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Scientific Investigation Plan for NNWSI WBS Element 1.2.3.4.1.5.A Sorption and Precipitation

Los Alamos National Laboratory

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Scientific Investigation Plan for
NNWSI WBS Element 1.2.3.4.1.5.A
Sorption and Precipitation

1. Objectives, Issues and Information Needs Addressed

The objective of this task is to provide data to predict radionuclide movement from the repository to the accessible environment. Sorption coefficients will be used to estimate radionuclide retardation along the flow path. However, sorption coefficients depend on several variables (such as groundwater composition, substrate material, sorbing species, presence of complexing agents, etc.). To interpret sorption coefficients correctly, these variables must be studied and must be taken into account in performance assessment calculations.

The charge of this task, therefore, is to determine sorption coefficients for elements of interest on pure minerals and on tuff samples representative of Yucca Mountain as a function of mineralogy, water composition, waste-element concentration, microbiological activity, presence of drilling fluids, and the presence of particulates and colloids. Work on the majority of elements using J-13 water and Yucca Mountain tuff samples is nearly complete. A major effort will now be focused on sorption of known species of actinides under various conditions to gain the understanding necessary to develop a model that predicts key radionuclide sorption at Yucca Mountain.

Sorption coefficients and models developed will be used to address the following issues:

1.1 Will the mined geologic disposal system meet the system performance objective for radionuclide releases to the accessible environment as required by 10 CFR Part 191, 10 CFR Part 60, and 10 CFR Part 960?

1.1.1. Site information needed to calculate the release of radionuclides to the accessible environment.

1.1.4 Calculational models to predict radionuclide releases to the accessible environment.

1.1.5 Determination of the radionuclide releases to the accessible environment associated with representative scenarios.

1.1.6 Probabilistic estimates of the radionuclide releases to the accessible environment considering anticipated and unanticipated scenarios.

1.9 Can the demonstration for favorable and potentially adverse conditions be made as required by 10 CFR 60.122?

1.10 (a) Can the higher-level findings required by 10 CFR Part 60 be made for the qualifying condition on the postclosure system guideline and the disqualifying and qualifying conditions on the technical guidelines for geohydrology, geochemistry, rock characteristics, climate changes, erosion, dissolution, tectonics and human interference, and (b) can the comparative evaluations required by 10 CFR 960.3-1-5 be made?

1.12.1 Site characterization information needed for design.

1.15.5 Radionuclide retardation by precipitation processes along flow paths to the accessible environment.

1.15.6 Radionuclide retardation by dispersive/diffusive/advective transport processes along flow paths to the accessible environment.

1.15.7 Radionuclide retardation by all processes along the flow paths to the accessible environment.

1.15.8 Information about the present and expected geochemical characteristics that is required to support postclosure higher level findings for repository performance.

3.13 Potential for impacts to surface and groundwater availability as a result of contamination or as a function of available resource potential.

3.1.10 Potential levels of radionuclides and dosages that regional populations will be exposed to, and their potential effects.

The application of the information generated from the work described to site characterization is obvious. However, this information is equally important to performance assessment. Performance assessment is charged with the task of calculating as accurately as possible any releases of radionuclides to the accessible environment under anticipated and unanticipated conditions. The data provided here are directly applicable to those calculations. It will not be possible to prove conclusively that groundwater will never find a shorter path to the accessible environment; however, with the data obtained from this work, it may be possible to show that the transport of key radionuclides will be retarded with respect to the groundwater travel time, whatever it may be. This is a valuable form of insurance for accurate performance assessment calculations.

2. Principal Investigators

Kimberly W. Thomas, Los Alamos National Laboratory

3. Statement of Work

Sorption studies are divided into eight subtasks:

1. Batch sorption studies.
2. Preparation of actinide tracers.
3. Sorption coefficients as a function of concentration of sorbing element (isotherms).
4. Sorption as a function of groundwater composition.
5. Sorption as a function of atmosphere.
6. Sorption on particulates and colloids.
7. Statistical analysis of sorption data.

