of oxidation states. The conceptual model involves processes referred to as "olation" and "oxolation" in which metal cations become bridged with hydroxyl groups, which in turn undergo irreversible elimination of water and concurrent formation of oxygen bridges. Johnson and Toth demonstrate that the model is consistent with the observed behavior of the Pu(IV) intrinsic colloid.

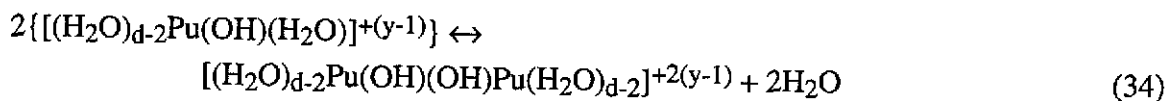
Hydrolysis reactions for metal cations such as plutonium may be written as follows:



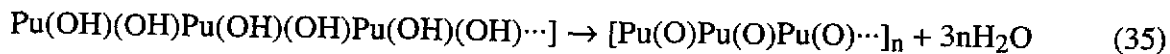
Johnson and Toth point out, however, that in interpreting the formation of the Pu(IV) intrinsic colloid, it makes better sense to include the implied waters of hydration that surround metal cations in solution. Hydrolysis equations (26) through (29) can be rewritten as follows, where n equals 4:



From the literature, it is clear that polymerization occurs nearly immediately after the first hydrolysis occurs (30). Johnson and Toth suggest the following reaction involving polymerization of two hydrolyzed species by loss of water (oxolation):



Aging or maturation of polymer then occurs by loss of water (olation) as follows:



Maiti et al. (1989) and Laul et al. (1985) describe similar reactions, but it appears as though they believe that the third hydrolysis reaction occurs, because they use the  $\text{Pu}(\text{OH})_3^+_{(\text{aq})}$  ion in their proposed polymerization reaction. Use of that ion does not appear to be consistent with observations by many workers that polymerization occurs immediately after the first hydrolysis

reaction.

A unique interpretation of the chemistry of Pu(IV) intrinsic colloids was presented by Lloyd and Haire (1978), also from Oak Ridge National Laboratory. Those authors conclude that what we refer to herein as Pu(IV) polyelectrolyte is not a polymer at all, but consists, in their terms, of a secondary aggregation of primary particles (in other words, coagulated mineral fragment type colloidal particles). Whereas the implications of that conclusion would be advantageous for the WIPP Site, their conclusions do not appear to be consistent with observations of the behavior of the initial Pu(IV) intrinsic colloid as a function of dispersant composition, electrolyte concentration, and reversibility of reactions.

Johnson and Toth (1978) noted that the Pu(IV) polyelectrolyte has a small positive charge (probably measured at low pH) and is precipitated by molar equivalents of nitrate, iodate, sulfate, oxalate, phosphate, and ferricyanate. In their review, Katz et al. (1986) reported that the positively charged polyelectrolyte can be precipitated by adding approximately 0.15 M of anions such as phosphate ( $\text{PO}_4^{3-}$ ), ferricyanate ( $\text{Fe}(\text{CN})_6^{3-}$ ), iodate ( $\text{IO}_3^-$ ), or oxalate ( $\text{H}_2\text{C}_2\text{O}_3^-$ ), regardless of charge or the type of anion. If the initial Pu(IV) intrinsic colloid were a mineral fragment type colloidal particle, it is likely that it would be destabilized by the 0.15 M salt concentration, especially for the trivalent anions (refer to section 2.5.1.3). In contrast, if the initial Pu(IV) intrinsic colloid is a polyelectrolyte, it is reasonable that anions could destabilize the colloid by specific interaction with surface moieties (much like Ca and Mg are able to destabilize negatively charged humic substances; refer to section 2.5.2). It is interesting to note that at least some of the anions cited are not particularly inert (see section 2.5.1.1). One of the methods used to disperse the Pu(IV) polyelectrolyte is the addition of dilute hydrochloric or nitric acid (Lloyd and Haire, 1978, p. 147). To produce kinetically stable dispersions of Pu(IV) polyelectrolyte at plutonium concentrations less than about 0.1M, the anion to plutonium molar ratio must be between 0.8 and 4 (Lloyd and Haire, 1978). Those dispersant concentrations are far more concentrated than the c.c.c. for mineral fragment type colloidal particles. The stability is apparently imparted by specific interaction of the  $\text{Cl}^-$  or  $\text{NO}_3^-$  anions with the positively charged Pu(IV) polyelectrolyte.

As part of the investigation discussed above, Lloyd and Haire (1978) conducted electron microscopy and diffraction analyses to determine the morphology, mineralogy, and crystallinity of the initial and aged Pu(IV) intrinsic colloids. Their microscopy appears to be very well done, but we question whether dehydrating the Pu(IV) polyelectrolyte sol would alter the composition of the colloidal particles. It is likely that the mature Pu(IV) mineral fragment type colloidal particle has not been denatured by dehydration. In fact Johnson and Toth (1978, p. 9) allude to this potential problem by stating that "... attempts to crystallize ("fresh" Pu-polymer) merely results in aging, loss of water, and the formation of the more stable  $\text{PuO}_2$  structure." It is also not surprising that if a polyelectrolyte were dehydrated, it would produce a diffraction pattern indicative of an



amorphous material.

It has been well demonstrated that the Pu(IV) intrinsic colloid becomes progressively more inert as it matures and efforts at converting it back to Pu(IV) aquo ion becomes increasingly more difficult. That observation also suggests that the intrinsic colloid initially consists of a polyelectrolyte that ages to become a mineral fragment type colloidal particle. Once maturation reactions have proceeded to produce a mineral fragment type colloidal particle, dissolution becomes very difficult. In fact, in his review, Kraus (1956), refers to the process of transformation of the Pu(IV) polyelectrolyte to a mineral fragment type colloidal particles as an "... 'irreversible' process ...," a recurring theme in later publications (e.g., Cleveland, 1979a,b). Realistically, the dissolution of the mature Pu(IV) mineral fragment type colloidal particle is not irreversible, but is simply very slow even under fairly harsh chemical conditions. Evidence from different rates of centrifugation and different absorption spectra of the "fresh" and "aged" Pu(IV) intrinsic colloid provide additional evidence that the two colloidal particles are significantly different in density and chemical composition (Ockenden and Welch, 1956, p. 3362).

A significant effort has been expended in controlling polymerization and depolymerization reactions to improve processing techniques. Polymerization is promoted by increased pH values, increased temperature, increased plutonium concentrations, and low concentrations of actinide complexants (Toth et al., 1981). For example, Rai and Swanson (1981) showed that, whereas the concentration of Pu<sup>4+</sup> aquo ion needs to be about 10<sup>-2</sup> M for the formation of Pu(IV) polyelectrolyte at pH 1, the minimum Pu<sup>4+</sup> aquo ion concentration required for polymerization decreases to about 10<sup>-7</sup> M at neutral pH. Competition of organic and inorganic complexants with polyelectrolyte formation is particularly intriguing in light of the expected waste forms at the WIPP. The pH required to accomplish nearly complete polymerization of an approximately 10<sup>-5</sup> M Pu(IV) aquo ion solution is increased by several pH units by the presence of nitrate, perchlorate, and bicarbonate ions in millimolar to molar concentrations. For organic complexants, the following even more dramatic increase in pH values is required:

organic anion	[anion]	pH for 90% polymerization
acetate	$5 \times 10^{-2}$ M	5.7
phthalate	$1 \times 10^{-1}$ M	7
citrate	$5 \times 10^{-4}$ M	$\geq 11$
ethylenediaminetetraacetate (EDTA)	$1 \times 10^{-4}$ M	$\geq 11$
diethylenetetraaminepentaacetate (DTPA)	$5 \times 10^{-4}$ M	$\geq 11$
triethylenetetraaminehexaacetate (TTHA)	$1 \times 10^{-4}$ M	$\geq 11$
2,2'-bis[di(carboxymethyl)-amino]diethyl ether (BAETA)	$1 \times 10^{-4}$ M	$\geq 11$

Of the ligands listed, acetate, citrate, and EDTA are present in WIPP waste. It is not known whether the remaining organic complexants will be present, but a variety of similar complexants will be (refer to Section 2.2.1; Table 3).

The explanation developed by Lloyd and Haire (1978) for the development of the Pu(IV) intrinsic colloid does not seem consistent with the numerous comments in the literature about Pu(IV) intrinsic colloid plugging process pipes. It is not likely that a mineral fragment type colloidal particle would be able to produce a floc with sufficient shear strength to cause clogging. Montmorillonite is an exception, in that it is known to form a gel. However, the unusual rheological properties of montmorillonite result from the formation of edge-to-face flocs because of the difference in surface charges on those surfaces (refer to van Olphen, 1991).

The formation of polymers has been reported to be a non-equilibrium process (Cleveland, 1979a). However, Savage and Kyffin (1986) showed that early in the polymerization process, polymerization could be reversed by acidification or by adding strong oxidizers such as fluorine or Ce(IV). The reversal of the polymerization process becomes increasingly difficult with time (Ockenden and Welch, 1956). Kim and Kanellakopoulos (1989) and Kim (1992) proposed a three-way equilibrium between  $\text{Pu}(\text{OH})_4(\text{am})$ , Pu(IV)-polymer, and the  $\text{Pu}^{4+}$  aquo ion. Again, our interpretation of discussion of equilibria and non-equilibria in the polymerization process presented in the literature is that the entire sequence is governed by chemical equilibria, but that the backwards reaction (i.e., dissolution of the Pu(IV) polymer) becomes increasingly difficult as the polyelectrolyte matures to a mineral fragment type colloidal particle. In other words, the backwards reaction is not kinetically favorable.

Rai and Serne (1978) and Rai and Swanson (1981) demonstrated that the solubilities of  $\text{Pu}(\text{OH})_4(\text{am})$  and Pu(IV)-polymer are similar and concluded that the concentration of  $\text{Pu}^{4+}$  aquo

ions had to exceed the concentration required for the precipitation of  $\text{Pu}(\text{OH})_{4(\text{am})}$ . Those workers also showed that, whereas the concentration of  $\text{Pu}^{4+}$  aquo ion needs to be about  $10^{-2}$  M for the formation of Pu(IV)-polymer at pH 1, the minimum  $\text{Pu}^{4+}$  aquo ion concentration required for polymerization decreases to about  $10^{-7}$  M at neutral pH. It is not known what effect ionic strength would have on minimum required concentrations. Nitsche et al. (1992) found that Pu(IV)-polymer added to Culebra brine simulants (hydrochemical facies C; see Section 2.3) to produce a concentration of  $10^{-8}$  M, resulted in chemically stable conditions for the polymer. No significant changes in polymer concentration were observed over a period of several hundred days.

A broad range of sizes has been reported for the Pu(IV) actinide intrinsic colloid, ranging from 1 to hundreds of nanometers. Triay et al. (1991) found that sizes ranged from about 1 to 370 nm, but that most were between about 2 and 6 nm. Rundberg et al. (1988) measured maximum widths of  $^{242}\text{Pu}(\text{IV})$  colloidal particles at  $2.9 \pm 0.2$  nm. They reported that  $^{239}\text{Pu}(\text{IV})$  colloidal particles were larger, with mean particles sizes of about 200 nm. They suggested, however, that the relatively large size of the particles of the latter isotope might be due to aggregation of 2 nm particles. That suggestion is consistent with observations by Lloyd and Haire (1978), who showed that the aged polymer actually consists of nanometer-sized mineral crystallites. Estimates of the number of plutonium ions contained in the aged polymer (actually a mature, or partially mature, Pu(IV) mineral fragment type colloidal particle) as large as  $10^{10}$  molecules were reported by Johnson and Toth (1978). Rundberg et al. (1988) reported that the density of the Pu(IV) intrinsic colloids was  $9.0 \pm 2.0$  g/cm<sup>3</sup>. They attributed the disparity between that measured density and the density of  $\text{PuO}_{2(\text{c})}$ , 11 g/cm<sup>3</sup>, to hydrolyzed surfaces or the presence of water in intercrystalline pores in the colloidal agglomerate. Similarities in densities lends further credibility to our polyelectrolyte interpretation of the polymerization process.

### 2.5.3.2 Intrinsic Colloids of other Actinides

Reference is made to a variety of intrinsic colloids of other actinides, but no systematic investigations of their formation and behaviors appear to have been made. Plutonium is apparently unique in its propensity to form an intrinsic colloid. To our knowledge, no mention is made in the literature of maturation of polyelectrolytes of other actinides to form mineral fragment type colloidal particles as plutonium does.

In general, the tendency of actinides to hydrolyze and to polymerize to form intrinsic colloids follows the order:



where An represents an actinide element (Cleveland, 1979a,b; Choppin, 1983; Kim, 1992; Lieser et al., 1991, p. 119). The order of oxidation states in the equation above results from the ionic charge to ionic radius ratios (Table 6). The tendency for hydrolysis of  $\text{An(VI)O}_2^{2+}$  is greater than for  $\text{Pu}^{3+}$  because the effective charge on the central cation on the linear  $[\text{O-An-O}]^{2+}$  ion is  $3.3 \pm 0.1$ , slightly greater than 3. This trend generally holds true for the actinide elements in general, because of the very small changes in ionic radii among the actinide elements (this is the oxidation state analogy; refer to Novak, in review). There are differences in the behaviors of the actinides from element to element that stem from very subtle changes in the charge to radius ratio and the nature of the configuration of the f molecular orbital.

Considering Pu as an example, hydrolysis becomes significant for  $\text{Pu}^{4+}$ ,  $\text{Pu(VI)O}_2^{2+}$ ,  $\text{Pu}^{3+}$ , and  $\text{Pu(V)O}_2^+$  at pH values of <1, 4-5, 6-8, and 9-10, respectively (Choppin, 1983). On the basis of the hydrolysis trend, it is not likely that An(III) and An(V) actinides will form actinide intrinsic colloids. That group includes  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Pu(V)O}_2^+$ , and  $\text{Np(V)O}_2^+$ . There are suggestions in the literature, however, that  $\text{Am}^{3+}$  may form an intrinsic colloid, which is surprising because it does not undergo hydrolysis until relatively high pH values. Thorium does not follow the trend described by equation (36) because its large size makes it resistant to hydrolysis (Cotton and Wilkinson, 1988). Nevertheless, thermodynamic data suggest that in almost all environments (near neutral or higher pH) thorium exists as  $\text{Th(OH)}_4^0_{\text{(aq)}}$ . Moreover, thorium has been reported to form a polymer (Kraus, 1956; Johnson and Toth, 1978).

Examples can be found in the literature of polymeric species of many of the actinides of importance to WIPP (see e.g., Baes and Mesmer, 1976; Kim, 1992). It is important, however, to note the sizes of polymers described in the literature. It is well known that as polyvalent metals, the actinides can form polynuclear species, but they are largely lower polymers (i.e., oligomers) such as dimers, trimers, tetramers, and hexamers (see, e.g., Choppin, 1983, p. 46). However, in terms of physical transport behavior, lower polymers will behave no differently than dissolved monomeric species. In contrast, the higher polymers, such as the Pu(IV)-polymer, may reach colloidal sizes (1 nm to 1  $\mu\text{m}$ ) and will have different hydrodynamic properties than the sub-colloidal-sized dissolved species. Johnson and Toth (1978) reported a molecular weight of 4000 for a Th polymer. Assuming that it consisted of  $\text{Th(OH)}_4$ , that polymer would consist of about 13 thorium metal ions (i.e., the degree of polymerization number, N). That observation is consistent with Kraus (1956), in which he quotes an N value of about 9 for Th polyelectrolyte.

Empirical evidence published in the literature does not always support the suggestion that Am, as a trivalent cation, will form an intrinsic colloidal particle. Avogadro and de Marsily (1984) suggested that, like Pu, Am is a likely candidate to form an insoluble hydroxide. Buckau et al. (1986) reported the formation of Am(III) intrinsic colloids at near neutral pH conditions, with a

particle size greater than 1 nm. In their study of the hydrolysis of Am(III) over a pH range from 3 to 13.5, however, Kim et al. (1984a) found only monomers of Am. Regardless of whether Am(III) intrinsic colloids will form under highly idealized laboratory environments, it would be highly unlikely that they would form in a geologic system, because of the tremendously strong sorption properties of the Am(III) ion.

### 2.5.3.3 Potential Impact of Actinide Intrinsic Colloids at the WIPP

Using the "oxolation-olation" conceptual model used by Johnson and Toth (1978) described above, the concentration of mobile actinides associated with actinide intrinsic colloids will vary depending on the relative proportion of the immature actinide polyelectrolyte form or the mature actinide mineral fragment type colloidal particle form.

There is ample evidence in the literature that the slightly positively charge polyelectrolytes would sorb onto a wide variety of materials in the repository environment and in the Culebra, if they were to be transported to the Culebra. The pH of zero-point-of-charge ( $\text{pH}_{\text{zpc}}$ ), which defines the pH at which those substrates are neutrally charged, for geologic substrates which have protons as the potential-determining ion (PDI) is presented in Table 7. At pH values below and above the  $\text{pH}_{\text{zpc}}$ , those geologic substrates will be positively and negatively charged, respectively. As can be appreciated from those  $\text{pH}_{\text{zpc}}$  values, many geologic substrates are likely substrates for sorption of the positively charged actinide polyelectrolytes. Ockenden and Welch (1956) showed that "fresh" Pu(IV) intrinsic colloid (i.e., polyelectrolyte) sorbs to artificial substrates that are expected to be present in the WIPP repository. They observed significant levels of sorption on glass ( $1.6 \mu\text{g Pu(IV)/cm}^2$ ), polished steel ( $4 \mu\text{g/cm}^2$ ), and unpolished steel ( $11 \mu\text{g/cm}^2$ ).

As the actinide polyelectrolytes mature through the olation process to become closer in composition to an actinide-oxide mineral, they will be kinetically destabilized by the high ionic strengths of the WIPP brines, and will not be mobile. Further, the solubilities of the mature solid phase cannot be exceeded. In fairly long-term experiments, Nitsche et al. (1992, 1994) showed that the concentration of Pu(IV) intrinsic colloid stabilized at about  $10^{-8}$  M. It is not known whether the form was Pu(IV) polyelectrolyte or Pu(IV) mineral fragment type colloid.

### 2.5.4 Microbes

Potentially important colloidal sized microorganisms include bacteria, fungi, yeast, and protozoa. Fungi and yeast are not important for the WIPP Site because of the anticipated anoxic environment of the repository. For the WIPP Site, we focus on the halophilic and halotolerant microbes that have been identified at the Site (see Brush, 1990; Francis and Gillow, 1994). Microbes are

important to consider in performance assessments of the WIPP because they may significantly affect the characteristics of the waste stored at the WIPP, but also participate in transport of actinides in the event of human intrusion. Microbes are known to actively bioaccumulate actinides intracellularly as well as act as substrates for passive extracellular sorption (Francis, 1985, p. 299, and references cited therein).

At the WIPP Site, concentrations of naturally occurring microbes are on the order of  $10^4$  to  $10^7$  cells per milliliter (Francis and Gillow, 1994, Table 1). In the presence of nutrients provided by WIPP waste constituents, including nitrates, sulfates, and cellulosic materials such as protective clothing and wood, the population of microbes is likely to increase. Lysis, a natural phenomenon whereby cells die and release their cell constituents to the solution, also provides a source of nutrients to microbes.

Below a certain radiation dose threshold, the impact of radiation and radionuclides on microbe population will not be significant because microbes routinely develop radioresistant strains. Laboratory experiments have shown, however, that microbial growth is completely halted at about  $2.7 \times 10^5$  pCi/mL of radioactivity (Francis, 1985).

#### **2.5.4.1 Interaction with Electrolytes**

The outer cell membrane contains polysaccharides which essentially act as steric stabilizing compounds (see Section 2.5.1.3). It is not clear whether those steric stabilizing effects are sufficient to render microbes kinetically stable in the very high ionic strengths of brines associated with the WIPP.

#### **2.5.4.2 Transport of Microbes**

In a microbial system, a biomass is generated that includes the actively growing cells, as well as fragments of dead cells which have been produced by lysis. In terms of transport, those two components of the biomass are likely to behave differently. The transport behavior of the bioaccumulated actinides will, of course, follow the transport behavior of the microbes and in general will be different from the transport behavior of solutes. The cell fragment portion of the biomass has been observed (Sonnenfeld, 1984) but its impact on radionuclide transport is not known. It may be appropriate to treat the remains of microbes as naturally occurring organic material, which have been discussed in Section 2.5.2.

Microbial processes may also indirectly affect colloidal actinide transport and retardation behavior by affecting the chemistry of dissolved radionuclides. Microbial processes change pH and Eh,

which may affect the oxidation state of radionuclides and other chemical properties such as adsorption and solubility. Microbes are also known to facilitate leaching or dissolution of various metals. Many subsurface microbes can metabolize a wide variety of naturally occurring organic compounds and ones present in the waste. The microbial metabolites and decomposition products often have quite different chemical reactivities and may significantly alter the solubility and transport behavior of radionuclides.

Field studies have shown that pathogens may travel large distances (e.g., Gerba and Goyal, 1985). Sorption studies have shown, however, that sorption of microbes to solids can be significant. Like sorption involving inorganic solutes and substrates, sorption of microbes is sensitive to ambient chemical environment, including the chemical composition of the liquid and the solid surfaces, ionic strength, and the presence of organic compounds and minerals (see, e.g., Gerba and Bitton, 1984; Enfield et al., 1989; Mills et al., 1994). Moreover, it has been observed in laboratory experiments that bacteria and viruses form agglomerates under many environmental conditions, which may clog porous media and slow down or block subsequent transport of solutes and colloids (see McDowell-Boyer et al., 1986, 1987, and references cited therein).

The transport behavior of microbes has not been extensively investigated in the laboratory. In one of the earliest laboratory transport studies of microbial transport, Smith et al. (1985) produced breakthrough curves that did not support the linear or Langmuir isotherm model for microbe sorption observed in later batch sorption studies by Mills et al. (1994) and other investigators. Although the shape of those breakthrough curves does not rule out the linear or nonlinear isothermal sorption behavior, it does indicate the possibility of other colloid transport processes in effect. Because microbes are typically one micrometer or larger in size, they are very likely to move through larger pores at a greater than average flow rate (see Section 2.4.1). Microbes may also be filtered out more readily than other smaller colloidal particles, although Smith et al. (1985) did not observe any loss of bacteria due to filtration or any other process. It is also not clear whether the structures are sufficiently rigid to preclude their transport into pore throats roughly equivalent to their mean diameters.

#### **2.5.4.3 Potential Impact of Microbes at the WIPP**

Research conducted to date on the impact of microbes on the performance of the WIPP has largely been directed at quantifying the concentration of gases that microbes generate as a byproduct of their metabolism, and include carbon dioxide, nitrous oxide, hydrogen sulfide, and methane. As part of the disposal-room gas-generation program, a broad base of knowledge has been gained about microbial activity in WIPP brines (Francis and Gillow, 1994, and references cited therein). Some of that information can be used to bound the concentration of actinides that could be transported by microbes.

The maximum concentration of actinides sorbed on or contained within an individual microbe is limited by geometrical constraints such as the size and surface area of the microbes and sorption site density. However, the total concentration of bioaccumulated actinides, a function of the concentration of microbes, must not result in environmental conditions that produces so much radiation that growth of the microbe colonies is hindered or stopped. For example, Francis (1985) showed experimentally that at radiation levels on the order of  $3 \times 10^7$  pCi/L, growth of bacteria, cultured from samples collected at the Maxey Flats, Kentucky disposal site, began to be inhibited.

Because the relative uptake of different actinide elements due to bioaccumulation is not known, it is not possible to determine explicitly the maximum concentration of actinides that could be bioaccumulated without producing so much radiation that growth is inhibited. Estimates can be made assuming that uptake of the five actinides of particular importance to the WIPP occurs proportionately. Using information on the WIPP waste inventory tabulated in the Baseline Inventory Report (US DOE, 1994c), mean radiation levels of Am, Np, Pu, Th, and U were determined to be approximately  $2 \times 10^{12}$  pCi/mole actinide (Table 4). Coupling that value with the threshold survivability value in the example cited above,  $3 \times 10^7$  pCi/L, indicates that the upper bound on concentrations of actinides that could be bioaccumulated by microbes is on the order of  $10^{-5}$  moles/L.

Using simple calculations based on limitations imposed by geometrical considerations, bounding estimates can be made for extracellular bioaccumulation (i.e., sorption of metal cations on the outer surfaces of the microbes) and for intracellular bioaccumulation (i.e., active uptake of metal cations by the microbe). The information available to make those calculations is described in the following paragraphs.

Measured concentrations of halophilic bacteria in repository (G-Seep; see Section 2.3) brine range from  $7 \times 10^4$  to  $3 \times 10^6$  cells/mL (Francis and Gillow, 1994). Concentrations of microbacteria in brines at the surface near the WIPP Site are greater, presumably because of more readily accessible nutrients, and range from  $6 \times 10^6$  to  $1 \times 10^7$  cells/mL (Francis and Gillow, 1994). The microbes are spherical or rod-shaped, with dimensions on the order of 1 to 2  $\mu\text{m}$ . Maximum adsorption site density of mineral substrates is typically on the order of 1 sites/nm<sup>2</sup>, although the site density may be as high as 10 sites/nm<sup>2</sup> in some particularly strongly sorbing minerals (e.g., goethite,  $\alpha\text{-FeO}\cdot\text{OH}$ ) under certain conditions. No equivalent information is available for microbes, but 1 sites/nm<sup>2</sup> is a reasonable site density, considering that the effective site density will be reduced by competition from other metal cations. Assuming a relatively large steady-state population of microbes of  $1 \times 10^7$  cells/mL, large spherical microbes with diameters of 2  $\mu\text{m}$ , and sorption site densities of 1 site/nm<sup>2</sup>, the concentration of actinides that could be sorbed extracellularly is  $2 \times 10^{-7}$  moles/L, corresponding on average to about  $5 \times 10^5$  pCi/L.



To estimate maximum concentrations of actinides bioaccumulated intracellularly, the following calculation was done by arbitrarily assuming that a dense form of actinide filled about 5 volume percent of the internal volume of the relatively large microbes. Using the molar concentration of Pu in crystalline PuO<sub>2</sub> (obviously an extreme case) calculated using cell parameters from Katz et al. (1986, Table 7.65; cubic,  $a=5.396 \text{ \AA}$ ,  $Z=4$ ) the concentrations of actinides bioaccumulated intracellularly are about  $1 \times 10^{-4}$  moles/L. That value is an order-of-magnitude greater than the  $10^{-5}$  moles/L threshold concentration calculated on the basis of radiation effects. Intracellular bioaccumulation is likely to be hindered due to size or steric (used in chemical rather than colloidal parlance) exclusion effects if actinides are complexed with organic ligands. Intracellular bioaccumulation is also not likely to concentrate actinides in as dense a form as PuO<sub>2</sub>.

The maximum concentration of total actinides potentially transportable by a large microbe population, therefore, cannot be greater than about  $10^{-4}$  moles/L based on geometrical constraints, and is likely to be at least an order of magnitude less,  $10^{-5}$  moles/L, because of radiation effects. Radiation effects alone may reduce the maximum potential concentration more, because of greater toxicity effects from  $\alpha$ -particle emitters such as plutonium.

## 2.6 Case Studies

To gain an appreciation for the potential impact of colloidal particles on the performance of the WIPP Site, it is useful to consider results from other sites. Several extensive studies have been performed to investigate the nature and abundance of colloidal particles in naturally occurring groundwaters and surface waters, at natural analog sites, and at anthropogenically contaminated sites (e.g., Fillela and Buffle, 1993; McCarthy and Degueldre, 1992; Penrose et al., 1990; Triay et al., 1995). Tables 8a and 8b present the compilations by McCarthy and Degueldre (1992), divided into results compiled from shallow subsurface sites and deep subsurface sites, respectively. Figure 13 shows typical concentrations of colloidal particles at several sites.

It is striking that most of the colloidal particles reported at the various sites are mineral fragment type colloidal particles that would not be kinetically stable in brines associated with the WIPP Site. The only frequently observed colloid listed in Table 8b that would likely be kinetically stable in WIPP brines is naturally occurring organic matter. McCarthy and Degueldre point out that, although colloids are ubiquitous in natural groundwaters, higher concentrations are observed when the groundwater system has been perturbed either naturally or anthropogenically (e.g., mixing of oxic surface and deep groundwaters, Table 8a, row 5; hydrothermal fracture zone, Table 8a, row 7; outside a nuclear detonation cavity, Table 8a, row 13). Deep subsurface groundwaters (Table 8b) generally have lower concentrations of colloidal particles than shallow groundwaters (Table 8a).

When reviewing colloid sampling and characterization work, results should be carefully scrutinized because of the strong possibility of artifacts, despite a substantial effort in improving methodologies to help reduce the potential for artifacts (see, e.g., Degueldre, 1990; Hurd and Spencer, 1991; Buffle et al., 1992; Beckett and Hart, 1993; Giddings, 1993; Laaksoharju et al., 1993; McCarthy and Degueldre, 1992). One of the most likely artifacts stems from inducing flow in the subsurface to collect samples. Another likely artifact may stem from subtle changes in groundwater chemistry during sampling. Further artifacts are introduced during the isolation of colloidal particles for further analysis. The impact of different colloidal particle types is frequently determined on the basis of differences in actinide concentrations measured in ultrafiltrates and ultrafilter retentates. These techniques are challenging because of the strong potential for introducing artifacts stemming from sorption of actinides onto vessel walls and in the filter membrane, precipitation of colloidal particles, etc. Differences between filtrates and the initial solution are not unusual, and are frequently attributed to the presence of colloidal particles, but unless further examination (e.g., electron microscopy examination of the filter membrane) is done to confirm the presence of colloidal particles, the results may be suspect. Many studies do not adequately differentiate between what may be very small colloidal particles with sorbed actinides or actinide intrinsic colloids. Evaluation of natural groundwaters is particularly complicated if humic substances are present, because of their strong complexation with actinides, which may confound the results.

Detailed characterization work has been done at natural analog sites (e.g., the Cigar Lake uranium deposit in Canada; the Koongarra uranium deposit in Australia; the Poços de Caldos uranium mine in Brazil), potential repository or research sites (e.g., the proposed Gorleben repository in Germany; the Grimsel Test Site in Switzerland; the Whiteshell research area in Canada; the El Berrocal experimental site in Spain; the Palo Duro Basin site in Texas), and at anthropogenic analog sites (e.g., the Nevada Test Site; Mortandad Canyon near Los Alamos, New Mexico). Triay et al. (1995) present concise summaries of the results of work conducted on many of those sites. Of those sites, WIPP is the only proposed repository site in which both the near-field and far-field environments are brines. The near-field environment at Gorleben consists of brine, but the far-field consists of humic-rich low-ionic strength groundwaters. The near-field environment does provide useful information, however. Other relevant work concerning colloidal particles in high ionic strength systems is seawater and the work related to the proposed nuclear waste repository in the Palo Duro Basin, Texas. Those studies involve characterization of naturally occurring colloidal particles in brines, formation of colloidal particles in artificially spiked brines, and the formation of colloidal particles during leaching of high-level waste glasses in brines. It is important to note that some of the studies were conducted with actinide concentrations much less than might be expected for the WIPP repository area, and some of the high-level waste glass studies were conducted at elevated temperatures (90-200°C).

Results from the Grimsel Test Site are especially useful because the sampling and characterization work was very carefully done and the data base produced is perhaps the most extensive data base of naturally occurring colloidal particles in the deep subsurface.

### 2.6.1 Grimsel Test Site, Switzerland

One of the most comprehensive evaluations of the nature and population of naturally occurring colloidal particles in the deep subsurface studies was coordinated by the Paul Scherrer Institute, Switzerland, in which a round-robin colloid sampling and characterization exercise was conducted on groundwater samples collected from fractured granite at the Grimsel Test Site. That exercise, sponsored by the Commission of the European Communities, was done to evaluate the accuracy and precision of colloid measurement techniques at different laboratories (Degueldre, 1990; see also McCarthy and Degueldre, 1992). Despite the variety of particle size and concentration measurement techniques used, the results are surprisingly consistent, varying by only one order of magnitude. In addition to evaluating reproducibility, the exercise has provided a comprehensive population data set for naturally occurring colloidal particles.

In the following paragraphs, we have taken the results from the Grimsel Test Site study, and have estimated the maximum concentration of actinides that could be transported by the population of colloidal particles that was measured at Grimsel.

Colloid concentration at the Grimsel Test Site was described (Degueldre, 1990) using a power function to fit the cumulative size distribution for colloidal particles with diameters ranging from 10 to 10,000 nm:

$$[\text{coll}] = 10^{15.82(\pm 0.36)} \Phi^{-3.17(\pm 0.16)} \quad (37)$$

where:

[coll] concentration of colloids (particles/L)  
 $\Phi$  colloid diameter (nm)

The cumulative size distribution as a function of colloid diameter ( $\Phi$ ) is the summed abundance of particles greater than or equal to  $\Phi$ . Particle and sediment distribution data are frequently presented as cumulative distributions, because that method most closely represents what is measured in the laboratory with sequential filters or sieves. The first derivative of the cumulative size distribution equation (37) provides the rate of change of colloid size as a function of colloid diameter:

$$\frac{d[\text{coll}]}{d\Phi} = - 10^{16.32} \Phi^{-4.17} \quad (38)$$

Combining size distribution equation (38) with the equation describing the concentration of actinides per unit surface area (22) provides the rate of change of actinide concentration for the colloidal particle population as a function of colloid diameter:

$$\frac{d[\text{An}]}{d\Phi} = - 10^{16.32} \Phi^{-4.17} \left( \frac{\pi \Phi^2 N_S}{N_A} \right) \quad (39)$$

where:

- [An]<sub>T</sub> total concentration of an actinide element (moles/L)
- Φ colloid diameter (nm)
- N<sub>S</sub> adsorption site density (sites/nm<sup>2</sup>)
- N<sub>A</sub> Avogadro constant

The total concentration of actinides carried by naturally occurring groundwater colloids over the 10 to 10,000 nm size range can be estimated by integrating equation (39) over that size range:

$$[\text{An}]_T = \frac{10^{16.32} \pi N_S}{(1.17) N_A} \left[ \Phi^{-1.17} \right]_{\Phi=10}^{\Phi=10000} \quad (40)$$

Solving equation (40) for total concentrations of an divalently charged actinide cation assuming a rather large adsorption site density estimate of 10 sites/nm<sup>2</sup> produce integrated actinide concentration estimates of 6 x 10<sup>-8</sup> moles/L (Figure 14).

The colloidal particles identified in Grimsel Test Site groundwater consist of silica, illite/muscovite, biotite, calcium silicate, very small amounts of natural organic matter, and some bacteria (McCarthy and Degueldre, 1992, p. 293). To interpret this information in terms of the WIPP Site, however, one must evaluate the dispersant. Whereas groundwater from the Grimsel Test Site contains about 75 mg/L total dissolved solids, Salado and Castile Formation brines contain in excess of 300,000 mg/L TDS and Culebra brines within the WIPP Site boundary contain between about 45,000 to 150,000 mg/L total dissolved solids (hydrochemical facies C and A, respectively; Siegel et al., 1991). Considering the destabilization effects of high ionic-strength electrolytes on mineral fragment type colloidal particles, the majority of the naturally occurring colloids at Grimsel would not be kinetically stable in WIPP brines. Of the Grimsel colloids identified, only natural organic matter and bacteria might be kinetically stable in WIPP brines.

### 2.6.2 Gorleben, Germany

A continuing effort has been underway since the middle 1980s to characterize the potential for colloid-facilitated transport at the Gorleben site in Germany. Kim et al. (1984b) studied the behavior of actinides [ $^{238}\text{Pu}$ ,  $^{241}\text{Am}$  ( $10^{-7.3}$ ,  $10^{-8.3}$ , and  $10^{-9.3}$  M); and  $^{244}\text{Cm}$  ( $10^{-9}$  M)] in several artificially spiked natural Gorleben groundwaters, containing different levels of humic materials and salinities up to 2.3 molar NaCl (from well Gohy-2122). They observed no evidence to indicate the formation of actinide intrinsic colloids or pseudocolloids collected on ultrafilters as small as  $0.001\ \mu\text{m}$ , and concluded that the high ionic strength of the Gorleben brines precludes the formation of colloids. In a later study, Kim et al. (1985) examined high-level-waste-glass leachates in 0.1 to 5 molar NaCl brines representative of the Gorleben area, at  $25^\circ\text{C}$  and  $200^\circ\text{C}$ . They were specifically interested in  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$  (Pu concentration in the leachate was  $10^{-9.6}$  to  $10^{-8.7}$  M), and  $^{241}\text{Am}$  (less than the detection limit of  $10^{-11}$  M). They speculated that americium and plutonium colloidal particles were present at sizes less than  $0.001\ \mu\text{m}$ , but were not able to determine whether they were intrinsic colloids or pseudocolloids.

Dearlove et al. (1991) characterized the physical and chemical characteristics of naturally occurring organic colloids as part of a study to investigate radionuclide loading on colloids in two groundwater samples obtained at the Gorleben site. One groundwater sample (from well Gohy-1231) contained high salinity and low concentrations of dissolved organic carbon (mainly humic and fulvic acids), whereas the other contained low salinity and high concentrations of dissolved organic carbon. Ultrafiltrates and ultrafilter retentates obtained with a series of filters with nominal pore sizes between  $1.0$  and  $0.001\ \mu\text{m}$  were analyzed for concentrations of Th ( $0.5 \times 10^{-10}$  and  $7.0 \times 10^{-9}$  M), U ( $2.0 \times 10^{-10}$  and  $0.24 \times 10^{-10}$  M), and organic material. In the less saline groundwater, strong evidence was presented that indicated that thorium and uranium were sorbed on humic materials. In the more saline groundwater, however, the evidence suggested that the radionuclides were dissolved or, perhaps, sorbed on organic material smaller than  $0.001\ \mu\text{m}$ , the pore size of the smallest filter used.

Lieser et al. (1986a,b) investigated the behavior of radionuclides in spiked Gorleben brines [ $^{137}\text{Cs}$  ( $5.3 \times 10^{-9}$  M);  $^{85}\text{Sr}$  ( $2.3 \times 10^{-7}$  M); and  $^{141}\text{Ce}$  ( $3.2 \times 10^{-7}$  M)] with low and moderate salinities. Using a  $0.002\ \mu\text{m}$  ultrafilter, their experimental results showed that Ce behaved differently than Cs and Sr. The difference in behavior was attributed to the tendency of Ce to form polynuclear hydroxy complexes, which would be expected to condense and agglomerate in relatively high salinities. Cerium was used in their experiments as an analog for the trivalent actinides, and the results suggest that, in general, actinides will form intrinsic colloids. Lieser et al. (1990) studied the behavior of radionuclides in spiked Gorleben brines [ $^{137}\text{Cs}$  ( $\sim 10^{-7}$  M);  $^{85}\text{Sr}$  ( $\sim 10^{-6}$  M);  $^{210}\text{Pb}$  ( $\sim 10^{-8}$  M);  $^{227}\text{Ac}$  ( $\sim 10^{-9}$  M); and  $^{234}\text{Th}$  ( $\sim 10^{-11}$  M)] ranging from low to moderate salinities (0.16 M NaCl). They attributed the absence of Th, Pb, and Ac intrinsic colloids (greater than  $0.002\ \mu\text{m}$ ) to the low initial concentrations of those elements. All five radionuclides investigated did form

pseudocolloids, however. One possible explanation for the absence of intrinsic colloids is that the available radionuclides were fixed on carrier colloids before they had time to produce intrinsic colloids.

