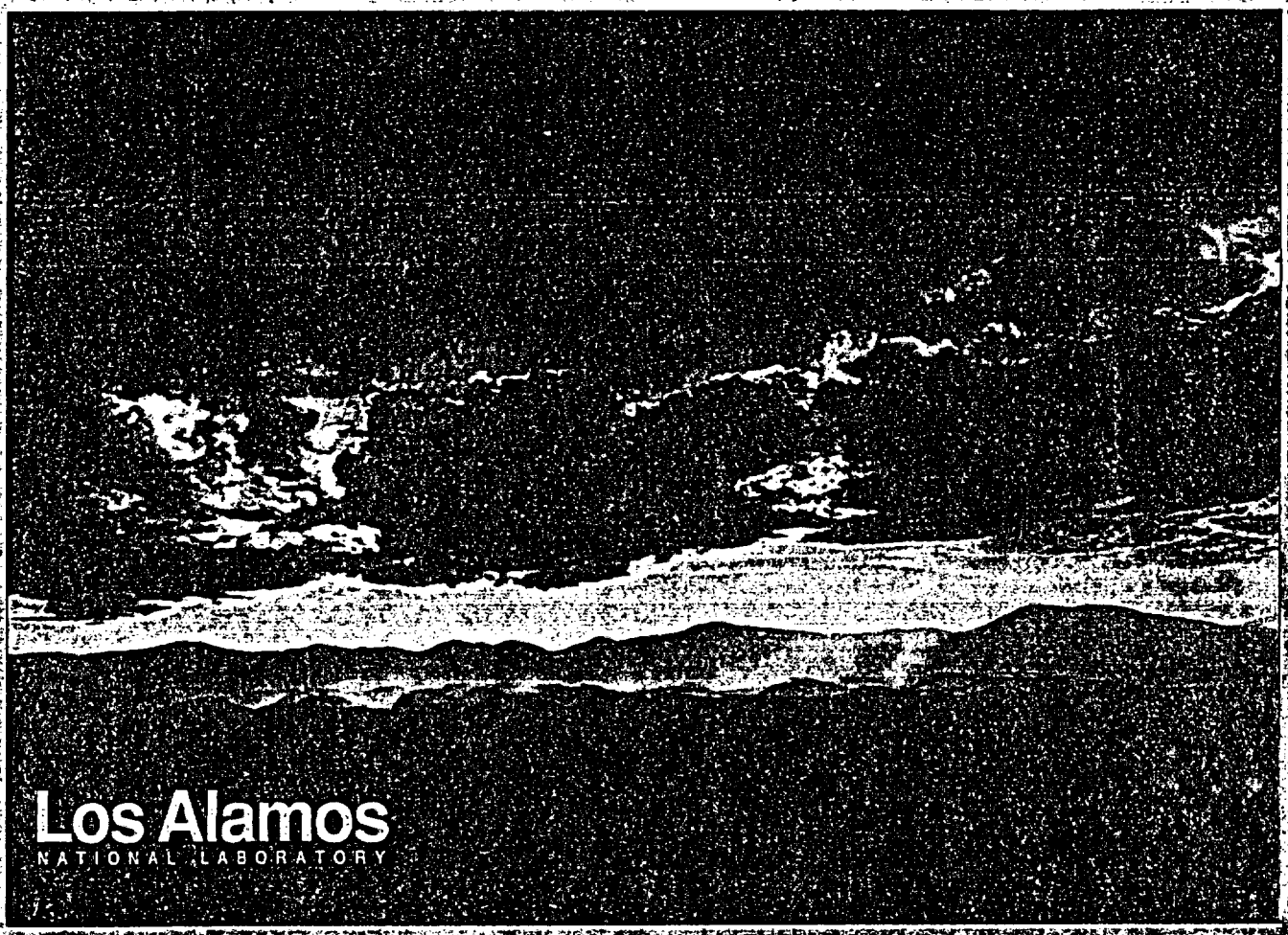
# Yucca Mountain Site Characterization Project

# Monthly Activity Report

*September 1992*





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# LOS ALAMOS NATIONAL LABORATORY

# YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

## Monthly Activity Report

## September 1992

### WBS 1.2.1 Systems

**Objective**

The objective of this task is to integrate systems with the Geologic Repository Program, to describe the Yucca Mountain Site Characterization Project Mined Geologic Disposal System, and to evaluate the performance of the natural, engineered barrier, and total systems for meeting regulatory standards.

### Technical Data (WBS 1.2.1.3.5)

**Activities and Accomplishments**

Reviewed AP-5.1 and AP-5.2 and provided comments on their contents.

**Planned Activities**

Submit data from Activities 8.3.1.8.1.3.2, 8.3.1.3.6.1.1, and 8.3.1.3.2.1.3 to the Technical Data Base (TDB) as soon as data acceptance resumes.

Submit calcite data to the TDB.

Submit erosion data to the TDB.

### Caisson Experiment (WBS 1.2.1.4.6)

**Activities and Accomplishments**

Staff consulted with K. Stetzenbach of the University of Nevada at Las Vegas (UNLV) to discuss analytical chemistry support of the caisson experiment. Sample treatment procedures, the type of analytical suite, and potential problems such as the use of a 0.1 M sodium-chloride solution as a background electrolyte, which may cause interference for some metal analyses, were considered. SNL and Los Alamos staff will provide a more specific set of needs, and UNLV will determine if the background solution should have a lower ionic strength.

Discussions were also held with B. Boehm about a possible collaboration on a column experiment at UNLV as it will provide an additional length scale or comparison of transport with the caisson.

All materials have been delivered for fabricating the lower-boundary device.

An extended summary on the design of the caisson experiment was submitted to the 1993 International High-Level Radioactive Waste Management Conference to be held April 26-30, 1993 in Las Vegas.

**Planned Activities** Fill caisson with sufficient sand to install lower-boundary device. Test porous cup assemblies for lower boundary before installing in the caisson. Obtain material to construct solution samplers for caisson.

**Publications** None

## Performance Assessment Calculational Support (WBS 1.2.1.4.7)

**Activities and Accomplishments** G. Zyvoloski met with W. Nelson of INTERA to discuss ground-water modeling capabilities within YMP. They also discussed future code development of the Los Alamos code FEHMN.

# WBS 1.2.3.1 Site Management and Integration

## Site Management (WBS 1.2.3.1.1)

**Objective**

The objective of this task is to manage and integrate site characterization activities.

**Activities and Accomplishments**

B. Carlos and S. Bolivar attended the September Sample Overview Committee meeting at the Sample Management Facility.

Review of the executive summary of the ITE report was completed by teleconference on 9 September.

Following the Thermal Loading Decision Workshop, various groups were assigned to develop needs for specific areas. Contributions were made by Los Alamos to the liquid transport modeling group, and Los Alamos studies and experiments that have or are now supporting thermal issues were included with budget information. A review of the draft Thermal Loading Decision Report was submitted through the Geochemistry Integration Team.