8. Sorption model development.

1. Batch Sorption Studies

The purpose of these studies is to complete the measurement of batch sorption coefficients for hazardous radionuclides on tuff samples representative of Yucca Mountain as a function of mineralogy and time. This will provide the main sorption data base for the statistical analyses and for developing a model to predict sorption at Yucca Mountain. Emphasis is now being placed on those elements considered most important (by the Solubility Task). Comparison of the batch sorption coefficients with those measured from crushed tuff column experiments will indicate if chemical species of an element are present that have differing sorption ratios. By performing these measurements on pure minerals, the minerals responsible for the sorption of the waste element may be identified.

Sorption coefficients and their dependence upon the variables studied will be used in WBS 1.2.3.4.1.6.A (Dynamic Transport Processes) to aid in predictions of fracture flow; in calculations of retardation by various mechanisms (WBS 1.2.3.4.1.7.A, Retardation Sensitivity Analysis); and in Performance Assessment calculations for Issue 1.1.

2. Preparation of Actinide Tracers

The purpose of this work is to prepare solutions of actinide tracers in known, stable, well-characterized oxidation states for use in batch sorption measurements and for use in Issue 1.15.6. Actinide elements such as plutonium, americium, and neptunium are among the key radionuclides. Most actinide elements in near neutral solutions (the expected repository conditions) can exist in more than one oxidation state, each of which may exhibit different sorption and transport behavior. In order to characterize these behaviors, sources of the individual species must be available. Emphasis will be placed on those species predicted most likely to be present under repository conditions (WBS 1.2.3.4.1.4.A, Solubility).

3. Sorption Coefficients as a Function of Concentration of Sorbing Element (Isotherms)

The purpose of this study is to characterize the dependence of sorption coefficients upon the concentration of the element being sorbed. Since the concentration of a waste element is expected to change as it is transported from the repository to the accessible environment, an accurate prediction of sorption along the flow path must account for the change in sorption coefficient with the concentration changes, if they are significant. The concentrations studied will try to reach an apparent concentration limit, i.e., the greatest radionuclide concentration that the solution phase can maintain when all other variables are held constant, so that it can be shown that precipitation is not contributing to the sorption ratio.

These isotherm data will be used as part of the general sorption data base; to determine where in element concentrations precipitation begins to contribute to the measured sorption ratio; and in modeling efforts (WBS 1.2.3.4.1.7.A, Retardation Sensitivity Analysis) that predict retardation along the flow path.

4. Sorption as a Function of Groundwater Composition

Since the groundwater composition will vary between the repository and the accessible environment, the dependence of sorption on this variable must be determined. Groundwater composition can control the waste element oxidation state, speciation, and solubility, and therefore, can have a great effect on the measured sorption ratio. These results will be used in the general sorption data base and in modeling efforts (WBS 1.2.3.4.1.7.A, Retardation Sensitivity Analysis) that predict retardation along the flow path to the accessible environment.

5. Sorption as Function of Atmosphere

The purpose of this study is to examine the dependence of sorption coefficients on atmospheric composition. In particular, comparisons will be made between sorption coefficients made under laboratory conditions (ambient atmosphere) and under a CO_2-controlled atmosphere that is regulated to maintain the pH of J-13 groundwater near 7. In experiments performed in the laboratory atmosphere, the pH of the solution gradually rises to approximately 8-8.5, presumably due to the loss of CO_2 from solution, whereas the field pH of Yucca Mountain groundwaters is much closer to 7. It is important to show what effect,

if any, the higher pH has on measured sorption coefficients. These results will be used to confirm that sorption coefficients measured under laboratory atmosphere conditions are valid.

6. Sorption on Particulates and Colloids

The purpose of this study is to determine if sorption occurs on particulates or colloids that may be present in groundwaters between the repository and the accessible environment. This is an interactive study with others described in Issue 1.15.5 and WBS 1.2.3.4.1.6.A, Dynamic Transport. If sorption does occur and if these particulates can be transported to the accessible environment, then the use of sorption coefficients alone will not accurately predict the transport of the sorbed radionuclides. Transport may also occur via microbes, either as sorption on their surfaces or by ingestion of the radionuclides by the microorganisms. It must be determined what role such colloidal and particulate matter might play in the transport of radioactivity. If sorption is found to occur on microbes or particulates, further experiments on their transport will be performed in WBS 1.2.3.4.1.6.A, Dynamic Transport.