### 2.6.3 Palo Duro Basin

Field and laboratory work characterizing the potential for colloid formation in Palo Duro Basin brines was conducted in the middle- to late-1980's. Laul et al. (1985) investigated the distribution of naturally occurring radionuclides in Palo Duro Basin NaCl brines containing 20 wt% total dissolved solids. They found no difference in the concentrations of radionuclides in filtered and unfiltered samples using membranes with nominal pore sizes of 0.8, 0.22, and 0.10  $\mu\text{m}$ , and concluded that colloids were not important in the transport of U, Th, and Ra radionuclides in those brines. That conclusion was corroborated by a later study by Laul and Smith (1988), who investigated Palo Duro Basin  $\text{MgCl}_2$ -NaCl brines with an ionic strength of approximately 9 molal. They found no difference in the concentrations of naturally occurring radionuclides [ $^{232}\text{Th}$  ( $\sim 7.1 \times 10^{-11}$  M);  $^{230}\text{Th}$  ( $\sim 7.5 \times 10^{-12}$  M);  $^{228}\text{Th}$  ( $\sim 1.9 \times 10^{-15}$  M);  $^{238}\text{U}$  ( $\sim 2.3 \times 10^{-10}$  M);  $^{234}\text{U}$  ( $\sim 1.5 \times 10^{-14}$  M);  $^{228}\text{Ra}$  ( $\sim 5.8 \times 10^{-17}$  M);  $^{226}\text{Ra}$  ( $5 \times 10^{-13}$  M)] in unfiltered samples and filtrates obtained using nominal filter pore sizes of 0.8, 0.22, and 0.10  $\mu\text{m}$ . Those measurements were followed by laboratory experiments with radionuclide spikes to determine the effects of increased concentrations. They found no appreciable difference in the concentrations of radionuclide spikes [ $^{232}\text{U}$  ( $2.8 \times 10^{-5}$  M and  $2.8 \times 10^{-6}$  M);  $^{232}\text{Th}$  ( $2.8 \times 10^{-5}$  M and  $2.7 \times 10^{-5}$  M);  $^{226}\text{Ra}$  ( $9.7 \times 10^{-11}$  M); and Pb ( $3.2 \times 10^{-5}$  M)] in unfiltered samples and filtrates obtained using nominal filter pore sizes of 1.0, 0.20, 0.10, and 0.015  $\mu\text{m}$ . They concluded that colloidal particles were not important in the transport of U, Th, and Ra in the Palo Duro Basin brine. Later work by Maiti et al. (1989) extended the Palo Duro Basin colloid investigation to 0.015  $\mu\text{m}$  in radionuclide-spiked 9 molar synthetic brines and to perhaps 0.0018  $\mu\text{m}$  in 1:1 diluted brines. Of the radionuclides investigated [ $^{232}\text{U}$  ( $2.8 \times 10^{-5}$  M and  $2.8 \times 10^{-6}$  M);  $^{232}\text{Th}$  ( $2.8 \times 10^{-5}$  M and  $2.7 \times 10^{-5}$  M);  $^{226}\text{Ra}$  ( $9.7 \times 10^{-11}$  M);  $^{210}\text{Po}$  ( $2.4 \times 10^{-14}$  M and  $2.7 \times 10^{-14}$  M); Pb ( $3.2 \times 10^{-5}$  M); Sr ( $5.1 \times 10^{-3}$  M); Rb ( $1.8 \times 10^{-3}$  M); and Cs ( $2.3 \times 10^{-4}$  M)] they found evidence that only Po might form colloids. Maiti et al. (1989) postulated that, in general, hydrolysis is unlikely to take place in the high ionic strength brines characteristic of the Palo Duro Basin. However, they speculated that colloid formation could occur over long periods of time, due to changes in aqueous composition.

In a related study, McGrail (1986) examined the formation of radionuclide ( $^{238}\text{U}$ ,  $^{99}\text{Tc}$ ,  $^{237}\text{Np}$ ,  $^{243}\text{Am}$ , and  $^{239}\text{Pu}$ ) colloids in leachates produced during prolonged exposure of high-level-waste glass (Savannah River) and steel with low and high Mg content brines at 90°C. They used a series of filters in the range of 0.002 to 20  $\mu\text{m}$  pore size to characterize particulates. Colloidal particles containing Np, Am, or Tc colloids were not observed. Fairly large ( $>1$   $\mu\text{m}$ ) U- and Pu-bearing pseudocolloids were formed, however, by sorption on iron oxide particles produced from

degradation of the steel. Plutonium-bearing pseudocolloids were not present under reducing conditions. Examination with scanning electron microscopy showed that the pseudocolloids were actually aggregates of 0.03  $\mu\text{m}$  diameter spheres. Avogadro and de Marsily (1984), in one of the most widely cited early papers investigating radiocolloid formation in brines, found that one-quarter of the Am released during high-level-waste-glass leaching experiments in brine was retained on a 0.1  $\mu\text{m}$  filter. It was not certain, however, whether the americium colloids were intrinsic colloids or pseudocolloids. The source or specific composition of that brine was not stated in their article.

### 3.0 Application of Previous Knowledge

In this Section, we have assimilated the discussion of previous work presented in detail in Section 2 to some well-founded hypotheses that will be experimentally tested as part of the WIPP Colloid Research Program. Where applicable, the baseline conceptual models and parameter values that were used in the SPM baseline calculations are noted (Table 9a). The baseline models and values are also used to define the null and alternative hypotheses as part of the Data Quality Objective process presented in Section 4.

- (1) Mineral fragment type colloidal particles are not kinetically stable in brines associated with the WIPP because of inert electrolyte effects. It is unlikely that agglomerates will be peptized or entrained by brine movement in the repository because of the relatively large amount of energy required for peptization. Surface charge reversal and steric stabilization effects are not important. The concentration of actinides associated with mobile mineral fragments was assumed to be zero for the SPM baseline calculations.
- (2) Actinide-intrinsic colloids initially consist of an actinide polyelectrolyte, which mature to form mineral fragment type colloidal particles. The former may not be effected by kinetic destabilization effects of WIPP brines, whereas the latter will be destabilized. Actinide intrinsic colloids other than the Pu(IV) intrinsic colloids are less likely to be important. Aside from kinetic destabilization of the mature form, actinide polyelectrolytes are not likely to form in the presence of anthropogenic organic complexants, and are strongly sorbing. The concentration of actinides associated with mobile actinide intrinsic colloids was assumed to be zero for the SPM baseline calculations.
- (3) Humic substances are kinetically destabilized by specific interaction with divalent cations in WIPP brines, which will reduce the concentration of actinides which they may mobilize, particularly under slightly acidic conditions. Humic substances are smaller than the pore throats in the Culebra and will be retarded by diffusion into matrix. The concentration of actinides associated with mobile humic substances was bounded by conservative estimates made on the soil component of the waste inventory for the SPM baseline calculations, but is likely to be far less due to the effects of the phenomena listed above.
- (4) Microbes may be kinetically stable in brines, but their abundance is limited by the presence of suitable nutrients and substrates. Microbes may act as substrates for sorption (passive bioaccumulation) of actinides or they may actively bioaccumulate actinides into or through their cell walls. The concentration of actinides that they



may mobilize is limited by radiation inhibiting their growth and survival. Lysed microbes may provide substrates for actinide transport or nutrients for viable microbes. The concentration of actinides associated with mobile microbes was bounded by conservative estimates for the SPM baseline calculations, but is likely to be far less due to the effects of the phenomena listed above.

- (5) The source of potentially mobile colloidal particles is nearly exclusively from wastes in the WIPP repository environment. Cellulose, nitrate, and sulfate provides substrates and nutrients for microbes. Soil-bearing wastes contain humic substances. The high concentrations of actinides provides the environment most conducive for formation of actinide intrinsic colloids. The quantity of actinide-bearing colloidal particles generated in the Culebra is likely to be small compared to the potential of the repository environment. The only potential colloid types that could be generated within the Culebra are microbes and humic materials. Mixing of repository brines with Culebra brines may result in precipitation of solids, and some may be colloidal in size. Those colloidal particles will be mineral fragment type particles and will immobilized by kinetic destabilization effects.
- (6) Colloid-facilitated actinide transport in the Culebra, a fracture advection-matrix diffusion flow system, could result in increased rates of contaminant transport relative to an ideal non-sorbing solute due to complete exclusion of particles from matrix diffusion because of large sizes or, to a lesser extent, reduced diffusion rates because of intermediate sizes. Increased transport rate due to flow in central regions of channels (hydrodynamic chromatography) is negligible.
- (7) Significant decreases in colloid-facilitated actinide transport (relative to an ideal non-sorbing solute, and in some cases relative to a sorbing solute) may occur due to surface filtration (sorption of the colloidal particles themselves), physical filtration (sieving), or pore clogging. Retardation effects are enhanced if actinides are sorbed to the immobilized colloidal particles (i.e., cosorption effects). The net effect of transport enhancing mechanisms and retardation mechanisms is likely to be a significant amount of retardation.

## 4.0 Data Quality Objectives

This section follows the outline for designing experimental programs described in the "Guidance for the Data Quality Objectives Process," published in September 1994 by the U.S. Environmental Protection Agency (US EPA, 1994). That document presents in a concise form, the thought process required to develop a logical, as well as reasonable and efficient, experimental program. The subsection headings exactly follow the seven steps described in US EPA (1994): Step 1: State the Problem; Step 2: Identify the Decision; Step 3: Identify the Inputs to the Decision; Step 4: Define the Study Boundaries; Step 5: Develop a Decision Rule; Step 6: Specify Tolerable Limits on Decision Errors; and Step 7: Optimize the Design. It is suggested in US EPA (1994, p. 5) that the recommended procedures may be modified and may not be entirely applicable for research programs (specifically, "... the DQO Process is a flexible planning tool that can be used more or less intensively as the situation requires."). The thrust of the procedures are obviously designed for planning and developing a sampling and analytical program to evaluate a potentially contaminated site. Nevertheless, the information is useful for the WIPP colloid research program.

### 4.1 Development of Data Quality Objectives

In the following subsections, the data quality objectives are developed following the seven steps in US EPA (1994). To guide the reader, we have underlined terms and phrases that correspond directly to information items specifically requested in US EPA (1994).

#### 4.1.1 Statement of the Problem

At the highest level, the problem addressed by SNL is to determine whether the performance of the WIPP complies with the regulatory standard described in 40 CFR Part 191 (US EPA, 1985). The problem addressed in this Test Plan, which will provide information to contribute to the solution of the high-level problem, is the quantification of the concentration of actinide elements reaching the accessible environment by colloidal particles, in a breach scenario. Colloid-facilitated transport of actinides has not been included in past performance assessments because of the lack of adequate information to model this phenomenon and to demonstrate its impact on compliance (see, e.g., WIPP PA Department, 1992a, p. 4-12, line 29). Transport of actinides by colloidal particles has been recognized only relatively recently as a phenomenon of critical importance to the performance of nuclear waste repositories. Additional discussion of the motivation for this work is included in the Section 1. Schedules driving this effort are discussed in Section 1.6. A literature review and interpretation of that literature in the context of the WIPP Site are presented in Sections 2 and 3. Resources to be utilized for the effort are described in Section 5.

#### 4.1.2 Identification of the Decision

Three principal study questions must be addressed in the colloid research program: (A) what are the kinetic and chemical stabilities of colloidal particle types that may be present in the repository and in the Culebra; (B) what is the concentration of actinides that are carried by kinetically and chemically stable colloidal particles; and (C) what are the transport characteristics of actinide-bearing colloidal particles that are present in the Culebra under a breach scenario.

The alternative actions for addressing the principal study questions are to: (1) disregard the potential impact of actinide-bearing colloidal particles on assessments of the performance of the WIPP (i.e., take no action); (2) design and implement an experimental program to address the principal study questions sequentially in the forward order (i.e., emphasis on stability screening experiments); (3) design and implement an experimental program to address the principal study questions sequentially in the reverse order (i.e., emphasis on transport experiments); or (4) design and implement an experimental program that strikes a logical and efficient balance between the three previous principal study questions (A, B, and C above).

The SPM calculations (refer to Sections 1.2 and 3; Prindle et al., 1996a,b) indirectly provided performance sensitivity analyses that have demonstrated that research activities on colloid-facilitated transport is critical to the evaluation of the performance of the WIPP. Therefore, alternative (1) above, which dictates that no action would be taken, can be dismissed from further consideration.

Because of the complexities of numerical modeling of colloid-facilitated actinide transport, it is not practical to conduct alternative (3), in which the emphasis is on transport modeling rather than attempting to simplify the colloid experimental program by stability screening experiments. Alternative (2) would be ideal, provided that there were no time constraints on completing the colloid research program. The aggressive schedule of the DOE/CAO Disposal Decision Plan (Figure 3; US DOE, 1995) dictates that recommendations for numerical model changes and associated model parameters must be submitted to the SNL WIPP PA Department by 30 September 1995 and 31 March 1996, respectively. Considering the Disposal Decision Plan schedule, the only logical alternative is (4), in which there is some overlap in the sequence of the activities.

The sequence of decision statements, in which the principal study questions and the appropriate alternative actions are combined, is the following: (A) determine whether or not different types of colloidal particles are kinetically and chemically stable and require further experimental evaluation; (B) determine whether or not the concentration of actinides associated with kinetically and chemically stable colloidal particles require further experimental evaluation; and (C) determine whether or not kinetically and chemically stable actinide-bearing colloidal particles are physically or

chemically retarded by interaction with the Culebra.

#### 4.1.3 Identification of Inputs to the Decision

Resolution of the decision statements will require information available from peer-reviewed published literature, laboratory experiments, a small component of field sampling, and a small component of mathematical and numerical modeling. In addition, resolution of the decision statements will require information from the Source Term Test Program being conducted at LANL as one of the three subprograms of the Actinide Source Term Program (refer to Section 1.5.1). That information is used to challenge conceptual models describing what types of colloidal particles may be present in a simulated repository environment as well as a qualitative check on the concentrations of actinides associated with colloidal particles.

Establishing action levels is largely driven by SNL WIPP performance assessment calculations. As part of the SPM process (Prindle et al., 1996a,b), calculations were conducted to evaluate the sensitivity of the total WIPP System to various phenomena and parameter values. Those sensitivity calculations provide information to define action levels.

#### 4.1.4 Definition of Study Boundaries

The spatial boundaries of the SNL WIPP Colloid Research Program investigation area is defined by the "accessible environment," a right parallelepiped extending from the Salado Formation to the surface, with lateral dimensions of approximately 5 km, with the WIPP Site located approximately in the geographic center (Figure 1). The rock unit that is investigated for transport is the Culebra, an approximately 8-meter thick fractured microcrystalline dolomite. Actinide-bearing colloidal particles may form in the repository environment, or in the Culebra under a breach scenario. The groundwaters that may interact with waste in the repository and groundwaters that may be involved in transport in the Culebra are all brines, with ionic strengths ranging from 0.8 to 8 molal. The temporal boundary is defined by regulations as 10,000 years after waste is emplaced. Detailed information on the study boundaries is presented in Section 2.

#### 4.1.5 Development of the Decision Rule

Development of a decision rule requires the consideration of four components: the parameter of interest, the scale of decision making, the action level, and alternative actions.

The parameters of interest are the following: concentrations of actinides (Th, U, Np, Pu, Am) associated with mobile colloid particles that form in the repository environment, concentrations of actinides associated with mobile colloid particles that form in the Culebra, physical retardation parameters quantifying the transport of colloidal particles in the Culebra; and chemical retardation parameters quantifying the transport of colloidal particles in the Culebra. In addition to those discrete parameters, additional parameters of interest describe how colloidal particles develop, how they interact with actinides, and how they interact with the Culebra during transport. Addressing the development of conceptual models for these interactions is not specifically addressed in US EPA (1994), but is consistent with the objectives described in that document. Development of the numerical model used for quantifying colloid-facilitated actinide transport is included in Section 7.2.

The scale of decision making, as used in US EPA (1994), concerns the spatial and temporal boundaries associated with sampling and analytical programs to evaluate sites with potential environmental contamination. That theme is applicable to the WIPP colloid research program in two ways. First, evaluation of the behavior of colloidal particles must be considered on both short and long time frames. Second, the applicability of local-scale laboratory experiments to transport of colloidal particles at the regional scale must be addressed.

The action levels for those parameters are defined by SNL WIPP performance assessment sensitivity analyses conducted as part of the SPM process (Prindle et al., 1996a,b). The action levels, therefore, are indirectly based on the regulatory requirements that stipulate the acceptable performance of the WIPP over the 10,000-year period. Results of the SPM process have shown that acceptable performance of the WIPP requires that concentrations of actinides associated with colloidal particles involved in transport in the Culebra must be on the order of  $1 \times 10^{-7}$  M and diffusion constant reduction factors must be on the order of 100 (Table 9b). Different levels are required for different types of colloidal particles.

Action levels for transport parameters were indirectly defined for the SPM process in terms of actinide release reduction factors, which describe the reduction of concentration of actinides that reach the accessible environment by colloid-facilitated actinide transport. With colloidal source term concentrations on the order of  $1 \times 10^{-7}$  M (Table 9b), reduction factors on the order of 10 to 100 provided a means for demonstrating compliance of the WIPP, according to the SPM process and its assumptions (Prindle et al., 1996a,b). Reduction factors, as opposed to actual retardation factors, were used in SPM calculations as a simple means to evaluate the need of quantifying colloid transport numerical modeling. The following equation provides a relationship between the simplistic reduction factor used in SPM calculations and a retardation factor for colloidal particles, a parameter that is more suitable for accurate evaluation of the performance of the WIPP:

$$R_f = \frac{K_r}{1 + \frac{(K_r - 1) T_t}{(10000 - T_0)}} \quad (41)$$

where:

- $R_f$  retardation factor (dimensionless) of actinide-bearing colloidal particles
- $T_t$  travel time (in years) for non-retarded front to move from the intrusion borehole to the accessible environment
- $T_0$  time interval (in years) between repository closure and breach
- $K_r$  reduction factor (dimensionless) for actinide release to the accessible environment due to colloid-facilitated transport

The travel time ( $T_t$ ) used in equation (41) is the time required for a hypothetical "particle" (idealized non-sorbing material) to reach the accessible environment (refer to LaVene et al., 1990). The relationship described in equation (41) is derived given the following reasonable assumptions: (1) contaminants are introduced into the Culebra move at a constant concentration (i.e., a step function) away from an intrusion borehole toward the accessible environment; (2) retardation occurs by slowing the velocity of the front of the contaminant relative to an unretarded front; and (3) once contaminants are introduced into the Culebra, the flow is continuous and constant for the duration of the period defined by  $(10,000 - T_0)$  years. Note that in equation (41) we have intentionally excluded effects of matrix diffusion so that the resulting target  $R_f$  values are independent of the hydrogeological conceptual model (i.e., target values are not dependent on selection of double- or single-porosity flow models).

In the SPM calculations, reduction factor values on the order of 10 to 100 provided significant levels of attenuation of colloidal actinides. Using (41), with a travel path of 2.5 km from the intrusion borehole to the accessible environment boundary, and assuming that the intrusion occurs immediately after waste is emplaced, we derive the following target retardation factors:

groundwater velocity (m/s)	$K_r = 10$	$K_r = 100$
10 <sup>-2</sup>	10	100
10 <sup>-3</sup>	10	100
10 <sup>-4</sup>	10	100
10 <sup>-5</sup>	10	90
10 <sup>-6</sup>	9	60
10 <sup>-7</sup>	6	10
10 <sup>-8</sup>	1	1

The range of groundwater velocities in the Culebra were taken from LaVenue et al. (1990). The retardation factors listed above will be used for guidance in the transport experiments described in Section 5.1.5.

Alternative actions were defined above in Step 2: Identify the Decision. As stated in that section, it would be preferable to conduct activities supporting the three decision statements sequentially in the forward order. However, because of the aggressive schedule dictated by the Disposal Decision Plan (Figure 3; US DOE, 1995), some overlap in the timing of conducting the activities is mandatory. Depending on the outcome of the decision rules, however, the intensity of effort and resources applied to subsequent activities or activities being conducted concurrently may be increased or decreased accordingly.

The statistical parameters used to describe the value and uncertainty of parameter values will generally be the mean and standard deviation, although the best method to convey parameter values and uncertainties will have to be evaluated on a case-by-case basis for each of the planned experiments.

The resulting decision rules are the following: (1) if the concentration of mobile colloidal particles (mineral fragments, actinide intrinsic colloids, humic materials, microbes) generated in the repository and the Culebra is less than the action level, then take no additional action, otherwise, evaluate the interaction of the particular colloid type with actinides (Th, U, Np, Pu, Am); (2) if the concentration of actinides (Th, U, Np, Pu, Am) associated with the particular mobile colloidal particle type is less than the action level, then take no additional action, otherwise, emphasize evaluation of the physical and chemical retardation parameters with transport experiments; and (3) if the determination of physical and chemical retardation parameters for the particular mobile colloid type and actinide result in a actinide release reduction factor that is greater than the action level, then take no action, otherwise, re-evaluate the colloid research program.

#### 4.1.6 Specification of Decision Error Limits

The total study error, which if large may lead to a decision error, is the combination of sampling design error, in which the sampling design does not capture the natural variability of the environment or the phenomenon being investigated, and measurement error. For the WIPP colloid research program, the primary source of error will be from sampling design error, which is more appropriately stated as error in conceptual models used to design the colloid experiments. By comparison, measurement error will be negligible.

The DQO Guidance Document (US EPA, 1994) uses standard statistical terminology to describe limits on decision errors. The null hypothesis,  $H_0$ , and the alternative hypothesis,  $H_a$ , represent

the baseline condition in the absence of any additional characterization work and the outcome of additional characterization work, respectively. A false positive, or Type I, error results when the  $H_0$  is rejected when it is true. A false negative, or Type II, error results when the  $H_0$  is not rejected when it is false.

Determination of the possible ranges of values for the parameters of interest was discussed in Section 3, Summary of Conceptual Models and Baseline Parameters. Where possible, estimates of the upper bounds for actinide concentrations associated with mobile colloidal particles were calculated based on existing information about the waste composition, known characteristics of the WIPP system, and known geochemical principles. Realistically, the lower bounds for concentrations of actinides associated with colloidal particles is the analytical minimum detection limit of actinides, generally about  $10^{-10}$  M. Because of the lack of relevant information, the upper bounds for transport of colloidal particles in the Culebra were simply estimated on the basis of colloid particle size. Assuming a fracture advection-matrix diffusion flow system, colloidal particles larger than the intercrystalline (matrix) pore throats (see Sections 2.4.1 and 2.4.3) of the Culebra are not retarded physically or chemically, whereas particles smaller than the intercrystalline pore throats of the Culebra are retarded physically. The lower bounds for transport of colloidal particles are difficult to estimate at this time, but are likely to result in retardation factors of ten or less (refer to Section 2.4), because of the number of phenomena that could lead to retardation of colloidal particles.

Evaluation of the performance of the WIPP is viewed from the standpoint that without further characterization work, parameter values used in performance assessment calculations must err on the conservative side, which would lead to an overprediction of releases of actinides to the accessible environment. That standpoint is consistent with US EPA (1994, p. 32), which states that, "... the planning team should define the null hypotheses (baseline condition) to correspond to the true state of nature for the more severe decision error and define the alternative hypothesis to correspond to the true state of nature for the less severe decision error."

In general, for WIPP research, the null hypothesis is corresponds to the current technically defensible position and the alternative hypothesis corresponds to some improvement, with respect to compliance, over the null hypothesis. A false positive decision error results when  $H_0$  is erroneously rejected in favor of  $H_a$ , which would result in erroneously underestimating the release of actinides to the accessible environment, relative to the true release of actinides. The consequence of the false positive decision error is that public health is potentially endangered from releases of actinides to the accessible environment that are greater than predicted. A false negative decision error results when  $H_0$  is erroneously not rejected when it is false. The consequence of the false negative decision error is that the WIPP Site might erroneously not comply with the regulations, leading to continued storage of waste at the surface and potential endangerment of public health, waste of taxpayer dollars, damaged credibility of the DOE and SNL, etc. However,



the burden falls on the side of demonstrating compliance, and so the false positive decision error is considered to have more severe consequences.

For the WIPP colloid research program the initial definitions for the null hypotheses correspond to the technical baseline parameters, determined from literature evidence, scoping experiments conducted to date, and the calculations described above (refer to Section 3 for summary). The definitions for the alternative hypotheses correspond to improvements in parameter values, with respect to compliance. As each decision rule is answered, the definitions for  $H_0$  are revised with  $H_a$ , the alternative hypothesis, provided that the answer supports the alternative hypothesis.

In summary, for the three decision rules stated above in Section 4.1.5 for the WIPP colloid research program, the following definitions apply:

- (1)  $H_0$ : The concentration of mobile colloidal particles (mineral fragments, actinide intrinsic colloids, humic substances, microbes) generated in the repository and the Culebra is equal to the baseline value.  
 $H_a$ : The concentration of colloidal particles is equal to the action level.
- (2)  $H_0$ : The concentration of actinides (Th, U, Np, Pu, Am) associated with the particular mobile colloidal particle type is equal to the baseline value.  
 $H_a$ : The concentration of actinides is equal to the action level.
- (3)  $H_0$ : The actinide release reduction factor determined from physical and chemical retardation parameters for the particular mobile colloidal particle type and actinide result in a actinide release reduction factor that is equal to the baseline value.  
 $H_a$ : The actinide release reduction factor is equal to the action level.

Because of the complexity of the WIPP System, the most appropriate way to establish limits to reflect the tolerable probability limits for the occurrence of decision errors for the WIPP colloid research program is by establishing an order-of-magnitude "gray region." In other words, for each of the decision rules, an experimental outcome must surpass the action level by at least one order-of-magnitude in order to reject  $H_0$  in favor of  $H_a$ .

#### 4.1.7 Design Optimization for Data Acquisition

The experiments described in subsequent sections have been designed using published information, which was reviewed and put into context for the WIPP Site in Sections 2 and 3. The most resource-effective data collection design that satisfies the data quality objectives is one that

utilizes screening experiments to allow rapid focus on issues that have the greatest bearing on answering the decision rules. Conventional data collection design alternatives, such as factorial design, systematic sampling, etc., are not practical for the WIPP colloid research program, because of the complexities of the phenomena. Instead, conceptual models based on existing geochemical knowledge have been used to design carefully thought-out experiments to test certain phenomenon. The empirical measurements obtained are always interpreted from a mechanistic perspective.

## **4.2 Description of Data Quality Objectives**

In this section, the data quality objectives (DQOs) for the proposed experiments have been established in terms of precision, accuracy, representativeness, completeness, and comparability. The primary purpose of these DQOs is to minimize the decision errors (see Section 4.1.6). In addition, the qualitative and quantitative DQOs will be developed following a graded approach, i.e., DQOs for each data item will be based on its relative importance to final results and conclusions. The data items of primary interest are the parameters of interest identified in Section 4.1.5. Not all parameters identified in Section 4.1.5 will be addressed in this Test Plan. As discussed in Section 4.1.6, the total study error is the combination of sampling design and measurement errors. It is expected that in the proposed experiments, the measurements errors will be relatively small compared to the sampling design error. Therefore, more effort has been expended to minimize the sampling design error in the measurement and modeling program described in this Test Plan.

### **4.2.1 Precision**

Precision is a measure of agreement between individual measurements of a physical quantity and is estimated through statistical analysis of replicate measurements. The proposed colloid characterization and transport experiments are designed to provide replicate measurements for only key parameters of interests such as critical coagulation concentrations. Due to scheduling and funding constraints, it may not always be possible to make adequate number of replicate measurements for statistical analysis, but enough replicate measurements will be performed to assure that the data can be judged reliable. This approach is consistent with the EPA guidelines which state that the sampling frequency of any measurement should be selected keeping in mind the uncertainties and the schedule and cost constraints (US EPA, 1994, p. 39). In many instances, replicate measurements may not be possible because samples cannot be duplicated. For example, in the case of transport experiments with core samples collected from the air intake shaft, replicate measurements are not possible because no two cores are physically or chemically identical (see also Section 4.2.3).

#### 4.2.2 Accuracy

Accuracy is a measure of how close the measured value of a parameter is to the true value. For the proposed column experiments, whenever possible the data accuracy will be assured through proper calibration of each instrument using standards traceable to standards approved by the National Institute of Standards and Technology. The recommended procedures of the manufacturers will be followed to minimize the impact of the potential sources of error identified by manufacturers. Some of these sources of errors are discussed in various technical operating procedures for the proposed experiments. Other sources of errors which may become apparent during the operation of various instruments will be addressed, to the extent practical, through improvements in procedures. In addition, whenever possible, the data from one instrument will be cross-checked with the data from another instrument employed in the experiment (see also Section 10.11).

#### 4.2.3 Representativeness

A great deal of effort has been expended to achieve a high degree of representativeness with respect to WIPP field conditions in the proposed laboratory experiments. Some of these efforts for collecting core samples and brine samples from the air intake shaft are described in the core column flow experiment Test Plan (Lucero et al., 1995). There are practical constraints limiting the simulation of field conditions in the laboratory. For example, the repository conditions likely to occur thousands of years after the waste is emplaced are known based on model results and therefore the laboratory simulations of the repository conditions can be only representative within the limitations of the models.

#### 4.2.4 Completeness

The colloid screening experiments will be performed at selected electrolyte concentrations covering the range of brine concentrations observed in the Culebra and likely to occur in the repository. The results of these experiments will be used in planning the remaining set of experiments described in Section 5 and will cover an appropriate range of the parameter space to address adequately the decision rule and to minimize decision error. The colloid column experiments will be performed for as many radionuclides as possible and their analogs with highest priority given to Pu and U, as recommended by the SNL WIPP PA Department (Section 1). If requested by the WIPP Project and adequate resources are made available, additional experiments can be performed for candidate analogs selected for field experiments to plan the field experiments.

#### 4.2.5 Comparability

Wherever possible, the results of these experiments will be compared with the relevant data sets available in the literature from radioactive waste repository programs in progress in several countries such as the Gorleben Radionuclide Migration Experiment Program (Germany), the Yucca Mountain Site Characterization Project (Nevada), the International El Berrocal Project (Spain), etc. Results from some of these programs have been reviewed in Section 2.6 of this Test Plan and have been used in planning the proposed experimental and modeling program for the WIPP.

## 5.0 Experimental Program

Working hypotheses describing the physicochemical behaviors of colloidal particles in the WIPP System were developed and defined above in Sections 2 and 3. The experimental program described below is designed to provide the information required to evaluate the working hypotheses and to determine whether we can justify accepting the alternative hypotheses defined in Section 4.1.6, and their associated action level parameter values defined in Section 4.1.5, developed as part of the DQO process.

It is highly likely that some of the experiments described below will be eliminated, that others will be substituted, or that modifications of the ones below will be made. The level of effort required to demonstrate within a reasonable doubt that we can defend rejecting the null hypotheses and accept the alternative hypotheses defined in Sections 4.1.5 and 4.1.6, is likely to vary between different colloidal particle types. For each of the five categories of experiments (four corresponding to colloidal particle types plus transport for a total of five), some of the later experiments provide contingencies in case unanticipated results or unsolvable experimental difficulties are encountered in earlier experiments.

The general experimental approach is to simplify the WIPP colloid research program by taking advantage of the kinetic destabilizing properties of the high ionic strengths of groundwaters present in both the repository environment and the Culebra. The initial thrust of the work is in defining the source term rather than focusing the effort on transport. Because of the complexities of developing a colloid transport model, it is desirable to begin with a well characterized source term.

Quantification of the impact of colloid-facilitated actinide transport on the performance of the WIPP requires consideration of the following steps:

- (1) develop a conceptual framework for the formation of radiocolloids and colloid-facilitated actinide transport based on information that is known about the Castile, Salado, and Rustler Formations, repository conditions, and the disturbed system (the E1, E2, and E1E2 scenarios; Figure 2);
- (2) identify colloidal particle types that potentially may impact the performance of the WIPP;
- (3) perform initial bounding calculations based on what is known to simplify and focus the laboratory and modeling programs where possible;
- (4) establish the Data Quality Objectives for the colloid source term and for colloid retardation factors;
- (5) evaluate the effects of high ionic strength and inorganic brine constituents on the behavior of colloidal dispersions;
- (6) evaluate the formation or behavior of colloidal particles with actinides;

- (7) evaluate transport behavior;
- (8) assist the SNL WIPP PA Department in using the results to evaluate the long-term performance of the WIPP.

The first four steps have been completed and described above in Sections 1 through 4. Steps (5) through (7) are the components of the experimental program and are described below. A general flow chart of the WIPP colloid research program is presented in Figure 15.

Throughout the implementation of the colloid experimental program, however, all steps will be revisited. It is important to challenge the conceptual models in step (1) with suitable experiments (including the real waste tests at LANL), but it is also mandatory to conduct bounding calculations and sensitivity analyses throughout the experimental program to determine whether demonstrated reductions in the impacts of colloidal particles on WIPP performance is sufficient to reduce the extent of the problem. The general strategy of the colloid program is to attempt to demonstrate that colloidal particles have a minor or negligible impact on the performance of the WIPP. However, the set of experiments planned will address phenomena that may increase the impact of colloids.

## 5.1 Components of the Experimental Program

The colloid laboratory research program includes four components that focus on the separate colloid types as described in Section 2: Mineral fragments, humic substances, actinide intrinsic colloids, and microbes. For each those four components, a series of static screening experiments has been designed according to the particular physicochemical behaviors of each colloid type. Division of the colloid research program according to colloid type has the additional advantage of allowing work to be contracted to organizations with specialized expertise and the necessary analytical equipment to conduct the work efficiently. The fifth component, transport research, may be reduced in scope if the static screening experiments show that a particular colloidal particle type is not important in transport. Technical Operating Procedures will be developed as required for the experiments described. Procedures described are for general guidance only. Note that pH is used here to indicate an operational pH, which is sufficient for our purposes. Refer to Novak (in review) and Rai et al. (1995) for discussions of complication of pH measurements in high ionic strength media, and the relationships of conventional pH (activity of  $H^+$ ), pC<sub>H</sub> (molarity of  $H^+$ ), pm<sub>H</sub> (molality of  $H^+$ ), and pH<sub>obs</sub> (observed pH, also designated pH<sub>r</sub> for meter reading).

### 5.1.1 Mineral Fragments—Screening Experiments

A review of the current knowledge of mineral fragment type colloidal particles was presented in Section 2.5.1. Because of the strong evidence that supports kinetic destabilization of colloidal

particle type under all WIPP conditions, only a few confirmation experiments need to be conducted. Candidate minerals and compounds for the experiments are listed in Table 2.

Well characterized monodisperse mineral fragment type colloidal particles such as iron oxide particles or titanium dioxide particles are available from commercial vendors (e.g., Polysciences, Inc., Warrington, Pennsylvania). Alternatively, mineral fragment colloidal particles may be synthesized with laboratory reagents (see, e.g., Matijević, 1985) or from mechanical milling of rocks, minerals, or other materials acquired from commercial vendors (e.g., Ward's Natural Science Establishment, Inc., Rochester, New York).

Experiment: MF-1

Title: Kinetic stability of mineral fragments in brine.

Hypotheses: The critical coagulation concentration (c.c.c.) for mineral-fragment type colloidal particles is less than the concentration of ions in undiluted brines associated with the WIPP. High concentrations of counterions in WIPP brines cannot result in a kinetically stable colloidal dispersion due to reversal of surface charge.

Description: In colloidal systems in which the dispersant has a high ionic strength, the presence of high concentrations of counterions collapse the electric double layer surrounding the colloidal particles and kinetically destabilize the colloidal system. The adsorption of counterions is non-specific and so reversal of surface charge will not occur. Colloidal dispersions are prepared by mechanical disaggregation of mineral and rock samples or other materials or are prepared by chemical precipitation from laboratory reagents. Brine simulants are prepared for the Salado and the Castile Formation. Those brines are sequentially diluted with deionized water by factors of ten and adjusted to acidic, neutral, and basic pH conditions. Sequential dilution of the Castile and Salado Formation brine simulants produces compositions that are sufficiently similar to the Culebra brines to evaluate the effect of Culebra brines. A small aliquot of the colloidal dispersion is injected into a series of test tubes or cuvettes with the sequentially diluted brine and mixed. The concentration of colloidal particles remaining near the top of the fluid column is measured as a function of time. The c.c.c. is the maximum brine concentration below which the concentration of colloidal particles does not rapidly decrease in the fluid column. The procedures for these experiments generally follows those described in Hunter (1991, p. 94).

Experiment: MF-2

Title: Residual mobile colloid concentrations.

Hypotheses: In dispersants with electrolyte concentrations in excess of the c.c.c. for a particular colloidal system, the concentration of colloidal particles in the fluid column is too small to mobilize a significant concentration of actinide elements, even with colloidal particles with strong sorptive properties for dissolved actinides. The objective of this experiment is to quantify the concentration

of colloidal particles in a colloidal dispersion that remain mobile in the fluid column after coagulation has begun.

Description: The number of colloidal particles required to mobilize a significant concentration of actinides is a function of colloid particle size and sorption capacity of the substance comprising the colloidal particle. Typically, it is the tremendously large number of relatively small diameter colloidal particles that have the greatest total surface area available for sorption in natural systems. Phase I of this activity consists of bounding calculations based on experiments conducted in MF-1. Phase II, if necessary, will be an experimental demonstration of the bounding calculations.

### 5.1.2 Humic Substances—Screening Experiments

A review of the current knowledge of humic substance type colloidal particles was presented in Section 2.5.2. Bounding calculations were described based on maximum values for relevant parameters such as sorption site density. It is likely that the kinetic stability of humic substances will be affected by specific interaction with divalent cations in WIPP brines, the metal complexation capacity will be reduced by both specific interaction and non-specific interaction with ions in WIPP brines. Experiments on transport and retardation of humic substances in Culebra rocks are described in Section 5.1.5.

The metal complexation experiments being conducted by Greg R. Choppin and co-workers (Florida State University) on WIPP anthropogenic organic ligands are very similar to some of the experiments required for humic substances (refer to Novak, in review). In that organic ligand research program, acidity constants are determined from information acquired at six NaCl concentrations. The effect of magnesium on metal complexation behavior is being investigated in NaCl concentrations of 0.3, 3, and 5 M to provide effects of ionic strength, with 0.01 M  $MgCl_2$ . Measurements of pH in that simple system is relatively straight forward.

As described in Section 2.5.2, determination of protonation constants for humic substances is hindered by interactions of the functional groups on the surface of the macromolecule, producing a smeared effect. Metal complexation experiments under a variety of chemical conditions are anticipated to be relatively straight forward, however.

Several options are available for the types of humic substances used in the experiments. Humic substances are typically highly variable in composition so it is either necessary to conduct experiments on the specific variety that is present, or conduct experiments on a variety of materials that span the range of behaviors (Stevenson, 1994). Isolating specific humic substances that may accompany the soils destined for the WIPP is not feasible, considering that soils may come from a variety of locals. Isolating samples of humic substances, if present, in Culebra groundwaters requires tedious and time-consuming sampling and concentration steps, but can be done.



For initial experiments, it will be preferable to conduct experiments with the well characterized standard reagent humic acid available from Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin), or humic substances available from a humic substance library at the Colorado School of Mines (Golden, Colorado), or humic substances isolated as part of this program. Experiments with model organic compounds that simulate the behavior of carboxyl, phenolic hydroxyl, and alcoholic hydroxyl functional groups present in humic substances may also be useful (acetate, malonate, phthalate, catechol, and salicylate; refer to Section 2.5.2.2).

Experiment: HS-1

Title: Kinetic stability of humic substances in brine.