A meeting was held on 18 September in Los Alamos with the lead auditor and lead technical specialist to determine those activities to be audited during the upcoming DOE audit scheduled for 2-5 November.

Los Alamos studies were ranked according to nine DOE priorities for budget allocation purposes. This information was submitted to the M&O for consideration by DOE.

## Test Management and Integration (WBS 1.2.3.1.2)

**Objective**

The objective of this task is to provide coordination for Los Alamos surface-based test planning and package development.

**Activities and Accomplishments**

Surfaced-based Test Coordination. Staff developed a draft submission of D&TRI to YMP for the reactive tracer testing planned in the C-well complex.

Staff continued to participate in Test Integration Group (TIG) meetings.

ESF Testing. Continued field construction and testing activities as defined by TPP 92-07, "Fran Ridge Test Pit Mapping," and its associated JP 92-7. The DRC, JP 92-7, "Field Implementation Record Package," is being assembled for submittal to the RPC. Los Alamos and USGS staff developed a technical data information form for mapping data to be collected at the Fran Ridge site.

**Planned Activities**

Surfaced-based Test Coordination. Continue support of the Los Alamos surface-based site characterization activities in response to Project program directives.

ESF Testing. Prepare test planning packages for launch-chamber tests. Continue gathering tracers, fluids, and materials information. Prepare Title II Test Planning Packages. Continue ESF sample and test-coordination efforts, participate in TIG meetings, and support the RSED director, as requested.

## WBS 1.2.3.2.1.1.1 Mineralogy, Petrology, and Rock Chemistry of Transport Pathways

**Objective**

The purpose of this activity is to define the important mineralogical and geochemical variables along fracture and rock-matrix transport pathways at Yucca Mountain, in support of performance assessment and to evaluate the impact of repository construction on natural waste-transport barriers.

**Activities and Accomplishments**

Staff continued to work on operating procedures and software for the INEL microdiffractometer.

Milestone 3137, "Geologic evaluation of six nonwelded tuff sites for a surface-based test facility for the Yucca Mountain Project," was revised and sent to the USGS and SNL for further modification. This report includes data on hydrologic properties (A. Flint, USGS) and mechanical properties (C. Rautman, SNL), as well as mineralogical and chemical data collected by Los Alamos.

Work continued on zeolites in fractures in existing drill holes. Chabazite was identified visually and by x-ray diffraction in the Prow Pass member of Crater Flat tuff in drill core UE-25b #1h; previously, chabazite had been identified only in the basal vitrophyre of the Topopah Spring Member in J-13 and USW VH-1, and all known occurrences of this mineral were below the static water level. Samples of zeolites were prepared for electron microprobe analysis. An extended abstract entitled "Distribution of Fracture-lining Zeolites at Yucca Mountain, Nevada" was prepared for the Zeolite '93 Conference (Boise, Idaho, June 1993).

Review comments were received on the paper "Fracture-lining Manganese Oxide Minerals in Silicic Tuff, Yucca Mountain, Nevada," and minor revisions were made. It will be resubmitted to *Chemical Geology* in October.

YMPO review comments on "Mineralogy as a Factor in Radioactive Waste Transport through Altered Pyroclastic Rocks at Yucca Mountain, Nevada" were addressed. The paper is being revised and will be submitted for publication early in FY93..

Samples from the first 530 ft of UE-25 UZ-16 were examined at the Sample Management Facility. Fractures containing silica, calcite, clay, zeolites, and manganese-oxide minerals were requested for further study.

**Planned Activities**

Work planned within the next few months includes the following activities: (1) continue analysis of fracture-coating zeolites in existing drill core and begin analysis of fracture-coating minerals in UE-25 UZ-16; (2) continue analysis of calcites to understand transport and precipitation mechanisms.

**Problem Areas**

The electron microprobe has been nonfunctional for approximately 6 weeks. The repair date is uncertain, and the new electron microprobe will not be available for some time.

**Milestone Progress**

3120
30 June 1992
*Calcite in the Upper Paintbrush Tuff*
Approved by YMPO.

3130
15 December 1992
*Fracture Mineralogy of the Paintbrush Tuff*
In preparation.

3137
30 September 1992
*Mineralogy of Calico Hills for Adit Development*
In technical review.

**Publications**

B. Carlos, D. Bish, S. Chipera, and S. Craven
*Fracture-Lining Manganese Oxide Minerals in a Silicic Tuff*
Journal article, *Chemical Geology*
Approved by YMPO; revised and resubmitted for publication.

B. Carlos, S. Chipera, and D. Bish
*Distribution of Fracture-Lining Zeolites at Yucca Mountain, Nevada*
Conference paper, *Zeolite '93*
In preparation.

G. D. Guthrie, D. L. Bish, and B. T. Mossman
*Quantitative Analysis of Zeolite-Bearing Dusts Using the Rietveld Method*
Journal article, *Science*
Submitted.

D. Vaniman, D. Bish, D. Broxton, B. Carlos, S. Chipera, and S. Levy
*Mineralogy as a Factor in Radioactive Waste Transport Through Pyroclastic Rocks at Yucca Mountain, Nevada*
Journal article, *Journal of Geophysical Research*
In YMPO approval process.

D. T. Vaniman
*Calcite Deposits in Drill Cores USW G-2 and USW GU-3/G-3 at Yucca Mountain, Nevada*
La-series report
Submitted to TPO.

## WBS 1.2.3.2.1.1.2 Mineralogical and Geochemical Alteration

**Objective**

The objective of this task is to characterize past and present natural alteration processes that have affected the potential geologic repository and to predict future effects of natural and repository-induced alteration.

**Activities and Accomplishments**

D. Vaniman and S. Levy reviewed the draft YMPO topical report on calcite-silica studies in Trench 14 and at Busted Butte and provided additional text and data tables.

Opal and zeolites from altered rocks at Harper Valley (Yucca Mountain) were separated for x-ray diffraction studies. A paper presenting interim results of the ongoing studies at Harper Valley will be submitted for the fall meeting of the Materials Research Society in November 1992. An abstract of this paper was published in the conference proceedings.

G. WoldeGabriel prepared mineral separates of altered tuffs from the Mojave and Amargosa deserts for K/Ar studies, and apparent ages from authigenic feldspars and clays will be used to evaluate the dating results for K-rich zeolites from these samples.

**Planned Activities**

Chemical and mineralogical characterization of samples from hydrothermal deposits exposed at the surface will continue, as will K/Ar and calcite-silica, laminated-deposit studies. We will continue work on the YMP topical report on calcite-silica and breccia deposits.

**Problem Areas**

Mechanical problems with our old electron microprobe have resulted in the loss of two weeks of analytical time; fortunately, our new microprobe is close to being operational.

**Milestone Progress**

3138
30 October 1992
*Chemical Transport in Zeolitic Alteration*
60% complete.

3141
31 March 1992 (delayed due to participation in the issue resolution process)
*Laminated Zone in Trench 14*
65% complete. (Technical review complete.)

3142
31 July 1992
*K/Ar Dating of Clays and Zeolites*
In technical review.