7. Statistical Analysis of Sorption Data

The purpose of this work is to use a variety of statistical approaches to the sorption data base in order to: 1) determine those variables (mineralogy, groundwater composition, atmosphere, etc.) having the most profound effect on the sorption coefficients; 2) predict sorption coefficients as a function of mineralogy and, perhaps, groundwater composition; 3) estimate errors associated with predicted sorption coefficients; 4) identify gaps in the experimental data. The results of these analyses will be used to bound sorption coefficients to be used in WBS 1.2.3.4.1.7.A, Retardation Sensitivity Analysis, and for Performance Assessment in Issue 1.1.

8. Model Development

The purpose of this work is to develop a model to predict sorption behavior of key radionuclides at Yucca Mountain using the data generated from the previously described studies. This model will be used in Performance Assessment Issue 1.1, by the Retardation Sensitivity task, and by the Dynamic Transport task as part of the description of radionuclide movement from the repository to the accessible environment.

4. Data and Materials Needed, Techniques, Procedures, and Computer Codes

Data:

Physical characteristics of the tuff samples studied such as core identification, depth of core, identification of stratigraphic unit.

Mineralogic content of the tuff samples.

Water composition.

Speciation data for the elements studied (provided by Solubility Task WBS 1.2.3.4.1.4.A).

Characterization of particulates, including their origin, size, and mineralogic composition.

Cation exchange capacity of tuff samples.

Materials:

These analyses require tuff samples representative of the various mineralogic and stratigraphic characteristics of Yucca Mountain. Primary attention is focused on samples from stratigraphic positions near and below the proposed repository horizon and on vitric vs. devitrified, zeolitized vs. nonzeolitized, welded vs. nonwelded, etc., mineralogic characteristics of tuff samples from these stratigraphic units.

Well J-13 groundwater has been chosen as the representative Yucca Mountain groundwater for these studies because it is pumped from the Topopah Spring unit, the proposed repository horizon. Water from Wells H-3 and UE-25p#1 is used to study the effect of groundwater composition on sorption.

Particulates will be provided by the Groundwater Chemistry task and the Microbiological task.

Radionuclide tracers are obtained from standard sources. Pure minerals, such as clinoptilolite and smectite clays, will be obtained from outside sources.

Techniques:

Standardized batch sorption techniques as described in the Los Alamos Quality Assurance Manual (TWS-CNC-DP-05, R1) and in report LA-9328-MS will be used. Cation exchange capacity has been measured by the National Soil Survey Laboratory using procedures in "Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey," Soil Survey Investigation No. 1 (USDA, Soil Conservation Service, Washington, DC, August 1982 rev.).

Plutonium and americium tracer solutions will be prepared in a carbonate buffer solution in the lowest concentration possible in which the species present can be identified. These solutions will then be diluted and immediately used in sorption experiments.

Standard statistical methods will be employed to evaluate the sorption data base generated by the previously discussed subtasks. The two primary goals are to identify trends in sorption coefficients associated with changing variables and to pinpoint gaps in the existing data base.

Various modeling routines will be employed to obtain the best fit to the existing sorption data.

Techniques being developed or explored include identification of actinide species at $<10^{-6}$M concentration by chemical separation methods and modifying the standard batch sorption procedure to accommodate much smaller amounts of solid material (for particulate studies).

Procedures:

TWS-CNC-DP-05, R1	Sorption, Desorption Ratio Determinations of Geologic Materials by a Batch Method
TWS-INC-DP-02, R3	Quality Control in Counting Radioactive Nuclides
TWS-MSTQA-DP-15, R0	NNWSI Measurement Control
TWS-INC-DP-35, R0	pH Measurement
TWS-INC-DP-30, R0	Partial CO_2 Atmospheric Control of Groundwater Chemistry
TWS-MSTQA-QP-14, R1	Research and Development (Experimental) Procedure

To be Prepared	Preparation of actinide tracers (when a suitable technique is developed)
	Collection of Yucca Mountain groundwater
	Preparation of crushed tuff for batch and column measurements.