Hypotheses: The moderate to high concentrations of Mg and moderate concentrations of Ca in brines associated with the WIPP undergo specific interaction (i.e., chemisorption) with functional groups in humic substances. The concentrations of those divalent cations in WIPP brines are sufficient to reduce surface charge to a level at which coagulation of humic substances occurs.

Description: Divalent cations Mg and Ca are particularly effective at complexing with inner-sphere functional groups and reducing surface charge. As surface charge is reduced, the macromolecules will coagulate and settle. This phenomenon is independent of the concentrations of actinide in solution or (within reason) the concentrations of actinides sorbed onto the humic substance. This experiment consists of two phases. In Phase I, thermodynamic calculations using oligoelectrolyte theory using the PHREEQEV computer code (Crawford, 1993) are conducted to evaluate the effect of electrolytes on the behaviors of humic substances. Laboratory experiments are conducted in Phase II to demonstrate concepts suggested by the thermodynamic modeling, which is likely to be limited to ionic strengths less than those observed at the WIPP. The laboratory experiments will be conducted similarly to experiments described in MF-1 above, except that analytical methods suitable for quantifying concentrations of humic materials are substituted. A second difference is that, because the concentrations of Mg and Ca in WIPP brines are relatively low compared to the concentration of "indifferent" ions (e.g., Na<sup>+</sup> and Cl<sup>-</sup>, which destabilize colloidal particles through non-specific interaction), the c.c.c. is likely to be much closer to the undiluted brine concentration. Rather than prepare sequential dilutions of factors of ten, it will probably be necessary to prepare sequential dilutions with much reduced dilution factors.

Experiment: HS-2

Title: Quantification of actinide complexation by humic substances and model compounds.

Hypotheses: The high ionic strength of WIPP brines, together with specific adsorption of divalent cations calcium and magnesium, results in a significant reduction in the extent of complexation of actinides by humic substances.

Description: Like HS-1, this experiment consists of two parts. Phase I consists of a

thermodynamic modeling effort that makes use of the published data base of information about metal complexation by humic substances. The PHREEQEV computer code described for activity HS-1 will be useful for modeling metal uptake in high ionic strength conditions. Phase II consists of a laboratory experimental program that is designed to confirm the results of the thermodynamic calculations. Metal complexation experiments with one or more of the five actinides of interest, Th, U, Np, Pu, and Am, may be conducted. In conducting this activity, results of the activity to define the aqueous geochemical environment in the Culebra (Papenguth and Behl, 1995) will be considered.

Experiment: HS-3

Title: Characterization of organics in Culebra brine.

Hypotheses: The concentration of total organic carbon present in Culebra brines is 1 mg/L or less and contains only a relatively low proportion of humic substances. The impact of total organic carbon constituents in Culebra brines will not have an appreciable impact on colloidal transport and may be disregarded.

Description: Because of the relatively old age and the high ionic strengths of Culebra brines, it is not likely that the total organic carbon concentrations in the brines consists of humic substances. Rather, it is more likely that the total organic carbon consists of short-chain carboxylic acids as has been observed in other brines collected from the deep subsurface. Isolating humic substances in groundwater requires collecting a fairly large quantity of pristine brine, followed by tedious and lengthy ultrafiltration and ion exchange steps. Rather than devote resources to a field sampling program initially, experiment HS-3 will be done in several phases. First, the results of experiments described in HS-1 and HS-2 will be used to re-evaluate the potential importance of humic substances on the performance of the WIPP. Second, several relatively small brine samples, collected from monitoring wells as part of the ongoing Westinghouse Water Quality Sampling Program, will be analyzed with a technique suitable for measuring small concentrations of total organic carbon. The potential impact of those measured concentrations on WIPP performance will be re-evaluated. Finally, if it is still justified, the rigorous sampling, isolation, and characterization program will be initiated. Phase I consists of quantification of total organic carbon. Phase II consists of quantification and characterization of humic substances.

### 5.1.3 Actinide Intrinsic Colloids—Screening Experiments

A detailed review of the current knowledge of actinide intrinsic colloids is presented in Section 2.5.3. In the following paragraphs, we focus on that information to develop our experimental approach.

Pu(IV) intrinsic colloid is the only actinide intrinsic colloid which has been conclusively shown to

mature to form a mineral fragment type colloidal particle, although several reports have been made for U(IV), Pu(IV), and Th(IV) forming polyelectrolytes. Intrinsic colloids of Pu(VI), Pu(V), Pu(III) are not important because the Pu(IV) dominates, perhaps exclusively. Pu(IV) seems to be the only actinide intrinsic colloid that has been reported to form large aggregates. Intrinsic colloids of U(VI) may exist, although it is puzzling why, with an actinide that is readily available and easy to work with, more information has not been published on it. The first hydrolysis reactions for Am(III) and Np(V) do not occur until pH is quite high, yet reports exist for the formation of Am(III) intrinsic colloid.

Polymerization does not occur until the first hydrolysis reaction has occurred, and is favored by higher pH and greater actinide concentrations. In the presence of chain-terminating molecules (e.g., organic complexants or uranyl), polymerization may not occur. Actinide polyelectrolytes are highly sorptive, and, at least for Pu(IV), are an intermediate form that matures to a amorphous or crystalline solid. The total concentration of that solid phase is limited by its solubility. When the actinide intrinsic colloid matures to form mineral fragment type colloidal particles, they are destabilized by electrolytes like mineral fragment colloidal particles. Polyelectrolytes may be destabilized by specific interaction with some anions.

It is not clear how quickly the Pu(IV) polyelectrolyte matures to form a mineral fragment type colloidal particle which would be kinetically destabilized by electrolytes. That maturation process takes on the order of weeks to months, a duration which is essentially instantaneous relative to the 10,000-year performance period, and even fracture-advective transport in the Culebra. Anion concentrations in brines associated with the WIPP may be sufficiently high to destabilize the polyelectrolyte. It has not been demonstrated whether the positive charge reported for the Pu(IV) polymer is independent of pH, although it should be. If surface charge does not become negative, then cation concentrations in WIPP brines will not affect the stability of the Pu(IV) polyelectrolyte. The mechanism for peptization by nitric and hydrochloric acid is not clear. Finally, although Pu(IV) may be a model intrinsic colloid and the only one of any significance, information may be needed to confirm the behaviors of intrinsic colloids of other actinides.

The strategy for simplifying the experimental program is to demonstrate that the mature actinide intrinsic polymers exhibit mineral fragment behavior and are thus kinetically destabilized in WIPP brines. Several contingencies are identified in the event that the primary hypothesis is not supported to provide, if required, additional assurance that actinide intrinsic colloids will not have a detrimental effect on the performance of the WIPP. The contingency identified is to gain a mechanistic understanding of the reactions responsible for the formation of the Pu(IV) actinide intrinsic colloid and to document that the conditions present in the repository are not amenable to their formation. These conditions include the effect of pH on the stability of Pu(IV) polymer suspensions, particularly in high ionic strength solutions, the ability of anions which are expected to be present to destabilize the colloids, the effect of organic complexants on the polyelectrolyte

formation, and the impact of metal ions which will be present in the repository on reducing the extent of polymerization by terminating chains.

Several of the experiments discussed below focus on demonstrating solubility relationships for the mature Pu(IV) mineral fragment type colloidal particle, and also on qualitatively determining the rate at which it forms. Those experiments are conducted in sodium chloride media rather than WIPP brine simulants because pH can be controlled more accurately, and there is less risk in introducing artifacts because of solute precipitation during ultrafiltration steps.

Colloidal solids may be characterized using a variety of analytical techniques including powder X-ray diffraction to determine mineralogy and high-resolution field-emission scanning electron microscopy coupled with energy-dispersive electron microprobe analysis to determine chemical composition. Concentrations of dissolved actinides may be determined using gamma spectroscopy, liquid scintillation counting techniques, and laser-induced photoacoustic spectroscopy.

Experiment: AIC-1

Title: Critical coagulation concentration for mature Pu(IV) mineral fragment type colloid.

Hypotheses: The mature Pu(IV) mineral fragment type colloidal particle is kinetically destabilized by non-specific interaction with counterions present in an indifferent electrolyte (refer to Sections 2.5.1.1 and 2.5.1.3). The colloidal particle, therefore, behaves like a mineral fragment and will not be kinetically stable in brines associated with the WIPP.

Description: Same as for experiment MF-1 above.

Experiment: AIC-2

Title: Inhibition of Pu(IV) polymerization due to organic complexants.

Hypotheses: In the presence of concentrations of organic complexants that will be present in the WIPP repository, polymerization of hydrolyzed Pu(IV) aquo ion will not take place because of the strong competition from those organic complexants.

Description: This experiment may be used as a contingency if in experiment AIC-1, it is found that the maturation rate of the Pu(IV) polyelectrolyte to the Pu(IV) mineral fragment colloid is exceedingly slow. If that maturation is slow, then kinetic destabilization by electrolytes may not be as effective as desired. Alternatively, this experiment can be used to demonstrate that secondary mechanisms exist to further reduce the potential negative impact of actinide intrinsic colloids on the performance of the WIPP. Evidence in the published literature shows that polymerization of Pu(IV) aquo ion does not occur in the presence of concentrations of organic complexants on the order of  $10^{-4}$  M. That concentration is within the anticipated concentrations of organic complexants in the WIPP repository (refer to Section 2.2.1 and Table 3).

Experiment: AIC-3

Title: Destabilization of Pu(IV) polyelectrolyte due to specific interaction with anions.

Hypotheses: The Pu(IV) polyelectrolyte is destabilized by relatively low concentrations of anions such as nitrate, sulfate, and phosphate, regardless of the valence of the anion or pH.

Description: This experiment may be used as a contingency if in experiment AIC-1, it is found that the maturation rate of the Pu(IV) polyelectrolyte to the Pu(IV) mineral fragment colloid is exceedingly slow. If that maturation is slow, then kinetic destabilization by electrolytes may not be as effective as desired. Alternatively, this experiment can be used to demonstrate that secondary mechanisms exist to further reduce the potential negative impact of actinide intrinsic colloids on the performance of the WIPP. Reports in the published literature that anions have been used to "precipitate" Pu(IV) polyelectrolyte suggests that the polyelectrolyte is neutralized by the negative charge, much like humic substances may be destabilized by specific interaction with divalent metal cations.

Experiment: AIC-4

Title: Polyelectrolyte chain termination by non-actinide metal cations.

Hypothesis: Certain metal ions have the ability to react with the polymer and function as a chain termination unit, thus limiting polymer and colloid formation.

Description: This experiment will be utilized as a contingency if it is found in experiment AIC-1 that the colloids are not kinetically destabilized in the high ionic strength brines. Metals that will have a significant concentration in the repository (e.g. U, Fe, Al) will be evaluated for their ability to limit or terminate polymer formation under conditions found in the literature to promote polymer formation.

Experiment: AIC-5

Title: Sorption effects of WIPP repository substrates on Pu(IV) actinide intrinsic colloid.

Hypotheses: In the presence of a variety of substrates present in the WIPP repository or in the Culebra, Pu(IV) polyelectrolyte is strongly sorbed.

Description: This experiment may be used as a contingency if in experiment AIC-1, it is found that the maturation rate of the Pu(IV) polyelectrolyte to the Pu(IV) mineral fragment colloid is exceedingly slow. If that maturation is slow, then kinetic destabilization by electrolytes may not be as effective as desired. Alternatively, this experiment can be used to demonstrate that secondary mechanisms exist to further reduce the potential negative impact of actinide intrinsic colloids on the performance of the WIPP. Evidence in the published literature shows that sorption of Pu(IV) polyelectrolyte is strong on glass, polished steel, and tarnished steel. Promising substrates present in the disposal room or the Culebra include kaolinite, montmorillonite, diatomaceous earth, iron-

bearing corrosion products, and dolomite.

Experiment: AIC-6

Title: pH/Stability Relationship

Hypothesis: The actinide intrinsic colloids are not kinetically (as opposed to thermodynamically) stable and thus immobile at pH values greater than 5. Establishing this threshold will allow the contribution of actinide intrinsic colloids to be reduced to a limited range of conditions.

Description: This work will provide for a contingency which reduces the overall contribution of actinide intrinsic colloids in the event that experiment AIC-1 does not demonstrate their instability. The experiment will consist of a matrix of conditions spanning the pH range expected in the repository versus the range of ionic strengths.

Experiment: AIC-7

Title: Surface charge of Pu(IV) polyelectrolyte and Pu(IV) mineral fragment colloid.

Hypotheses: The surface charge of the Pu(IV) polyelectrolyte is positive regardless of the pH conditions. The surface charge of the Pu(IV) mineral fragment colloid varies as a function of pH, and becomes more neutral and probably negative at high pH values.

Description: Evidence in the published literature shows that the Pu(IV) polyelectrolyte is destabilized by concentrations of anions, regardless of charge, on the order of 0.15 M. Provided that the destabilization effect is due to specific interaction with the polyelectrolyte, the concentrations of anions required to destabilize the polyelectrolyte should vary as a function of pH. Electrophoretic mobility measurements will be made on Pu(IV) polyelectrolyte at concentrations below the solubility of the mature Pu(IV) mineral fragment colloid at several pH concentrations between 3 and 11. A second set of measurements will be made on Pu(IV) mineral fragment colloid to demonstrate that its charge is affected by pH.

Experiment: AIC-8

Title: Formation of Pu(IV) intrinsic colloid, from oversaturation without  $p\text{CO}_2$ .

Hypotheses: (A) At moderately acidic as well as basic conditions, Pu(IV) polyelectrolyte will form because pH conditions are conducive for the Pu(IV) aquo-ions to undergo the first hydrolysis reaction, even at very low concentrations of the aquo ion. However, because the initial concentration ( $10^{-4}$  M) of the Pu(IV) aquo ion exceeds the solubility of the likely mature form [e.g.,  $\text{Pu}(\text{OH})_4$  (am),  $\text{Pu}(\text{OH})_4$  (c),  $\text{PuO}_2$  (c)], the Pu(IV) mineral fragment colloid will form from the Pu(IV) polyelectrolyte under both acidic and basic conditions. (B) Ionic strength suppression of hydrolysis at a constant pH value is not great enough to inhibit the formation of Pu(IV) polyelectrolyte even at 5 M. (C) The Pu(IV) mineral fragment colloid becomes more crystalline as it matures. In conjunction with maturation, the Pu(IV) mineral fragment colloid is kinetically

destabilized by electrostatic effects of the electrolyte, aggregates, and settles by gravity.

**Description:** This initial set of experiments is designed to test the formation of the Pu(IV) intrinsic colloid under conditions in which they are known to form. Experiments will be conducted as a function of ionic strength of NaCl ranging from 0.05 m to 5 m, acidic and basic conditions, and time. The initial concentration of Pu(IV) aquo-ions will be  $10^{-4}$  M, a concentration that exceeds the solubility of Pu (hydr)oxide in NaCl media by two or more orders-of-magnitude. The experiment is conducted over a period of four weeks, with samples collected for analysis immediately on introduction of Pu stock solution to the experimental matrix solution, and periodically over the following several weeks. Examination of solids isolated from samples collected at those times will provide qualitative information on the rate of maturation of Pu(IV) polyelectrolyte. It is anticipated that the initial amorphous Pu(IV) mineral fragment type colloidal solid will become more crystalline over the duration of the experiment. The size of individual crystallites, which are expected to be agglomerated in all but the most dilute concentration of NaCl, may also increase over the duration of the experiments. Formation and agglomeration of Pu(IV) mineral fragment type colloidal particles is expected to occur within the first few days. In a small test tube, Stokes law settling times for colloidal agglomerates of Pu(IV) should only be several hours. Consequently, the concentration of Pu(IV) aquo ion and Pu(IV) polyelectrolyte at the top of the sample vessels should stabilize within a few days to the expected solubility of the Pu(IV) (hydr)oxide solid in NaCl media. If the hypotheses are correct, then the Pu(IV) concentration at the bottom of the vessels, which will consist primarily of the Pu(IV) mineral fragment type colloid of varying crystallinity (along with minor concentrations of Pu(IV) aquo-ion and Pu(IV) polyelectrolyte).

**Experiment:** AIC-9

**Title:** Formation of Pu(IV) intrinsic colloid, from undersaturation without  $p\text{CO}_2$ .

**Hypotheses:** At moderately acidic as well as basic conditions, Pu(IV) polyelectrolyte will form because pH conditions are conducive for the Pu(IV) aquo-ions to undergo the first hydrolysis reaction, regardless of the concentration of the aquo ion. However, because the initial concentration ( $10^{-8}$  M) of the Pu(IV) aquo ion does not exceed the solubility of the likely mature form (e.g.,  $\text{Pu}(\text{OH})_4$  (am),  $\text{Pu}(\text{OH})_4$  (c),  $\text{PuO}_2$  (c)), the Pu(IV) mineral fragment colloid will not form from the Pu(IV) polyelectrolyte under either acidic and basic conditions.

**Description:** Experiments will be conducted as a function of ionic strength of NaCl ranging from 0.05 m to 5 m, acidic and basic conditions, and time. The initial concentration of Pu(IV) aquo-ions will be  $10^{-8}$  M, a concentration that does not exceed the solubility of Pu (hydr)oxide in NaCl media by two or more orders-of-magnitude. The experiment is conducted over a period of four weeks, with samples collected for analysis immediately on introduction of Pu stock solution to the experimental matrix solution, and periodically thereafter for several weeks. It is anticipated that the Pu(IV) mineral fragment type colloidal solid will not form over the duration of the experiment. Consequently, the total Pu(IV) concentrations at the top and bottom of the sample vessels should be identical, both containing the Pu(IV) aquo ion and Pu(IV) polyelectrolyte.

Experiment: AIC-10

Title: Formation of Pu(IV) intrinsic colloid, from oversaturation with high  $p\text{CO}_2$ .

Hypotheses: The formation and maturation of Pu(IV) polyelectrolyte to form mature Pu(IV) mineral fragment colloid will not be changed by the presence of high  $p\text{CO}_2$  because cation bridging by hydroxyl- and oxo-anions is dominant.

Description: The bridging anion in the Pu(IV) polyelectrolyte is thought to be hydroxyl ions. It is highly possible that the geochemical environment in the repository will contain a high  $p\text{CO}_2$ . The carbonate ion, which will dominate the carbonic acid-bicarbonate-carbonate system at high pH values, may compete with hydrolysis of actinides. If that is true, then Pu(IV) polyelectrolyte may not develop, or it may have a different form. If Pu(IV) mineral fragment colloids do develop in this experiment, their mineralogy will be determined by powder X-ray diffraction. Like experiment AIC-8, this experiment is conducted from over-saturation to ensure that colloidal particles will form. The experiment will be conducted at acidic and basic pH values. Under acidic conditions, the dominant carbon-bearing species is carbonic acid, which will not compete with hydrolysis. Consequently, results of the experiment conducted under acidic conditions are expected to be identical to experiment AIC-8 conducted in the absence of  $\text{CO}_2(\text{g})$ , under acidic conditions. Under basic conditions, the dominant carbon-bearing species is the carbonate ion. If the hypothesis is correct, the results of the experiment should also be identical to experiment AIC-8 conducted in the absence of  $\text{CO}_2(\text{g})$ , under basic conditions.

Experiment: AIC-11

Title: Formation of U(IV) or U(VI) intrinsic colloid, from over- and undersaturation.

Hypotheses: Repeat of AIC-1 and perhaps others for U(IV) and/or U(VI) which may form intrinsic colloids.

Description: As above.

#### 5.1.4 Microbes—Screening Experiments

A review of the current knowledge of microbe type colloidal particles was presented in Section 2.5.4. Microbes are isolated from cultures made from samples collected from saline ponds in the vicinity of the WIPP, from brine samples collected from the repository, from rock samples collected from the repository, and from brine samples collected from the Culebra. Experiments may be conducted with pure (axenic) cultures, mixed cultures, or indigenous bacteria isolated from Culebra brine samples.

Experiments involving transport and retardation of microbes are described in Section 5.1.5.



Experiment: B-1

Title: Steady-state concentration of mobile microbes.

Hypotheses: The population of mobile microbes is significantly less than the total concentration of microbes in a culture.

Description: In general, the concentrations of microbes in most experiments, including the work done in support of the WIPP gas-generation program (Brush, 1990; Francis and Gillow, 1994), have been determined by filtering the entire population of microbes and measuring the biomass. In terms of microbe-facilitated transport, the critical measurement is the free, or mobile, concentration of microbes in the culture. Much of microbe population is likely to be immobilized due to fixation on substrates (cellulosics in the case of WIPP). These experiments will be conducted with pure and mixed WIPP-relevant cultures under free-drift nutrient conditions. The microbial concentration remaining in the fluid column of batch experiments will be measured as a function of time. Bacterial cell numbers, sizes, and shapes will be evaluated. This activity consists of two phases. Phase I consists of a newly initiated series of experiments specifically designed for testing the above hypothesis and will also provide a means to develop appropriate experimental and analytical protocols. For Phase II, a small aliquot will be withdrawn from test vessels started several years ago as part of the microbial gas-generation program. The total numbers of bacterial cells, the portion of respiring or metabolically active cells, and cell morphologies will be determined using light microscopy. The Phase II activity will provide information on long-term effects.

Experiment: B-2

Title: Concentration of microbes in Culebra brines.

Hypotheses: The population of naturally occurring microbes present in Culebra brines will be significantly less than the population of microbes present in the WIPP repository, considering the increased amount of substrates and nutrients in the repository.

Description: In an intrusion scenario, dissolved actinides introduced to the Culebra could be bioaccumulated by indigenous microbes present in Culebra brines. Moreover, nutrient concentrations in the Culebra could be boosted by introduction of nutrients from the repository, which could cause a bloom of microbes in the Culebra. Because microbes may be the most effective vehicle for transport of actinides in the Culebra, it is important to characterize the total bacterial numbers, respiring or metabolically active cells, and bacterial size and morphology of naturally occurring microbes in brine samples collected from boreholes in the Culebra. In addition, brine samples collected from the Culebra will be amended with a low concentration of carbon and nitrogen to determine the potential impact of introduction of nutrients to the Culebra. Changes in mobile and immobile microbes will be determined including cell number, sizes, morphologies, and metabolic states.

Experiment: B-3

Title: Toxicity effects of U and Th actinides resulting from microbial bioaccumulation.

Hypotheses: Uptake of actinides, either by extracellular passive sorption or by active intracellular bioaccumulation, eventually leads to the death of the organism because of radioactive poisoning or heavy-metal toxicity. The presence of dissolved actinides in a dispersion may also have toxicity effects from radiation produced. Bioaccumulation of actinides is reduced in WIPP brines because of competition for microbial sorption sites by other cations in the brines. Dissolved actinide complexes, perhaps forming because of high carbonate ion concentration, are not actively bioaccumulated because of steric effects.

Description: Laboratory experiments on microbes cultured from samples collected at the Maxey Flats, Kentucky disposal site have shown that growth of those microbes became inhibited at elevated actinide concentrations (Francis, 1985). The experimental and analytical protocol will be similar to those used in B-1, except that actinide concentrations associated with the mobile and total biomass will also be evaluated. Mechanisms of bioaccumulation and biotransformation, such as microbial reduction of actinides perhaps leading to precipitation, will be investigated. Phase I of this experimental activity will be conducted with pure and mixed WIPP-relevant microbe cultures. Phase II of this activity will be conducted with indigenous microbes isolated from Culebra brine samples. Initial experiments will be conducted under nutrient deficient conditions. Subsequent experiments will be conducted with additions of low concentrations of carbon and nitrogen nutrients (see B-2).

Experiment: B-4

Title: Toxicity effects of Np, Pu, and Am actinides resulting from microbial bioaccumulation.

Hypotheses: Same as for B-3.

Description: Same as for B-3. This activity is separated from activity B-3 because of greater logistical complications working with Np, Pu, and Am.

### 5.1.5 Transport and Retardation Experiments

The objective of experiments described in this section is to provide information required to develop conceptual models of colloid transport and retardation in Culebra rocks and to develop numerical models and parameter values to provide the SNL WIPP PA Department with a means to implement the results. A variety of phenomena will be tested, including matrix diffusion, chemical interactions between colloidal particles and the host rock, and physical filtration (sieving). Retardation factors will be determined from the results.

The conceptual model used to describe hydrogeological flow in the Culebra is a fracture advection-matrix diffusion model (refer to Sections 2.4.1 and 7.2). That conceptual model may or may not be appropriate for interpreting the means by which colloidal particles are transported through the Culebra. In support of the transport experimental program, a review of existing information will be conducted in parallel with the development of the conceptual model for sorbents as described in Papenguth and Behl (in review). A substantial portion of the information required to develop conceptual models describing the interaction between the Culebra and dissolved actinides and colloidal actinides will come from the field non-sorbing tracer test and associated tests. Additional information will come from macroscopic and petrographic analysis of cores housed in the WIPP core library (Carlsbad, New Mexico), the horizontal core extracted from the air intake shaft at the WIPP (Lucero et al., 1995), outcrop inspection, etc.

To evaluate and quantify the transport and retardation of colloidal particles, two types of column experimental approaches will be utilized. Crushed-rock column flow experiments conducted with crushed Culebra core provide an economical means to conduct a relatively large number of experiments with a greater degree of variability. Core column flow experiments with large diameter (approximately 6 in) Culebra core provide confirmation that results from the crushed-rock column flow experiments are representative. The apparatus and experimental approach for the core column flow experiments is described in detail (Lucero et al., 1995). In addition to the column experiments, diffusion experiments may be conducted. A field-scale test involving colloidal particles as tracers is listed as an experiment in this section, but will be described in detail elsewhere in association with the field sorbing tracer test. The decision to conduct a field sorbing tracer test has not yet been made.

In designing crushed-rock column flow experiments, values for several parameters must be carefully selected. Those parameters and the rationale for the values selected are described.

In the field, it is believed that the double porosity nature of the Culebra results in advective flow in fractures coupled with diffusion into the matrix. Although core samples provide the best simulation of fracture advection-matrix diffusion in the laboratory, crushed-rock column flow experiments can provide an adequate simulation, because of the microcrystalline nature of the Culebra. As shown in Figure 16, crushed rock particles with diameters of 1 mm have a ratio of intragranular to extragranular surface area on the order of 100, which is quite large, and actually only one to two orders of magnitude less than the ratio for the core columns. Nevertheless, it is desirable to keep the crushed rock size as large as possible to simulate the possible effects of matrix diffusion. Again, because the microcrystalline nature of the Culebra, we believe that it is not necessary to use the approach devised by Toran and Palumbo (1992), in which plastic tubes mixed with sediment simulated double porosity flow in column experiments.

In his review of design considerations for column flow tests conducted to quantify retardation of

dissolved solutes, Relyea (1982) provided selection criteria for several key parameters which are useful in designing crushed-rock column flow experiments. Whereas those suggestions were for dissolved solutes, they provide a starting point for evaluating the retardation of colloidal particles. A tabulation of possible configurations that are consistent with suggestions by Relyea is presented in Table 10. A review and application of the suggestions of Relyea is presented in the following paragraphs. Additional information on experimental design is available in several publications (e.g., Enfield et al., 1989; Enfield, 1990; Amirbahman and Olson, 1993; Ivanovich et al., 1994; Read et al., 1994; Schlautman and Morgan, 1994; Zachara et al., 1994).

First, groundwater flow velocity should be sufficiently high so that broadening of elution peaks due to dispersion and diffusion, is less than the column length. Relyea suggested the following criteria for most dissolved solutes:

$$V_w \geq \frac{80 D}{C_L} \quad (42)$$

where:

- $V_w$  flow velocity (cm/s)
- $C_L$  column length (cm)
- $D$  diffusion coefficient (cm<sup>2</sup>/s)

For dissolved ions, Relyea (1982) used  $2 \times 10^{-5}$  cm<sup>2</sup>/sec. For colloidal particles,  $D$  will have to be reevaluated.

Second, flow velocity should not be so high, however, that the effective porosity of the packed column is reduced substantially below the actual (i.e., static) porosity. Effective porosity of the column can be determined empirically by comparing the pore volumes eluted and the pore volumes required for a non-sorbing tracer to elute. Actual porosity can be determined using the mass of an unsaturated and saturated column, with known volume. Relyea has found that longer columns provide better results, and that the column geometry should be:

$$C_L \geq 4 C_D \quad (43)$$

where:

- $C_L$  column length (cm)
- $C_D$  column diameter (cm)

However, once the crushed-rock column geometry has been selected, a series of experiments using flow velocities that bracket the desired flow velocity should be conducted to ensure that the effective porosity is constant for the geometry and velocity range selected. Further, replicate tests

with a range of column aspect ratios should be conducted to ensure that edge effects do not occur in elongated columns.

Third, flow velocity should not be so high that equilibrium is not reached between the sorbate and the sorbent. Though colloid transport was not addressed by Relyea, flow velocity should not be so high that equilibrium (or perhaps steady state) is not reached between the colloidal particles, the sorbate, and the host rock. Preferably, flow velocities should be kept low and column length should be long, to provide greater time for equilibrium to be reached. As equilibrium is approached, the ratio between the measured retardation factor and the equilibrium retardation factor approaches unity. Relyea provided a relationship for determining whether the flow velocity is appropriate, in terms of mass transfer units:

$$n = \frac{\rho_b K_d C_L}{\phi V_w} (k) \quad (44)$$

where:

n	number of mass transfer units
$\rho_b$	bulk density of the medium (cm <sup>3</sup> /g)
$K_d$	distribution coefficient
$\phi$	porosity of the medium (fractional)
$V_w$	flow velocity (cm/s)
$C_L$	column length (cm)
k	sorption rate constant

Equilibrium is approached to within 90 percent for 15 mass transfer units, whereas 30 mass transfer units are required to reach 95 percent of equilibrium. Equation 44 may not be particularly useful, however, because the sorption rate constant (k) is not well known.

Fourth, to avoid artifacts introduced by channeling, Relyea suggests that the column diameter should be at least 30 times the maximum particle size used in packing the column.

Fifth, consideration should be given to the design of the tubing, pumping apparatus, flow gauges, flow-through measuring cell, fraction collector, injection valves, etc., so that the dead-space volume is small compared to the porosity in the column.

Transport experiments with crushed rock will be conducted in standard glass chromatography columns and supplies. Spike injections and constant feed injections (step function) may be used. Depending on the tracers used, effluent may be analyzed in real time using a flow-through analytical cell or effluent may be collected with a fraction collector and analyzed later. As part of

the crushed-rock column flow experimental methods development, variations will be made in the experimental protocol to demonstrate that artifacts have not been inadvertently introduced. Analytical techniques that may be used include: Inductively coupled argon plasma-atomic emission spectrophotometry; nephelometry; ion-selective electrodes; light scattering photometry; ultraviolet/visible light spectrophotometry; fluorometry; ion chromatography; or light scattering particle sizing techniques (Table 11). The interpretation of elution curves will be made using standard computer codes such as CXT-Fit (Parker and Genuchten, 1984) or with COLUMN (Budge, in review), a computer code developed for interpretation of the core column flow tests being conducted as part of the WIPP chemical retardation program (Lucero et al., 1995).

**Experiment:** T-1 (MF,AIC,HS,B)

**Title:** Entrainment of agglomerated colloidal particles in the repository following intrusion.

**Hypotheses:** The energy required to entrain colloidal particles in a coagulated colloid system is higher than would be expected in the repository or in the Culebra. Entrainment of colloidal particles in a destabilized colloidal dispersion requires rather large hydrodynamic flow rates.

**Description:** In an E1, E2, or E1E2 scenario the repository will contain flowing brines, particularly for the E1 and E1E2 scenarios, in which pressurized brine from the Castile Formation enters the repository. In the repository environment, coagulated colloidal particles will settle by gravity to the floor of any microenvironment where they exist. This activity investigates the potential for entrainment of those coagulated colloidal particles under flowing conditions. Phase I consists of calculations using fluidized-bed reactor theory. Phase II is a laboratory evaluation of entrainment, in which the minimum hydrodynamic flow required to entrain agglomerated colloidal particles under simulated repository conditions is measured.

**Experiment:** T-2 (MF,AIC,HS,B)

**Title:** Orthokinetic coagulation of colloidal particles following entrainment.

**Hypotheses:** Orthokinetic destabilization of colloidal particles occurs significantly more rapidly than perikinetic destabilization. If destabilized colloidal particles are entrained during an intrusion scenario, tortuous flow paths with the repository environment or in the Culebra will result in rapid orthokinetic destabilization.

**Description:** Kinetic destabilization experiments to demonstrate the rapid agglomeration of mineral fragment type colloidal particles, actinide intrinsic colloids, and humic substances described above are conducted under static, i.e., perikinetic, conditions. In general, kinetic destabilization is enhanced under turbulent, i.e., orthokinetic, conditions. In the event that calculations or experiments conducted as part of T-1 demonstrate that significant concentrations of mobile actinide-bearing colloidal particles are entrained following an intrusion scenario, this experimental activity may be conducted. In the repository environment, entrained colloidal particles would have to flow through a series of microenvironments in which they come in close proximity to a variety

of waste components, such as iron corrosion products, cellulose, miscellaneous laboratory wastes, soils, etc. In the Culebra, coagulated colloidal particles would primarily interact with dolomite. Movement of colloidal particles through a subsurface environment is affected by several factors including ionic strength, surface charges of the colloidal particles and the matrix, pH (which affects surface charge), and hydrodynamic conditions such as tortuosity, porosity, and average linear velocity. Crushed rock column flow experiments are used to test attenuation of colloidal dispersions. One method for evaluating the impact of perikinetic agglomeration is through titrating the eluent of crushed-rock column experiments with electrolyte during the course of an experiment.

Experiment: T-3 (HS,B)

Title: Crushed-rock column flow experiments to quantify retardation of actinide-bearing colloidal particles.

Hypotheses: Transport of kinetically stable colloidal particles is retarded as a result of chemical and physical interaction with Culebra substrates.

Description: Colloidal particles that may be used in these experiments may include any of the four colloidal particle types. It is likely, however, that quantifying transport and retardation behaviors of humic substances and microbes will be emphasized. For humic substances, it is likely that some of the same humic and fulvic materials or analog compounds described in Section 2.5.2.2 will be used. For microbes, initial experiments will be conducted with latex microspheres. A wide range of sizes of microspheres are available commercially. In addition to neutral surfaces, latex microspheres are available with various surface functional groups, such as carboxyl and amino groups, that may simulate the surface chemistry of bacterial cells. Because many of the latex microspheres may be kinetically destabilized by high ionic strength dispersants, experiments may be conducted with low ionic strength eluents, to evaluate physical filtration effects, or perhaps to isolate physical filtration and chemical filtration effects. Once an understanding of microbe transport and retardation behavior has been established based on experiments with latex microspheres, a smaller number of additional experiments will be conducted with pure or mixed cultures of WIPP-relevant microbes. Potential non-sorbing tracers in experimental activity T-4 may include fluorescent dyes such as fluorescein, Rhodamine B, Rhodamine WT, or Sulforhodamine B, or inorganic ions, such as bromide or lithium (see, e.g., Davis et al., 1985). Whereas non-radioactive tracers are preferable from a safety and resource efficiency standpoint, radioactive tracers such as deuterated or tritiated water may need to be used. Selection of suitable conservative tracers will be conducted as part of the experimental protocol for this activity. Experimental activity T-4 will be conducted in three phases. For Phase I, colloidal particles with no cation sorbents (other than the elements present in the brine eluent) will be used, in order to simplify the experimental protocol while a basic understanding of colloidal particle rock interaction is achieved. For Phase II, surrogates for the actinides, such as lanthanide elements europium, neodymium, or gadolinium, will be used. Experiments with non-radioactive surrogates provides a

means to conduct a larger number of experiments over a broader range of conditions. Finally, some experiments may be conducted with actinide-bearing colloidal particles in Phase III. General guidance for column transport experiments was described in Section 5.1.5.

Experiment: T-4 (HS, B)

Title: Intact-core column flow experiments to quantify retardation of actinide-bearing colloidal particles.

Hypotheses: Transport of kinetically stable colloidal particles is retarded as a result of chemical and physical interaction with Culebra substrates.

Description: Same as activity T-4, but using large diameter (approximately 6 in) intact core acquired from the WIPP air intake shaft. Experimental protocol described in Lucero et al. (1995) will be adapted for testing colloidal actinides rather than dissolved actinides. These experiments will be confirmation experiments for information gained in activity T-4.

Experiment: T-5 (HS, B)

Title: Measurement of diffusion constants for humic substances

Hypotheses: Diffusion constants for humic substances in WIPP brines will be much lower than predicted by radius ratios because of the compressing effect that high-ionic strength solutions have on macromolecules with surface functional groups such as humic substances.

Description: Means for estimating the diffusion constants of colloidal particles were discussed in Section 2.4.3. By quantifying diffusion constants experimentally, it is likely that the diffusion values will be greater than those determined by estimation, resulting in a greater attenuation of colloidal particles.

Experiment: T-7 (HS, B)

Title: Batch  $K_d$  measurements of cosorption of microbes and/or humic substances, actinides, and Culebra host rock.

Hypotheses: In the presence of microbes or humic substances, sorption of actinides onto Culebra substrates is enhanced due to ternary sorption effects.

Description: This activity will be done to support microbial and humic substance transport experiments described in T-4 and T-5. Empirical batch sorption experiments with crushed Culebra rock samples under appropriate aqueous geochemical conditions will be used to determine minimum  $K_d$  values and sorption isotherm shapes. These experiments would be similar to the empirical batch sorption experiments being conducted in support of the dissolved actinide chemical retardation program. Refer to Papenguth and Behl (in review) for a description of those experiments.



## 5.2 Laboratory Equipment and Materials

In this section we describe the facilities at which the above listed work is likely to be conducted.

### 5.2.1 Facilities

Facilities that are scheduled to be used for the work described in this Test Plan include the following laboratories at SNL:

Surface- and Colloid-Chemistry Laboratory  
Technical Area 1, Building 823, Room B-45

Geochemistry Engineering Laboratory  
Technical Area 1, Building 823, Room B-59

Water Chemistry Laboratory  
Technical Area 1, Building 823, Room 2079

Core Column Flow Laboratory  
Technical Area 3, Building 6600

In general, static screening and transport experiments which do not involve the use of actinides will be conducted in the first three laboratories listed above. Transport experiments with actinides will be conducted at the Core Column Flow Laboratory. Each of the SNL laboratory facilities has a Standard Operating Procedure (SOP) that defines how laboratory activities are conducted in a manner consistent with Environment, Safety, and Health requirements (note that at SNL, methodologies used in WIPP experiments are described in Technical Operating Procedures, not SOPs).

Some of the experiments, particularly static screening experiments with actinides, will be conducted at other facilities, including Lawrence Livermore National Laboratory (Glenn T. Seaborg Institute for Transuranic Science), Brookhaven National Laboratory, Los Alamos National Laboratory, and Florida State University.

### 5.2.2 Analytical Equipment

A variety of analytical equipment is used for measurements in support of the experimental activities

described in this Test Plan. Equipment that has been identified for use is listed in Table 11. It is likely that other equipment will also be used. Analytical equipment will be used for the following general activities: particle sizing and population measurement; general aqueous chemistry; solute characterization; and solids characterization and surface chemistry. Measurements will be conducted in accordance with Technical Operating Procedures developed for specific instruments.

### 5.2.3 Reagents and Standards

Laboratory reagents and standards may be acquired from a variety of commercial vendors including Fisher Scientific and Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin). Mineral and rock samples may be acquired from cores of the Culebra housed at the WIPP Core Library (Carlsbad, New Mexico), from core acquired from the air intake shaft which was obtained primarily for the core column flow experiments (Lucero et al., 1995), and from commercial vendors, such as Ward's Natural Science Establishment, Inc. (Rochester, New York). Clay minerals may be obtained from the Clay Minerals Society Library (Columbia, Missouri).