3143
30 April 1992
*Experimental Dehydration of Volcanic Glasses*
In program review.

3150
15 April 1993
*Final Report on Bedrock*
30% complete.

**Milestone Progress (cont.)**

3341
30 October 1992
*Surface-discharging hydrothermal systems at Yucca Mountain -- examining the evidence*
Technical review complete.

**Publications**

D. Bish and J. Aronson
*Paleothermal and Paleohydrologic Conditions in Silicic Tuff from Yucca Mountain, Nevada*
Journal article, *Clay and Clay Minerals*
Approved by YMPO; submitted.

S. Levy
*Surface-discharging hydrothermal systems at Yucca Mountain -- examining the evidence*
Conference paper, *Scientific Basis for Nuclear Waste Management XVI.*
Technical review complete.

S. Levy and C. Naeser
*Bedrock Breccias Along Fault Zones near Yucca Mountain, Nevada*
Chapter in USGS Bulletin on Yucca Mountain studies
In USGS editorial review.

S. Reneau
*Maganese Accumulation in Rock Varnish in a Desert Piedmont, Mojave Desert, California, and Application to Evaluating Varnish Development*
Journal article, *Quaternary Research*
Approved by YMPO.

D. Vaniman, D. Bish, and S. Chipera
*Dehydration and Rehydration of a Tuff Vitrophyre*
Journal article, *Journal of Geophysical Research*
In YMPO approval process.

D. Vaniman, S. Chipera, and D. Bish
*Pedogenesis of Siliceous Calcretes at Yucca Mountain, Nevada*
Journal article, *Science*
Approved by YMPO.

## WBS 1.2.3.2.1.2 Stability of Minerals and Glasses

**Objective**

The objective of this activity is to produce a model for past and future mineral alteration in Yucca Mountain. The model is intended to explain the natural mineral evolution resulting from the transformation of metastable mineral assemblages to more stable assemblages and the effects of a repository emplacement.

**Activities and Accomplishments**

This activity has been deferred.

## WBS 1.2.3.2.5 Postclosure Tectonics

### Objective

The objective of these volcanism studies is to determine the hazards of future volcanic activities with respect to siting a high-level radioactive waste repository at Yucca Mountain.

### Activities and Accomplishments

A preliminary draft of Study Plan 8.3.1.8.1.2, "Physical Process of Magmatism and Effects on the Repository," has submitted to the DOE for submission to the NWTRB.

A large trench was constructed on the north side of the Lathrop Wells center. The scoria mound beneath the $Ql_4$ lava, an older scoria unit ($Qs_7$) below the scoria mound, and a sequence of primary and reworked pyroclastic surge deposits were exposed on the south end of this trench. On the north end, the base of the $Ql_7$ lava, which lies on a thin interval of flow clinker and minor scoria, was exposed. The pyroclastic surge deposit originally thought to underlie the $Ql_7$ lava was not discovered, and the trench exposure revealed that the pyroclastic surge deposits draped the $Ql_7$ and probably do not underlie the lava flow. The lava flow edge of the $Ql_7$ unit is composed of a flow rubble, which explains the scatter obtained in the field-magnetic directions of this unit. The trench walls were unstable so that the deposits could not be described and logged.

Trace-element data were evaluated for the Black cone and the Lathrop Wells cone. The data for both cones show that they were formed by separate magma batches. Each magma batch cannot be related to other magma batches by fractional crystallization.

An U-Th isochron age of 120±20 ka was obtained for the $Ql_6$ lava.

Cosmogenic helium ages of about 65-70 ka were obtained for the $Ql_3$ lava.

A three-day meeting was held with the Nuclear Waste Technical Review Board (NWTRB). Talks were presented by the YMP, State of Nevada, NRC, USGS, and external consultants for the first two days, and a field trip to the Lathrop Wells volcanic center and Crater Flat was conducted on the third day.

A meeting was held with participants from DOE, Los Alamos, SNL, and the M&O to discuss future interactions with the NRC, possible revisions of the volcanism study plans, and the interfaces between volcanism studies and performance assessment.

Work in progress. Staff prepared for an upcoming meeting with the NWTRB.

Staff continued to determine the U-Th disequilibrium ages for volcanic units of the Lathrop Wells volcanic center.

Using the software SURFER, the volume of volcanic units of the Lathrop Wells volcanic center was calculated.

### Planned Activities

Further studies of the trench LW-1 will be completed in October.

Sampling of $Ql_6$ and $Qs_1$ will be completed for cosmogenic helium studies.

**Problem Areas**

We will delay field mapping of the 3.7 Ma basalt centers of Crater Flat to concentrate on completion of the Issue Resolution Report.

Completion of the Issue Resolution Report has been delayed because of the large amount of time required to prepare for the NRC video conference and the NWTRB meeting.

The volcanism issue resolution report was originally scheduled to be completed by June 1992. It will be completed in October 1992 because of meeting commitments with the NRC and the NWTRB.

**Milestone Progress**

3174
8 January 1992
*Effects of Magmatic Disruption on the Repository* (Study Plan 8.3.1.8.1.2, R0)

3034
30 September 1992
*Report on Magma System Dynamics*

3109
30 September 1992
*Report of Subsurface Effects*

3111
30 September 1992
*Preliminary Geologic Mapping of Volcanic Centers*

3164
30 September 1992
*Progress Report on Thermoluminescence*

R482
30 October 1992
Issue Resolution Report

**Publications**

B. M. Crowe, *et al.*
*Issue Resolution Report*
First draft complete.

S. G. Wells, *et al.*
*Multiple Eruptive Events at Small Volume Basaltic Centers: Evidence From the Cima and Crater Flat Volcanic Fields*
Journal article
In preparation.

## WBS 1.2.3.3.1.2.2 Water-Movement Tracer Tests

**Objective**

The objective of the water-movement tracer tests is to obtain measurements of chlorine isotope distributions to help quantify the percolation of precipitation in the unsaturated zone.

**Activities and Accomplishments**

Over 20 samples from neutron-access boreholes USW N-37, N-54 and N-55 and Midway Valley soil were prepared by Hydro Geo Chem and subsequently analyzed by the University of Rochester and LLNL for chlorine-36 .

Staff began to streamline the organization of data generated by Hydro Geo Chem.

Collection of cutting samples for $^{36}Cl$ analysis from UZ-16 and new neutron access boreholes continued this month.

**Planned Activities**

Address study plan review comments; revise existing DPs; prepare new DPs; process soil samples for Cl/Br and $^{36}Cl/Cl$ ratios; process cuttings samples from neutron-access boreholes; collect additional soil samples from Yucca Mountain area as opportunities arise.

**Problem Areas**

None

**Milestone Progress**

3191
*Procedure for Chlorine-36 Analysis of Unsaturated Zone Samples*
30 September 1992
95% complete

**Publications**

None

## WBS 1.2.3.3.1.2.5 Diffusion Tests in the ESF

**Objective**

The objective of this task is to determine *in situ* the extent to which the nonsorbing tracers diffuse into the water-filled pores of the Topopah Spring welded unit.