Computer Codes:

SOSI	Data base management (sorting)
SAS	Statistical Analysis System
DATATRIEVE	Data base management
MAPPER	Graphics
RAYGUN	Gamma-ray data analysis
GAMANAL	Gamma-ray data analysis
SPECANAL	Gamma-ray data analysis

5. Nonstandard Methods or Techniques

None.

6. Location of Work Performed

Most work will be performed at the Los Alamos National Laboratory and at and adjacent to the Yucca Mountain exploration block. Cation exchange capacity measurements will be contracted out.

7. Quality Assurance Requirements

This task has been determined to be Quality Level I. See QALAS submission for details.

8. Application of Results

The investigations in this task will be used to assess licensing requirements of the Nuclear Regulatory Commission as specified in 10 CFR Part 60 with specific application to sections 60.122 (b)(1), 60.122(b)(3), and 60.122(c)(8). Within the NNWSI Project, the results of these studies will be applied to the issues listed under Item 1, and to specific tasks such as Dynamic Transport Process Task (WBS 1.2.3.4.1.6.A, Los Alamos) Retardation Sensitivity Analysis Task (WBS 1.2.3.4.1.7.A, Los Alamos), Performance Assessment (SNL), SCP, and EIS preparation.

9. Schedule

Starting date: in progress. Ending date: FY 1990.

10. Past and Expected Achievements

Significant Achievements to Date

Demonstrated that zeolitized tuffs possess high sorption coefficients for many elements (see LA-9328-MS).

Developed a model to predict sorption coefficients for simple cations based on sorptive mineral content (LA-9328-MS).

Preliminary results show groundwater composition does have an effect on sorption coefficients.

Demonstrated that drilling fluids in use at Yucca Mountain support microbial activity.

Preliminary results indicate that the presence of bacteria increase the sorption coefficient of plutonium.

Published a summary report of sorption in J-13 groundwater on Yucca Mountain Tuff (M313).

Published a survey of C-14 literature applicable to Yucca Mountain (R310).

Planned Achievements For FY 86 And Later Years

Determine the effect of CO_2-enriched atmosphere on sorption coefficients.

Statistically examine the effect of mineralogy on sorption coefficients.

Determine sorption coefficients under vadose zone groundwater conditions.

Evaluate relationships between sorption and water chemistry.

Model sorption data using various equilibrium and nonequilibrium models.

Previous Work and QA Controls on Previous Work

The previous work to be used in support of these investigations is summarized in the reports listed below.

K. W. Thomas, "Summary Report on Sorption Measurements Performed with Yucca Mountain Tuff Samples and Water from Well J-13," Los Alamos National Laboratory Report (to be published).

Daniels et al., "Summary Report on the Geochemistry of Yucca Mountain and Environs," Dec. 1982, Los Alamos National Laboratory Report, LA-9328-MS.

Daniels at al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, Jan-Mar, 1982," Los Alamos National Laboratory Report, LA-9327-PR.

Wolfsberg et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April-June, 1982," Los Alamos National Laboratory Report, LA-9484-PR.

Daniels et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July-Sept, 1982," Los Alamos National Laboratory Report, LA-9577-PR.

Ogard et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, Oct-Dec, 1982," Los Alamos National Laboratory Report, LA-9666-PR.

Wolfsberg et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, Jan-Mar, 1983," Los Alamos National Laboratory Report, LA-9793-PR.

Ogard et al.,"Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April-June, 1983," Los Alamos National Laboratory Report, LA-9846-PR.

Bryant et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July-Sept, 1983," Los Alamos National Laboratory Report, LA-10006-PR.

Wolfsberg et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, Oct-Dec, 1983," Los Alamos National Laboratory Report, LA-10032-PR.