Colloidal particles, including latex microspheres of various sizes and functionalizations and macromolecules such as blue Dextran (a polysaccharide used in colloid transport studies), are available from Polysciences, Inc. (Warrington, Pennsylvania). Humic substances are available from a library at the Colorado School of Mines (Golden, Colorado). Microbes can be cultured from samples collected from saline ponds near the WIPP Site and from rock and fluid samples collected in the subsurface.

Where possible, standards will be purchased that are traceable to the National Institute for Standards and Technology (NIST). For some of the colloid characterization analysis techniques (e.g., electrophoretic mobility), no NIST-traceable standards exist. Similar problems may be encountered with some actinide isotopes. For those cases, independent analytical methods will be utilized where possible as a cross check on the methodology.

### 5.3 Milestones and Schedule

Logic charts showing the key experiments that were described in Section 5.1, their linkages, and the prioritization are shown in Figure 17. As noted above, many of the experiments are contingencies in case the hypotheses are not demonstrated. Those experiments are designated with dashed lines. Gantt charts showing the planned schedules and milestones are presented in Figure 18.

## 6.0 Application of Information from Source-Term Test Program

A detailed discussion of how the data resulting from the Source-Term Test Program (STTP) component of the SNL WIPP Actinide Source Term Program (ASTP; refer to Section 1.5.1) will be utilized and managed is the subject of a separate document titled "Plan for the Utilization and Interpretation of Actinide source Term Waste Test Program Data," included in Appendix A.

With regard to the SNL WIPP Colloid Research Program, a primary objective of the STTP component of the SNL WIPP ASTP is to test the following hypothesis: For actinide-bearing colloidal particles, the largest concentration within the uncertainty range (i.e., error bar) predicted for the repository environment for applicable STTP test containers will not be exceeded by the colloidal concentration measured for that STTP test container when at steady-state conditions.

## 7.0 Deliverables

Deliverables from the colloid characterization and transport research program are focused toward providing the SNL WIPP PA Department the information that they require to quantify the impact of actinide-bearing colloidal particles on the performance of the WIPP. We anticipate providing three deliverables.

First, we will provide a description of defensible conceptual models generated from the results of our experiments and information gained from the literature. The conceptual models will describe how colloidal particles are generated, what types are important to consider in performance assessment calculations, how those colloidal particles are mobilized, and their transport and retardation behaviors. As part of this first deliverable, we will provide recommendations on how the SNL WIPP PA Department can numerically implement those conceptual models. This step will require interaction with representatives of the SNL WIPP PA Department to reach a viable approach. We will provide mathematical models where appropriate. As discussed in Section 1.6, the WIPP Disposal Decision Plan (Figure 3; US DOE, 1995) dictates that this deliverable was to be provided to the SNL WIPP PA Department by 30 September 1995.

Second, we will provide parameter values to support the recommended numerical implementation. As discussed in Section 1.6, the WIPP Disposal Decision Plan (Figure 3; US DOE, 1995) dictates that critical experimental results be completed by 31 March 1996.

Third, we will provide detailed written documentation of the experimental methods, experimental results, and interpretation. Detailed explanations will be prepared justifying the conceptual models, the recommendations for numerical implementation of those conceptual models, and limitations of the results. This deliverable will be initiated after that date, so that we can devote the time until 31 March 1996 on the experimental program.

The first deliverable is described in the remainder of this Section.

### 7.1 Mobile Colloidal-Actinide Source Term

In the repository environment, actinide solids present in the waste will dissolve according to thermodynamic principles until an equilibrium<sup>4</sup> is established between the following entities: (1) the actinide-bearing solid phase; (2) dissolved actinide ions and complexes with anthropogenic organic ligands; (3) actinide polyelectrolyte macromolecules (i.e., the immature actinide intrinsic colloid or polymer); (4) actinides sorbed on fixed substrates (e.g., iron corrosion products); (5)

<sup>4</sup> Note that the actinide-bearing precipitates will be metastable initially, and become more stable with time. Consequently, the concentration of dissolved actinides will decrease with time.

actinides sorbed onto immobile colloidal substrates; and (6) actinides sorbed onto mobile colloidal sorbing substrates (e.g., humic substances). Because of the complexities of evaluating the equilibrium relationships between those entities, the WIPP Project has elected to not take credit for item (4), sorption onto fixed substrates, and has also elected to disregard the effects of competition associated with the equilibrium between dissolved actinides and actinides associated with colloidal particles. Consequently, the repository source term is reduced to two independent components that are not linked, resulting in an overestimation of the total concentration of mobile actinides that may leave the repository environment.

It is likely that the concentration of actinides sorbed on or contained within colloidal particles will be a function of a variety of physicochemical conditions, such as pH,  $p\text{CO}_2$ , concentration of major brine constituents, ionic strength, oxidation speciation of the actinides, and concentration of organic ligands. Information on chemical conditions within the repository are likely to be used for determining dissolved actinide concentrations and could also be used as input parameters in determining concentrations of actinides associated with the different colloidal particle types. The intrusion scenario selected for a particular PA realization will dictate the major ion composition of the repository brine. In the event of an E1 or E1E2 intrusion scenario, the repository brine will be dominated by the brines introduced from the Castile Formation, because of the relatively high hydrostatic pressure anticipated in the Castile Formation. In an undisturbed scenario or an E2 intrusion scenario, the repository brine will consist of Salado Formation brine. Key parameters associated with the intrusion scenario then, are magnesium concentration and ionic strength (refer to Table 5). The partial pressure of carbon dioxide and the pH will be controlled by the extent to which microbial degradation of wastes and corrosion of iron in the repository occurs. In practice, microbial gas production, pH, and  $p\text{CO}_2$  will be sampled parameters within each PA realization. The concentration of actinides associated with microbes could be linked to the selection of whether microbial gas generation is occurring. We have elected not to make that linkage, however, because lysed microbes may take part in actinide transport, yet not produce gas. The concentration of a set of five organic ligands will be sampled within each PA realization from a distribution that reflects the concentrations anticipated in the waste inventory and the uncertainties in those concentrations. Acetate, citrate, EDTA, lactate, and oxalate will be considered.

For the repository portion of the mobile colloidal-actinide source term, actinide concentrations will be selected from a table of concentrations and uncertainties on the basis of magnesium concentration, ionic strength, pH,  $p\text{CO}_2$ , and organic ligand concentration. We have suggested that a table format (actually a series of tables) identical to the dissolved actinide solubility program be used to provide flexibility. In practice, however, we recognize that our experimental program will not enable us to address the effects of many of the input parameters, and the look-up table will be reduced to a significantly simplified format. In its simplest form, the colloidal particle source-term table will consist of values and uncertainties, in a four-by-five nodal-element matrix, defining actinide concentrations (Th, U, Np, Pu, Am) associated with each the four colloidal particle types.

Each of those values will represent the steady state concentration of actinides associated with that particular colloid type in terms of molarity or molality.

In the event that the sum of the concentration of a particular dissolved actinide element (the sum of contributions of all of its possible oxidation states) and the concentration of that actinide associated with mobile colloidal particles exceeds the inventory-limited concentration of that actinide (i.e., total mass of actinide in repository divided by the amount of brine in the repository; see Section 2.5.4.3 and Table 4), then a partitioning scheme must be utilized. Rather than basing the partitioning on an equilibrium approach, we have elected to use a simpler approach based on conservatism. The total concentration of a particular actinide element in the inventory is made available first to the most efficient transport mode, which may be microbes for example. If the concentration of actinide is not exhausted, then next most efficient transport vehicle is filled. That process is continued until the actinide inventory is exhausted by assignment to the five categories of transport vehicles (four colloidal particle types and dissolved actinide elements).

After introduction of colloidal actinides and dissolved actinides into the Culebra, realistically a new equilibrium condition will be established, with the stipulation that the total concentration of actinide must be preserved. Components participating in establishing a new equilibrium include: (1) actinides precipitated or coprecipitated with carbonate or sulfate salts resulting from the mixing of repository and Culebra brines; (2) dissolved actinide ions and complexes with anthropogenic organic ligands introduced from the repository; (3) actinide polyelectrolyte macromolecules (i.e., the immature actinide intrinsic colloid or polymer) from the repository; (4) actinides sorbed onto mobile colloidal sorbing substrates (e.g., humic substances) from the repository; (5) actinides sorbed onto mobile colloidal sorbing substrates (e.g., humic substances) present in Culebra brines; (6) sorption of dissolved actinides or complexes onto the Culebra host rock; and (7) cosorption of colloidal actinides onto the Culebra host rock. As in the repository, quantifying an equilibrium assemblage is beyond our capabilities. Consequently, we have elected not to attempt to link processes, which is a conservative approach provided that retardation of dissolved actinides exceeds colloid-facilitated actinide retardation.

The effect of naturally occurring colloidal particles in the Culebra is included in the source term by supplementing the repository colloidal actinide source term with the potential contribution from Culebra colloidal particles. A more obvious approach would have been to modify the repository source term as it was introduced to the Culebra, perhaps by assigning a portion of the dissolved actinide to the concentration of naturally occurring colloidal particles in the Culebra. That approach is not consistent with the implementation of SECO-TP, however, as is seen in the following example. In a particular time step within a PA realization, a mass of actinides is introduced into the nodal block in the Culebra intersected by the intrusion borehole, and immediately mixed with the contents of that nodal block. The impact of naturally occurring colloidal particles in the Culebra must be defined by the mass of actinides that may sorb to those particles, which, therefore is

specified as a mass per unit volume (i.e., concentration) term. In the event that colloidal particles are not retarded, the two colloidal source terms may be added at the Culebra without introducing artifacts. If, however, retardation of colloidal actinides does occur, then the concentration of colloidal actinides in that nodal block continually increases with subsequent time steps as Culebra colloidal particles are added. Supplementing the repository source term avoids that artifact, although the approach is probably overly conservative.

## 7.2 Transport and Retardation

Because of schedule constraints imposed by the Disposal Decision Plan (US DOE, 1995; Figure 3, Section 1.6), the program to quantify transport is being conducted in parallel with the source term quantification. As stated in the previous subsection, we anticipate that the effort to quantify transport will definitely result in a demonstration that actinides associated with colloidal particles will be retarded relative to an ideal non-sorbing dissolved species. After completing the colloidal actinide source term experiments, we may conclude that the colloidal actinide source term is negligible. In that case, the transport effort may be useful in demonstrating the existence of a "secondary barrier," that provides increased confidence that actinide-bearing colloidal particles will not result in a health and safety risk to the public. We intend to continually reevaluate the focus of the colloid research program. If a change in the emphasis on transport experiments and model development is warranted, we will refocus the program accordingly.

Quantification of actinide transport by colloidal particles is a particularly challenging area of contaminant transport modeling, because it requires coupling of various aspects of hydrogeology, geochemistry, and colloid chemistry (see, e.g., McDowell-Boyer et al., 1986, 1987; Hwang et al., 1991; Mills et al., 1991; Nuttall et al., 1991; Bennett et al., 1993; van der Lee et al., 1993, 1994; Gauthier, 1994). Those aspects may be grouped into the following categories: (1) the physicochemical behavior of colloidal particles in the dispersant, including the formation of the particles and their kinetic and thermodynamic stabilities; (2) interaction of the colloidal particles with actinides; and (3) the hydrologic behavior of colloidal particles in the subsurface environment.

Several phenomena were described in Section 2.4 that could result in increases or decreases in the rate of actinide transport by colloidal particles relative to the rate of movement of an idealized non-sorbing dissolved species. Relative to that idealized tracer, actinide transport by colloidal particles may be increased by a reduction in the rate of diffusion into intercrystalline pores or size exclusion from intercrystalline pores. Increased relative transport rates associated with flow due to size and surface charge effects (equations 3 and 5) is negligible considering uncertainties associated with other aspects of transport and retardation. A variety of mechanisms for reducing the relative rate of colloid-facilitated transport of actinides was also described, including ionic strength destabilization, gravitational settling, surface filtration, adsorption onto the host rock, sieving, clogging, and

diffusion into intercrystalline pores in a direction normal to the net groundwater flow direction.

Three approaches could be used in quantifying colloid-facilitated actinide transport at the WIPP. First, the transport of one or more types of actinide-bearing colloidal particles in the Culebra could be assumed to be instantaneous. In other words, as actinides associated with that type of colloidal particle migrate to the Culebra from the repository, or are generated within the Culebra, the mass of actinides associated with those colloidal particles becomes part of the integrated release of actinides at the accessible environment boundary (Figure 1). That approach may be useful if the concentrations of actinides associated with one or more types of colloidal particles is very low. Treating colloid-facilitated actinide transport as instantaneous, however, is a significant shortcoming, because of the potentially large anticipated retardation effects of colloidal particles. Second, relatively minor modifications could be made in the existing advection-dispersion numerical code (SECO-TP; Roache, 1993) and supporting codes, to simulate the effects of one or more of the colloid retardation phenomena. Phenomena identified that may significantly increase the rate of actinide transport by colloidal particles would also be included. This approach was used for the SPM calculations (Prindle et al., 1996a,b). Specifically, microbes, because of their relatively large sizes, were excluded from matrix diffusion and limited to advective flow in fractures. Humic substances were allowed to diffuse into intercrystalline pores, but at a reduced rate relative to dissolved actinide species. It is likely that additional colloidal particle retardation phenomena can be accurately simulated by minor modifications in SECO-TP. This numerical simulation approach has been used by other organizations in performance assessments of other sites. Third, colloid-facilitated actinide transport could be quantified by a rigorous numerical modeling code developed for the WIPP. As described in Section 2.4, such a rigorous transport model would address all physical and chemical processes which could affect the movement and fate of the four colloidal particle types, including colloid generation, interactions with solutes, the dispersant, and rock, advection, dispersion, diffusion, filtration, gravitational settling, attachment and detachment, adsorption and desorption, coagulation, flocculation, peptization, etc. Ideally, permeability reduction due to pore clogging by colloids, which would impact solute transport as well, would also be considered. Currently available models do not include all the processes, and it is not possible to develop a model of this complexity with reasonable resources within the current Disposal Decision Plan schedule (Figure 3; US DOE, 1995).

Among the most sophisticated rigorous numerical models are those being developed by van der Lee et al. (1993, 1994) and Bennett et al. (1993). Many of the colloid transport numerical models described in the literature focus on simulating solute transport through fractured media with double porosity flow characteristics, and have been generalized to include unique features of colloid transport (e.g., Hwang et al., 1989; Grindrod and Worth, 1990; Light et al., 1990; Smith and Delguedre, 1993; Harmand and Sardin, 1994). Some numerical models, such as the population balance model by Travis and Nuttall (1985), assume equilibrium colloid concentrations. That is, the loss of colloidal particles by attachment to the medium wall is compensated by the generation of



new colloidal particles by various mechanisms such as condensation and entrainment ("simultaneous birth and death"). The modeling approach developed by Travis and Nuttall (1985), however, is quite similar to the double porosity transport model equation.

To our knowledge, none of the rigorous numerical codes were designed for long-term performance assessment calculations, such as those required for the WIPP Project. One means to simplify the numerical modeling approach, is to isolate complicated mechanisms from the colloid-facilitated contaminant transport numerical models. For evaluation of the performance of the WIPP, we have done this, by quantifying kinetic stability outside of any transport model. The remaining phenomena, can be treated empirically with retardation factors which include the composite effects of surface filtration, physical filtration (sieving), clogging of pore throats, diffusion, and perhaps cosorption. As discussed at length in Section 2, a significant reduction in the potential impact of colloidal particles on the performance of the WIPP can be made at the source term level, without consideration of the transport properties of those colloidal particles.

The most practical approach to evaluating the transport of colloidal actinides is the second option presented above, in which we use the existing SECO-TP numerical code (Roache, 1993). Where possible, we will reduce the number of phenomena that need to be treated in the transport code, and address them from a source-term perspective. For example, the effect of ionic strength on colloid stability will be included in the colloid source term. Retardation of colloidal particles will be quantified using a retardation factor, which includes the integrated effects of chemical and physical retardation phenomena that cannot be isolated from the transport code.

In its current implementation, SECO-TP allows for four types of retardation: (1) retardation within matrix porosity accessed by advective flow, following a matrix advection single porosity type conceptual model for hydrogeologic flow; (2) retardation within matrix porosity accessed by diffusion, following a fracture advection-matrix diffusion double porosity type conceptual model for hydrogeologic flow; (3) retardation within a thin layer (e.g., a "clay-lining," refer to Papenguth and Behl, 1995) adjacent to fracture surfaces; or (4) retardation on a fracture surface. The choice of implementation will depend on the final conceptual model chosen to describe the transport and retardation of each of the four colloidal particle types. Assuming that the field non-sorbing tracer tests demonstrate that the most appropriate hydrogeological conceptual model is a fracture advection-matrix diffusion model, we would select the corresponding SECO-TP implementation to evaluate retardation of colloidal particles small enough to diffuse into the rock matrix. If that is the case, a complication arises in the treatment of large-diameter colloidal particles such as microbes, if they are too large to diffuse into the matrix porosity. Instead, retardation of microbes would be simulated by sorption onto fracture surfaces, which is essentially a  $K_a$  approach (refer to Section 2.5.1.4). For the 30 September 1995 deliverable, we have recommended that the three types of retardation be retained in SECO-TP, and that provisions are made within the code to allow unique transport treatment of each of the four colloidal particle types in addition to the dissolved actinides.

That approach provides us with flexibility to select from several conceptual models describing hydrogeologic flow in the Culebra, and the behavior of the four colloidal particle types according to that conceptual model.

A complication associated with quantifying colloid-facilitated actinide transport (as well as transport and retardation of dissolved actinide species) is that the heterogeneous properties of the Culebra must be considered. As described above in Section 2.3, groundwater composition in the Culebra is variable, especially when considering an intrusion scenario in which Salado and Castile Formation brines will be introduced. The rock fabric, both locally and regionally, of the Culebra is also variable, and may affect hydrogeologic flow. That variability of physical and chemical properties along a potential flow path cannot be measured directly. Several types of rock fabrics have been observed in core collected from the air intake shaft and elsewhere (refer to Papenguth and Behl, in review). An evaluation of the representativeness of those cores is being evaluated as part of the Culebra dissolved actinide species Chemical Retardation Program (Papenguth and Behl, in review).

From a performance assessment perspective, incorporating the effects of heterogeneity can be approached in several ways. Ideally, the spatial and temporal extents of heterogeneity could be defined and an exact weighted distribution of parameter values would be prepared that reflect that heterogeneity. A more realistic approach is to treat this variability and related phenomena in a probabilistic manner. In this probabilistic approach, known variability is accounted for by sampling probability distribution functions describing the variability of the desired parameter with respect to all relevant parameters that affect the value of the desired parameter. Finally, perhaps the most appropriate approach is to identify the parameters and their ranges which may effect the value of the desired parameter, and then establish a bounding value for the desired parameter. Bounded values must be selected such that they reflect conditions under which releases to the accessible environment are not underestimated (i.e., it should be conservative). Bounded values for some of the parameters that might be included in a rigorous transport models are embodied in the colloidal actinide source term. Included in that category are the destabilization effects of ionic strengths and sorption of actinides onto carrier colloids.

## 8.0 Provisions for Significant Events

Not applicable to the work described in this Test Plan.

## 9.0 Operational Regulatory Requirements

The SNL Environment, Safety, and Health (ES&H) Department has developed procedures and guidelines for various activities to ensure that SNL is in compliance with all applicable federal, state, and local regulatory requirements concerning public health concerns. Any changes in regulatory requirements will be addressed by revising those Standard Operating Procedures as required.

The experiments described herein will be conducted following SNL ES&H procedures and guidelines. Standard Operating Procedures have been developed in accordance with ES&H guidelines for experimental activities proposed in this Test Plan. Standard Operating Procedures are in place for all SNL laboratory facilities listed in Section 5.2.1: Water Chemistry Laboratory (Robinson, 1995b); Core Column Flow Test Laboratory (Lucero, 1995); Colloid-Chemistry and Surface-Chemistry Laboratory (Robinson, 1995a).

Note that at SNL, Standard Operating Procedures are documents addressing only ES&H concerns, whereas Technical Operating Procedures are documents that address laboratory procedures for operation of analytical equipment and conduct of experiments.

## 10.0 Quality Assurance

All activities conducted by SNL and its contractors in support of this Test Plan will be conducted in accordance with the Quality Assurance (QA) requirements described in the Quality Assurance Program Description (QAPD, Revision R) and the QA Procedures (QAPs). The relevant elements of the QAPD and the related QAPs are addressed in this Section.

Contractors to SNL are required to develop a Quality Assurance Project Plan (QAPP) for their work.

### 10.1 Training

All personnel involved in the experiments described in this Test Plan will be trained and qualified for their assigned work. This requirement will be implemented through QAP 2-2 (Orientation and Training Program). All qualification and QA training records will be submitted to, and maintained by the SNL WIPP Central File office. The training records for the following ES&H courses are maintained in the SNL Laboratory Information System training database TIDBITS:

- EMG 145: SNL Emergency Response Awareness
- EMP 100: Employee Rights
- FRP 100: Fire Extinguisher Awareness
- LTO 100: Lock Out/Tag Out Awareness
- PRS 102: Basic Pressure Safety
- RAD 101: Radiological Worker Training
- RAD 102: Radiation Awareness
- SAF 110: Safety Meeting

### 10.2 Design Control

This Test Plan is a part of the Five-Year Program Plan (US DOE, 1994a), and is a DOE requirement. The experimental approach for planned experiments is described in detail in Section 5. The proposed experiments require off-the-shelf commercial equipment as well as some special equipment built commercially to the specifications supplied by the Principal Investigator to individual manufacturers. These experiments have been designed after an extensive literature review (see Section 2). The independent peer review of the experiment design will be conducted as part of the review of this Test Plan. The experiments being proposed in this Test Plan do not require modifications to underground facilities. Core samples that may be used in some transport experiments have been obtained from the air intake shaft (Lucero et al., 1995).

### 10.3 Procurement Document Control

The procurement documents associated with any procurement of items or services in support of the proposed experiments will be prepared following the guidelines provided in QAP 4-1 (WIPP Supplier Quality Assurance Program Requirements). The review and approval requirements for the procurement documents and any changes to them are also provided in QAP 4-1. The QA review requirement for commercial grade items is waived if they meet certain criteria specified in QAP 4-1.

### 10.4 Instructions, Procedures, and Drawings

The acceptance criteria for these experiments were developed in Section 4 as part of the Data Quality Objective process, and are in the format of action levels (i.e., target values). However, unexpected problems cannot be ruled out completely in spite of careful planning. In such cases, this Test Plan will be amended or revised to address the unexpected problems. These changes will be implemented through QAP 20-1 (Preparing, Reviewing, and Approving Test Plans), used in generating the original Test Plan (see Section 10.5). In addition, the experimental results will be periodically reviewed by the DOE and review groups to determine if they are technically acceptable. Those technical reviews may result in modifications to the acceptance criteria for satisfactory completion of these tests. The QA records that are anticipated to be generated as a result of various activities associated with the proposed tests are identified in Section 10.16.

### 10.5 Document Control

According to the QAPD (Revision R) Test Plans are not controlled documents. The preparation and issuance of this Test Plan, and any major changes to it in the future will be controlled through QAP 20-1 (Preparing, Reviewing, and Approving Test Plans).

### 10.6 Control of Purchased Items and Services

Procurement of items and services required for the proposed experiments will be controlled by QAP 4-1 (WIPP Supplier Quality Assurance Program Requirements), which provides QA controls and guidelines for the following, as appropriate:

- source evaluation and selection;

- evaluation of objective evidence of quality furnished by the supplier;
- source inspection;
- audit; and
- examination of items or services upon delivery or completion.

### **10.7 Identification and Control of Items**

The requirements for identification and control of data, materials, parts, samples, specimens, and components are provided in QAPs 13-1 (Conducting and Documenting Sample Control) and 13-2 (Chain-of-Custody) will be followed during the conduct of the proposed experiments.

### **10.8 Control of Processes**

The QAPD (Revision R) and various QAPs establish processes and procedures to ensure that activities conducted in support of the WIPP are completed in accordance with federal and industrial quality requirements. For example, the scientific investigation described in this Test Plan will be conducted in accordance with this Test Plan, which has been developed following the guidelines specified in QAP 20-1 (Preparing, Reviewing, and Approving Test Plans). The data analysis will be controlled by QAP 9-1 (Quality Assurance Requirements for Conducting Analyses). Any special processes affecting the quality of the activities described in this Test Plan will be controlled by Technical Operating Procedures according to the QA requirements specified in QAP 5-3 (Preparing, Reviewing, and Approving Technical Operating Procedures). A special process is defined in NQA-1 as "a process, the results of which are highly dependent on the control of the process or the skill of the operators, or both, and in which the specified quality cannot be readily determined by inspection or test of the product."

### **10.9 Inspections**

In addition to periodic QA inspections for any aspect of the experiments (see Section 10.10 below), routine safety inspections are anticipated which are discussed in ES&H Standard Operating Procedures for the laboratories where these tests will be performed (refer to Section 9 for list of relevant ES&H Standard Operating Procedures).

### **10.10 Test Control**

Experimental activities will be controlled and conducted in accordance with the approved Test Plan,

a copy of which will be maintained in the laboratory. At the discretion of SNL WIPP management, a readiness review may be conducted according to the guidelines provided in the QAPD (Revision R). The QA records will be submitted to the SNL WIPP Central File in accordance with QAP 17-1 (WIPP Quality Assurance Records and Source Requirements). Test and experiment results will be documented laboratory notebooks and, as appropriate, an automated data acquisition system. Periodic QA overviews will be conducted at the discretion of the SNL QA staff. Any deficiencies identified through these inspections will be corrected and documented following the requirements of QAP 16-2 (Conditions Adverse to Quality and Corrective Action).

### **10.11 Control of Measuring and Testing Equipment**

The calibration requirements for measuring and testing equipment used in the experiments will be controlled according to QAP 12-1 (WIPP Calibration Laboratory Quality Assurance Program). The calibration procedures for each instrument are described in the documentation provided by its manufacturer and/or various TOPs. These procedures will be followed and the calibration data will be kept in the data package for this activity. If these procedures are unavailable or deficient, calibration procedure will be developed and reviewed following the guidelines provided in QAP 12-1. In addition, all requirements identified in QAP 12-1 regarding staff qualification and training, calibration records including calibration labels, and measurement standards will be observed.

### **10.12 Handling, Storage, and Shipping**

Standard operating procedures (SOPs) or instructions for handling, storage, and shipping laboratory equipment and materials related to the proposed experiments have been documented in ES&H Standard Operating Procedures. Those SOPs also include guidance for safety related equipment and materials (e.g., radioactive materials). In addition, QAPs 13-1 (Conducting and Documenting Sample Control) and 13-2 (Chain-of-Custody) identify requirements and appropriate forms for documenting and tracking sample possession.

### **10.13 Inspection, Test, and Operating Status**

Many of the instruments to be used in the proposed experiments will require periodic inspections and testing for their satisfactory operation. This requirement will be controlled through calibration stickers, tags, and markings on each item and also through notations in laboratory notebooks. These stickers on each instrument will clearly show its operating status so that instruments that are due for an inspection/testing or do not pass the required inspection/testing are not inadvertently



used.

The status of these experiments will be provided through monthly progress reports conveyed verbally to SNL WIPP Project Management, SNL reports, through presentations at meetings, workshops, and conferences, and through peer-reviewed journal publications.

#### **10.14 Control of Non-conformances**

If any deficiency is identified in the conduct of these experiments which would make the data obtained in the experiments unacceptable or indeterminate, immediate actions will be taken to assess the impact of the deficiency, to prevent recurrence of the deficiency, and to document the deficiency and related activities in a Non-conformance Report. Detailed guidelines for preparing a Non-conformance Report and the related review and approval process are given in QAP 16-2 (Conditions Adverse to Quality and Corrective Action).

#### **10.15 Corrective Actions**

Conditions adverse to data quality such as power failures during data acquisition, instrument malfunctions or failures, and defective items and their root cause will be immediately evaluated to assess their impact on the experiments and to determine what corrective actions are needed. This evaluation and any corrective actions taken will be documented in a Non-conformance Report using the guidelines of QAP 16-2 (Conditions Adverse to Quality and Corrective Action), including appropriate forms.

#### **10.16 Quality Assurance Records**

QA records generated through the activities of this Test Plan are:

- Test Plan
- Training and qualification records
- Procurement documents
- Readiness review documents
- ES&H SOPs
- Logbooks
- Inspections/testing documents
- Technical and operating procedures
- Assessment reports

- Calibration/certification reports
- Uninterpreted data
- Technical progress reports and SAND reports
- Non-conformance reports

These records will be submitted to the SNL WIPP Central File as required by QAP 17-1 (WIPP Quality Assurance Records Source Requirements). Document records and test data will be submitted to the SNL WIPP Central File when they are finalized or completed, respectively. During the test, the data collected using an automated data acquisition system will be downloaded and backed up in duplicate at least daily.

### **10.17 Computer Software**

Any computer software development in support of these tests will be controlled through documentation requirements specified in Section 6 of the QAPD (Revision R), and QAP 19-1 (WIPP Computer Software Requirements).

## 11.0 Health and Safety

All of the health and safety requirements relevant to the colloid experiments and the procedures that will be used to satisfy these requirements are described in the ES&H Standard Operating Procedures identified in Section 10. Those ES&H Standard Operating Procedures identify radiation and other hazards associated with these experiments and describe the procedures to deal with these hazards including all the training requirements for personnel involved in conducting these experiments. In addition, the experimental procedures take into consideration all the relevant ES&H requirements. General experimental procedures have been discussed in Section 5. For most cases, the safety requirements are expected to have no direct impact on the technical aspects of these experiments. Note, however, that some of the experiments described herein must be conducted within glove boxes due to safety considerations, which significantly impede the rate at which experiments can be conducted. That reduction has been considered in developing the schedules included in Figures 17 and 18, but it does limit the number of experiments that may be conducted.

## 12.0 Acknowledgments

The SNL WIPP Colloid Research Program has benefited from ongoing discussions with a large number of scientists and engineers at SNL and elsewhere since it was initiated in Fall 1992. The initial planning benefited from a series of technical discussions held in early 1993 with Robert J. Silva, Brian Viani, Marilyn S. Buchholtz-ten Brink, Ken J. Jackson, Susan A. Carroll, M. Susan Martin, and Kevin G. Knauss (LLNL); Heino Nitsche (formerly at LBL); Bruce D. Honeyman (Colorado School of Mines); Joseph N. Ryan (University of Colorado); and Inés R. Triay, Alan J. Mitchell, Joseph L. Thompson, Wilfred L. Polzer, Mark Paffett, and Edward H. Essington (LANL). Review comments on a draft precursor to this Test Plan, the "Actinide Source Term Model Development Plan," (see Section 1.3) written by Hans W. Papenguth, Craig F. Novak, and E. James Nowak, have also been useful in developing the WIPP Colloid Research Program.

The SNL WIPP Colloid Research Program has benefitted from extensive and ongoing technical discussions with E. James Nowak (SNL), R. Vann Bynum (SAIC Inc.), and representatives from the SNL WIPP PA Department and their contractors. The experimental approach for actinide intrinsic colloids, humic substances, and microbial colloids has been significantly improved from discussions with Cynthia E. A. Palmer (LLNL), Greg R. Choppin (FSU), and A. J. Francis (BNL), respectively. Discussions with Robert A. Stroud and Richard J. Lark (DOE/CAO); Patrick V. Brady, Thomas F. Corbet, Fred Gelbard, John W. Kelly, Malcolm D. Siegel, Peter N. Swift, Robert C. Moore, Laurence H. Brush, Mark L. F. Phillips, W. Graham Yelton, and Kurt W. Larson, Kent G. Budge (SNL); Linda Marquez and David A. Wruck (LLNL); Richard E. Westermann (PNL); Jeff B. Gillow (BNL); and David G. Bennett (Galson Sciences Ltd., United Kingdom) have resulted in improvements in the Colloid Program.

We also acknowledge our immediate contacts at DOE/CAO, Richard J. Lark and Robert A. Stroud, who have assisted in developing this program. Review comments received from Aldred L. Stevens, Harlan W. Stockman, and Wendell D. Weart (SNL); David G. Bennett (Galson Sciences Ltd., United Kingdom); and Richard J. Lark (DOE/CAO) and his WTAC staff, have resulted in a significant improvement of this document. Carol Crawford (SNL) conducted a reference review.

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**Appendix A. Plan for the Utilization and Interpretation of STTP Data**

**Plan  
for the Utilization and Interpretation  
of  
Actinide Source Term Waste Test Program  
Data**

**December 20, 1995**

**Plan for the Utilization and Interpretation  
of  
Actinide Source Term Waste Test Program  
Data**

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Chemical & Disposal Room Processes

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Date

Chemical & Disposal Room Processes





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## 1.0 Objective of the Plan for Utilization and Interpretation of STTP Data

The objective of this document is to define how the data resulting from the Actinide Source-Term Waste Test Program (STTP) will be utilized and managed. To accomplish this objective, the interface requirements and responsibilities for the Department of Energy, Carlsbad Area Office (DOE/CAO), Sandia National Laboratories (SNL) and Los Alamos National Laboratory (LANL) are defined, and evaluation criteria and protocols for data interpretation are established.

This plan supersedes any previous description of the management and utilization of data from the STTP which may be contained in other plans, but is not intended to replace any detailed plans or procedures being utilized by the participants in carrying out their responsibilities as outlined in this plan.

## 2.0 Introduction

The WIPP Actinide Source Term Program (ASTP) is the set of activities with the objective of quantifying the concentrations of actinides that could be mobilized by WIPP brines and thus could be transported by several mechanisms from the WIPP facility to the accessible environment. The overall goal of the ASTP is to provide defensible data to demonstrate that WIPP will be in compliance with 40 CFR 191. The ASTP is composed of three principal activities:

- Dissolved Species Submodel Development
- Colloidal Species Submodel Development
- STTP

The Dissolved Species Submodel Development and Colloid Species Submodel Development are described in separate Test Plans (Novak 1995 and Papenguth 1995, respectively). The technical requirements for the STTP were defined by Phillips and Molecke (1993) and were incorporated into the Test Plan by Villarreal and Phillips (1993). The relationship of these activities with each other and with the other activities within the WIPP program are described in the Test Plan for the WIPP Actinide Source Term Conceptual Model and Actinide Dissolved Concentration Submodel (Novak 1995).

### **3.0 Objectives of the STTP**

A primary objective of the STTP is to test the following hypotheses:

1. For each dissolved actinide, the highest concentration within the uncertainty range (as expressed by error bars) of the maximum solubility as predicted by the Dissolved Species Submodel for applicable STTP test containers will not be exceeded by the highest measured dissolved concentration within the uncertainty range of composition analyses for that STTP test container when at steady state conditions. For the Dissolved Species Submodel, the STTP will not be used to lower the maximum, thermodynamically predicted solubility limit for dissolved actinides under the conditions evaluated by the model because of the potential in the STTP for sorption on immobile substrates and the impossibility of isolating and identifying the solubility-limiting, actinide-bearing minerals from the waste matrix.
2. For colloidal species containing actinides, the largest concentration within the uncertainty range (error bar) as predicted by the Colloidal Species Submodel for applicable STTP test containers will not be exceeded by the colloidal concentration measured for that STTP test container when at steady state conditions.

A secondary objective of the STTP is to corroborate information and hypotheses on the oxidation state distribution of the actinides under anticipated repository like conditions. To accomplish this objective, those containers with sufficiently high actinide concentrations will be analyzed to establish the oxidation state distribution under the conditions of the tests. Based on preliminary analytical methods development, it is anticipated that a concentration of approximately  $1 \times 10^{-6}$  moles/liter will be required to determine by spectrophotometry the oxidation state distribution of applicable actinides in brine samples taken from STTP containers. Although lower concentration limits may be achievable by using other solvent extraction, and co-precipitation techniques, spectrophotometric techniques are preferred to minimize the potential of the oxidation state distribution being corrupted by the analytical procedures. The details of this work are covered in "Actinide Redox Reactions Important in WIPP Site" Rev. 0 by Rai et. al.

The STTP is being performed by LANL with technical guidance provided by SNL. The tests were initiated in February 1995 and the first data collected in April 1995. The STTP is projected to continue for approximately 3-5 years to allow each of the containers to reach or approach steady state conditions and to allow for the potential to modify experiments that may provide mechanistic information on the concentrations of actinides in brine in contact with actual waste, if deemed necessary.

#### **4.0 Management of Source and Interpreted STTP Data**

##### **4.1 SNL Responsibilities**

SNL is designated as the Scientific Advisor to the WIPP. In this role, SNL has the responsibility to define the technical requirements for the tests, verify that appropriate Quality Assurance measures are in place and effective, and take the lead role in the data analysis and interpretation. SNL will perform the analysis of the data consistent with the protocol as outlined in Section 6.0.

Consistent with SNL Quality Assurance Procedure (QAP) 17.1 , SNL has the responsibility to maintain and store all items which are designated as project records.

#### 4.2 LANL Responsibilities

LANL has responsibility for carrying out the required experimentation in accordance with the requirements of the Technical Requirements Document and LANL's contract with the Department of Energy Carlsbad Area Office (DOE/CAO). LANL shall generate all data in accordance with the approved STTP Quality Assurance Project Plan (#CLS1-STP-QAP1-002/0), perform the required data management according to the STTP Data Reduction, Validation, and Reporting Procedure (CST1-STP-QAP5-017/0), provide the data to SNL in the format as prescribed later in this section, and assist in interpreting the experimental results as requested by the SNL Principal Investigator (PI). LANL must also transfer all items designated as project records to SNL in accordance with QAP 17.1.

In addition to providing the raw data and the compiled data in the form of approved data packages, LANL shall provide a matrix of the analytical results of each test container by analyte and a graphical representation of each actinide by container. The matrix should be provided to the SNL PI in the form of an Excel or Excel importable spreadsheet in both hard copy and electronic forms. The electronic form transfer should take place via electronic mail to WIPPMA@NWER.SANDIA.GOV. A diskette copy should also accompany the transmittal of the data packages.

To assist SNL and DOE/CAO in understanding the progress of the experiments, LANL will participate in meetings to discuss the results of the experiments and present the extrapolated prediction of the achievement of steady state by curve fitting techniques. The choice of curve fitting techniques is left to LANL's discretion within the bounds as described in Section 6.0.

#### 4.3 DOE/CAO Responsibilities

DOE/CAO is the direct customer for SNL and LANL. In that role, DOE/CAO has the responsibility to provide contractual direction to both SNL and LANL, perform technical and programmatic oversight of the program, ensure that the Quality Assurance requirements are fulfilled, and serve as the primary interface to stakeholder groups.

### 5.0 Test Matrix and Analytical Protocol

Since preparation of the Technical Requirements document (Phillips and Molecke, 1993) and the Test Plan (Villarreal and Phillips, 1993), several changes have been made to the test matrix because of revisions in scope, unanticipated nature of the waste, and the need to evaluate the effects of Castile Formation brines as well as Salado Formation brines. In its current configuration, the STTP consists of 33 low pressure test containers of nominal 3 liter internal volume ("liter-scale vessels") and 15 65-gallon test containers ("drum-scale vessels"). There are also six of the vessels of two liter nominal internal volume which will be operated at 60-bar pCO<sub>2</sub>. Each of the low pressure, liter-scale and drum scale test containers will be sampled approximately eight times per year. The pressurized liter-scale test containers will be sampled three times per year. The liter-scale vessels were sealed and the experiments initiated in March 1995. The drum-scale vessels were sealed and experiments initiated in May 1995. The loading matrix for these vessels is provided in Table 1.