**Activities and Accomplishments**

No significant activity in this study.

**Milestone Progress**

No Level II milestones are planned for this fiscal year.

## WBS 1.2.3.3.1.3.1 Site Saturated Zone Ground-water Flow System (Reactive Tracer Testing)

**Objective**

Experiments will be conducted at the C-Well complex (holes UE-25c #1, UE-25c #2, and UE-25c #3) and other wells in the vicinity of Yucca Mountain using reactive tracers to characterize retardation and transport properties at a larger scale than currently used in laboratory experiments.

**Activities and Accomplishments**

Software Qualification. Z. Dash and B. Robinson continued to serve as temporary software configuration manager and CCB chair, respectively.

Modeling. No significant progress this month; effort was diverted to SQA and other activities.

Two papers will be submitted to the special edition on the Yucca Mountain Project of the *Radioactive Waste and the Nuclear Fuel Cycle*. B. Robinson continued to prepare a paper, "A Strategy for Validating a Conceptual Model for Radionuclide Migration in the Saturated Zone Beneath Yucca Mountain," and W. Polzer submitted a paper, "The Use of Selectivity Coefficients to Estimate Modified Langmuir Isotherm Parameters as a Function of Experimental Conditions," for YMPO review.

Lithium (Li) Batch Sorption Experiments. An additional suite of experiments was conducted to examine the effect of rock-water ratio on Li sorption. The data were being analyzed.

**Planned Activities**

Contribute to the SQA effort by serving as Software Configuration Manager (Z. Dash) and CCB Chair (B. Robinson).

Complete documentation of lithium-bromide batch sorption experiments.

Continue modeling field test design using FEHMN.

**Problem Areas**

None

**Milestone Progress**

3188
30 September 1992
*Documentation for SORBEQ*
Delayed due to personnel reassignment.

3194
30 September 1992
*Batch Sorption Experiments with Lithium*

T112
22 June 1992
*Final Documentation for FEHMN*
Delayed due to personnel reassignment.

3196
27 July 1992
*FRACNET Documentation*
Delayed due to personnel reassignment.

**Milestone Progress (cont.)**

R529
*Evaluation of Preliminary Application of FEHMN to Yucca Mountain*
Completed.

**Publications**

B. A. Robinson
*FRACNET—Fracture Network Model for Water Flow and Solute Transport*
LA-series report
In preparation.

B. A. Robinson
*SORBEQ—A One-Dimensional Model for Simulating Column Transport Experiments*
LA-series report
In preparation.

B. A. Robinson
*A Strategy for Validating a Conceptual Model for Radionuclide Migration in the Saturated Zone Beneath Yucca Mountain*
Journal article, *Radioactive Waste Management and the Nuclear Fuel Cycle - Special issue on the Yucca Mountain Project*
In preparation.

W. L. Polzer and E. H. Essington
*The Use of Selectivity Coefficients to Estimate Modified Langmuir Isotherm Parameters as a Function of Experimental Conditions*
Journal article, *Radioactive Waste Management and the Nuclear Fuel Cycle - Special issue on the Yucca Mountain Project*
Submitted to TPO.

W. L. Polzer, M. G. Rao, H. R. Fuentes, and R. J. Beckman
*Thermodynamically Derived Relationships Between the Modified Langmuir Isotherm and Experimental Parameters*
Journal article, *Environmental Science and Technology*
Published.

## WBS 1.2.3.4.1.1 Ground-water Chemistry Model

**Objective**

The goal of this investigation is to provide conceptual and mathematical models of the ground-water chemistry at Yucca Mountain. These models will explain the present ground-water composition in relation to interactions of minerals and ground-water and will be used to predict ground-water compositions as a result of anticipated and unanticipated environments.

**Activities and Accomplishments**

Study Plan. Staff reviewed comments and continued to revise the Ground-water Chemistry Model Study Plan, R0.

Other Activities. Staff continued refining the matrix for "most-active" ground-water modeling to categorize ground-waters by compositional variables that affect radionuclide solubility and/or sorption properties. Variables of interest are measured Eh potential, pH, and bicarbonate content. EQ3/6 is being used to simulate different ground-water compositions. A letter report on these results due 30 September 1992 was postponed to 30 October 1992.

Modeling of pH and Eh stability was underway. Milestone report 3006 will be delayed until 30 October 1992.

QA Activities. No additional progress to report on the IMOU between LLNL and Los Alamos. IMOU is in review in Las Vegas.

**Planned Activities**

Continue to resolve comments on study plan. Complete letter report on "most-active" ground-water. USGS collaboration will continue. Continue support of QA efforts. Continue tracking IMOU mentioned above.

**Problem Areas**

Delays in material and equipment for the USGS down-hole sampler could slow progress on testing of conceptual models of ground-water chemistry at Yucca Mountain.

**Milestone Progress**

3006
30 October 1992
*Eh and pH Buffering Capacity*

3415
30 October 1992
*Letter report on Most-Active Ground-water Chemistry*

**Publications**

None

## WBS 1.2.3.4.1.2.1/3 Batch Sorption Studies and Sorption Models

**Objective**

The objective of this task is to provide sorption coefficients for elements of interest to predict radionuclide movements from the repository to the accessible environment.

**Activities and Accomplishments**

Experiments to measure batch sorption coefficients of neptunium (Np) on crushed tuff samples under a variety of pH values, $CO_2$ partial pressures, and water compositions continued. The reaction between the rock samples and Np-traced solutions was completed, the solution and solid phases were separated by centrifugation, and the amount of Np in the solution samples was determined using liquid scintillation counting.

A new type of filter for separating solution and solid (+colloidal) phases following batch sorption experiments was evaluated. Because the filter retained over 10% of the Np in a 5 ml aliquot, it was unacceptable for measuring sorption of Np on tuff samples. (Filters with a molecular weight cut-off of 30 000 are required by TWS-INC-DP-05, R2, but the filters last used for this purpose are no longer manufactured.)

P. Rogers continued to prepare a milestone report on the influence of particle size and water composition on sorption coefficients. This paper will be presented at the fall meeting of the Materials Research Society; an abstract was published in the conference proceedings. Rogers found that grinding had no affect on the batch sorption coefficients she obtained; consequently, previous experiments using particle sizes between 2 mm and 75 µm should not have been biased by the extent of grinding. (Most previous batch experiments used a tuff size fraction between 75 and 250 µm, which appears to be ideal for minimizing sampling error and sample mineral fractionation caused by excessive grinding.)

**Planned Activities**

Batch sorption experiments for Np will be continued with emphasis on studying the desorption behavior of Np from the tuff samples We will continue to search for a suitable filter replacement.

**Problem Areas**

None

**Milestone Progress**

3009
30 September 1992
*Variation of Water-Rock Ratio Sorption Coefficients on Zeolitic Tuff*

3212
30 September 1992
*Progress Report on Single Mineral Experiments*

**Publications**

A. Meijer
*A Strategy for the Derivation and Use of Sorption Coefficients in Performance Assessment Calculations for the Yucca Mountain Site*
Conference proceedings, *Proceedings of the DOE/Yucca Mountain Site Characterization Project Radionuclide Adsorption Workshop at Los Alamos National Laboratory September 11-12, 1990.* (LA-12325-C, 1992)
Published.