Crowe et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, Jan-Mar, 1984," Los Alamos National Laboratory Report, LA-10154-PR.

Rundberg et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April-June, 1984," Los Alamos National Laboratory Report, LA-10297-PR.

Ogard et al., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July-Sept, 1984," Los Alamos National Laboratory Report, LA-10299-PR.

A. E. Ogard and J. F. Kerrisk, "Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment", Nov. 1984, Los Alamos National Laboratory Report, LA-10188-MS.

E. N. Treher, and N. A. Raybold, "The Elution of Radionuclides Through Columns of Crushed Rock from the Nevada Test Site", Oct. 1982, Los Alamos National Laboratory Report, LA-9329-MS.

The Quality Assurance controls under which this previous work was performed are summarized in Tables I and II. Table I is a summary of the administrative controls under which the previous work was performed. Table II is a summary of the Work Plans and Detailed Procedures under which the previous work was performed.

Work used in support of this investigation and completed before the implementation of NVO-196-17, Revision 0, August 1980, will be processed in accordance with NNWSI-SOP-03-03.

For work completed subsequent to August 1980, where approved QA procedures were not implemented, the data or data interpretations to be used will be processed as a nonconformance in accordance with NNWSI-SOP-15-01 (TWS-MSTQA-QP-16, R0).

11. Milestones and Deliverables

Milestones

Number	Level	Descriptive Title	Delivery Date
R311	II	Preliminary report on statistical evaluation of sorption data	9/86
R309	II	Preliminary report on sorption modeling	9/86
M316	II	Report: sorption coefficients as a function of groundwater composition	9/86
R720	II	Interim report: letter report on sorption isotherms	3/87
R503	II	Progress report on sorption measurements with known species of actinides	9/87

Number	Level	Descriptive Title	Delivery Date
R505	II	Summary report on the effects of groundwater composition on sorption	9/87
R722	II	Letter report on sorption under CO_2 enriched atmospheric conditions	9/87
R512	II	Progress report on statistical evaluation of sorption data	9/87
R514	II	Progress report on sorption modeling	9/87
R721	II	Letter report on sorption isotherms	3/88
R515	II	Progress report on sorption modeling	9/88
R513	II	Progress report on statistical evaluation of sorption data	9/88
R726	II	Letter report on sorption on particulates	9/88
R723	II	Letter report on sorption under CO_2 enriched atmospheric conditions	9/88
R504	II	Report: sorption measurements with known oxidation states of actinides	9/88
M315	II	Report: Sorption isotherms	3/89
R506	II	Report: Effects of CO_2-enriched atmosphere on sorption coefficients	9/89
R727	II	Letter report on sorption on particulates	9/89
R384	II	Report: Statistical evaluation of sorption data	9/89
R385	II	Sorption model complete	9/89
R383	II	Report: sorption on particulates	9/90
M376	I	Final report on sorption at Yucca Mountain	9/90