As outlined in the responsibilities section above, LANL will perform the data validation, reduction, and reporting, prepare matrices of analytical results, and prepare a graphical representation of the results for each container by actinide. This information will be transmitted to SNL as available, but not less than quarterly, by the LANL Project Leader.

## 6.0 Protocol for Assessing Challenges to the Hypotheses

Prior to assessing the outcome of the test of the hypothesis, it is necessary to determine that the vessels are at steady state with respect to the actinide being assessed or that the steady state concentration can be estimated with a high level of confidence. For the purposes of the STTP and the testing of the hypotheses, a container will be considered to have reached steady state when the measured concentrations of the actinides does not change between three successive measurements (covering a period of at least two months) by more than the greater of 20% of the measured value or 4 times the analytical uncertainty.

### 6.1 Challenges to the Dissolved Species Submodel Hypothesis

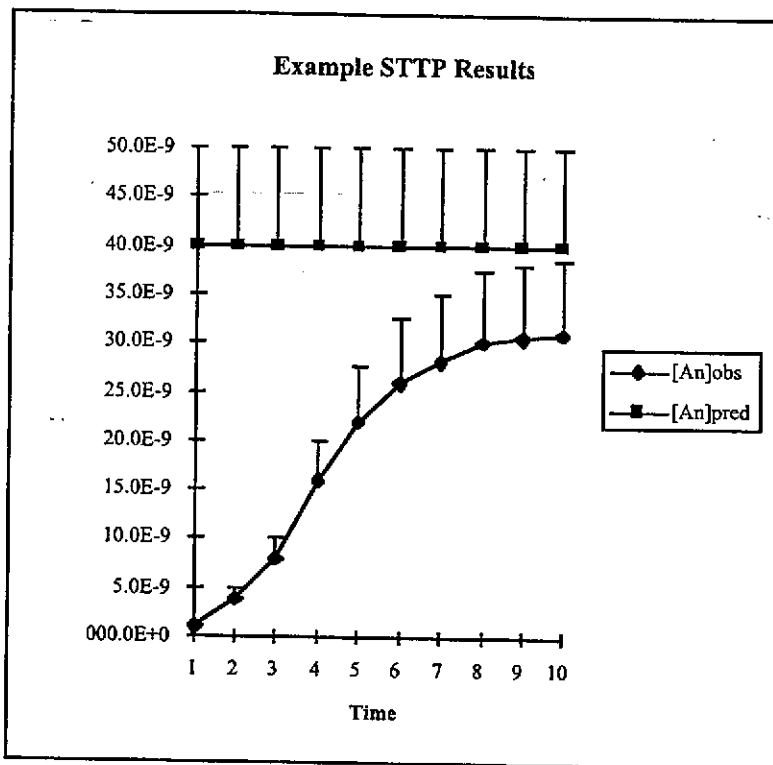
Once a test container has been determined to have reached steady state, or a point where steady state can be estimated as described in Section 6.0, with respect to the particular dissolved actinide being evaluated, the hypothesis as described in Section 3.0 can be tested. For the hypothesis to be confirmed, the upper bound (which includes the analytical uncertainty) of the measured value of the actinide concentration must be less than or equal to the upper bound (including the model uncertainty) of the predicted value.

example 1 The Dissolved Species Submodel predicts that container 'x' will have a steady state concentration of dissolved plutonium of  $10^{-5.7} \geq M \geq 10^{-7.7}$  moles/liter. Three successive analytical results provide total dissolved plutonium values of  $(5.6 \pm 2.2) \times 10^{-8}$ ,  $(6.1 \pm 1.1) \times 10^{-8}$ , and  $(6.0 \pm 1.1) \times 10^{-8}$  moles/liter. Because the upper bound of the measured values ( $7.8 \times 10^{-8}$ ,  $7.2 \times 10^{-8}$ , and  $7.1 \times 10^{-8}$  moles/liter, respectively) is less than the upper bound of the predicted value ( $2 \times 10^{-6}$  moles/liter), the hypothesis is upheld.



example 2 The Dissolved Species Submodel predicts that container 'y' will have a steady state concentration of dissolved plutonium of  $10^{-5.5} \geq M \geq 10^{-7.5}$  moles/liter. Three successive analytical results provide total dissolved plutonium values of  $(7.7 \pm 3.2) \times 10^{-6}$ ,  $(6.8 \pm 3.1) \times 10^{-6}$ , and  $(7.5 \pm 2.2) \times 10^{-6}$  moles/liter. Because the upper bound of the measured values ( $1.1 \times 10^{-5}$ ,  $9.9 \times 10^{-6}$ , and  $9.7 \times 10^{-6}$  moles/liter, respectively) is greater than the upper bound of the predicted value ( $3 \times 10^{-6}$  moles/liter), the validity of the hypothesis is brought into question.

If the upper bound of the measured value is greater than the upper bound of the predicted value, the outcome is considered anomalous and the observation must be investigated.



Upon discovery of an anomalous comparison, the SNL STTP PI will contact the SNL ASTP and LANL STTP PIs to notify them of the situation and request that they review their documentation leading to the predicted and/or measured values to ensure that the observation is not a result of

an analytical, sampling, or reporting error. If no such error is found, a meeting of the SNL ASTP and STTP PIs and the LANL STTP PI will be convened. This group will review all of the results and possible influencing variables to determine if there is a reasonable explanation for the disparity. All efforts by this group will be carefully documented in accordance with SNL QAP 19.1 to provide a clear and documented record. Additional analytical and/or modeling activities may be requested to help clarify the anomalous results.

## 6.2 Challenges to the Colloidal Species Submodel Hypothesis

Once a container has been determined to have reached steady state, or a point where steady state can be predicted as described in Section 6.0, with respect to the particular actinide-bearing colloidal particle being evaluated, the hypothesis that the largest concentration within the uncertainty range (error bar) of the actinide-bearing colloidal particle prediction for any STTP test container will not be exceeded by the largest measured actinide-bearing colloidal particle concentration within the uncertainty analyses for that STTP test container when at steady state conditions may be tested.

The form of the prediction and what is being tested for the Colloidal Species Program will be significantly different from that of the Dissolved Species Program. The actinide-bearing colloidal particles expected to potentially exist in the repository are not sensitive to many of the chemical and physical parameters to which the dissolved species are sensitive but are sensitive to other parameters. The key parameter that impacts the existence of colloids is the ionic strength of the brine, and experiments have shown that the mineral fragments are kinetically destabilized at any of the ionic strengths possible within the regulated environment. The only potential exception to this is in the area of the actinide intrinsic colloids where formation and stability are chemically dependent; however, we anticipate being able to confirm the hypothesis that the actinide intrinsic colloids if formed will be kinetically destabilized in the high ionic strength brines. At this time there is no basis for discounting the existence of actinide-bearing microbial

colloids in the repository, and efforts are underway to quantify this parameter. In consideration of the above factors, the results utilized in the Performance Assessment (PA) will be a two dimensional matrix of colloid types and upper bound concentrations (Table 2).

PA may have to track the different categories of colloids through side calculations in the event that they cannot be proved to be destabilized and they have different transport properties.

For the purposes of assessing the challenge of the assertion for colloidal properties, the analysis will be a simple comparison to verify that the value determined experimentally in the STTP with its associated experimental error is less than or equal to the maximum predicted concentration from the completed matrix. Upon discovery of an anomalous comparison, the SNL STTP PI will contact the SNL Colloid Source Term and Transport and LANL STTP PIs to notify them of the situation and request that they review their documentation leading to the predicted and/or measured values to ensure that the observation is not a result of an analytical, sampling, or reporting error. If no such error is found, a meeting of the SNL Colloid Source Term and Transport and STTP PIs and the LANL STTP PI will be convened. This group will review all of the results and possible influencing variables to determine if there is a reasonable explanation for the disparity. All efforts by this group will be carefully documented in accordance with SNL QAP 19.1 to provide a clear and documented record. Additional analytical and/or modeling activities may be requested to help clarify the anomalous results.

## 7.0 Utilization of STTP Data

### 7.1 Use of the STTP Data in the Dissolved Species Submodel Development

While it is not anticipated that the data generated within the STTP will generally be utilized beyond being used to test the hypothesis as described in Section 3.0, the STTP will generate a

wealth of empirical data. These data can well be utilized as a contingency in the event that the Dissolved Species Submodel does not achieve all of its objectives. Additionally, the use of these data for testing other hypotheses may evolve as the experiment progresses.

## 7.2 Use of the STTP Data in the Colloidal Species Submodel Development

It is not anticipated that, beyond being used to test the hypothesis as described in Section 4.2, the data from the STTP will be directly utilized in the Colloidal Species Submodel Development.

## 8.0 Assurance of Independence of Evaluation

The work being carried out in support of the ASTP, and indeed the entire WIPP Project, is subject to a rigorous Quality Assurance Program which includes checks and balances to ensure that all data are accurately portrayed, all assumptions are appropriately documented, and an auditable trail exists for all conclusions. Through this Quality Assurance Program and its auditability, the assurance of the independence of the model predictions from the STTP experimentally derived results is maintained.

## 9.0 References

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## 10.0 Tables

TABLE 1. STTP LOADING MATRIX (Part A, Drums)

STTP TEST	STAMPED (vessel ID)	VOI [L]	BRINE	TRU CON	ID#drum sampled}	WASTE TYPE	Fe	NdCl3 *6H2O	Special Conditions	Liq/Sol , g solid	brine wt, #	Th U Np by plan	Archive Pu reads ug/g 239	Archive Total g Pu239	Archive Am rea ug/g 241	Archive Total g Am-241
D1	#08	246	A	116	54546	COMBUSTIBLES	yes	9.18g		na	740.2-200.2	5g each	Pu 5g+	na	na	na
D2	#012	246	A	116	52896	COMBUSTIBLES	yes	9.18g		na	728.4-211.4	5g each	per 55gal	na	na	na
D3	#013	246	ERDA6	116	54129	COMBUSTIBLES	yes	9.18g		na	730.2-200.0	5g each	waste	na	na	na
D4	#06	246	A	116	52114	COMBUSTIBLES	yes	9.18g	Bentonite 10kg**	na	765.0-266.0	5g each	Pu 5g+	na	na	na
D5	#03	246	A	116	53565	COMBUSTIBLES	yes	9.18g	Bentonite 10kg**	na	723.4-275.8	5g each	per 55gal	na	na	na
D6	#010	246	ERDA6	116	52410	COMBUSTIBLES	yes	9.18g	Bentonite 10kg	na	746.4-250.4	5g each	waste	na	na	na
D7	#01	246	A	116	52047	COMBUSTIBLES	yes	9.18g	chelators	na	783.3-276.0	5g each	Pu 5g+	na	na	na
D8	#04	246	A	116	54409	COMBUSTIBLES	yes	9.18g	chelators	na	726.0-206.4	5g each	per 55gal	na	na	na
D9	#011	246	ERDA6	116	54174	COMBUSTIBLES	yes	9.18g	chelators	na	720.6-211.4	5g each	waste	na	na	na
D10	#07	246	A	116	52878	COMBUSTIBLES	yes	9.18g	[ 159.0g NaNO3,	na	728.0-220.6	5g each	Pu 5g+	na	na	na
D11	#05	246	A	116	53217	COMBUSTIBLES	yes	9.18g	258.1g NaH2PO4	na	754.6-201.0	5g each	per 55gal	na	na	na
D12	#02	246	ERDA6	116	53211	COMBUSTIBLES	yes	9.18g	these 3 drums]	na	717.8-219.6	5g each	waste	na	na	na
D13	#018	246	A	117	54371	METALS	yes	9.18g		na	867.4-324.4	5g each	Pu 5g+	na	na	na
D14	#003	246	A	117	52109	METALS	yes	9.18g		na	846.2-297.4	5g each	per 55gal	na	na	na
D15	#014	246	ERDA6	117	54871	METALS	yes	9.18g		na	860.0-315.6	5g each	waste	na	na	na
D16	#017	246	A	na	N/A	NONE	na	9.18g		na		no		na	na	na
D17	#014	246	ERDA6	na	N/A	NONE	na	9.18g		na		no		na	na	na
NOTE:	drum 17	now	"D18"	SO	"#"/3=	ERDA 6.			**Brine A equil'b'd							

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TABLE 1. STTP LOADING MATRIX (Part B, literscales)

STTP TEST	STAMPED (vessel ID)	VOI [L]	BRINE	TRU CON	ID#drum sampled)	WASTE TYPE	Fe	NdCl3	Liq/Sol. , g solid	brine wt, #	Th U Np by plan	Pu reads ug/g 239	Total P g	Archive Am rea	Archive Total gAm
L1	#010	3 L	A	111	55111	DEWATERED	yes	78mg	r10/1, 264	75mg ea		68	0.017	1.12	2.79E-04
L2	#002	3 L	A	111	55110	AQUEOUS	yes	78mg	r2/1, 1320	75mg ea		80	0.105	1.41	1.85E-03
L3	#001	3 L	ERDA6	111	55107	PROCESS	yes	78mg	r2/1, 1320	75mg ea		93	0.124	1.45	1.94E+03
L4	#HP001	2L	A	111	55112	SLUDGE	yes	52mg	CO2 pressurized r10/1, 184	75mg ea		103	0.021	1.27	2.59E-04
L5	#HP002	2L	A	111	55113	WITH PORTLAN	yes	52mg	CO2 pressurized r3/1, 613	75mg ea		83.5	0.051	0.97	5.94E-04
L6	#HP003	2L	ERDA6	111	55103	CEMENT	yes	52mg	CO2 pressurized r2/1, 920	75mg ea		95	0.086	1.08	9.80E-04
L7	#027	3 L	A	111	55105	DEWATERED	no	78mg	r10/1, 264	75mg ea		94.5	0.026	1.198	3.26E-04
L8	#028	3 L	A	111	55108	AQUEOUS	no	78mg	r2/1, 1320	75mg ea		88.5	0.118	1.095	1.47E-03
L9	#029	3 L	ERDA6	111	55102	PROCESS	no	78mg	r2/1, 1320	75mg ea		81	0.108	0.955	1.28E-03
L10	#030	3 L	A	111	55101	SLUDGE	no	na	AmCl3 75mg r10/1, 264	75mg ea		86	0.021	1.005	2.50E-04
L11	#031	3 L	A	111	55109	WITH PORTLAN	no	na	AmCl3 75mg r2/1, 1320	75mg ea		98	0.131	1.195	1.60E-03
L12	#032	3 L	ERDA6	111	55104	CEMENT	no	na	AmCl3 75mg r2/1, 1320	75mg ea		81.5	0.107	1.021	1.34E-03
L13	#018	3 L	A	112	5133P8-A	[ ORG. LIQUID	yes	78mg	r2/1, 1320	75mg ea		2575	3.386	1.92	2.52E-03
L14	#007	3 L	A	112	5133P8-B	SOLIDIFIED W	yes	78mg	r2/1, 1320	75mg ea		2592	3.368	2.54	3.40E-03
L15	#017	3 L	ERDA6	112	5133Y8	ENVIROSTONE	yes	78mg	r2/1, 1320	75mg ea		31.5	0.041	0.019	2.50E-05
L16	#005	3 L	A	113	5131A4	IAQ LAB WASTE	yes	78mg	r2/1, 1320	75mg ea		470	0.618	0.25	3.29E-04
L17	#006	3 L	A	113	5133A7	SOLIDIFIED W	yes	78mg	r2/1, 1320	75mg ea		1140	1.474	2.05	2.65E-03
L18	#019	3 L	ERDA6	113	5133U3	ENVIROSTONE	yes	78mg	r2/1, 1320	75mg ea		1970	2.591	26.48	3.48E-02
L19	#008	3 L	A	114	53822	[ INORG SLUD	yes	78mg	r2/1, 1320	75mg ea		380	0.508	12.75	1.71E-02
L20	#011	3 L	A	114	53754	SOLIDIFIED W	yes	78mg	r2/1, 1320	75mg ea		60.5	0.08	7.07	9.30E-03
L21	#009	3 L	ERDA6	114	53720	ENVIROSTONE	yes	78mg	r2/1, 1320	75mg ea		190	0.25	24.75	3.25E-02
L22	#004	3 L	A	126	54054	ORG. SLUDGE	yes	78mg	r2/1, 1320	75mg ea		180	0.233	6.51	8.45E-03
L23	#013	3 L	A	126	54029	SOLIDIFIED W	yes	78mg	r2/1, 1320	75mg ea		380	0.5	9.55	1.26E-02
L24	#003	3 L	ERDA6	126	54066	ENVIROSTONE	yes	78mg	r2/1, 1320	75mg ea		231	0.309	8.19	1.10E-02
L25	#014	3 L	A	124	SLTFP3122A	PYROSALT	yes	78mg	r2/1, 1320	75mg ea		285	0.381	0.3	4.01E-04
L26	#015	3 L	A	124	SLTFP31241A	PYROSALT	yes	78mg	r2/1, 1320	75mg ea		3075	1.044	1.71	2.25E-03
L27	#016	3 L	ERDA6	124	SLTFP31241B	PYROSALT	yes	78mg	r2/1, 1320	75mg ea		2585	3.4	1.18	1.55E-03
L28	#HP006	2 L	A	124	SLTFP3125A	PYROSALT	yes	78mg	CO2 pressurized r2/1, 920	75mg ea		11530	10.46	1.35	1.22E-03
L29	#HP005	2 L	A	124	SLTFP3137A1	PYROSALT	yes	78mg	CO2 pressurized r2/1, 920	75mg ea		4715	4.277	2.59	2.35E-03
L30	#HP004	2 L	ERDA6	124	SLTFP3137A2	PYROSALT	yes	78mg	CO2 pressurized r2/1, 920	75mg ea		2185	2.03	1.44	1.34E-03
L31	#020	3 L	A	124	XBRCW198E	PYROSALT	yes	78mg	Bentonite** r2/1, 1320	75mg ea		612.5	0.806	0.49	6.44E-04
L32	#021	3 L	A	124	XBRCW199E	PYROSALT	yes	78mg	Bentonite** r2/1, 1320	75mg ea		3105	4.083	2.21	2.91E-03
L33	#022	3 L	ERDA6	124	XBRCW200E	PYROSALT	yes	78mg	Bentonite r2/1, 1320	75mg ea		860	1.151	0.83	1.11E-03
L34	#023	3 L	A	124	XBRCW201E	PYROSALT	yes	78mg	[chelators+Ca(OH) r3/1, 880	75mg ea		2325	2.004	3.06	2.64E-03
L35	#024	3 L	A	124	SLTFB3117A	PYROSALT	yes	78mg	these three vesse r3/1, 880	75mg ea		510	0.451	0.79	6.99E-04
L36	#025	3 L	ERDA6	124	SLTFB3123A	PYROSALT	yes	78mg	Ca(OH)2 96.2g 0. r3/1, 880	75mg ea		12575	11.13	5.61	4.96E-03
L37	#033	3 L	A	124	SLTFP3124A	PYROSALT	no	na	AmCl3 75mg r2/1, 1320	75mg ea		3295	4.333	0.83	1.09E-03
L38	#034	3 L	A	124	XBRCW197E	PYROSALT	no	na	AmCl3 75mg r2/1, 1320	75mg ea		2045	2.736	5.55	7.43E-03
L39	#035	3 L	ERDA6	124	XBRCW1807	PYROSALT	no	na	AmCl3 75mg r2/1, 1320	75mg ea		3350	4.482	8.695	1.16E-02

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**Table 2**

Colloid Type	Maximum Concentration (moles actinide/liter)
Mineral Fragments	0.0
Actinide Intrinsic Colloids	TBD
Humic Materials	TBD
Microbial Colloids	TBD



## Appendix B. Figures

Figure 1.—Artist's concept of the WIPP disposal system showing the controlled area and accessible environment for 40 CFR 191, Subpart B, and the repository/shaft system. The repository/shaft system scale is exaggerated. On the land surface, the land-withdrawal boundary is shown at the same scale as the maximum extent of the controlled area (modified from Bertram-Howery and Hunter, 1989b). The disposal-unit boundaries for 40 CFR 268 for the WIPP Test Phase are shown for reference (US EPA, 1990a). Figure and caption from WIPP PA Department (1992a, Figure 3-2).

Figure 2.—Conceptual models for (a) the E1 scenario; (b) the E2 scenario; and (c) the E1E2 scenario. Arrows indicate assumed direction and relative magnitude of flow.  $R_c$  is the release of cuttings and eroded material.  $R_{acc}$  is the release at the subsurface boundary of the accessible environment. Illustrated plugs are assumed to remain intact for 10,000 years. DRZ indicates the disturbed rock zone adjacent to the disposal room; MB indicates anhydrite-rich marker bed horizons within the Salado Formation. Figure and caption from WIPP PA Department (1992a, Figures 4-2b, 4-3a, and 4-3b).

Figure 3.—WIPP Disposal Decision Plan schedule (Revision 1, 15 March 1995, updated 1 June 1995; US DOE, 1995).

Figure 4.—Nature and size domain of the most important particles of aquatic systems. Figure and caption from Buffle and van Leeuwen (1992b, Foreword). Note that "simple" hydrated anions and cations are on the order of 1 ångstrom in size, that humic and fulvic acids are among the smallest colloidal particles, and that bacteria and mineral fragment type colloidal particles (e.g.,  $FeO\cdot OH$  and  $MnO_2$ ) are among the largest colloidal particles.

Figure 5.—Possible excursions and eventual conditions of disposal rooms in Eh/pH space. Figure courtesy of L. H. Brush. Figure and caption from Phillips and Molecke (1993, Figure 2). The ranges shown in this figure are currently being defined as part of the WIPP gas generation program.

Figure 6.—Total organic carbon concentrations measured in Culebra groundwaters. Compiled from information presented in Myers et al. (1991). Note that most of the total organic carbon concentrations are below 1 mg/L.

Figure 7.—Schematic representation of the electric double layer surrounding a negatively charged colloidal particle in an aqueous environment. The electric double layer is comprised of the Stern layer, a relatively dense concentration of counterions immediately adjacent to the negatively charged particle, and the Diffuse layer surrounding the Stern layer. As the colloidal particle undergoes electrokinetic motion, the plane of shear is the interface between the Stern and Diffuse layers, and the surface electrical potential at the plane of shear relative to the bulk solution is described by the  $\zeta$ -potential. The graph at the bottom left illustrates the increase in anion concentration and decrease in cation concentration within the Diffuse layer that occurs with increasing distance from the plane of shear. The graph at the bottom right illustrates the magnitude of electrical potentials between the surface of the colloidal particle and the plane of shear (Nernst-potential), and between the plane of shear and the bulk solution ( $\zeta$ -potential). Figure from Hirtzel and Rajagoplian (1985).

Figure 8.—Potential energy curves for interaction between two spherical mineral-fragment type colloidal particles calculated from DLVO theory. Positive interaction energies correspond to repulsion between particles (solid circles), and negative energies correspond to attraction (solid squares). The total energy between particles is shown by solid triangles. Interparticle distance is defined by the distance between the surfaces of the two colloidal particles. For the calculations illustrated in Figures 8a, b, and c, the electrolyte type (symmetrical 1:1 cation:anion salt such as NaCl), dielectric constant for the dispersent (80), Hamaker constant for the colloidal particle material ( $3.0 \times 10^{-20}$  joules is representative of many geologic materials; see Ross and Morrison, 1988), particle diameter (0.1  $\mu\text{m}$ ), and surface charge (surface charge was approximated by equating it to a  $\zeta$ -potential of 30 mV) were kept constant. Ionic strength was varied. Note that the attraction energy (solid squares) does not vary as a function of ionic strength. As ionic strength increases, however, the magnitude of the repulsion energy decreases significantly.

(a) At an ionic strength of 1 mM, the colloidal particles must come within extremely close proximity to one another for coagulation to occur. The dispersion, therefore, is considered to be kinetically stable. (b) At an ionic strength of 10 mM, repulsion and attraction forces are similar in magnitude and range, and the colloidal dispersion is kinetically metastable. The slightly negative total interaction energy occurring in this case at interparticle separations of about 8-15 nm, referred to as the secondary minimum, results in the formation of loosely coagulated flocs. (c) At an ionic strength of 100 mM, the colloidal dispersion is kinetically unstable. Even at relatively long interparticle distances of 25 nm, the magnitude of attraction forces are greater than repulsion forces. No secondary minimum is observed as was in Figure 8b.

Figure 9.—Gravitational settling velocities (Stokes Law) of destabilized colloidal particle agglomerates. Brine density was assumed to be  $1.1 \text{ g/cm}^3$ , a value that is representative of Culebra brines (Yeh, 1993a-c). Brine densities of Castile and Salado Formation brines are slightly greater at approximately  $1.2 \text{ g/cm}^3$  (Yeh, 1993a-c). Most mineral fragment type colloidal particles have densities greater than 2.0 (Deer et al., 1966). Note that for particles with densities in the mineral fragment range, the settling velocities are of similar orders of magnitude as the groundwater flow velocities in the Culebra (see Section 4.1.5; LaVenue et al., 1990). Consequently, even relatively small aggregates of colloidal particles could not be transported very far even if they were entrained.

Figure 10.—Actinide adsorption capacity of a single spherical colloidal particle estimated using various adsorption site densities. For  $0.01 \text{ }\mu\text{m}$  and  $1 \text{ }\mu\text{m}$  diameter colloidal particles, the actinide carrying capacities are on the order of  $10^{-21}$  and  $10^{-17}$  moles actinide per particle, respectively, assuming reasonable adsorption site densities on the order of 2 to 10 sites/ $\text{nm}^2$ . Those adsorption site densities are within the range of values reported by Kent et al. (1988, Table 3-1) for oxide minerals. Much larger site densities have been reported for ternary (cosorption) systems involving complex organic molecules, such as humic substances.

Figure 11.—A proposed structure for a "generic" humic substance (after Stevenson, 19xx).

Figure 12.—Schematic conceptual model in terms of relative reaction rates for the formation of Pu(IV)-polyelectrolyte and Pu(IV) mineral fragment type colloidal particle. Time is dimensionless, but may be on the order of weeks.

Figure 13.—Size distributions based on particle number for different natural aquatic systems.  $N$  represents particle number;  $d_p$  represents particle diameter. The population number of colloidal particles in naturally occurring dispersions in surface and subsurface waters increases inversely with approximately the fourth power of colloidal particle size. That relationship is also observed in natural colloidal dispersions collected from the Grimsel Test Site (see equations 38 and 39 in the text). From Filella and Buffle (1993).

Figure 14.—Total potential actinide concentrations contained in Grimsel Test Site colloidal particles ranging in diameter from  $0.001 \text{ }\mu\text{m}$  to  $10 \text{ }\mu\text{m}$ , estimated assuming a conservative adsorption site density of 10 sites/ $\text{nm}^2$ . Generated using information in Degueldre (1990) and McCarthy and Degueldre (1993).

Figure 15.—Flow chart of the SNL WIPP Colloid Research Program.

Figure 16.—Surface area ratios in transport experiments. The dependent variable is the ratio of intraparticle porosity (i.e., the intercrystalline surface area within a piece of rock, accessed primarily by diffusion) to interparticle porosity (i.e., the surface area of the piece of rock, accessed predominantly by advection) in pieces of the Culebra. For these estimates we assumed microcrystalline particles of 2  $\mu\text{m}$  with spherical morphologies (zone a). The grain size in crushed rock flow experiments is controlled by sieve size and is typically 0.5 to 1 mm (zone b). The "grain size" in intact rock column flow experiments is controlled the scale of textural features, and may range from 10 mm to 100 mm (zone c) in the 6-inch diameter cores acquired from the air intake shaft. The scale of features that might participate in a field tracer test might be as large as 1-m blocks (zone d). Note that because of the microcrystalline nature of the Culebra, crushed rock experiments provide a substantial improvement over experiments with individual crystallites, and may not produce results that are substantially different than the intact core column flow experiments. For these calculations, we used crystallite sizes of 2  $\mu\text{m}$  cubes and an intercrystalline porosity of 5 percent.

Figure 17.—Logic chart of the SNL WIPP Colloid Research Program. The first four pages correspond to screening experiments planned for each of the four colloidal particle types. The fifth page covers transport experiments, including transport from the disposal room environment (e.g., entrainment and orthokinetic coagulation experiments) and transport in the Culebra.

Figure 18.—Schedules and milestones for the SNL WIPP Colloid Research Program.

Figure 1.—Stratigraphy and controlled area.

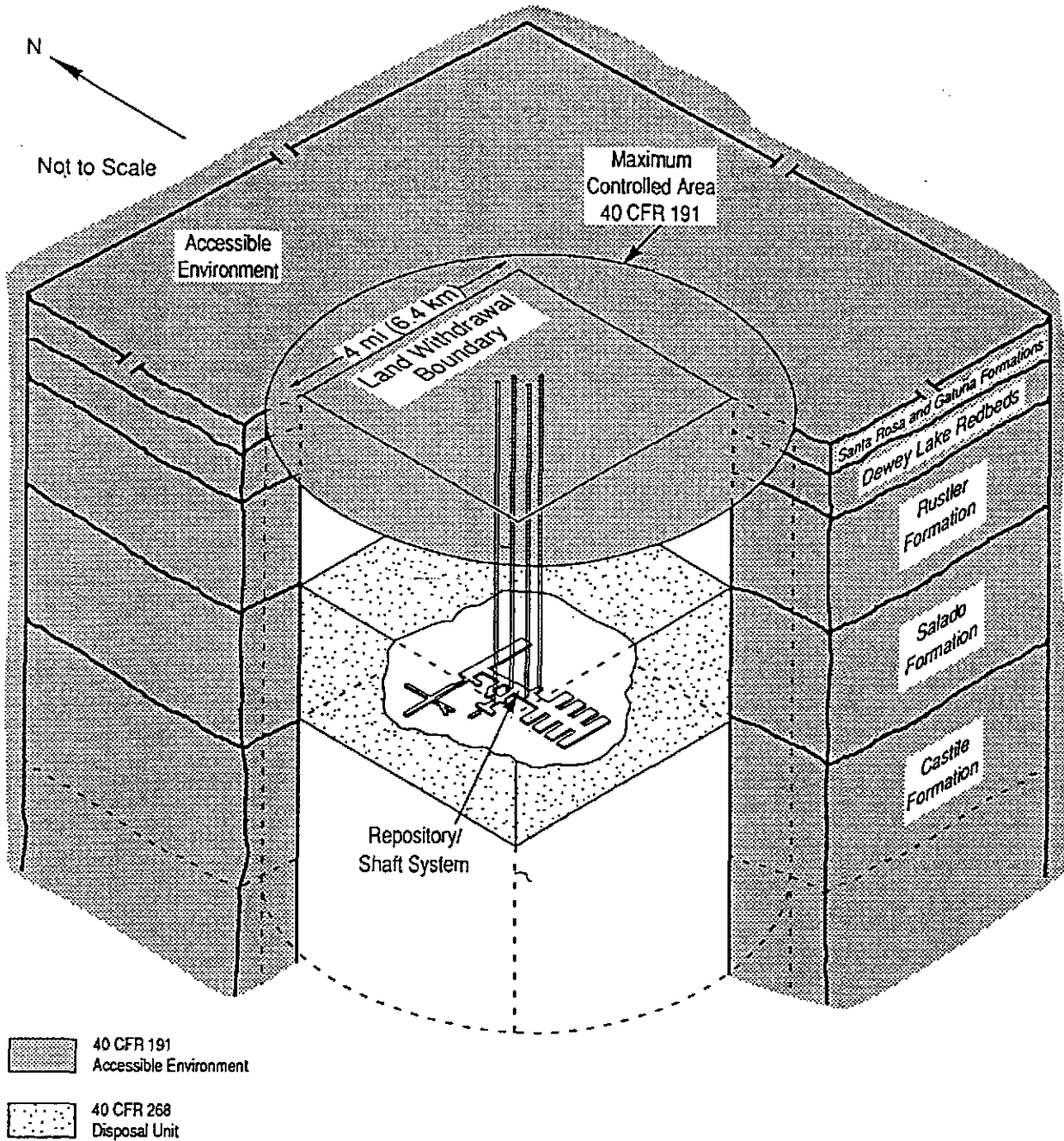
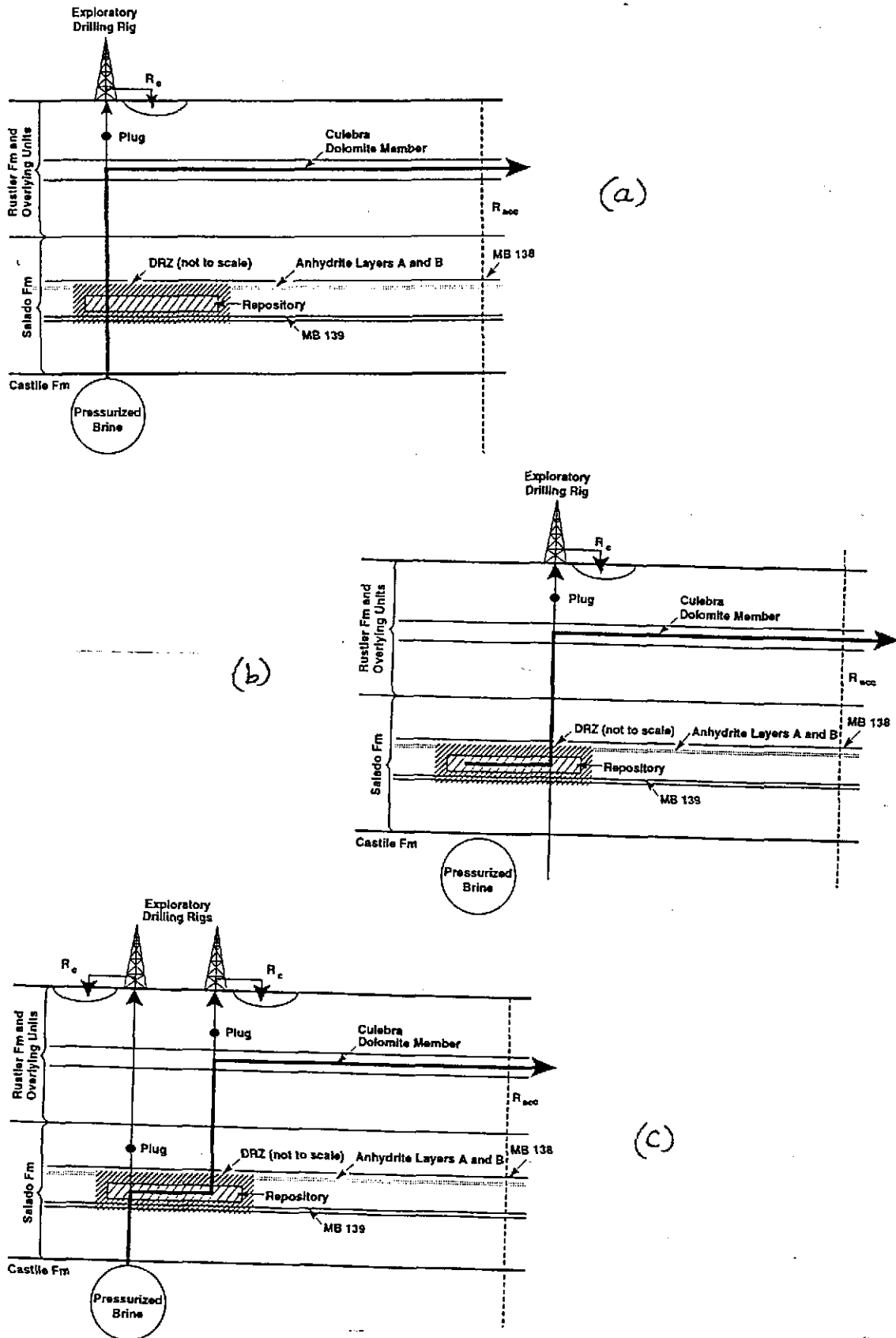


Figure 2.—Intrusion scenarios.



# WIPP Disposal Decision Plan

Revision 2  
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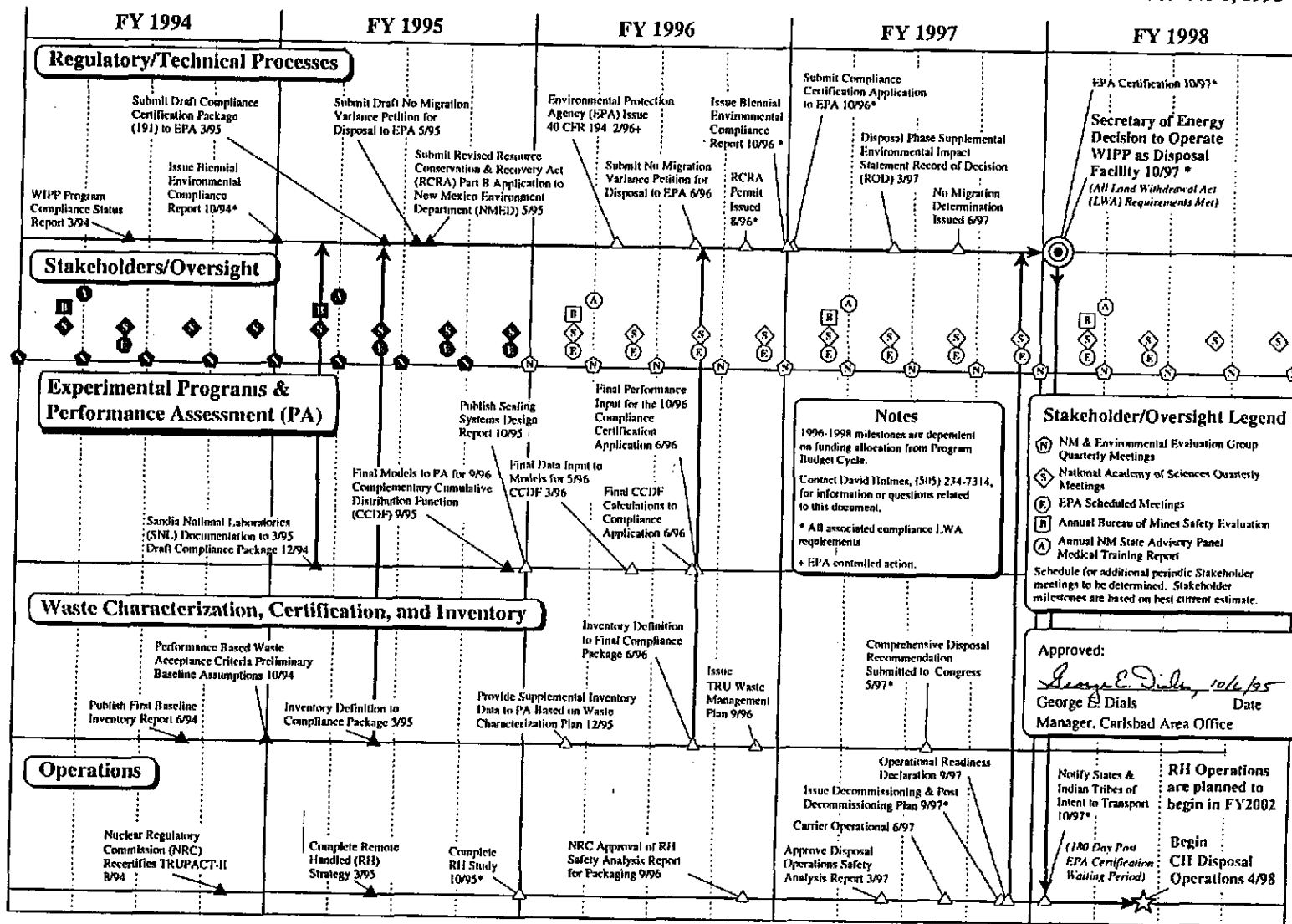


Figure 3.—Disposal Decision Plan Schedule.