P. Rogers, A. M. Meijer, and K. H. Kung,
*Sorption Characteristics of Yucca Mountain Tuffs as a Function of Particle Size*
Conference paper, *Fall meeting of the Materials Research Society, November 30 - December 4, 1992*
In preparation.

## WBS 1.2.3.4.1.2.2 Biological Sorption and Transport

**Objective**

The purpose of this research is to determine whether microbial activity can influence the movement of plutonium in tuff. Because fluids are used extensively in the exploration of locations for a nuclear repository, those micro-organisms capable of utilizing drilling fluids as growth substrates are of special interest.

**Activities and Accomplishments**

L. Hersman began a year's sabbatical leave working with G. Sposito of the Soil Science Department at UC Berkeley. During this time he will conduct experiments on mineral dissolution (particularly of Fe oxides) as they are affected by soil microorganisms. The UC Berkeley experiments are related to the siderophore work at Los Alamos because the ligand attack of a Pu oxide may be similar to Fe oxide.

Work continued on the milestones listed below; all are near completion.

**Planned Activities**

L. Hersman will work on plutonium formation constants in Los Alamos from 8-16 October.

Continue work on soil columns.

**Problem Areas**

None

**Milestone Progress**

3080
30 September 1992
*Report on Chelation*
In preparation.

3092
30 September 1992
*Report on Colloidal Agglomeration*
In preparation.

3176
30 September 1992
*Procedure for Determination of Formation Constants*
In preparation.

3177
30 September 1992
*Procedure for Determination of Effects on Colloidal Agglomeration*
In preparation.

**Publications**

L. R. Hersman, D. E. Hobart, and T. W. Newton
*Preliminary Evidence of Siderophore/Plutonium Complexation*
Journal article, *Journal of Applied and Environmental Microbiology*
Resubmitted.

## WBS 1.2.3.4.1.3 Radionuclide Retardation by Precipitation Processes

### Objective

The objective of the solubility determination task is to determine the solubilities and speciation of important waste elements under conditions characteristic of the repository and along flow paths from the repository into the accessible environment.

### Activities and Accomplishments

Revisions to the study plan were completed.

H. Nitsche, a task member at Lawrence Berkeley Laboratory met with Los Alamos staff on 28 September to discuss scientific and administrative aspects of his solubility subtask.

Speciation Studies. In preparation for Pu(IV) carbonate-speciation studies by NMR and single-crystal x-ray diffraction, a new 1-gram batch of $PuO_2$ was processed to produce an oxidation-state pure-stock solution of Pu(IV). Because only small quantities of the $^{17}O$-labeled actinyls can be prepared, a microelectrode system will be used to prepare $^{17}O$-labeled actinyl species (uranyl, neptunyl, and plutonyl) for NMR studies. Staff also devised a method to prepare $^{17}O$-labeled $CO_3^{2-}$ for carbonate-speciation studies with all the actinides by NMR; this labeling will allow us to study Pu(IV) and Am(III) speciation directly with the very high molecular structure specificity made possible by NMR spectroscopy.

In an effort to pin down the structure of the most highly carbonate-complexed Pu(IV) species (often presumed to be but never substantiated as $Pu(CO_3)_5^{6-}$), UV-vis absorption spectral data were obtained for Pu(IV) [0.2 M] in approximately 2 M total carbonate. These solution conditions should favor the formation of the most highly carbonate-complexed species, assuming the stepwise formation constants are sufficiently large. The characteristic Pu(IV) absorption band in the midvisible region for this sample was found at approximately 486 nm, consistent with one of the dominate species observed in our recent PAS work in extremely dilute plutonium solutions.

Staff aligned the PAS dye laser to maximize the readily accessible wavelength range; we can now achieve extended wavelength ranges (approximately 100–200 nm) by simply changing the dye solutions. This is important because investigations into the possible presence of multiple oxidation states in our solutions require an extended wavelength coverage in a short time period. The multiple oxidation state issue is now under investigation with Pu in carbonate.

Milestone Report 3031, "Plutonium(IV) and Plutonium(VI) Carbonate Speciation Studies by NMR and PAS Spectroscopies," was completed and submitted for technical review. This paper discusses our multifaceted spectroscopic approach to determining radionuclide speciation, recent results in determining Pu(IV) carbonate speciation by PAS, and carbonate complexation studies in $PuO_2^{2+}$ by $^{13}C$ NMR spectroscopy.

Solubility Studies. The neptunium (Np) undersaturation experiments in UE-25p #1 at 60°C have now run nearly as long as the comparable oversaturation experiments; their concentration profiles from the undersaturation experiments for the pH 6 and 8.5 solutions have virtually reproduced results obtained by oversaturation. This set of Np experiments will be completed by determining the species present in the supernatant, measuring the Eh of the solutions, and examining the solid phase by x-ray diffraction.

**Activities and Accomplishments (continued)**

The plutonium undersaturation experiments in UE-25p #1 water at 60°C are approaching thirty days in duration. At all three pH values, the aqueous plutonium concentration is approximately $10^{-7}$ M; these concentrations agree very well with those obtained from the oversaturation experiments at pH 6 and 7. Sampling of these experiments will continue until steady-state is established. Samples taken in September from the Am/Nd undersaturation experiments in UE-25p #1 at 60°C are being analyzed. The results will be reported next month.

Milestone Report 3329, "Measured Solubilities and Speciations from Oversaturation Experiments of Neptunium, Plutonium, and Americium in UE-25p #1 Well Water from the Yucca Mountain Region," detailing oversaturation experiments in UE-25p #1 well water, was prepared. A talk, "Far-Field Radionuclide Solubility and Speciation Studies for the Yucca Mountain Site Characterization Project," was prepared for the 1993 International High-Level Radioactive Waste Management Conference to be held April 26-30, 1993 in Las Vegas.

Reviewer comments were incorporated into the following detailed technical procedures: (1) "Operating and Calibrating the Mettler H6T Analytical Balance" (LANL-LBL-DP-14, R0), (2) "X-ray Powder Diffraction by the Debye-Scherrer Method" (LANL-LBL-DP-03, R1), (3) "Operating and Calibrating a Low-energy Gamma-ray Counting System" (LANL-LBL-DP-02, R1), and (4) "Concentration Determination of Soluble Radionuclides from Data Provided by a Low-energy Gamma-ray Counting System" (LANL-LBL-DP, R1).

**Planned Activities**

Efforts in all areas will continue.

**Problem Areas**

None

**Milestone Progress**

3010
30 June 1991
*Report on Measured Solubilities of Pu, Am, and Np in J-13 Groundwater from Oversaturation Conditions*
Submitted 7/29/91
YMPO comments were addressed.

3031
30 September 1992
*Plutonium(IV) and Plutonium(VI) Carbonate Speciation Studies by NMR and PAS Spectroscopies*
On schedule.