Table I. NNWSI Quality Assurance Procedures

Title	Identifier	Date Effective	Date Superseded
QA Program Plan	TWS-CMB QA-QP-01, R0	24-Oct-78	16-Aug-79
QA Program Plan	TWS-CMB QA-QP-01, R1	16-Aug-79	09-Apr-80
QA Program Plan	TWS-CMB QA-QP-01, R2	09-Apr-80	13-Sep-82
QA Program Plan	TWS-CMB QA-QP-01, R3	13-Sep-82	01-Feb-84
QA Program Plan	TWS-MSTQA-QP-01, R4	01-Feb-84	19-Sep-85
QA Program Plan	NNWSI-QP-01, R0	19-Sep-85	
Document Control	TWS-CMB QA-QP-03,R0		14-Nov-78
Document Control	TWS-CNC-11-10/78-9, R1	14-Nov-78	16-Jul-79
Document Control	TWS-CMB QA-QP-03, R2	16-Jul-79	13-Sep-82
Document Control	TWS-CMBQA-QP-03, R3	13-Sep-82	03-Jan-84
Document Control	TWS-MSTQA-QP-03, R4	03-Jan-84	19-Mar-85
Document Control	TWS-MSTQA-QP-03, R5	19-Mar-85	21-Feb-86
Document Control	TWS-MSTQA-QP-03, R6	21-Feb-86	
Handling, Storage	TWS-CMBQA-QP-04, R0	12-May-79	13-Sep-82
and Shipping Procedure	TWS-CMBQA-QP-04, R1	13-Sep-82	02-Apr-85
	TWS-MSTQA-QP-04, R2	02-Apr-85	
NNWSI Procurement	TWS-CMBQA-QP-06, R0	14-Sep-82	-03-Jan-84
Procedures	TWS-CMBQA-QP-06, R1	03-Jan-84	21-Oct-85
	TWS-MSTQA-QP-06, R2	21-Oct-85	
Procedure for Technical	TWS-CMBQA-QP-07, R0	02-Aug-82	04-Mar-85
Review of Publications	TWS-MSTQA-QP-07, R1	04-Mar-85	
Personnel Certification	TWS-MSTQA-QP-08, R0	01-Jun-83	03-Jan-84
Procedure for NNWSI	TWS-MSTQA-QP-08, R1	03-Jan-84	20-Dec-84
	TWS-MSTQA-QP-08, R2	20-Dec-84	19-May-86
	TWS-MSTQA-SP-08, R3	19-May-86	
Records Control	TWS-MSTQA-QP-09, R0	03-Jan-84	
Procedure			

Table I. (cont)

Title	Identifier	Date Effective	Date Superseded
NNWSI Surveillance Procedure	TWS-MSTQA-QP-11, R0	01-Sep-84	
NNWSI Receiving Inspection Procedure	TWS-MSTQA-QP-12, R0	21-Oct-85	
NNWSI Los Alamos Conflict Resolution Committee	TWS-MSTQA-QP-13, R0	22-May-85	30-Dec-85
Quality Assurance Procedure for One-Time Research and Development Work	TWS-MSTQA-QP-14, R0 TWS-MSTQA-QP-14, R1	22-May-85 19-May-86	19-May-86
NNWSI Control of Nonconformances	TWS-MSTQA-QP-16, R0	19-May-86	
Assignment of Quality Levels for Los Alamos NNWSI Items and Activities	TWS-MSTQA-QP-18, R0	17-Dec-85	
NNWSI Change Requests	TWS-MSTQA-QP-19, R0	19-May-86	
Los Alamos Quality Assurance Manual		02-Jul-84	19-Sep-85

Table II. Work Plans And Detailed Procedures

Identifier	Date	Title
TWS-CNC-11-11/78-5	11-13-78	Tuff experiments-sorption coefficients and migration measurements in CNC-11
TWS-CNC-11-11/78-5, R1	03-05-79	Tuff experiments-sorption coefficients and migration measurements in CNC-11
TWS-CNC-11-WP-03, R2	07-16-79	Tuff experiments-sorption coefficients and migration measurements in CNC-11
TWS-CNC-11-WP-03, R3	01-22-82	Tuff experiments-sorption coefficients and migration measurements in CNC Division
TWS-CNC-WP-03, R4	08-30-82	Tuff experiments-sorption ratios and migration measurements
TWS-CNC-11-10/78-10/ R0	11-02-78	Quality control in counting radioactive nuclides
TWS-CNC-11-DP-02, R1	01-18-80	Quality control in counting radioactive nuclides
TWS-CNC-DP-02, R2	08-30-82	Quality control in counting radioactive nuclides
TWS-CNC-11-DP-05, R0	06-13-79	Sorption, desorption ratio determinations of geologic materials by a batch method
TWS-CNC-11-DP-08, R0	08-13-79	TWS procurement procedures
TWS-CNC-11-DP-08, R1	12-02-80	TWS procurement procedures
TWS-CNC-WP-11, R0	08-30-82	Actinide chemistry in near-neutral solutions work plan
TWS-CNC-WP-16, R0	01-16-84	Oxidation state investigations of plutonium work plan