Figure 4.—Sizes of colloidal particles.

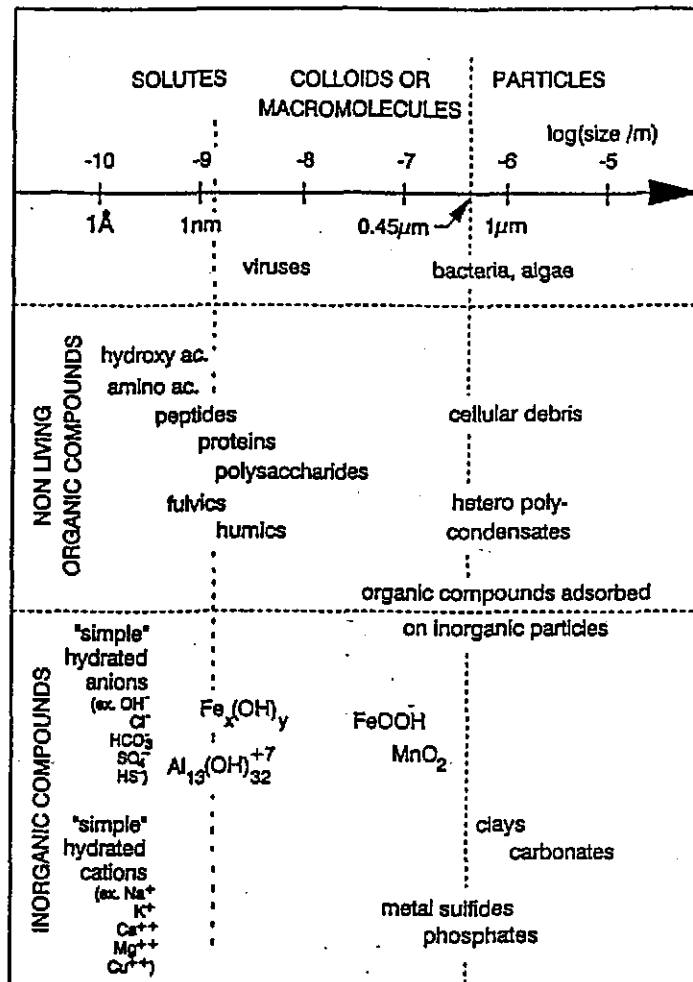
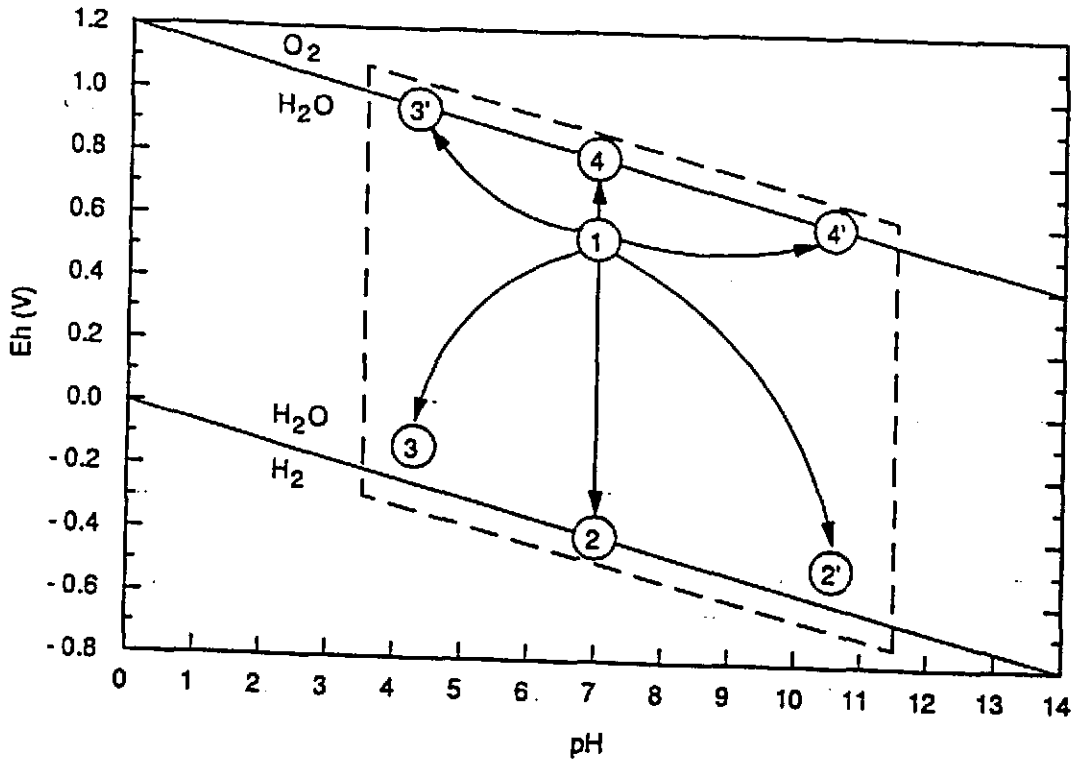




Figure 5.—Conditions of Eh-pH in disposal room.



- |                             |                                    |                       |
|-----------------------------|------------------------------------|-----------------------|
| 1. Start                    | 3. Microbial Activity              | 4. Radiolysis         |
| 2. Anoxic Corrosion         | 3'. Microbial Activity, Radiolysis | 4'. Radiolysis, Grout |
| 2'. Anoxic Corrosion, Grout |                                    |                       |

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Figure 6.—Concentrations of total organic carbon in Culebra brines.

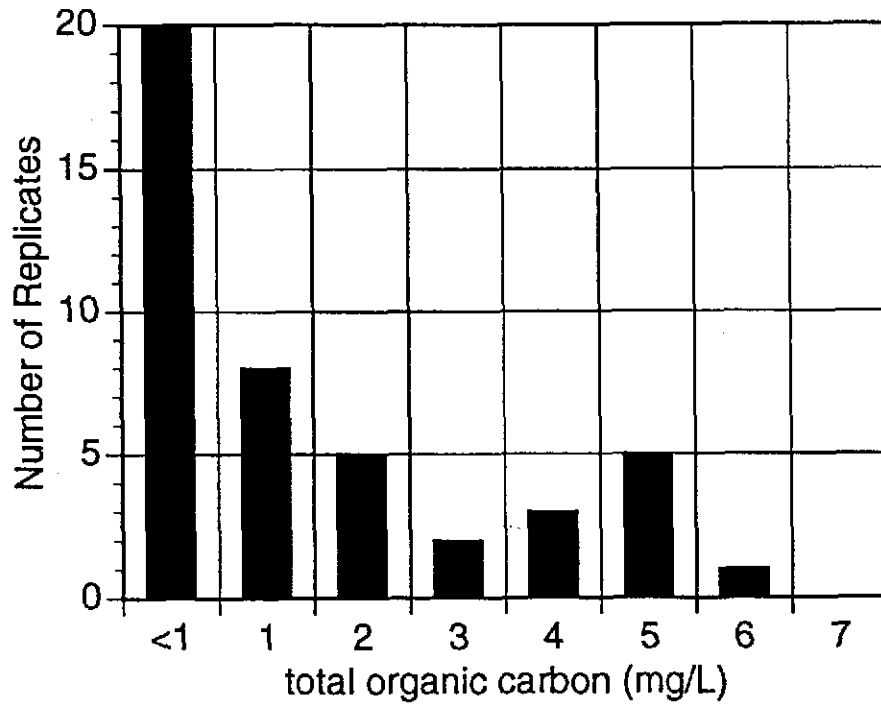


Figure 7.—Electric double layer.

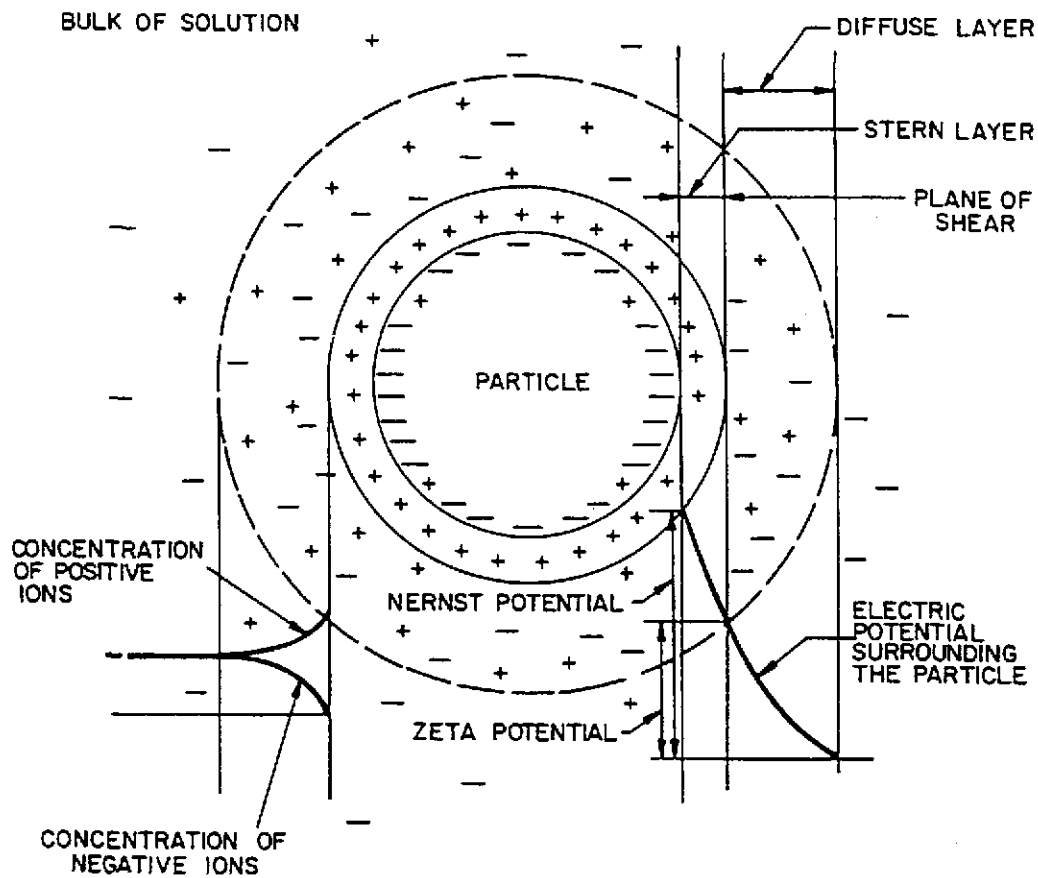


Figure 8a.—Ionic strength effects on kinetic stability. Ionic strength of 1 mM.

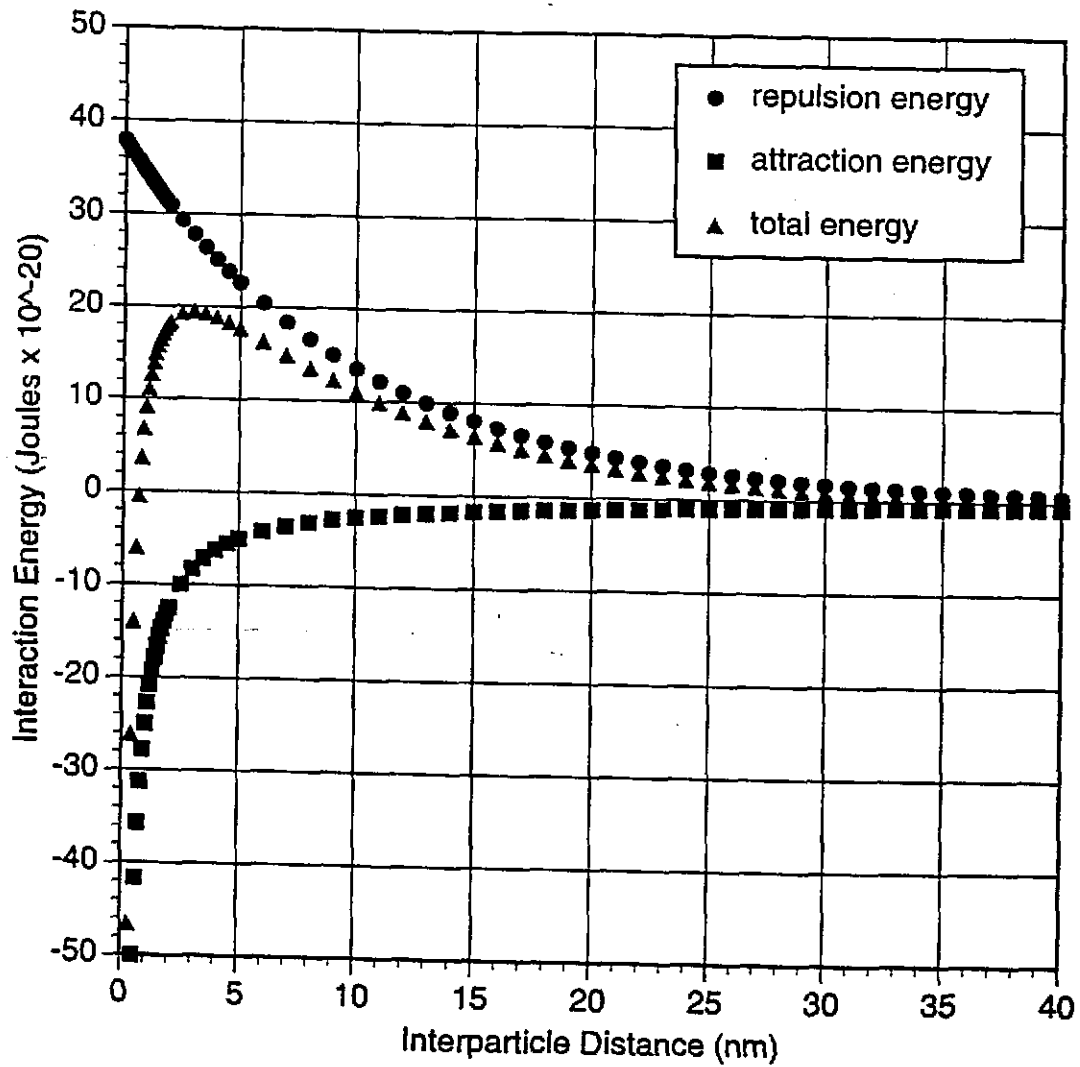


Figure 8b.—Ionic strength effects on kinetic stability. Ionic strength of 10 mM.

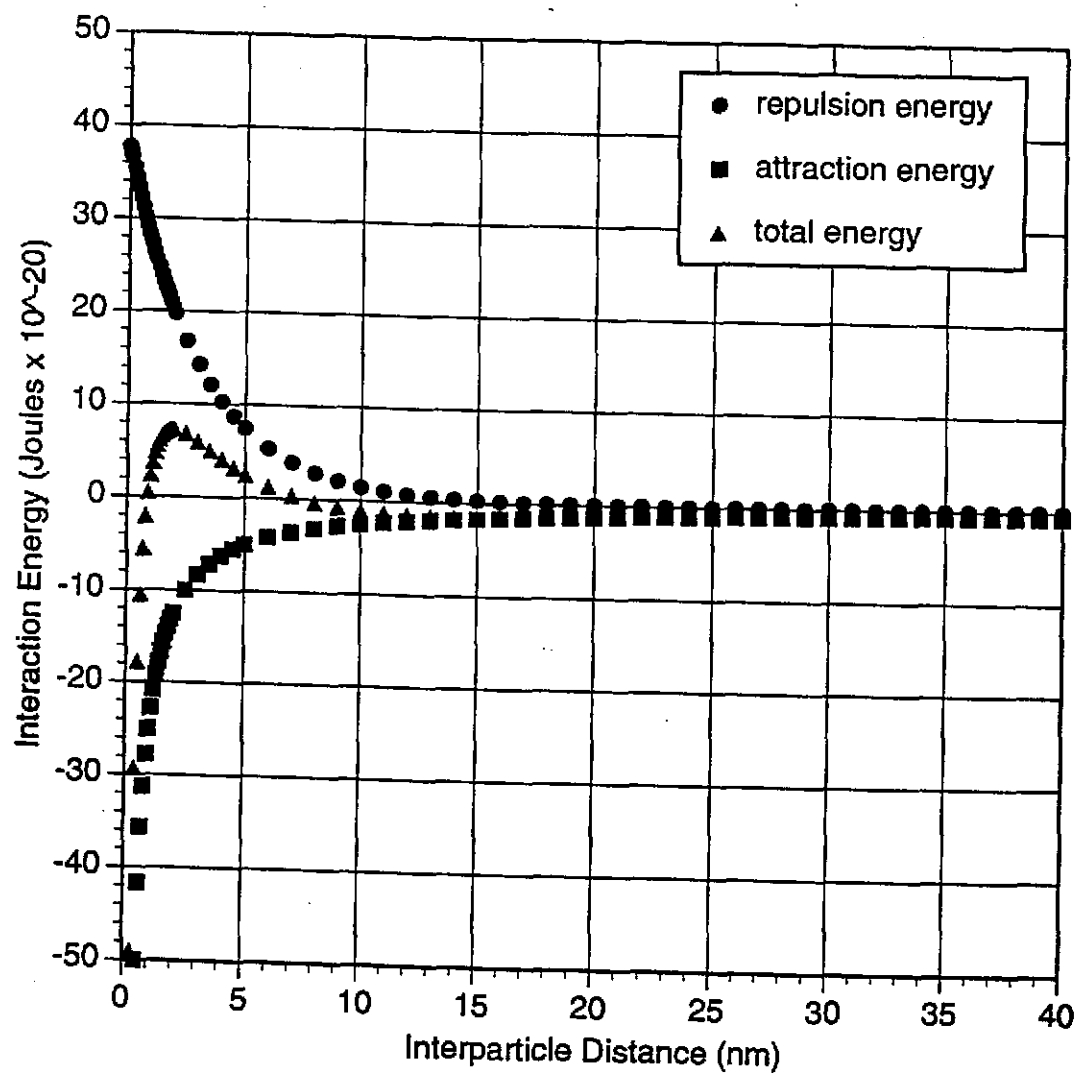


Figure 8c.—Ionic strength effects on kinetic stability. Ionic strength of 100 mM.

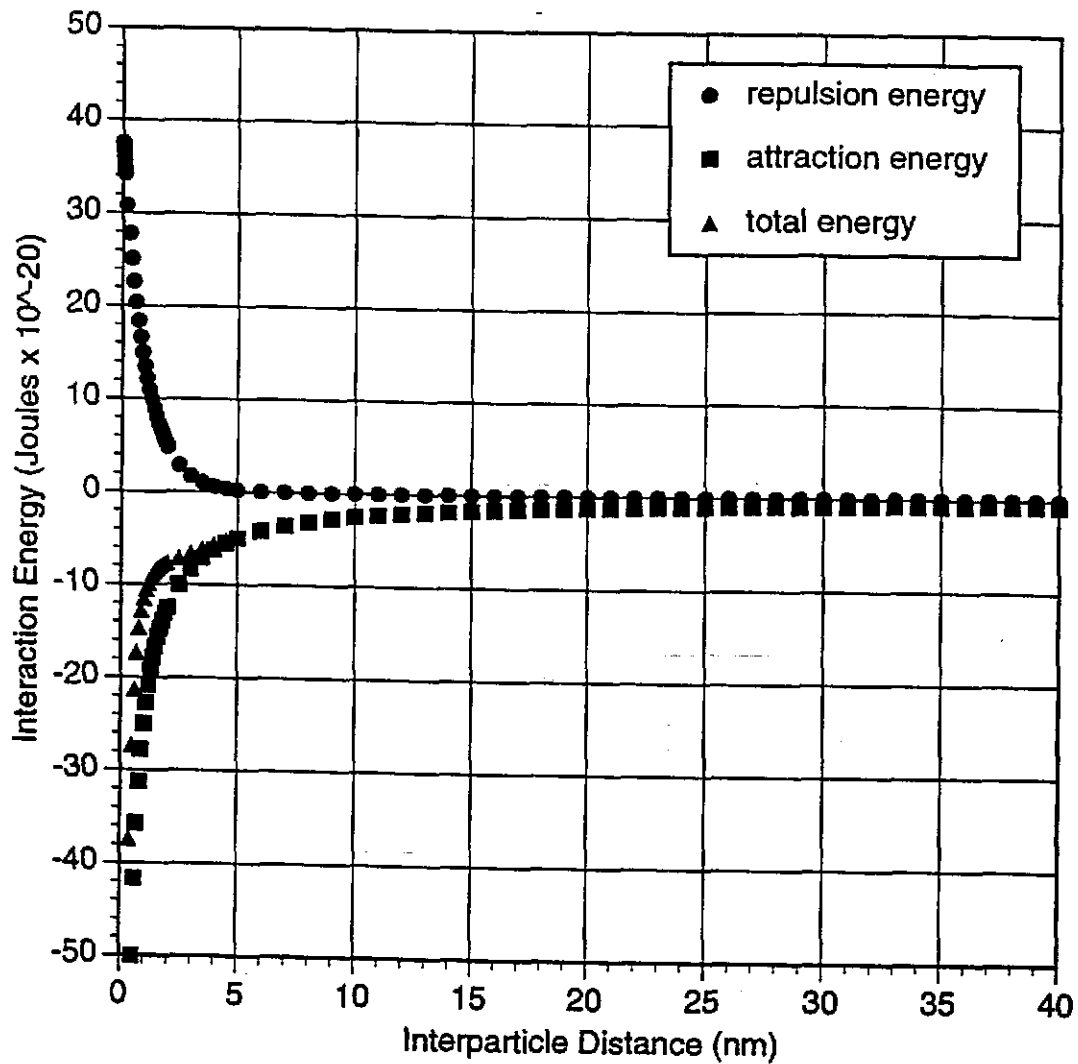


Figure 9.—Stokes law settling velocities.

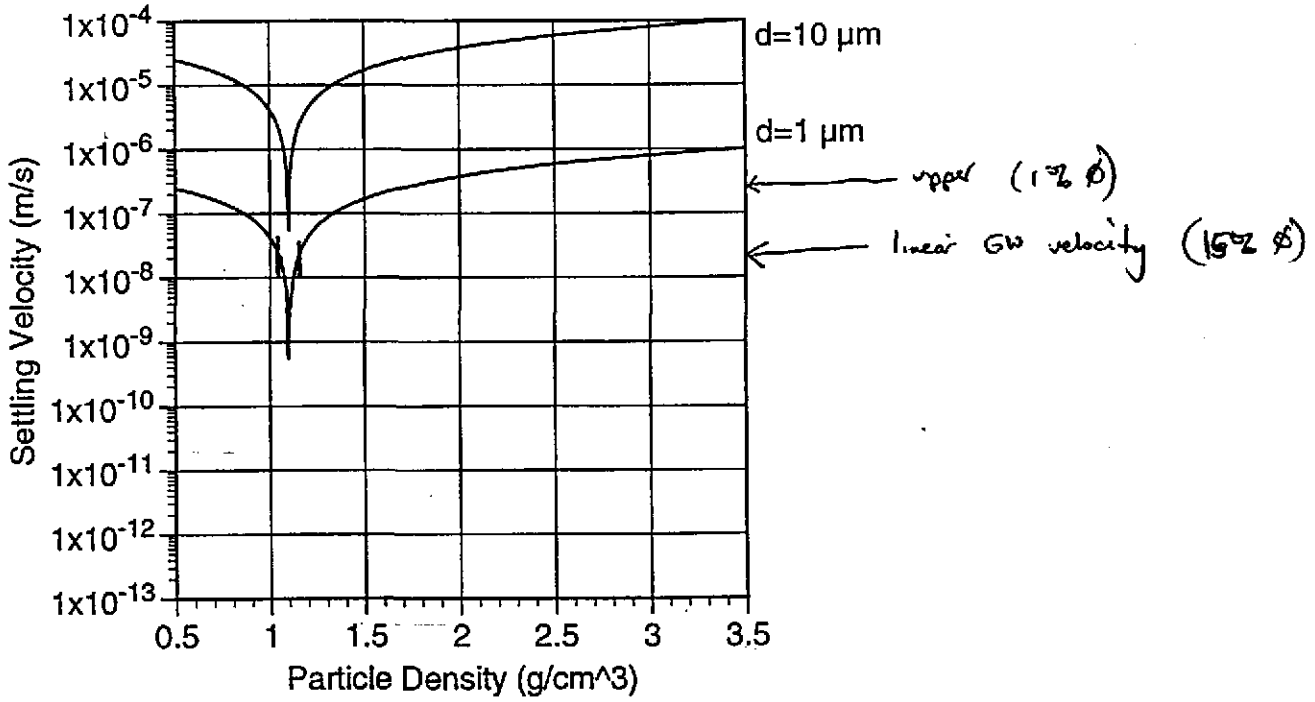


Figure 10.—Transport capacity of mineral-fragment type colloidal particles.

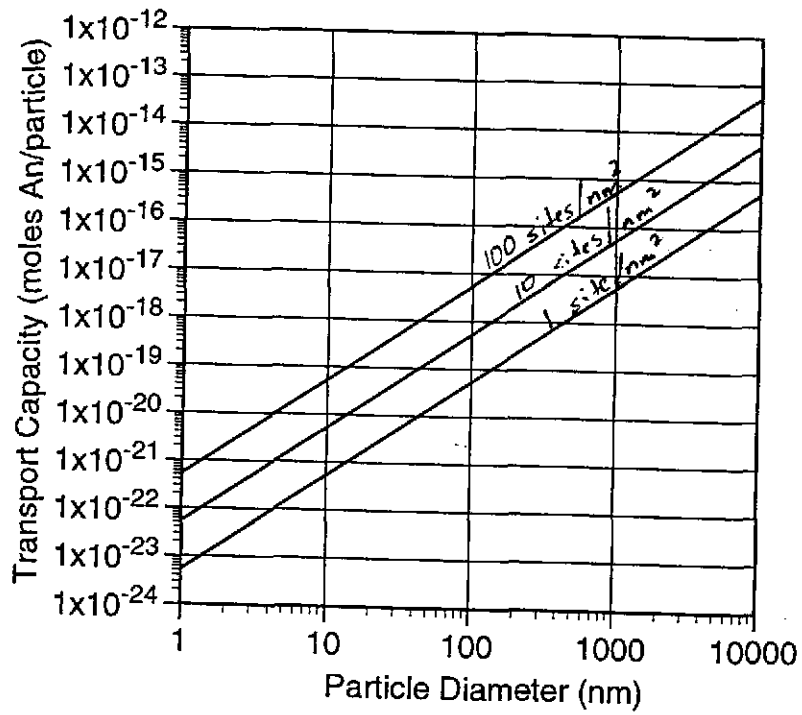
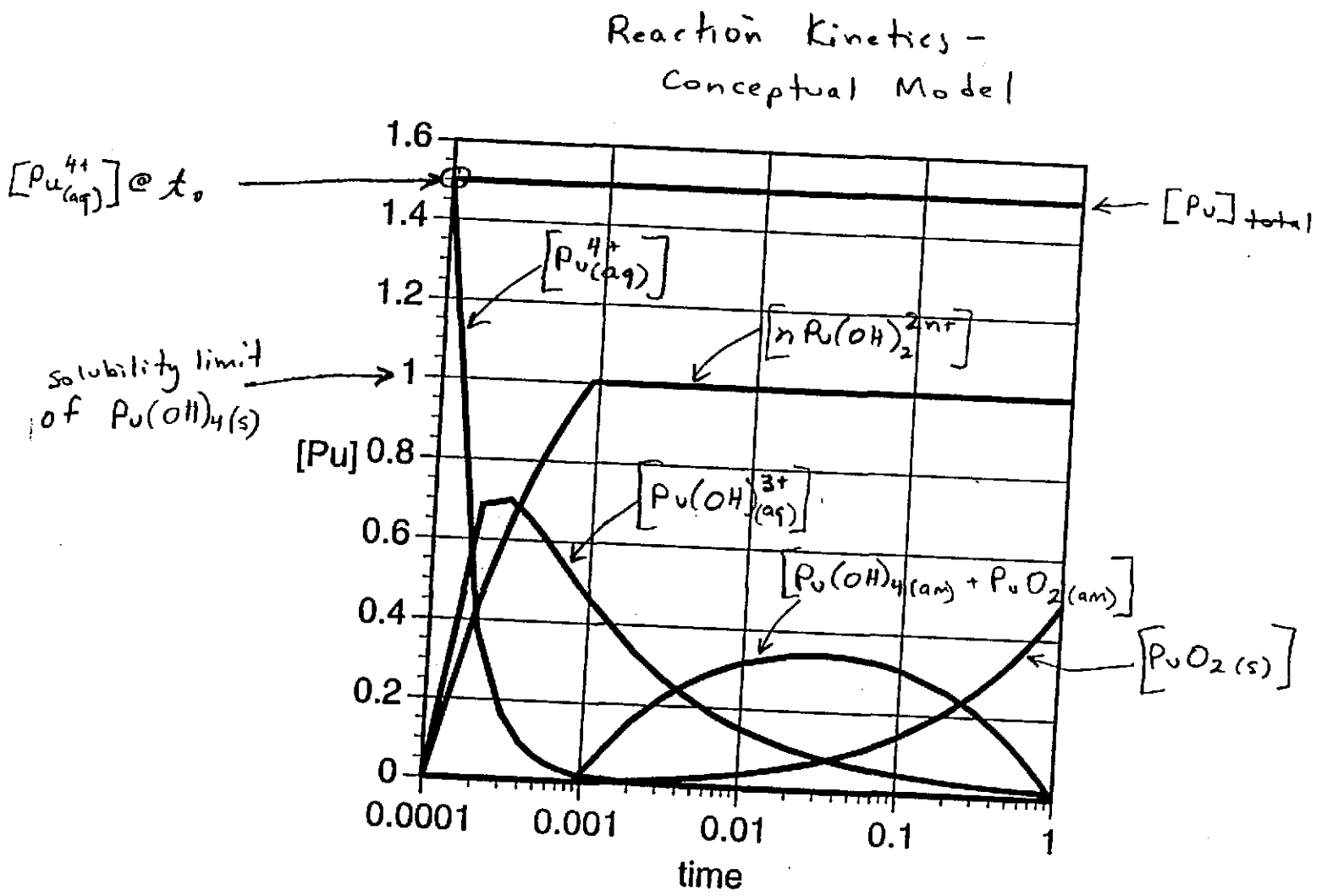






Figure 12.—Conceptual model for formation of Pu(IV)-intrinsic colloid.



Information Only

Figure 13.—Colloidal particle populations in natural waters.

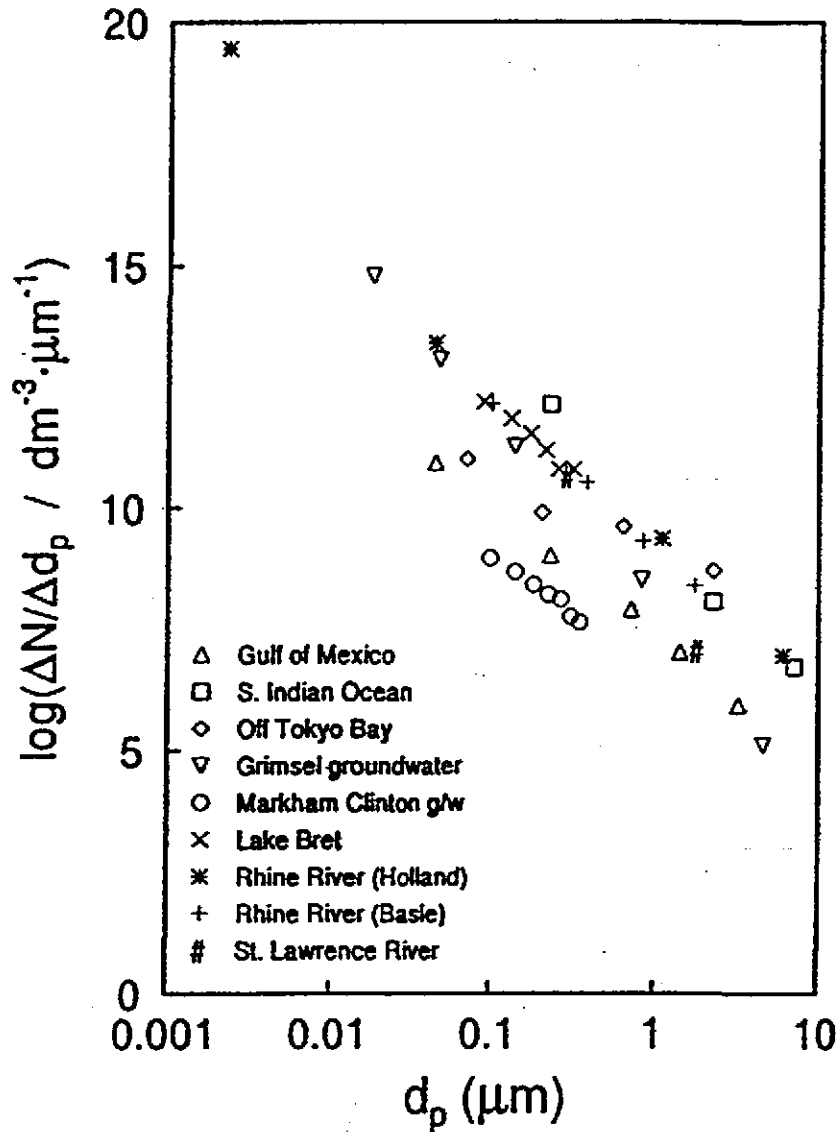
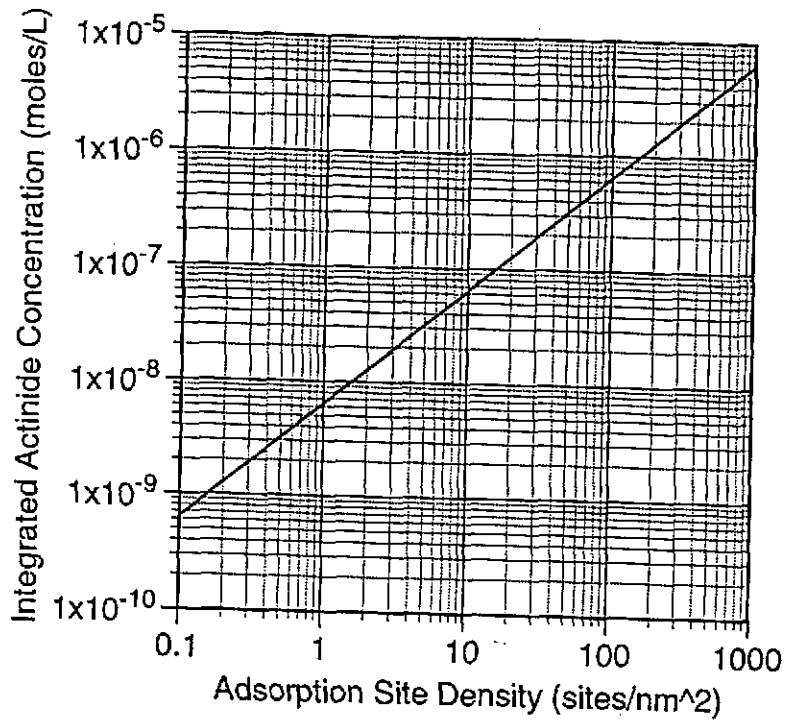
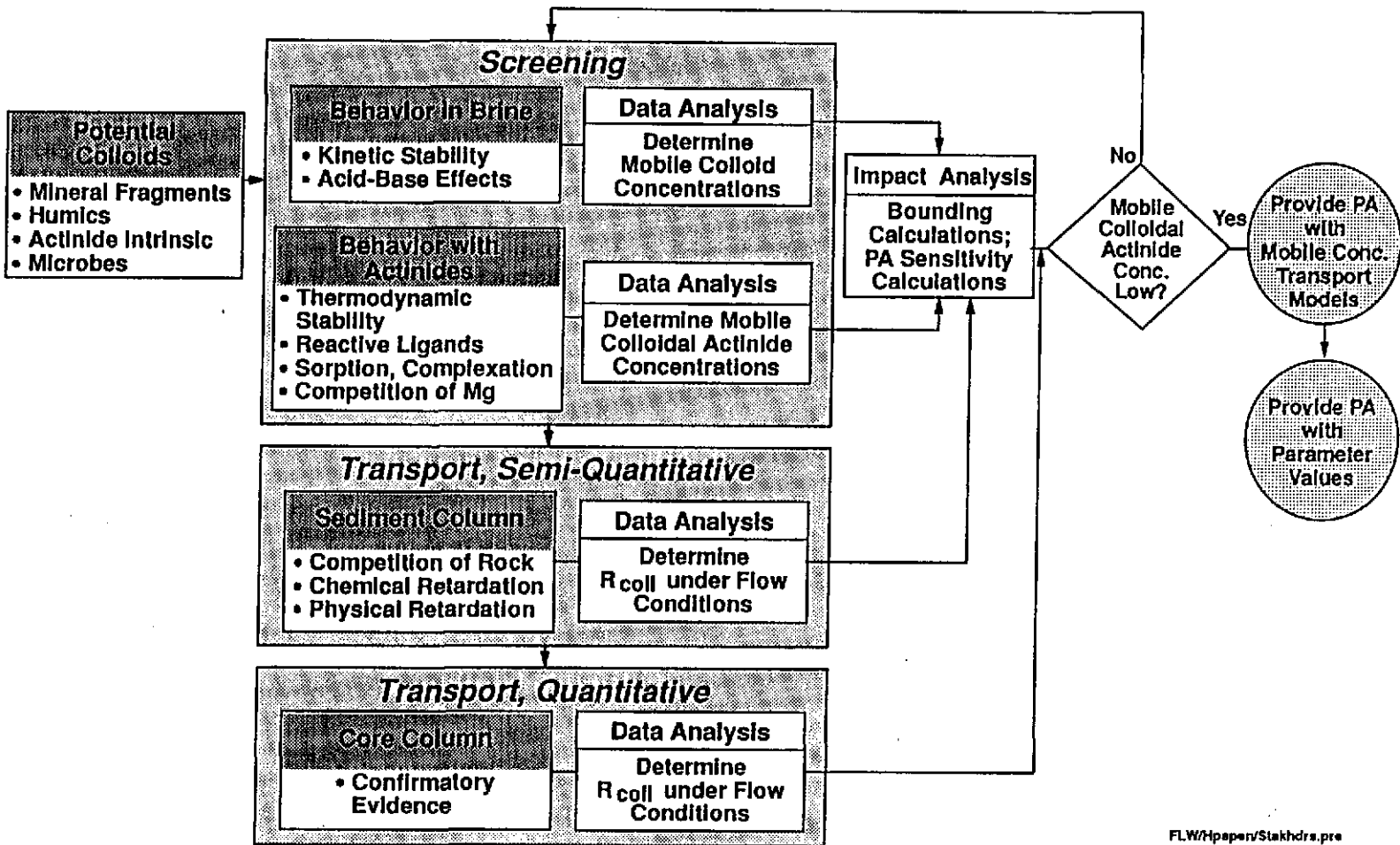


Figure 14.—Transport capacity of colloidal particles at Grimsel.



# Quantification of Colloidal Actinide Source and Transport



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Figure 15.—Flow chart of SNL WIPP Colloid Research Program.

Figure 16.—Surface areas in transport experiments.