3329
30 September 1992
*Measured Solubilities and Speciations from Oversaturation Experiments of Neptunium, Plutonium, and Americium in UE25p #1 Well Water from the Yucca Mountain Region*
On schedule.

3330
1 January 1993
*Evaluation of Alternative Detection Schemes in Photoacoustic Spectroscopy*
Early completion anticipated.

Letter Report
*Spectroscopic Studies of the Hydrolysis of $UCl_4$: Spectral Effects of Ligand Exchange*
In preparation.

## Publications

D. L. Clark, D. E. Hobart, P. D. Palmer, J. C. Sullivan, and B. E. Stout
*Carbon-13 NMR Characterization of Plutonyl(VI) Aqueous Carbonate Complexes*
Journal article, *Journal of the American Chemical Society*
In preparation.

D. L. Clark, C. D. Tait, D. E. Morris, D. E. Hobart, S. A. Ekberg, and P. D. *Palmer*
*Plutonium(IV) and Plutonium(VI) Carbonate Speciation Studies by NMR and PAS Spectroscopies*
LA-series report
In preparation.

D. L. Clark, J. G. Watkin, D. E. Morris, and J. M. Berg
*Molecular Models for Actinide Speciation*
LA-series report
In preparation.

L. E. Hersman, P. D. Palmer, and D. E. Hobart,
*Preliminary Evidence of a Siderophore/Plutonium Complex*
Journal article, *Journal of Applied and Environmental Microbiology*
In preparation.

D. E. Hobart, D. L. Clark, P. D. Palmer, J. C. Sullivan, and B. E. Stout
*Carbon-13 NMR Characterization of Americyl(VI) Aqueous Carbonate Complexes*
Journal article, *Inorganic Chemistry*
In preparation.

D. E. Morris and D. L. Clark
*Spectroscopic Studies of the Hydrolysis of $UCl_4$: Spectral Effects of Ligand Exchange*
LA-series report.
In preparation.

D. E. Morris, C.D. Tait, S. A. Ekberg, and P. D. Palmer
*Speciation of Plutonium in Carbonate Media*
Conference abstract, *Materials Research Society*
Approved by YMPO.

H. Nitsche, R. C. Gatti, E. M. Standifer, S. C. Lee A. Miller, T. Prussin,
R. S. Deinhammer, H. Maurer, K. Becraft, S. Leung, and S. A. Carpenter
*Measured Solubilities and Speciations of Neptunium, Plutonium; and Americium in a Typical Ground-water (J-13) from the Yucca Mountain Region*
LA-series report
In YMPO review.

C. D. Tait, D. E. Morris, J. M. Berg and W. H. Woodruff
*Evaluation of Alternative Detection Schemes in Photoacoustic Spectroscopy*
Journal article, *Analytical Chemistry* or *Reviews of Scientific Instrumentation*
In preparation.

C. D. Tait, S. A. Ekberg, and P. D. Palmer, and D. E. Morris
*Plutonium Carbonate Speciation Changes*
Journal article, *Inorganic Chemistry*
In preparation.

## WBS 1.2.3.4.1.4 Radionuclide Retardation by Dispersive, Diffusive, and Advective Processes

**Objective**

The objectives of this task are to determine the rate of radionuclide movement along the potential flow paths to the accessible environment and to examine the effect of diffusion, adsorption, dispersion, anion exclusion, sorption kinetics, and colloid movements in the flow geometries and hydrologic conditions expected to exist along the flow path to the accessible environment in the scenarios used for perform assessment.

**Activities and Accomplishments**

We completed the neptunium (Np) transport experiments using crushed-tuff columns and Np batch sorption experiments with tuffs G4-1530 and G4-275 and ground-waters from USWH-3, UE-25p #1, and J-13. We also completed batch sorption experiments with Np solutions and pure mineral separates found in the following: hematite, montmorillonite, clinoptilolite, and quartz. The results of these studies will be reported next month.

A letter report entitled "Far-Field Transport of Carbon Dioxide: Retardation Mechanisms and Possible Validation Experiments" was prepared by A. Meijer and appears in the Appendix. He describes the retardation mechanisms for C-14 at Yucca Mountain, evaluates potential experimental efforts to determine C-14 retardation, and makes recommendations for site characterization activities and modeling studies. He identified three main chemical retardation mechanisms for C-14 as carbon dioxide in Yucca Mountain: equilibration with carbonate species in ground-water, isotope exchange with carbonate minerals, and sorption on non-carbonate minerals. He also recommended the following: experimental evaluation of C-14 retardation should include batch sorption experiments, column experiments, and field experiments; batch sorption experiments with pure minerals (such as iron oxides, oxyhydroxides, aluminum oxides and clays) as well as tuffs should be performed; and column experiments should be carried out under unsaturated conditions at near-atmospheric pressure. The following additional data will be required for a more detailed modeling of C-14 transport at Yucca Mountain: alkalinity distributions in unsaturated zone waters, spatial distributions of matrix and fracture minerals critical to C-14 transport, and accessibility of C-14 to critical minerals. Based on a review of published models, Meijer recommended a more comprehensive chemical models for C-14 transport in Yucca Mountain that includes probability distributions for C-14 retardation factors based on probability distributions for alkalinity in Yucca Mountain waters, sorption potentials as measured in representative whole-rock samples, and a near-field calcite precipitation model coupled with a waste container failure model.

A letter report entitled "Measurement of Unsaturated Hydraulic Conductivity in Yucca Mountain Tuff" was prepared by J. Conca and is in internal technical review. Experimentally determined hydraulic conductivities were reported as a function of water content, and the feasibility of applying an innovative unsaturated-flow technique (using usaturated-flow apparatus) to transport studies was evaluated. (This report is listed as Milestone 3044, "Letter Report on Assessment of Available Techniques for Unsaturated Column Transport Experiments.")

The staff continued to organize the Colloid Workshop to be held on 3-5 May in Santa Fe, NM.

**Planned Activities**

Continue all work discussed above.

**Problem Areas**

None

**Milestone Progress**

3040
15 November 1992
*Kinetics of Sorption on Columns of Pure Minerals*
In preparation.

3044
31 August 1992
*Letter Report on Assessment of Available Techniques for Unsaturated Column Transport Experiments*
In preparation.

**Publications**

I. R. Triay
*Radionuclide Migration in Tuff under Diffusive Conditions*
Conference Paper, *Proceedings of the Migration '91, Jerez de la Frontera, Spain, 14–18 October 1991*
Approved by YMPO.

I. R. Triay, A. J. Mitchell, and M. A. Ott
*Radionuclide Migration Studies for Validating Sorption Data—Past, Present, and Future*
Conference paper, *Proceedings of the DOE/Yucca Mountain Site Characterization Project Radionuclide Adsorption Workshop at Los Alamos National Laboratory September 11-12, 1990. (LA-12325-C, 1992)*
Published.

I. R. Triay, M. A. Ott, A. J. Mitchell, and C. M. Overly
*Transport of Np through Yucca Mountain Tuffs*
Conference paper, *Proceedings of the fall meeting of the Materials Research Society, November 30 - December 4, 1992 .*
In preparation.