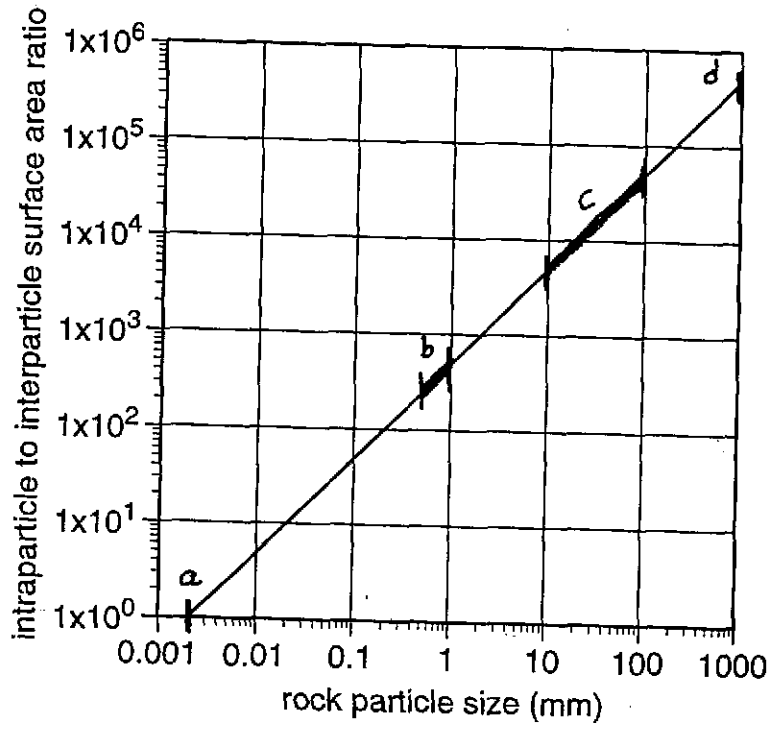


Figure 17a.—Logic charts for the SNL WIPP Colloid Research Program. Static screening experiments with mineral fragments.

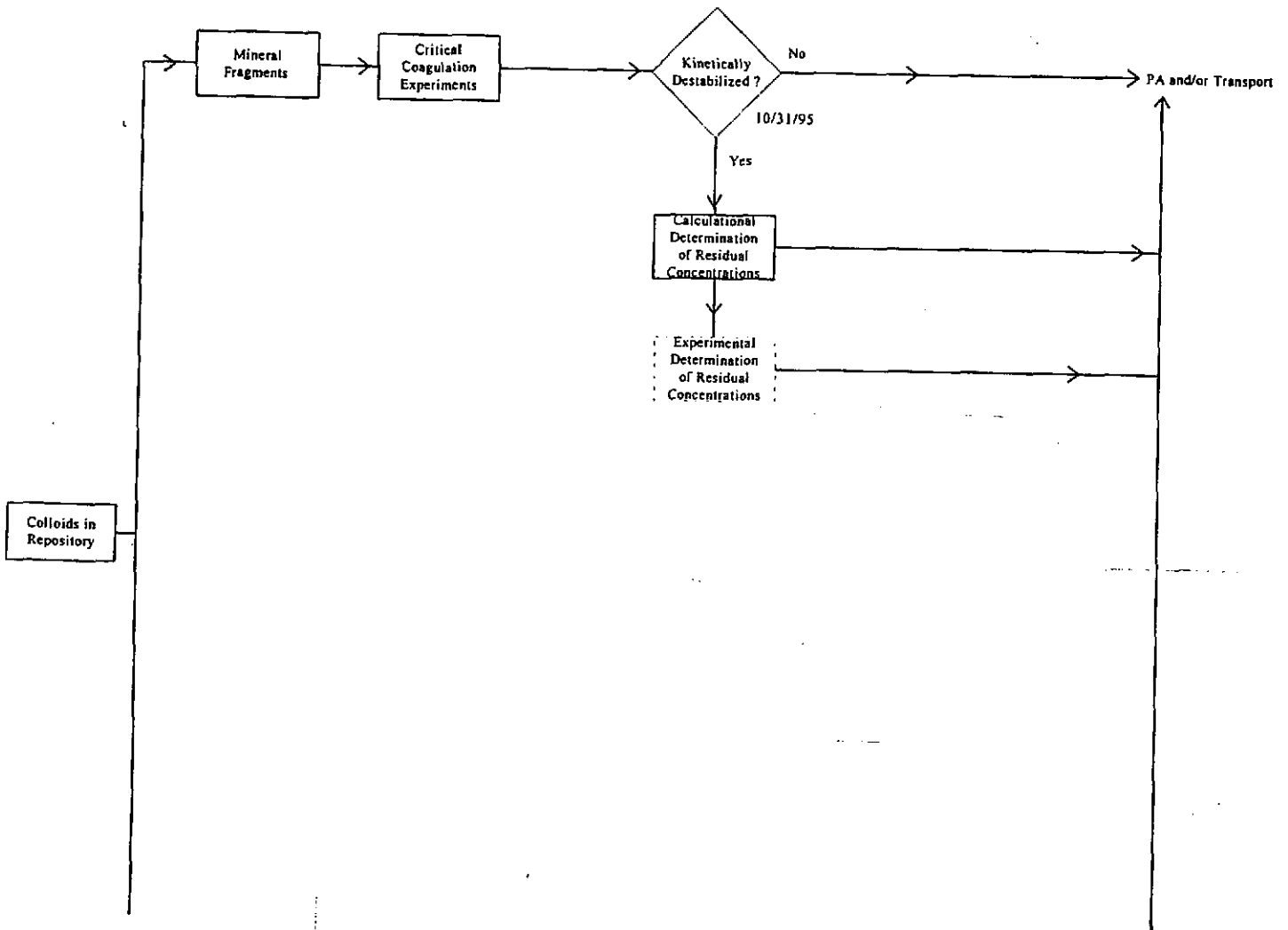


Figure 17b.—Logic charts for the SNL WIPP Colloid Research Program. Static screening experiments with humic substances.

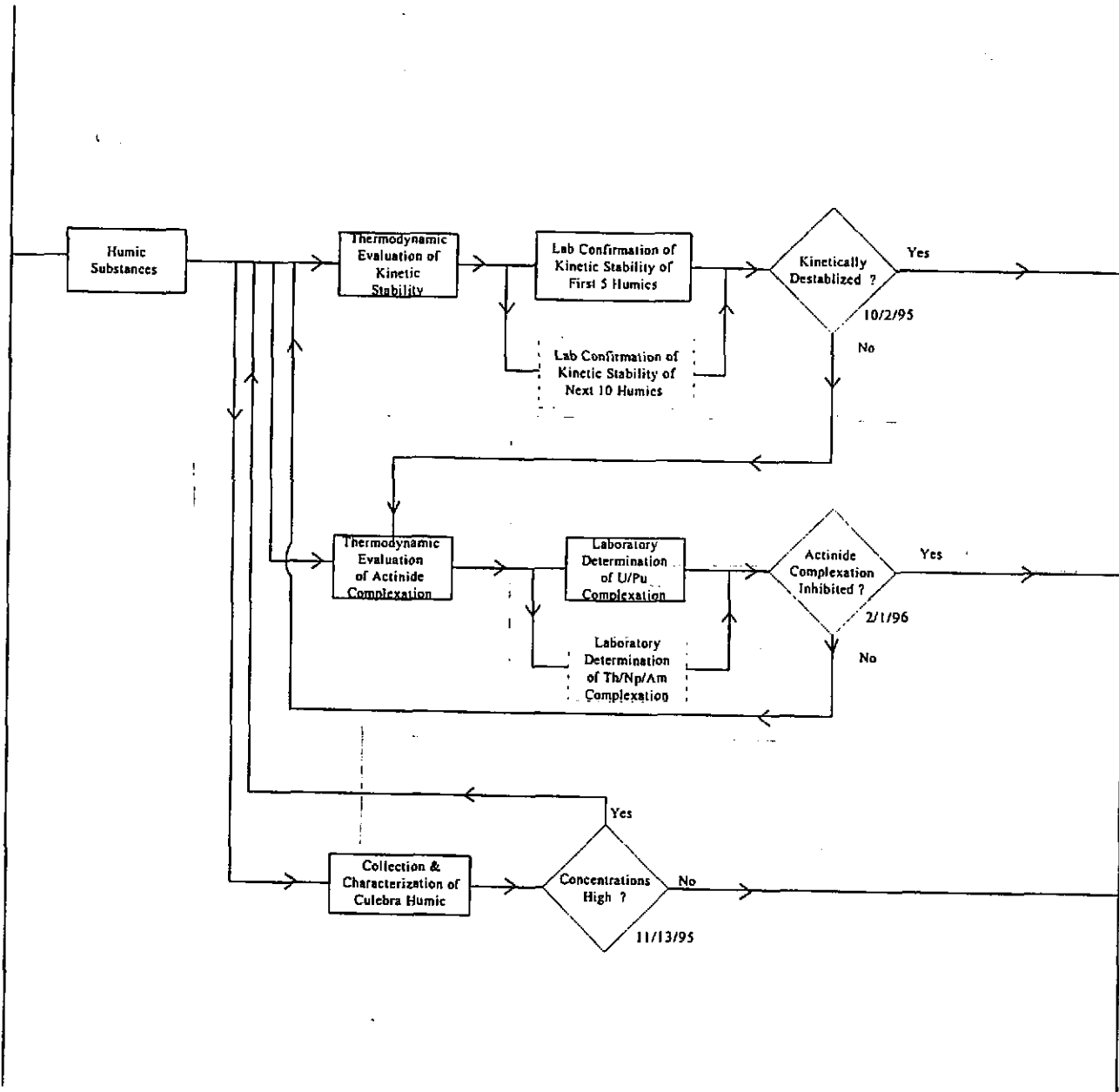




Figure 17c.—Logic charts for the SNL WIPP Colloid Research Program. Static screening experiments with actinide intrinsic colloids.

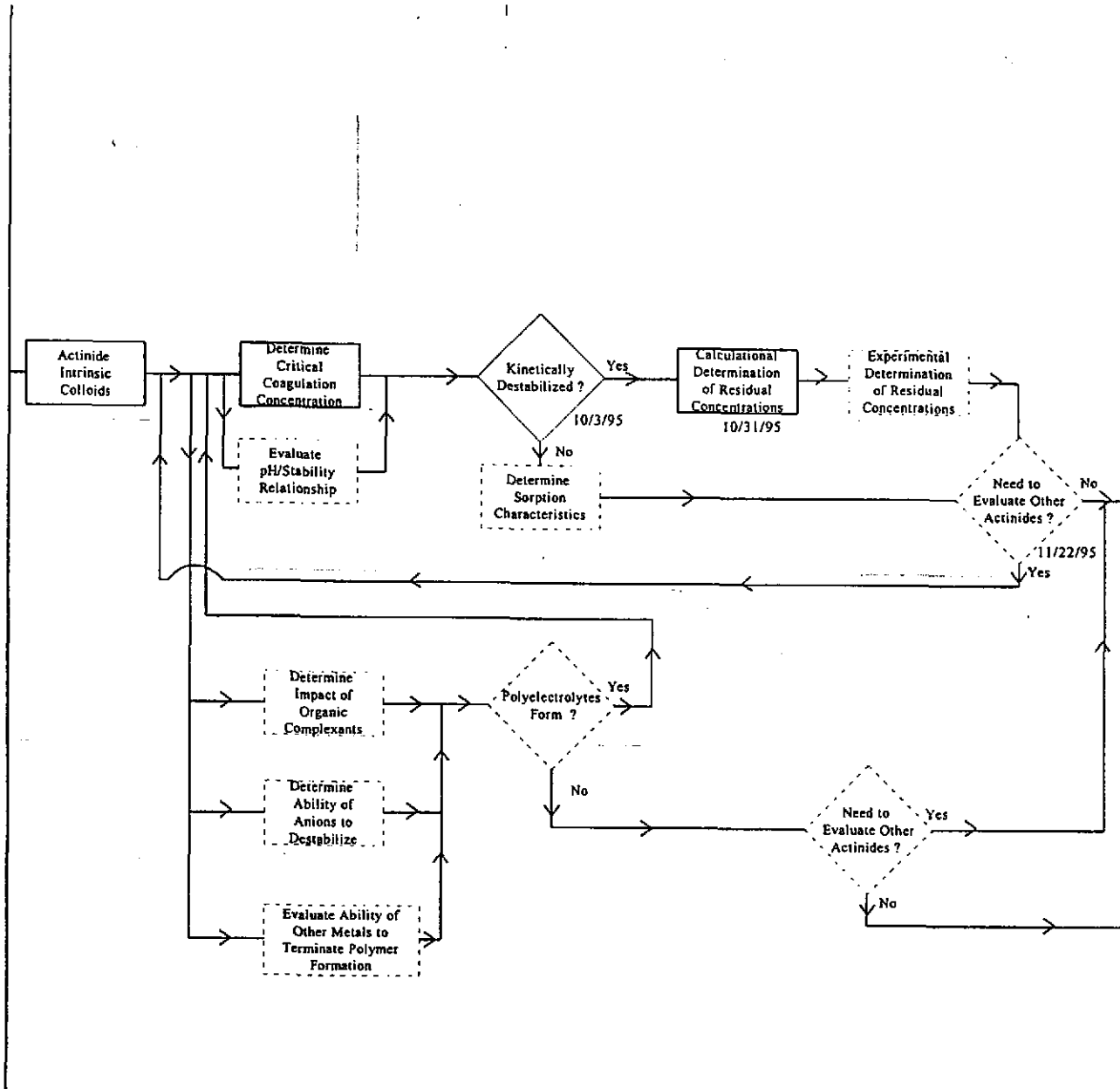


Figure 17d.—Logic charts for the SNL WIPP Colloid Research Program. Static screening experiments with microbes.

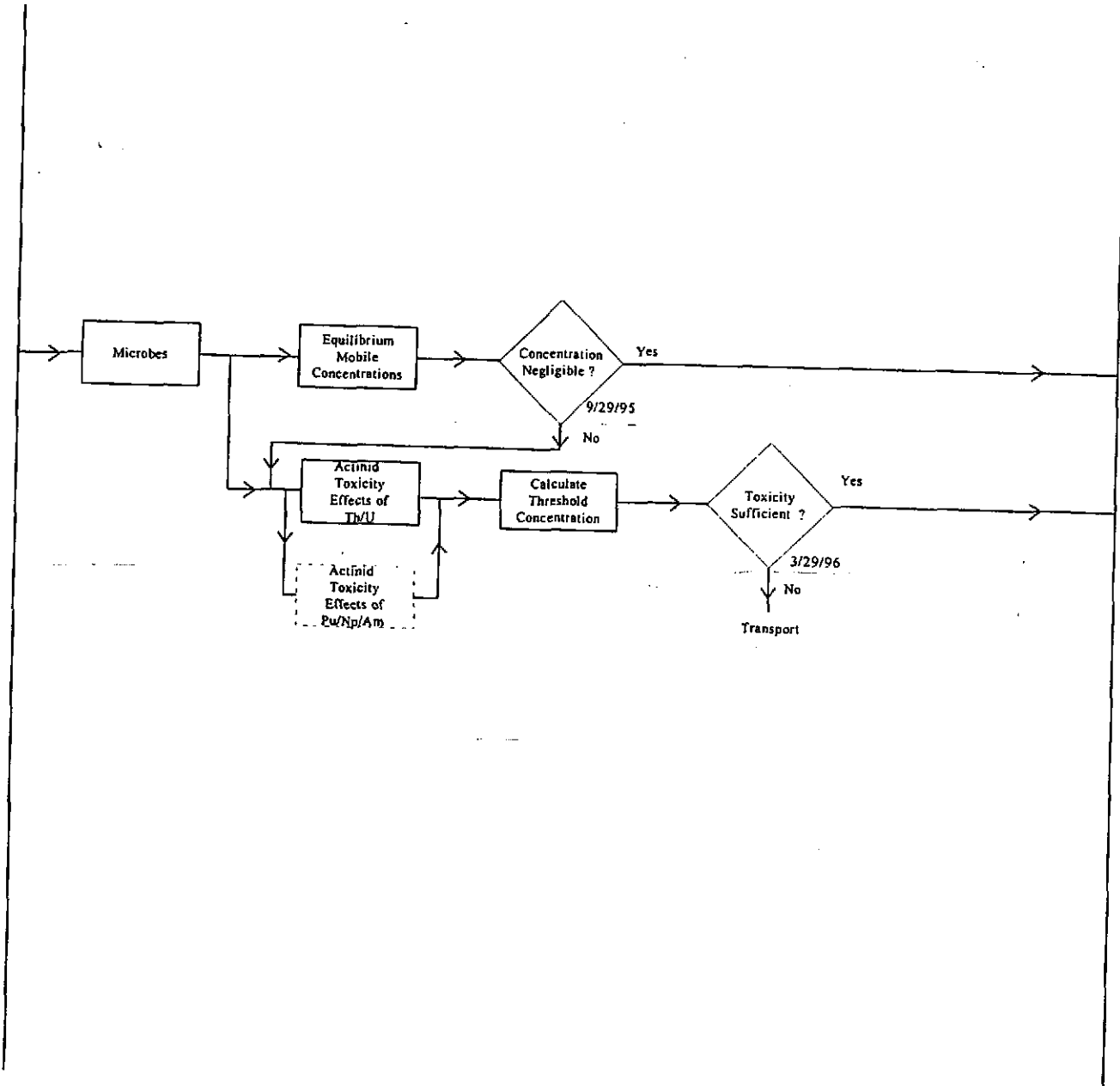
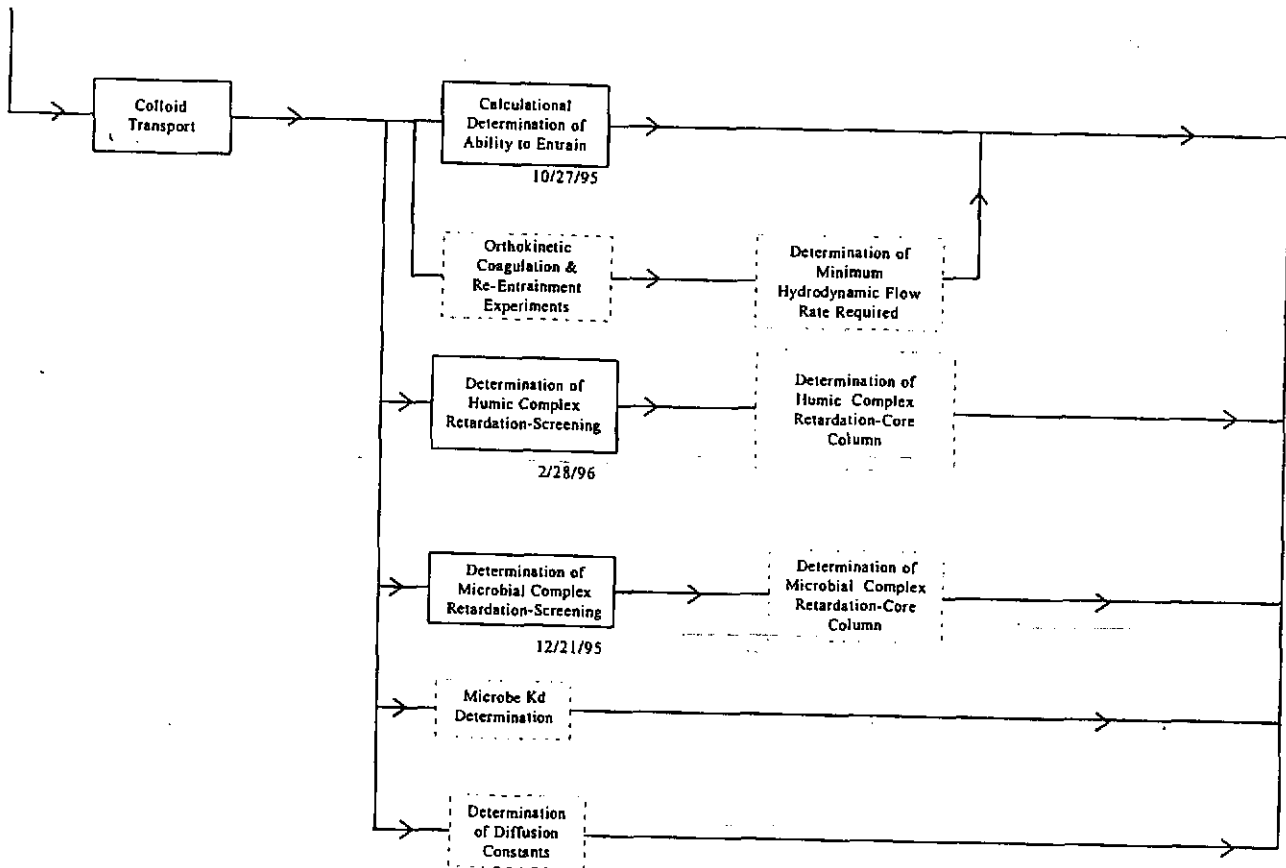


Figure 17e.—Logic charts for the SNL WIPP Colloid Research Program. Transport experiments.



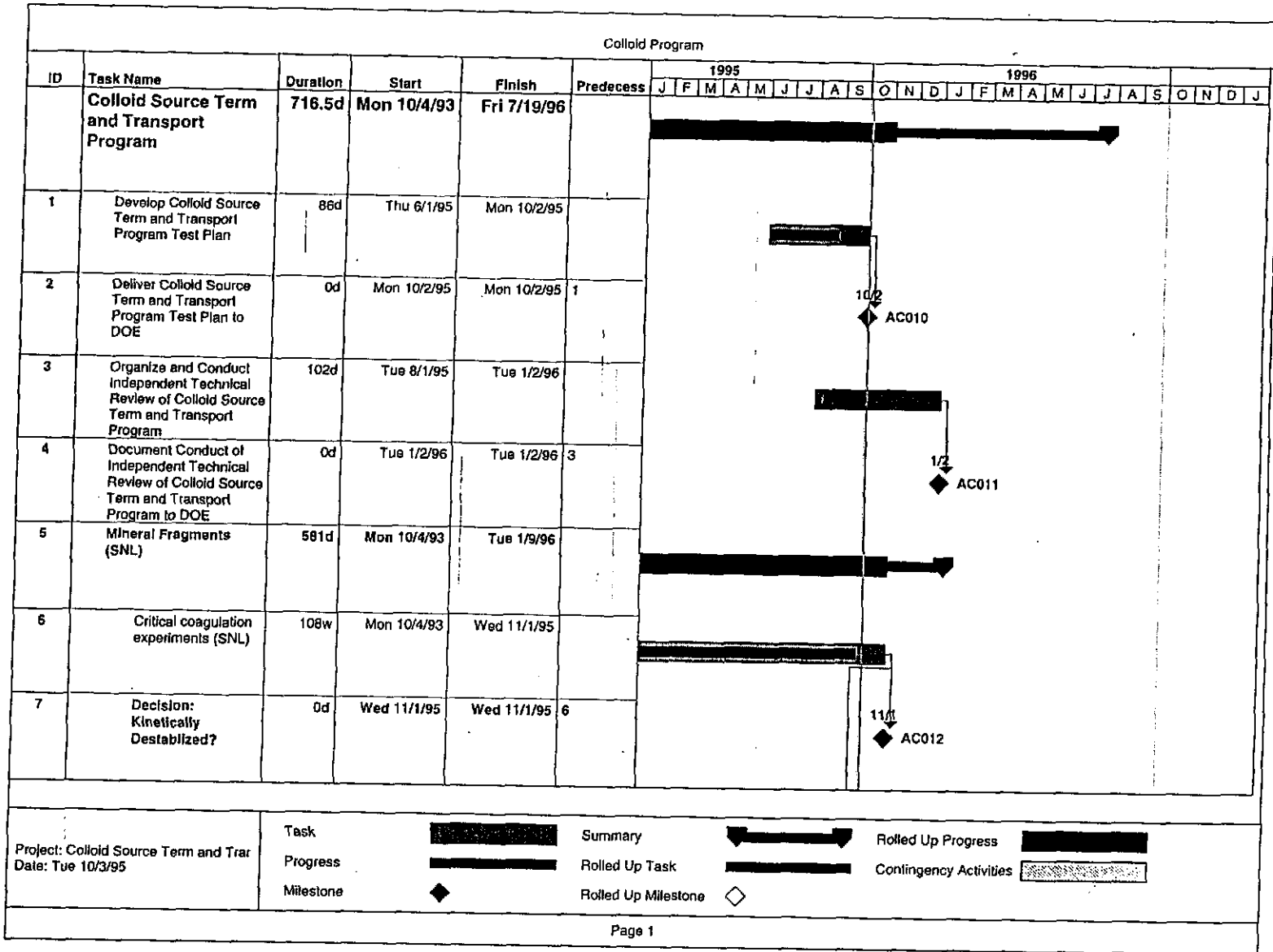


Figure 18.—Schedules and milestones.



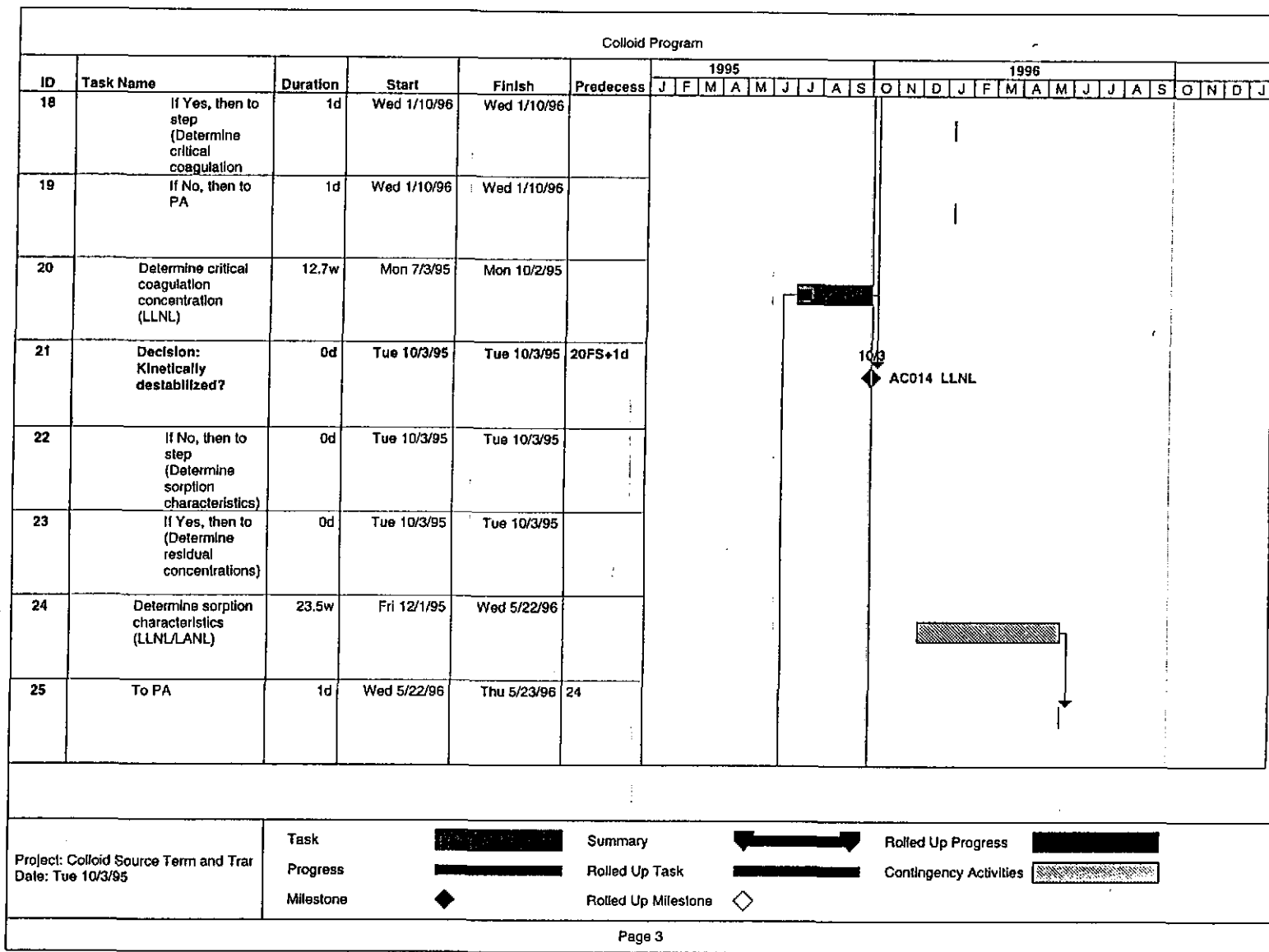


Figure 18, cont.—Schedules and milestones.















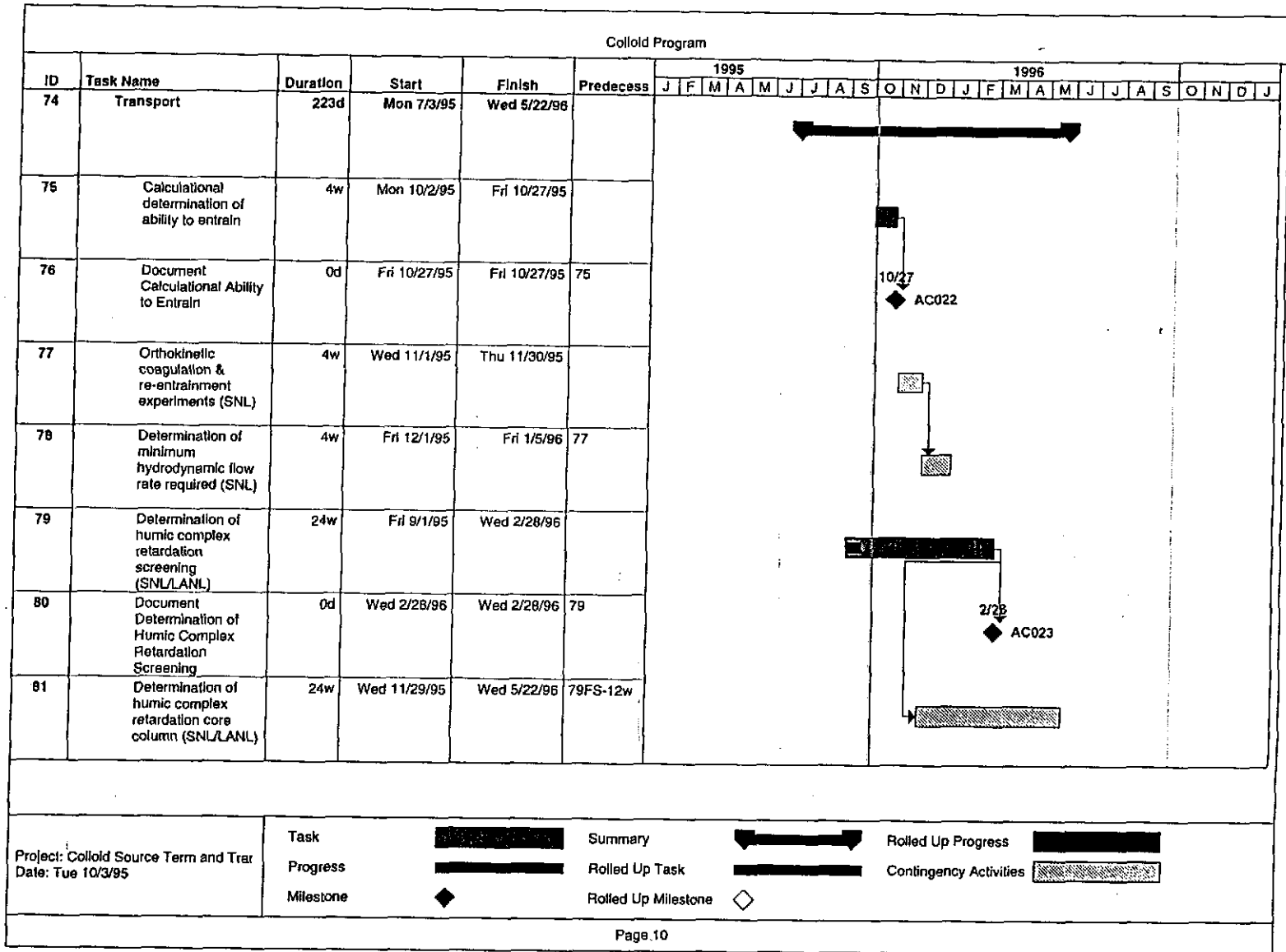


Figure 18, cont.—Schedules and milestones.



## Appendix C. Tables

Table 1.—Source of actinides by waste type. Summary of the anticipated waste inventory at the WIPP, compiled from information in the Baseline Inventory Report (US DOE, 1994c). Total masses of contact-handled and remote-handled wastes were calculated assuming total volumes of  $1.3 \times 10^5$  and  $2.6 \times 10^3$  m<sup>3</sup>, respectively.

Table 2.—Potential mineral fragment type colloidal particles that could be present in kinetically stable or destable forms in the disposal room or in the Culebra. Compiled from a variety of sources, including information in Brush (1990), Krumhansl et al. (1990), Sowards et al. (1992), and Telander and Westerman (1994).

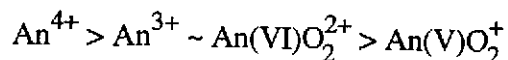
Table 3.—Summary of organic ligands and microbial degradation products anticipated in the WIPP disposal room environment. Estimated concentrations listed for anthropogenic ligands are from Brush (1990). Concentrations for microbially produced organic compounds are from A. J. Francis (Brookhaven National Laboratory, personal communication, 1994).

Table 4.—Inventory-limited actinide elemental and activity concentrations. For each of the eleven radioisotopes of the five most important actinide elements, curie totals from the Baseline Inventory Report (US DOE, 1994, Table 5-3) for contact- and remote-handled wastes are summed and multiplied by the appropriate activity conversion factor (WIPP PA Department, 199c, Table 3.3-1) to obtain masses. Total masses for each of the five actinide elements are converted to moles. Assuming that the fluid volume of the WIPP disposal room is  $5 \times 10^7$  L under fully inundated conditions, the inventory limited concentrations are determined (right-hand column). In the lower few rows, the average actinide activity concentration is estimated. Curie totals and mass totals for the eleven radioisotopes are summed. Assuming an representative gram molecular weight of 240, an average radiation level of  $2.2 \times 10^{12}$  pCi/mole actinide is estimated.

Table 5.—Summary of chemical compositions of naturally occurring brines associated with the WIPP.

Table 6.—Ionic radii for relevant actinides and lanthanide surrogates for the actinides. Ionic radii are from Allard et al. (1980) for eight-fold coordination. Parentheses indicate relatively rare oxidation states for that particular element. Note the similarity in radii in each column, which is the basis for the oxidation state analogy. Considering the ratio of charge to ionic radii, the following

trend is observed for complexation and sorption behavior:



Polymerization is thought to follow the hydrolysis trend:

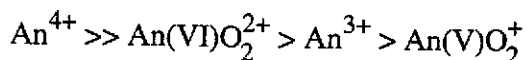


Table 7.—pH at zero-point-of-charge ( $\text{pH}_{\text{pzc}}$ ) for some minerals (Ross and Morrison, 1988, Tables B.1 and B.2).

Table 8.—Compilation of the nature and abundance of colloidal particles at a variety of sites (modified from McCarthy and Degueldre, 1993). (a) Deep (>100m) subsurface systems. (b) Shallow (<100m) surface and subsurface sites. (c) References.

Table 9.—Baseline (maximum bounding values) and action-level parameter values for mobile actinide-bearing colloidal particles used in SPM calculations (refer to Prindle et al., 1996a, Table 2-3 and Section 3.7.9.3). This information is used herein to develop target values as part of the Data Quality Objective process. (a) Baseline values determined on the basis of bounding calculations for humic substances, bacteria, and diffusion constant (refer to text) and speculation based on review of literature and preliminary experimental results for mineral fragments and actinide intrinsic colloids. (b) Anticipated outcomes of the SNL WIPP Colloid Research Program based on the experimental program described in this Test Plan. SPM calculations using these anticipated outcomes resulted in a performance assessment calculation showing compliance of the WIPP. The anticipated outcomes are used in the development of target values (i.e., action levels) for the experiments described herein.

Table 10.—Design considerations for crushed-rock column experiments. Based on discussions in Relyea (1982). For most of the transport experiments, we anticipate selecting an optimal column geometry, injection spike volume, eluent flow rate, and crushed-rock particle diameter. A subset of replicate experiments will be conducted with other parameter values, however, to evaluate the possibility of artifacts resulting from selection of optimal values.

Table 11.—Analytical equipment required for experiments (at SNL only). The list presented will



almost certainly be augmented with additional equipment identified as useful during the course of the experimental program. A variety of other specialized equipment will also be used by contract laboratories.

Table 1.—Source of actinides by waste type.

waste category	waste type	contact-handled waste; average mass fraction (kg/m <sup>3</sup> )	contact-handled waste; total (kg)	remote-handled waste; average mass fraction (kg/m <sup>3</sup> )	remote-handled waste; total (kg)	grand totals of contact and remote-handled wastes (kg)	percent of total mass
organics	cellulose	200	2.6E+7	34	8.8E+4	2.6E+7	29%
containers	steel	142	1.8E+7	2600	6.8E+6	2.5E+7	29%
inorganics	iron based	40	5.2E+6	71	1.8E+5	5.4E+6	6%
SUBTOTAL							64%
organics	plastics	65	8.5E+6	32	8.3E+4	8.5E+6	10%
inorganics	other inorganics	52	6.8E+6	130	3.4E+5	7.1E+6	8%
containers	plastic liners	39	5.1E+6	0	0.0E+0	5.1E+6	6%
SUBTOTAL							23%
solidified materials	inorganic	19	2.5E+6	70	1.8E+5	2.7E+6	3%
organics	rubber	20	2.6E+6	2.9	7.5E+3	2.6E+6	3%
inorganics	other metals	16	2.1E+6	5	1.3E+4	2.1E+6	2%
solidified materials	organic	12	1.6E+6	5.30E-03	1.4E+1	1.6E+6	2%
containers	lead	0	0.0E+0	460	1.2E+6	1.2E+6	1%
soils		5.3	6.9E+5	0	0.0E+0	6.9E+5	1%
inorganics	aluminum based	3	3.9E+5	3.8	9.9E+3	4.0E+5	1%
SUBTOTAL							13%
TOTAL							100.0%

Table 2.—Potential mineral fragment type colloidal particles.

mineral	source	chemical formula
hematite	corrosion	$\alpha\text{-Fe}_2\text{O}_3$
ferric oxide	corrosion	FeO
ilmenite	corrosion	FeTiO <sub>3</sub>
anatase	corrosion	TiO <sub>2</sub>
rutile	corrosion	TiO <sub>2</sub>
brookite	corrosion	TiO <sub>2</sub>
magnetite	corrosion	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> O <sub>4</sub>
maghemite	corrosion	$\gamma\text{-Fe}_2\text{O}_3$
goethite	corrosion	$\alpha\text{-FeO}\cdot\text{OH}$
akaganeite	corrosion	$\beta\text{-FeO}\cdot\text{OH}$
lepidocrocite	corrosion	$\gamma\text{-FeO}\cdot\text{OH}$
feroxyhyte	corrosion	$\delta\text{-FeO}\cdot\text{OH}$
limonite	corrosion	Fe·OH·nH <sub>2</sub> O
iron hydroxide	corrosion	Fe(OH) <sub>2</sub>
iron-chloride hydroxide	corrosion	$\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$
reevesite	corrosion	(Ni,Fe) <sub>6</sub> Fe <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>16</sub> ·4H <sub>2</sub> O
iron-magnesium hydroxide	corrosion	Fe,Mg(OH) <sub>2</sub>
mackinawite	corrosion	FeS <sub>1-x</sub>
troilite	corrosion	FeS
pyrrhotite	corrosion	Fe <sub>1-x</sub> S
marcasite	corrosion	FeS <sub>2</sub> (orthorhombic)
pyrite	corrosion	FeS <sub>2</sub> (cubic)
chalcocite	corrosion	Cu <sub>2</sub> S
siderite	corrosion	FeCO <sub>3</sub>
copper carbonate	corrosion	CuCO <sub>3</sub>
oligonite	corrosion	(Fe,Mn,Zn)CO <sub>3</sub>
brucite	precipitate	Mg(OH) <sub>2</sub>
vermiculite	waste	(Mg,Ca) <sub>0.7</sub> (Mg,Fe <sup>3+</sup> ,Al) <sub>6.0</sub> [(Al,Si) <sub>8</sub> O <sub>20</sub> ](OH) <sub>4</sub> ·8H <sub>2</sub> O
diatomaceous earth	waste	SiO <sub>2</sub>
tetracalcium aluminoferrate	waste	hydrated 4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> (C <sub>4</sub> AF) [Portland cement]
tricalcium aluminate	waste	hydrated 3CaO·Al <sub>2</sub> O <sub>3</sub> (C <sub>3</sub> A) [Portland cement]
tricalcium silicate	waste	hydrated 3CaO·SiO <sub>2</sub> (C <sub>3</sub> S) [Portland cement]
dicalcium silicate	waste	hydrated 2CaO·SiO <sub>2</sub> (C <sub>2</sub> S) [Portland cement]
Envirostone	waste	CaSO <sub>4</sub> + melamine formaldehyde
calcite	natural geologic	CaCO <sub>3</sub>
magnesite	natural geologic	MgCO <sub>3</sub>
strontianite	natural geologic	SrCO <sub>3</sub>
ankerite	natural geologic	Ca(Fe <sup>2+</sup> ,Mg,Mn)(CO <sub>3</sub> ) <sub>2</sub>
dolomite	natural geologic	CaMg(CO <sub>3</sub> ) <sub>2</sub>
anhydrite	natural geologic	CaSO <sub>4</sub>
gypsum	natural geologic	CaSO <sub>4</sub> ·2H <sub>2</sub> O
quartz	natural geologic	$\alpha\text{-SiO}_2$
corrensite	natural geologic	mixed layer chlorite/smectite
illite	natural geologic	K <sub>1-1.5</sub> Al <sub>4</sub> [Si <sub>7-6.5</sub> Al <sub>1-1.5</sub> O <sub>20</sub> ](OH) <sub>4</sub>
serpentine	natural geologic	Mg <sub>3</sub> [Si <sub>2</sub> O <sub>5</sub> ](OH) <sub>4</sub>
chlorite	natural geologic	(Mg,Al,Fe) <sub>12</sub> [(Si,Al) <sub>8</sub> O <sub>20</sub> ](OH) <sub>16</sub>

Table 2, cont.—Potential mineral fragment type colloidal particles.

mineral	source	chemical formula
calcium oxide ("lime")	grout, backfill	hydrated CaO
magnesium oxide ("lime")	grout, backfill	hydrated MgO
calcium hydroxide	grout, backfill	Ca(OH) <sub>2</sub>
calcium-aluminum silicate	grout, backfill	CaAlSi
montmorillonite ("bentonite")	grout, backfill	$(\frac{1}{2}\text{Ca},\text{Na})_{0.66}(\text{Al}_{3.34}\text{Mg}_{0.66})(\text{Si})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$
beidilite ("bentonite")	grout, backfill	$(\frac{1}{2}\text{Ca},\text{Na})_{0.66}(\text{Al})_4(\text{Si}_{7.34}\text{Al}_{0.66})\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$
kaolinite	grout, backfill	Al <sub>4</sub> [Si <sub>4</sub> O <sub>10</sub> ](OH) <sub>8</sub>

Table 3.—Organic ligands and functional groups.

organic compound	source	chemical formula (non-dissociated form)	reactive functional group	estimated maximum concentration
citrate (2-hydroxy-1,2,3-propanetricarboxylic acid; citric acid, trisodium salt, dihydrate)	anthropogenic	$\text{NaOOCCH}_2\text{C}(\text{OH})(\text{COONa})\text{CH}_2\text{COONa}\cdot 2\text{H}_2\text{O}$	-COOH -OH	$7 \times 10^{-3} \text{ M}$
ethylenediaminetetraacetate (EDTA tetrasodium salt hydrate)	anthropogenic	$(\text{NaOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2\cdot x\text{H}_2\text{O}$	-COOH	$1 \times 10^{-5} \text{ M}$
acetate (acetic acid, sodium salt dihydrate)	anthropogenic	$\text{CH}_3\text{COONa}$	-COOH	$7 \times 10^{-2} \text{ M}$
acetate	biogenic	$\text{CH}_3\text{COOH}$	-COOH	$\leq 200 \text{ ppm}$
lactate (lactic acid, sodium salt)	anthropogenic	$\text{CH}_3\text{CH}(\text{OH})\text{COONa}$	-COOH	$2 \times 10^{-3} \text{ M}$
lactate	biogenic	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	-COOH	$\leq 50 \text{ ppm}$
oxalate (oxalic acid dihydrate)	anthropogenic	$\text{HOOC}\text{COOH}\cdot 2\text{H}_2\text{O}$	-COOH	$9 \times 10^{-2} \text{ M}$
bis(2-ethylhexyl) phosphoric acid (DHP; di(2-ethylhexyl)-phosphoric acid; ?bis(2-ethylhexyl) hydrogen phosphate)	anthropogenic	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}]_2\text{P}(\text{O})\text{OH}$	-P(O)OH	
ascorbate (ascorbic acid)	anthropogenic	$\text{C}_6\text{H}_8\text{O}_6$	-OH	$1 \times 10^{-1} \text{ M}$
tartrate (tartaric acid, disodium salt dihydrate)	anthropogenic	$\text{NaOOCCH}(\text{OH})\text{CH}(\text{OH})\text{COONa}\cdot 2\text{H}_2\text{O}$	-COOH	
acetamide (acetic acid amide)	anthropogenic	$\text{CH}_3\text{CONH}_2$	-NH <sub>2</sub>	
2-hydroxybutyrate (?2-hydroxybutyric acid, Na salt)	anthropogenic	? $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COONa}$	-COOH	
1,10-phenanthroline	anthropogenic	$\text{C}_{12}\text{H}_8\text{N}_2\cdot \text{H}_2\text{O}$	-NH	$4 \times 10^{-6} \text{ M}$
thenoyltrifluoroacetate (TTA; 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; 1-thenoyl-3,3,3-trifluoroacetone)	anthropogenic	$\text{C}_4\text{H}_3\text{SCOCH}_2\text{COCF}_3$	-F	$2 \times 10^{-4} \text{ M}$
thiocyanate (sodium or ammonium thiocyanate)	anthropogenic	$\text{NaSCN}$	-SCN	
oxine (8-hydroxyquinoline; 8-quinolinol)	anthropogenic	$\text{C}_9\text{H}_6\text{NOH}$	-NH	$1 \times 10^{-3} \text{ M}$
a-hydroxyisobutyrate (a-hydroxy isobutyric acid)	anthropogenic	? $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$	-COOH	$4 \times 10^{-6} \text{ M}$
dihexyl-N,N-diethylcarbamoylmethylenephosphonate (DHDECMP)	anthropogenic		-P(O)OH	
tributyl phosphate (TBP)	anthropogenic		-P(O)OH	
tri-N-octylphosphine oxide (TOPO)	anthropogenic		-P(O)OH	
CMPO	anthropogenic		-P(O)OH	
HDEHP?				

Table 3, cont.—Organic ligands and functional groups.

formate	biogenic	HCOOH	-COOH	
isobutyrate	biogenic	(CH <sub>3</sub> ) <sub>2</sub> CHCOOH	-COOH	
butyrate	biogenic	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	-COOH	≤100 ppm
isovalerate	biogenic	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> COOH	-COOH	
valerate	biogenic	CH <sub>3</sub> (CH <sub>2</sub> )CCOOH	-COOH	

Table 4.—Inventory-limited actinide concentrations.

radionuclide isotope	Curie totals (scaled) for contact-handled (CH) waste (Ci)*	Curie totals for remote-handled (RH) waste (Ci)*	sum of Curie totals for CH (scaled) and RH waste (Ci)	activity conversion factor (Ci/kg)**	sum of masses for CH (scaled) and RH waste (kg)	radionuclide element	sum of masses of isotopes in CH (scaled) and RH waste (kg)	gram atomic weight	sum of quantities of isotopes in CH (scaled) and RH waste (moles)	WIPP liquid volume under fully inundated conditions (L)	calculated inventory-limited concentration under fully inundated conditions (moles/L)
Am241	5.78E+04	8.98E+04	1.48E+05	3.43E+03	4.30E+01	americium	4.30E+01	243	1.77E+02	5.0E+07	3.5E-06
Np237	2.35E+01	7.66E-01	2.43E+01	7.05E-01	3.44E+01	neptunium	3.44E+01	237.0482	1.45E+02	5.0E+07	2.9E-06
Pu238	8.12E+05	6.17E+04	8.74E+05	1.71E+04	5.11E+01						
Pu239	1.72E+05	4.08E+04	2.13E+05	6.22E+01	3.42E+03						
Pu240	2.28E+04	9.98E+03	3.28E+04	2.28E+02	1.44E+02						
Pu241	4.54E+05	1.78E+05	6.32E+05	1.03E+05	6.14E+00						
Pu242	6.89E+02	9.48E-01	6.90E+02	3.93E+00	1.76E+02	plutonium	3.80E+03	244	1.56E+04	5.0E+07	3.1E-04
Th232	1.41E-01	3.33E-01	4.74E-01	1.10E-04	4.31E+03	thorium	4.31E+03	232.0381	1.86E+04	5.0E+07	3.7E-04
U233	3.00E+02	1.04E+03	1.34E+03	9.68E+00	1.38E+02						
U235	1.39E+00	3.67E+02	3.68E+02	2.16E-03	1.71E+05						
U238	8.51E+00	2.30E+00	1.08E+01	3.36E-04	3.22E+04	uranium	2.03E+05	238.029	8.52E+05	5.0E+07	1.7E-02
	sum	sum	sum		sum		sum	mean atomic weight of actinides (g/mole)	mean radiation level of Am, Np, Pu, Th, U in WIPP waste (Ci/mole)	(pCi/mole)	
Am+Np+Pu+Th+U	1.52E+06	3.82E+05	1.90E+06		2.11E+05	Am+Np+Pu+Th+U	2.11E+05	240	2.2E+00	2.2E+12	
Notes:											
*Curie totals from Baseline Inventory Report (US DOE, 1994c, Table 5-3)											
**Curie to mass conversion factors from Sandia WIPP Project (1992c, Table 3.3-1)											

Table 5.—Chemical compositions of WIPP brines.

brine name	AIS	VPX series	H-17	G Seep	DH36	ERDA-6	Union
brine source	Culebra facies "C," AIS seep	Culebra facies "C," AIS boreholes	Culebra facies "A," well sample	Salado Fm., disposal room seep	Salado Fm., well sample	Castile Fm., well sample	Castile, well sample
Na <sup>+</sup> (M)	0.601	0.585	2.288	4.110	3.670	4.870	4.830
K <sup>+</sup> (M)	0.008	0.008	0.028	0.350	0.472	0.097	0.100
Ca <sup>2+</sup> (M)	0.023	0.021	0.042	0.008	0.010	0.012	0.009
Mg <sup>2+</sup> (M)	0.021	0.018	0.074	0.630	0.817	0.019	0.086
Cl <sup>-</sup> (M)	0.560	0.542	2.522	5.100	5.370	4.800	4.800
HCO <sub>3</sub> <sup>-</sup> (M)	0.001	0.001	0.001	0.012	0.012	0.043	0.036
SO <sub>4</sub> <sup>2-</sup> (M)	0.079	0.074	0.077	0.303	0.173	0.170	0.230
B (M)	0.003	0.002	0.004	0.144	0.137	0.063	0.100
Br (M)	0.000	0.000	0.001	0.017	NA	0.011	0.006
approximate ionic strength (M; without B, Br)	0.8	0.8	2.8	6.7	6.8	5.3	5.5
calculated TDS (g/L; without B, Br)	43	41	154	334	331	306	312
Σcations (meq/L)	698		2549	5735	5795	5029	5119
Σanions (meq/L)	719		2675	5718	5728	5183	5296
(Σcations - Σanions)/ (Σcations + Σanions) in percent	-1.5		-2.4	0.2	0.6	-1.5	-1.7
information source	1	2	3	4	5	6	6

Notes:

1. Average of analyses listed in Robinson (1991, Table 2).
2. Average of VPX-25, VPX-26, VPX-27, and VPX-28; see Lucero et al. (1994, Table 3).
3. From Robinson (1991, Table 1).
- 4, 5, 6. From Brush (1990, Tables 2.2, 2.1, 2.3, respectively).



Table 6.—Actinide oxidation states and ionic radii.

actinide/lanthanide	III	IV	V	VI
thorium		Th <sup>4+</sup>		
uranium	1.03 Å	U <sup>4+</sup> 0.93 Å	0.87 Å	UO <sub>2</sub> <sup>2+</sup> 0.83 Å
neptunium	1.01 Å	(Np <sup>4+</sup> ) 0.92 Å	NpO <sub>2</sub> <sup>+</sup> 0.88 Å	(NpO <sub>2</sub> <sup>2+</sup> ) 0.82 Å
plutonium	Pu <sup>3+</sup> 1.00 Å	Pu <sup>4+</sup> 0.90 Å	PuO <sub>2</sub> <sup>+</sup> 0.87 Å	PuO <sub>2</sub> <sup>2+</sup> 0.81 Å
americium	Am <sup>3+</sup> 0.99 Å	0.89 Å	(AmO <sub>2</sub> <sup>+</sup> ) 0.86 Å	0.80 Å
neodymium	Nd <sup>3+</sup> 1.12 Å			

Table 7.—pH at zero-point-of-charge for some minerals.

mineral	chemical formula	pH at PZC
quartz	SiO <sub>2</sub>	2-3.7
cassiterite	SnO <sub>2</sub>	4.5
rutile	TiO <sub>2</sub>	6.0
hematite (natural)	Fe <sub>2</sub> O <sub>3</sub>	4.8
hematite (synthetic)	Fe <sub>2</sub> O <sub>3</sub>	8.6
corundum	Al <sub>2</sub> O <sub>3</sub>	9.0
magnesia	MgO	12
fluoroapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,OH)	6
hydroxyapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	7
calcite	CaCO <sub>3</sub>	9.5

Table 8a.—Colloidal particles identified at other sites. Deep (>100m) subsurface systems.

Row No.	Site Location	Site Location	Site Location	Geology	Depth from Surface (m)	pH	Eh (mV)	T (°C)	Colloid Diameter (nm)	Colloid Concentration (mg/L)	Colloid Composition	Comments	Reference(s)
1	Switzerland	Grimsel Test Site	Grimsel Test Site	Granite/mylonite	500	9.6	-250	12	10-1000	0.1	Clay/silica	Stable hydrogeochemical system; stable groundwater flow rate	Degeldre et al. (1989); Degeldre et al. (1989)
2	Switzerland	Zurzach		Granitic/fractured; 2 sources	470	8	-180	37	10-1000	0.025	Silica/clay	Stable hydrogeochemical system; steady flow from artesian system	Brütsch et al. (1991)
3	Switzerland	Leuggem		Granitic/fractured	1680	8	-150	66	10-450	0.025	Silica/clay	Stable hydrogeochemical system; steady flow from artesian system	Degeldre et al. (1990)
4	Germany	Bad Sackingen		Granitic/fractured	82-201	6.5	+340 to +400	30	10-450	0.025	Silica/clay	Stable hydrogeochemical system; water pumped	Degeldre and Wernli (1987)
5	Germany	Menzenschwand		Granitic/fractured	240	6.5	+ (O <sub>2</sub> detected)	12	10-1000	0.4	Clay/silica	Mixed groundwaters (introduced oxic surface waters)	Alexander et al. (1989)
6	Switzerland	Transitgas tunnels Grimsel	Sources 1-8	Granitic/fractured; 8 sources	200	8-9	0	8	100-10,000	0.1-2	Clay/silica	Mixed groundwaters	
7	Switzerland	Transitgas tunnels Grimsel	Sources 9-13	Granitic/fractured; 5 sources	200	8-9	-80 to 0	20-30	100-10,000	5-20	Clay/silica	Hydrothermal fracture zone	
8	Switzerland	Transitgas tunnels Grimsel	Sources 14-16	Granitic/fractured; 5 sources	200	8-9	+200 to +300	5	100-10,000	0.5	Clay-silica	Direct transit of surface water	
9	France	Fanay-Augères, Massif-Central		Granitic formation	280	6.0	+398	16	100-1000	>0.2	Silica, NOM	Mixed water (groundwater and surface water with high levels of NOM [~2 mg C/L])	Billon et al. (1991)
10	Switzerland	Wellenberg	SB6	Marlstone	360-420	9.0	-500	12	100-1000	2-3	Clay	-2 mg/L of Fe(II) presents the potential for artifacts resulting from oxidation; low Ca <sup>2+</sup> ~1-2 mg/L	Degeldre et al. (in press)

Table 8a, cont.—Colloidal particles identified at other sites. Deep (>100m) subsurface systems.

11	Sweden	10 sites: Tavununnanen, Kamlunge, Gideå, Svartoberget, Forsmark, Finnsjön, Fjällveden, Ävrå, Äspö, Laxemar, Klipperås	total of 22 deep boreholes with 305 observations (depths 45-260 m)	Crystalline rock, mostly granitic, but one location with basalt; rock age of 1.5-2.0 x 10 <sup>9</sup> y; fracture fillings have been repeatedly activated by hydrothermal and low temperature fluids  Concentrated (deep) groundwater (Cl <sup>-</sup> >50 mg/L)	deep groundwater	7.4	-149	11	50-450	0.35 ± 1.06	Calcite, troilite, Fe-hydroxide, clay, quartz, Mn-oxide	Calcite precipitation is probably an artifact and increases the reported mean concentration by four-fold	Laaksoharju and Degueldre (in press); Tuilborg (1992)
12	Gabon	Okelobondo	fractures	Argillaceous rocks, pelites  Dilute groundwater (Cl <sup>-</sup> <50 mg/L)	300	7.08	+350 ± 50	26	50-450	0.14 ± 0.23	Fe-hydroxide, pyrophyllite	Samples from fractures gave lower values on Al and Si; drilling is therefore believed to increase silica and clay colloids	Smellie et al. (1992)
13	United States	Nevada Test Site		Fractured rhyolitic lava	800	8.4	+	40	4-55	4.5	Quartz, feldspars	Outside nuclear detonation cavity	Bucklemeier (1986)
14	United States	Jackass Flats, Nevada	Well 13	Rhyolitic welded tuff		7.2		32	100-2000	1.43	Oxides of Ca-Si, Al, Al-Si, Ca-Si-Ti	Sampled from water supply wells (800 L/min); bulk of pore volume in pores ≤100 nm, suggesting limited transport paths for colloids	Buchholtz-ten Brink et al. (1993)
15	United States	Nevada Test Site	Well 20	Rhyolitic welded tuff		7.7	+300	40	15-450	5.08	Layer silicates, plagioclase, carbonate, quartz	Sampled from water supply wells (800 L/min); average pores about 2000 nm (much larger than colloids)	Buchholtz-ten Brink et al. (1992)
16	United States	central or southern Nevada	Indian Spring Well	Volcanic (predominantly ash-flow tuff, ash-fall tuff and rhyolite lava flows)	46-131	8.4		30	30-1000; >1000	1.35; 0.18	Silica (cristobalite, fused silica, or amorphous silica), and possibly small amounts of clay or zeolite	Calcite and organic material also identified, but may be sampling artifacts or contaminants; No discernible trends were observed between water chemistry and either concentration or composition	Kingston (1989)
17	United States	Nevada Test Site	Well 4	Volcanic (as above)	229-424	8.0		38	30-1000; >1000	0.72; 0.30	(as above)	(as above)	Kingston (1989)
18	United States	Nevada Test Site	Water Well 20	Volcanic (as above)		8.0		27	30-1000; >1000	0.48; 0.15	(as above)	(as above)	Kingston (1989)

Table 8a, cont.—Colloidal particles identified at other sites. Deep (>100m) subsurface systems.

19	United States	Nevada Test Site	UE19c	Volcanic (as above)	2587	8.7		31	30-1000; >1000	0.68; 0.13	(as above)	(as above)	Kingston (1989)
20	United States	Nevada Test Site	Well 8	Volcanic (as above)	381-543	7.7		27	30-1000; >1000	0.73; 0.13	(as above)	(as above)	Kingston (1989)
21	United States	Nevada Test Site	Well C-1	Carbonate aquifer with fractures containing secondary calcite, calcareous clay, or calcareous clay and iron oxide	468-503	6.6		36	30-1000; >1000	0.55; 0.03	(as above)	(as above)	Kingston (1989)
22	United States	Nevada Test Site	UE16d	Carbonate (as above)	914	7.6		23	30-1000; >1000	0.35; 0.10	(as above)	(as above)	Kingston (1989)
23	United States	Nevada Test Site	Well A	Alluvial deposits of sand and gravel cemented by calcium carbonate	490-570	7.8		27	30-1000; >1000	0.31; 0.43	(as above)	(as above)	Kingston (1989)
24	United States	central or southern Nevada	Lathrop Well	Alluvial deposits (as above)	125-155	8.2		26	30-1000; >1000	0.54; 0.43	(as above)	(as above)	Kingston (1989)
25	Germany	Gorleben	Gorleben 8	Sedimentary	115	7.7		20	2-450	<0.5	Silica/clay	Off-line sampling and analysis; groundwater and sediment samples	Lieser et al. (1986); Kim et al. (1984)
26	Germany	Gorleben	Gorleben 9	Sedimentary	133	7.8		20	2-450	<0.5	Silica/clay	Off-line sampling and analysis; groundwater and sediment samples	Lieser et al. (1986); Kim et al. (1984)
27	Germany	Gorleben	Gorleben 214	Sedimentary				20	10-450	0.005	Silica/NOM	Off-line sampling and analysis of groundwater and sediment	Degueldre et al. (1988)
28	Canada	Cigar Lake, Saskatchewan	Hole 75	Upper sandstone	154-159	6.6	+65	7	10-450; >450	0.85 ± 0.26; 0.63 ± 0.42	Clay minerals, Fe-Si precipitates, NOM, quartz, carbonate	Well-consolidated sandstone; all Cigar Lake sampling conducted at pumping rates of 30-300 mL/min	Vilks et al. (1993)
29	Canada	Cigar Lake, Saskatchewan	Hole 71	Lower Sandstone	243-245	7.5	-304	10	10-450; >450	0.73 ± 0.16; 1.76 ± 0.42	(as above)	Well-consolidated sandstone	Vilks et al. (1993)
30	Canada	Cigar Lake, Saskatchewan	Hole 139	Lower sandstone	437	6.5	+235	5	10-450; >450	0.75 ± 0.2; 1.2 ± 0.4	(as above)	Well-consolidated sandstone	Vilks et al. (1993)
31	Canada	Cigar Lake, Saskatchewan	Hole 219	Lower sandstone	414-426	6.5	+124	9	10-450; >450	0.85 ± 0.16; 0.85 ± 0.21	(as above)	Well-consolidated sandstone	Vilks et al. (1993)
32	Canada	Cigar Lake, Saskatchewan	Hole 67	Lower sandstone	346-348	7.2	-9	5	10-450; >450	1.0 ± 0.2; 1.9 ± 0.3	(as above)	Formation contains lenses of friable sand, but not near the borehole	Vilks et al. (1993)
33	Canada	Cigar Lake, Saskatchewan	Hole 91	Clay-rich zone	407	6.1	+209	8	10-450; >450	0.6 ± 0.09; 4.9 ± 1.5	(as above)	Borehole near altered fracture zone; high hydraulic conductivity	Vilks et al. (1993)
34	Canada	Cigar Lake, Saskatchewan	Hole 197	Clay/uranium ore contact	416-421	6.0	+238	10	10-450; >450	0.72 ± 0.16; 0.64 ± 0.13	(as above)	Highly structured clay	Vilks et al. (1993)
35	Canada	Cigar Lake, Saskatchewan	Hole 79	Uranium ore	432	6.7	+80	15	10-450; >450	0.91 ± 0.26; 3.4 ± 0.9	(as above)		

Table 8a, cont.—Colloidal particles identified at other sites. Deep (>100m) subsurface systems.

36	Canada	Cigar Lake, Saskatchewan	Hole 220	Uranium ore	220	8.0	-243	11	10-450; >450	1.4 ± 0.4; 1.9 ± 0.4	(as above)	Ore zone contains lenses of friable sand	Vilks et al. (1993)
37	Canada	Cigar Lake, Saskatchewan	Hole 199	Altered basement	446-452	7.9	+109	15	10-450; >450	7.8 ± 4.1; 106 ± 3	(as above)	Near a major fracture (metapelite rock)	Vilks et al. (1993)

Table 8b.—Colloidal particles identified at other sites. Shallow (<100m) surface and subsurface sites.

Row No.	Site Location	Site Location	Site Location	Geology	Depth from Surface (m)	pH	Eh (mV)	T (°C)	Colloid Diameter (nm)	Colloid Concentration (mg/L)	Colloid Composition	Comments	Reference(s)
41	Sweden	10 sites: Tavinnunanen, Kamlunga, Gideå, Svartboberget, Forsmark, Finnsjön, Fjällveden, Ävrå, Äspö, Laxemar, Klipperås	total of 22 deep boreholes with 305 observations (depths 45-260 m)	Crystalline rock, mostly granitic, but one location with basalt; rock age of 1.5-2.0 x 10 <sup>9</sup> y; fracture fillings have been repeatedly activated by hydrothermal and low temperature fluids  Dilute (shallow) groundwater (Cl <sup>-</sup> <50 mg/L)	shallow groundwater	6.7	-191	12	50-450	0.3 ± 2.7	Clay, Fe-hydroxide, calcite, quartz, Mn-oxide	Fe-hydroxides, in some cases, can be artifacts resulting from oxidation during sampling	Laaksoharju and Degeldre (in press); Tullborg (1992)
42	Gabon	Oklo	drillhole	Argillaceous rocks, pelites  Dilute groundwater (Cl <sup>-</sup> <50 mg/L)	21				50-450	1.58 ± 1.57	Fe-hydroxide, pyrophyllite	Samples from fractures gave lower values on Al and Si; drilling is therefore believed to increase silica and clay colloids	Smellie et al. (1992)
43	United States	central or southern Nevada	Pahroe Spring	Volcanic (predominantly ash-flow tuff, ash-fall tuff and rhyolite lava flows)		7.9		16	30-1000; >1000	1.3; 0.18	Silica (cristobalite, fused silica, or amorphous silica), and possibly small amounts of clay or zeolite	Calcite and organic material also identified, but may be sampling artifacts or contaminants; No discernible trends were observed between water chemistry and either concentration or composition	Kingston (1989)
44	United States	central or southern Nevada	Peavine Canyon	Volcanic (as above)		7.8		11	30-1000; >1000	>0.28; 0.38	(as above)	(as above)	Kingston (1989)
45	United States	central or southern Nevada	Peavine Ranch Well	Volcanic (as above)	63-93	7.7		12	30-1000; >1000	0.51; 0.68	(as above)	(as above)	Kingston (1989)
46	United States	central or southern Nevada	Sidehill Spring	Volcanic (as above)		7.8		18	30-1000; >1000	0.82; 0.18	(as above)	(as above)	Kingston (1989)
47	United States	central or southern Nevada	Lower Indian Spring	Volcanic (as above)		7.8		22	30-1000; >1000	0.66; 0.34	(as above)	(as above)	Kingston (1989)
48	United States	Nevada Test Site	Cane Springs	Volcanic (as above)		7.5		16	30-1000; >1000	0.36; 3.89	(as above)	(as above)	Kingston (1989)
49	United States	Nevada Test Site	Topopah Spring	Volcanic (as above)		6.9		16	30-1000; >1000	>25.2; 2.01	(as above)	(as above)	Kingston (1989)

Table 8b, cont.—Colloidal particles identified at other sites. Shallow (<100m) surface and subsurface sites.

50	United States	central or southern Nevada	Crystal Pool	Carbonate aquifer with fractures containing secondary calcite, calcareous clay, or calcareous clay and iron oxide		7.1		33	30-1000; >1000	0.34; 0.03	(as above)	(as above)	Kingston (1989)
51	United States	central or southern Nevada	Ash Spring	Carbonate (as above)		7.1		31	30-1000; >1000	0.40; 0.10	(as above)	(as above)	Kingston (1989)
52	United States	central or southern Nevada	Cold Creek Spring	Carbonate (as above)		8.1		10	30-1000; >1000	0.87; 0.10	(as above)	(as above)	Kingston (1989)
53	United States	central or southern Nevada	Fairbanks Spring	Carbonate (as above)				27	30-1000; >1000	0.38; 0.28	(as above)	(as above)	Kingston (1989)
54	United States	central or southern Nevada	Indian Spring	Carbonate (as above)		8.0		25	30-1000; >1000	0.59; 0.13	(as above)	(as above)	Kingston (1989)
55	United States	central or southern Nevada	Beatty Well 2	Alluvial deposits of sand and gravel cemented by calcium carbonate	21-40	8.2		23	30-1000; >1000	6.48; 0.38	(as above)	(as above)	Kingston (1989)
56	Brazil	Morro de Ferro, Poços de Caldas	Well MF12	Clay/phonolite	50	6.0	+200 to +300	20	10-450	0.25	Fe(OH) <sub>3</sub> , NOM	Analyses of bore holes along flow path provides no evidence of colloid transport through saturated porous rock	Mickeley et al. (1991)
57	Jordan? (JD)	Maqarin		Sedimentary rock; 5 sources of basic groundwater		12.5	+	25	10-450	<1	Portlandite	Oxic groundwater containing chromate; highly alkaline due to portlandite produced by natural bitumen combustion	West et al. (1991)
58	United States	Pinal Creek, Arizona	Well 451	Fine-grained alluvium from a granitic porphyry	<50	4.7	+250	19		20		Downgradient from inputs of acidic mining wastes; in zone where groundwater pH is rapidly changing	
59	United States	Pinal Creek, Arizona	Well 503	Unconsolidated alluvium from a granitic porphyry	<50	5.7	+320	19	300-1300	0.1	Gypsum, Fe-oxide, kaolinite	Downgradient from Well 451 and plume of acidic waste	
60	United States	Laughlin, Nevada		Sand/gravel alluvium below evaporation ponds and ash dump	20-60	7.1-7.6	+100	12	100-2000	10-100	Silicates	Postulate dissolution of cementing carbonates due to microbially induced increase in groundwater CO <sub>2</sub>	Gschwend et al. (1990)



Table 8b, cont.—Colloidal particles identified at other sites. Shallow (<100m) surface and subsurface sites.

61	Israel	Tel Aviv	Well WT4	Coastal plain phreatic aquifer; calcareous sandstones	0-16	6.5-7.0			100-3000	11-33	Calcite and quartz	Postulate detachment of colloids resulting from dissolution of carbonate aquifer matrix; dissolution promoted by long-term irrigation of municipal sewage that resulted in microbially-induced increase in pCO <sub>2</sub>	Ronen et al. (1992)
62	United States	Cape Cod, Massachusetts		Glacial outwash	7	6.2	-100 to -400 (estimated)	13	100	0.9 to 2	Ferrous phosphate (monodispersed)	Downgradient from infiltration of secondary treated sewage; colloids formed from sewage phosphate and aquifer Fe(II)	Gschwend and Reynolds (1987)
63	United States	Connecticut	Coal gasification plant (operated from 1853-1923)	Glacial fluvial	6	6.2	+300 to +780	12	100-3000	~2 to 3	Silica and clay	Did not observe expected enhancement in transport of polycyclic aromatic hydrocarbons from coal tar deposits	Backhus (1990)
64	United States	McDonalds Branch Watershed, Pine Barrens, New Jersey	"Swamp Deep"	Unconsolidated sandy coastal plain aquifer	8	4.5	+290	12		60	Organic-coated kaolinite, chamosite, some goethite	Anaerobic under swamp; reductive dissolution of Fe-oxide cements postulated to mobilize organic-coated clays	
65	United States	McDonalds Branch Watershed, Pine Barrens, New Jersey	"Upland Deep"	Unconsolidated sandy coastal plain aquifer	10	4.8	+340	12		<1	Kaolinite	Oxic aquifer in same formation; Fe-oxide cements postulated to bind colloids to aquifer particles	
66	United States	Harrington, Delaware	Well Lc42-01	Unconsolidated coastal plain aquifer	15	6.2	+100	14		6	Organic-coated muscovite and kaolinite, Fe-oxides	Anoxic aquifer; postulate dissolution of Fe-oxide cements mobilizes colloids	
67	United States	Harrington, Delaware	Well Md22-01	Unconsolidated sandy coastal plain aquifer	5	4.3	+380	18		<1	Muscovite	Oxic aquifer in same formation; Fe-oxide cements postulated to bind colloids to aquifer particles	
68	United States	Alligator River		Uranium ore body in sandstone	15-25	6.8-7.2	+170 to +375		18-1000	0.1 to 1.2	Fe and Si species with sorbed U and U daughters	Prefiltration	Short et al. (1988)

Table 8c.—Colloidal particles identified at other sites. References.

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Table 9.—Baseline and action-level parameter values.

a. Baseline Levels							
Colloidal Particle Type	Plutonium Concentration (moles/L)	Uranium Concentration (moles/L)	Thorium Concentration (moles/L)	Neptunium Concentration (moles/L)	Americium Concentration (moles/L)	Diffusion Constant Reduction Factor*	
mineral fragments	0	0	0	0	0	not required	
bacteria	1E-04	1E-04	1E-04	1E-04	1E-04	not applicable	
humic substances	2E-04	2E-04	2E-04	2E-04	2E-04	100	
actinide intrinsic colloids	0	0	0	0	0	not required	
b. Action Levels							
Colloidal Particle Type	Plutonium Concentration (moles/L)	Uranium Concentration (moles/L)	Thorium Concentration (moles/L)	Neptunium Concentration (moles/L)	Americium Concentration (moles/L)	Diffusion Constant Reduction Factor*	Transport Reduction Factor
mineral fragments	0	0	0	0	0	not required	not applicable
bacteria	1E-07	1E-07	1E-07	1E-07	1E-07	not applicable	10
humic substances	2E-06	2E-06	2E-06	2E-06	2E-06	100	10
actinide intrinsic colloids	0	0	0	0	0	not required	not applicable
<b>Notes:</b>							
* used to reduce the free water diffusion constants for dissolved actinides in Reeves et al. (1991, Table 2.7), (i.e., divide the free water diffusion constants by the Reduction Factor shown)							

scenario	design constraint: column diameter (mm)	design constraint: column length (mm)	design constraint: pore volume (cm <sup>3</sup> )	design criterion 1: minimum V <sub>w</sub> to produce distinct peaks (cm/min)	minimum Q to produce distinct peaks (cm <sup>3</sup> /min)	design criterion 2: aspect ratio (should be ≥ 4) (length/diameter)	design criterion 3: maximum V <sub>w</sub> to reduce kinetic artifacts (cm/min)	mass transfer units (should exceed 15 to 30) (n)	design criterion 4: maximum particle diameter to reduce channeling (mm)
1	10	100	3.9	9.6 x 10 <sup>-3</sup>	3.8 x 10 <sup>-3</sup>	10	9.6 x 10 <sup>-1</sup>	58	0.25
2	10	150	5.9	6.4 x 10 <sup>-3</sup>	2.5 x 10 <sup>-3</sup>	15	6.4 x 10 <sup>-1</sup>	130	0.25
3	10	250	9.8	3.8 x 10 <sup>-3</sup>	1.5 x 10 <sup>-3</sup>	25	3.8 x 10 <sup>-1</sup>	360	0.25
4	10	300	12	3.2 x 10 <sup>-3</sup>	1.3 x 10 <sup>-3</sup>	30	3.2 x 10 <sup>-1</sup>	530	0.25
5	10	500	20	1.9 x 10 <sup>-3</sup>	0.75 x 10 <sup>-3</sup>	50	1.9 x 10 <sup>-1</sup>	1500	0.25
6	10	1000	39	0.96 x 10 <sup>-3</sup>	0.38 x 10 <sup>-3</sup>	100	0.96 x 10 <sup>-1</sup>	5800	0.25
7	25	150	37	6.4 x 10 <sup>-3</sup>	16 x 10 <sup>-3</sup>	6	6.4 x 10 <sup>-1</sup>	130	0.625
8	25	250	61	3.8 x 10 <sup>-3</sup>	9.4 x 10 <sup>-3</sup>	10	3.8 x 10 <sup>-1</sup>	360	0.625
9	25	300	74	3.2 x 10 <sup>-3</sup>	7.9 x 10 <sup>-3</sup>	12	3.2 x 10 <sup>-1</sup>	530	0.625

constants (see text):

total porosity (intercrystalline + interparticle) = 50%

bulk density of solid = 2.8 g/cm<sup>3</sup>

K<sub>d</sub> = 10

k = 0.1

Table 10.—Design considerations for crushed-rock column experiments.

Table 11.—Analytical equipment required for experiments.

Principle Task(s)	Instrument/Device	Manufacturer
Electrophoretic mobility measurements	Coulter DELSA 440 Zeta Potential Analyzer	Coulter Corp., Hialeah, Florida
Size determination of colloidal particles; nephelometric turbidity measurements of dilute dispersions	Coulter N4-MD Sub-Micron Particle Size Analyzer	Coulter Corp., Hialeah, Florida
Particle counting of supra-micron particles	Coulter Multisizer IIe	Coulter Corp., Hialeah, Florida
Particle counting of dilute dispersions of sub-micron sized colloidal particles	Particle Measurement Systems Model HSLIS-S50;S100 High-sensitivity Liquid Particle-Counting Spectrometers	Particle Measurement Systems Inc., Boulder, Colorado
Nephelometric turbidity measurements of concentrated dispersions	Monitek Model 21 Laboratory Nephelometer	Monitek
Quantification of surface area of solids by gas adsorption	Micromeretics ASAP 2000 BET Surface Area Analyzer	Micromeretics Instrument Corp., Norcross, Georgia
Quantification of organic and inorganic ions concentrations	Beckman Model DU-640 UV/Visible light spectrophotometer	Beckman Instruments, Inc., Fullerton, California
Quantification of fluorescent tracer concentrations	Turner Model 450 Fluorometer	Turner,
Preparation of colloidal dispersions	McCrone Micronizing mill	McCrone Associates, Westmont, Illinois
Generation of controlled atmospheres for experiments	Labconco Model 50801 Controlled-Atmosphere Glovebox	Labconco Corp., Kansas City, Missouri
Quantification of masses in the microgram to gram range ( $10^{-6}$ to $10^0$ g)	Mettler UMT-2 Microbalance	Mettler-Toledo, Inc., Hightstown, New Jersey

Table 11, cont.—Analytical equipment required for experiments.

Quantification of inorganic ion concentrations	TJA AtomScan 25 sequential inductively coupled argon plasma - atomic emission spectrometer	Thermo Jarrell-Ash Corp., Franklin, Massachusetts
Quantification of inorganic and organic anions concentrations	Dionex DX-300 ion chromatography system, gradient pump, conductivity detector and spectral array detector	Dionex Corp., Sunnyvale, California
Quantification of total organic carbon, total inorganic carbon, and total carbon concentrations in solutions	UIC Model CM150 Carbon Analyzer	UIC Inc. Coulometrics, Joliet, Illinois
Measurement of pH	Orion Model 940 pH meter	Orion Research Inc., Boston, Massachusetts
Measurement of pH; control of pH	Orion Model 960 Autotitration System	Orion Research Inc., Boston, Massachusetts