## WBS 1.2.3.4.1.5.1 Retardation Sensitivity Analysis

**Objective**

The objectives of this task are to construct a geochemical/geophysical model of Yucca Mountain and to use this model to examine the physical and chemical controls on radionuclide transport along flow paths to the assessable environment.

**Activities and Accomplishments**

QA and Programmatic Certification of TRACRN continued. The Implementation Phase Baseline was submitted and is under review. Four final verification runs, which compared results from TRACRN and FEHMN for unsaturated flow and transport problems in two and three dimensions, were conducted.

Certification of FEHMN and GZSOLVE continued. G. Zyvoloski worked with B. Robinson and Z. Dash (C-Wells Reactive Tracer Task) on documentation and verification of these software applications.

**Planned Activities**

Continue certification of TRACRN.

**Problem Areas**

None

**Milestone Progress**

3052
30 September 1992
*Baseline Documentation for TRACRN*

**Publications**

K. Birdsell, K. Eggert, and B. Travis
*Three-Dimensional Simulations of Radionuclide Transport at Yucca Mountain*
Journal article, *Radioactive Waste Management and the Nuclear Fuel Cycle - Special issue on the Yucca Mountain Project*
Approved by YMPO; submitted.

K. Birdsell, K. Campbell, K. Eggert, and B. Travis
*Sensitivity Analysis of Integrated Radionuclide Transport Based on a Three-dimensional Geochemical/Geophysical Model*
Conference proceedings, *Proceedings of the DOE/Yucca Mountain Site Characterization Project Radionuclide Adsorption Workshop at Los Alamos National Laboratory September 11-12, 1990.* (LA-12325-C, 1992)
Published.

## WBS 1.2.3.4.1.5.2 Demonstration of Applicability of Laboratory Data

**Objective**

The purpose of this study is to design and conduct experiments to evaluate the applicability of laboratory data and to test models used in the Radionuclide Transport Program to determine far field radionuclide transport. Both intermediate- and field-scale experiments and natural analogs will be assessed for their potential to provide the required data.

**Activities and Accomplishments**

Comments on the USGS study plan entitled "Saturated Zone Modeling and Synthesis" were verified.

The annual progress report has been completed and is included in the Appendix.

**Planned Activities**

Continue to develop study plan.

**Problem Areas**

None

**Milestone Progress**

No FY91 milestones.

**Publications**

C. Loeven
*A Summary and Discussion of Hydrologic Data from the Calico Hills Nonwelded Hydrogeologic Unit at Yucca Mountain, Nevada* (LA-12376-MS, 1992)
LA-series report
In press.

## WBS 1.2.5 Regulatory and Institutional

**Objective**

The purpose of this task is to coordinate the regulatory and institutional Project requirements within the Los Alamos programmatic structure. The focus of this coordination effort is on the integration of the technical work within the regulatory and institutional framework.

**Management and Integration**

Support for the erosion topical report continued.

**Study Plans**

**Water Movement Test, R1 (8.3.1.2.2.2).** Review comments on Rev. 1 of the study plan were received from the YMPO in May 1992; they are now being addressed.

**Diffusion Test in the Exploratory Studies Facility, R0 (8.3.1.2.2.5).** In April 1992 this study plan was accepted by DOE; in June 1992 it was submitted to the NRC for review.

**Testing of the C-Hole Sites With Reactive Tracers, R0 (8.3.1.2.3.1.7).** In February 1990 DOE/HQ issued the study plan as a controlled document; it was then sent to the NRC for comments. In January 1992 we were requested by DOE to review revised NRC comments addressed by the USGS. The revision was completed and all comments were accepted by Los Alamos.

**Ground Water Chemistry Modeling, R0 (8.3.1.3.1.1).** This study plan was returned in May 1992 with review comments by YMPO; these comments are now being addressed.

**Mineralogy, Petrology, and Chemistry of Transport Pathways, R0 (8.3.1.3.2.1).** In August 1992 we were requested to make final word processing changes to Revision 0 of the study plan; those changes are in progress.

**History of Mineralogy and Geochemical Alteration at Yucca Mountain, R0 (8.3.1.3.2.2).** YMPO approved the study plan on 18 December 1991 and submitted it to the NRC on 31 January 1992.

**Natural Analog Hydrothermal System in Tuff (8.3.1.3.3.1).** This is an out-year activity.

**Kinetics and Thermodynamics of Mineral Evolution and Conceptual Model of Mineral Evolution, R0 (8.3.1.3.3.2; 8.3.1.3.3.3).** No progress during the recording period because of a lack of funding.

**Sorption Studies and Sorption Modeling, R0 (8.3.1.3.4.1; 8.3.1.3.4.3).** A new study plan has been issued for internal review. The review was completed in August 1992 and returned to the principal investigator for comment resolution.

**Biological Sorption and Transport, R0 (8.3.1.3.4.2).** A revision addressing the exploratory shaft design was submitted in September 1992.

**Study Plans (continued)**

**Dissolved Species Concentration Limits, and Colloid Formation and Stability, R0 (8.3.1.3.5.1; 8.3.1.3.5.2).** All YMPO comments on the study plan were resolved by the principal investigator in September 1992. Rev. 0 will be submitted to YMPO for comment resolution verification and approval.

**Dynamic Transport Column Experiments, R0 (8.3.1.3.6.1).** All YMPO comments on the study plan were resolved by the principal investigator in September 1992. Rev. 0 will be submitted to YMPO for comment resolution verification and approval.

**Diffusion, R0 (8.3.1.3.6.2).** All YMPO comments on the study plan were resolved by the principal investigator in September 1992. Rev. 0 will be submitted to YMPO for comment resolution verification and approval.

**Retardation Sensitivity Analysis, R0 (8.3.1.3.7.1).** This study plan was approved by the DOE and sent to the NRC for review in July 1992.

**Demonstration of the Applicability of Laboratory Data to Repository Transport Calculations, RO (8.3.1.3.7.2).** This study plan is in preparation.

**Gaseous Radionuclide Transport Calculations and Measurements, (8.3.1.3.8.1).** Funds have not been allocated.

**Probability of Magmatic Disruption of the Repository, R0 (8.3.1.8.1.1).** A detailed technical review was complete in July 1992 by the NRC. In August 1992, a one-day video conference was held with the NRC to discuss their technical review comments. These comments are now being addressed.

**Physical Processes of Magmatisim and the Effects on the Repository, R0 (8.3.1.8.1.2).** A draft study plan was completed in September 1992; it will be submitted to the DOE in October 1992.

**Characterization of Volcanic Features, R0 (8.3.1.8.5.1).** Accepted by NRC on 4 September 1990.

## WBS 1.2.6 Exploratory Studies Facility

**Objective**

These Exploratory Studies Facility (ESF) tasks address the issues and information needs associated with the ES-based characterization of Yucca Mountain to determine the suitability of permanently isolating high-level nuclear waste from biosphere in a geologic repository.

**Activities and Accomplishments**

Staff continued to gather information on the use of tracers, fluids, and materials (TFM) used at the Yucca Mountain. Waste isolation impact and test interference analysis for the TFMs were requested from CRWMS M&O and SNL. Staff continued to support M&O efforts to develop a position paper on prototyping. Staff prepared briefings for biweekly ESF management meetings and attended biweekly ESF Engineering Development Division (ED&D) meetings.

**Planned Activities**

Continue to develop definitive design-related information for tests to be performed in the launch chamber. Support integration meetings such as ESF design, TIG, SMF, and surface-based testing and its interface with ESF testing. Support the ED&D effort in justifying the prototype test facility and preparing ESF budget options and strategies. Develop interfaces for testing and the ESF design.

Revise and update the PSAR as required. Begin to identify IDS needs. Develop new networks for ESF testing.

Participate in biweekly ED&D ESF Management Review Meetings.

Finalize abstracts for high-level waste management conference and 34th Rock Mechanics Symposium at Madison, Wisconsin. Prepare paper on the IDS for the ESF for the 2nd International Symposium on Mine Mechanization and Automation in Sweden.

**Problem Areas**

None

**Milestone Progress**

No milestones for FY91.

**Publications**

None

## WBS 1.2.6.8.4 Integrated Data System

**Objective**

The integrated data system (IDS) supports the Exploratory Studies Facility (ESF) test program by providing a central facility to automatically measure and control aspects of the ESF tests. The primary purposes of the IDS are to assist the principal investigators (PI's) in acquiring high-quality test data in a uniform, controlled fashion and to transfer those data to the PI's organizations for data management and analysis.

**Activities and Accomplishments**

This activity has been deferred.

## WBS 1.2.9.1.4 Records Management

**Objective**

The objective of this task is to manage records and documents related to the licensing of a geologic repository for the disposal of high-level radioactive waste by developing, implementing, and maintaining a comprehensive, automated, and integrated information management system.

**Activities and Accomplishments**

Thirty-seven records and/or record packages were received by the RPC; nine of these returned to the originators for corrections.

The CRF rejected two records and/or records packages; the RPC resubmitted eleven corrected records to the CRF.

Staff conducted inventories and interviews to update the Records Inventory Disposition Schedule (RIDS). It was determined that approximately 1071.26 cubic feet of YMP records and/or nonrecord material were in possession of Los Alamos and Los Alamos contractors. YMPO will determine the records disposition schedule at a later date.

## WBS 1.2.9.3 Quality Assurance

**Objective**

The Quality Assurance (QA) Program supports Los Alamos Yucca Mountain Site Characterization Project participants and ensures that their efforts provide data and evidence admissible for the repository-licensing process.

**Activities and Accomplishments**

**Software.** One meeting of the Configuration Control Board was held. A new configuration manager was selected.

**Records/Document Control.** Two quality administrative procedures (QPs), QP 02.4, R1, "Management Assessment," and QP 16.2, R2, "Trending," were approved and distributed. One detailed technical procedure, DP 131, R0, "Cameca SX-50 Electron Microprobe Operating Procedure," was approved and distributed.

**Training.** M. Clevenger attended training programs in software quality assurance (QA) and Framemaker software.

**Program Development.** Eighteen QPs are in various stages of revision. S. Bolivar, J. Day, and T. Morgan attended the 19th Annual National Energy and Environmental Quality Division Conference, and they presented a paper on the role of the QA liaison.

**Audits/Surveys.** YMPO conducted a scoping meeting for the November DOE audit, and appropriate corrective action for CAR-057 was verified at this time. An amended response for CAR-058 was also approved by the YMPO. The LANL-AR-92-11 audit plan (Hydro Geo Chem) is in preparation. The report on the annual management assessment of the Los Alamos QA program is in review by the TPO.

**Planned Activities**

A software configuration management status report will be distributed, and a new QAL will be assigned to replace T. Morgan, who is leaving YMP. An internal audit of Hydro Geo Chem will be conducted. The audit schedule will be revised because of conflicts, and an outstanding internal audit and survey reports will be completed. QP revisions will continue; comments on the notebook procedure (QP 03.5) will be resolved.

**Problem Areas**

None

**Milestone Progress**

No milestones for FY91.

**Publications**

S. L. Bolivar and J. L. Day
*The Role of the Los Alamos National Laboratory Quality Assurance Liaison for the Yucca Mountain Site Characterization Project*
Conference paper, *Proceedings of the ASQC Energy Division Annual Meeting*
Published.

# Appendix

## Attachments and Level III Milestone Reports

# Annual Progress Report for FY 1992

## SCP Study 8.3.1.3.7.2

# Demonstration of Applicability of Laboratory Data to Repository Transport Calculations

by Everett Springer

## Introduction

During FY92, staff from Lawrence Berkeley Laboratory (LBL) and Los Alamos (LANL) developed a conceptual design for the Calico Hills drift program in the Exploratory Studies Facility (ESF); to better organize the study, four separate activities were created. At midyear, the Project began Mission 2001, and this study was scheduled and resource-loaded through 2001. Lack of funding precluded further progress on the study plan in FY92.

## Study Plan

To better organize, manage, and provide visibility for this study within YMP, on 6 February a change request to revise the Site Characterization Program Baseline was submitted and approved. In accordance with the revision, the study plan for this task will be based on the following four activities:

Activity 8.3.1.3.7.2.1—Intermediate-scale experiments

Activity 8.3.1.3.7.2.2—Field-scale experiments to study radionuclide transport at Yucca Mountain

Activity 8.3.1.3.7.2.3—Natural analog studies of radionuclide transport

Activity 8.3.1.3.7.2.4 —Data on radionuclide transport from other DOE sites (anthropogenic analogs).

## Accomplishments

During FY92, staff from LBL and LANL developed a conceptual design for a field test to be conducted in the Calico Hills drifts of the ESF. This design was presented informally to the DOE in March and April, and a formal presentation was made during the OCRWM site tour of Los Alamos on 28 May.

A schematic design, which is based on the assumption that relatively fast flow paths will exist in conjunction with discontinuities (for example, faults, fracture zones, bedding planes, and lithologic changes such as the vitric/zeolitic interface) in the Calico Hills, is presented in Fig. 1. The test blocks may vary in size, but the initial target will be a cube with dimensions of 10 x 10 x 10 m. As soon as a test location is confirmed, two boreholes will be drilled from the access drift, and a series of geophysical, geological, and hydrological tests to determine if the site is suitable for further testing will be conducted. (The criteria for suitability have not been determined.)

When a location is ruled acceptable for further testing, the test gallery (see Fig. 1) will be constructed, and intensive characterization of the test block will take place: a series of boreholes, which will be used for geophysical, hydrological, and tracer tests, will be drilled across the test block, and to enable staff to sample any tracer breakthrough, an alcove beneath the test block will be mined. Following borehole testing, the test gallery area can be reconfigured for alcove-to-alcove testing of solute transport.

The sequence of borehole and alcove testing will permit different spatial and temporal scales to be characterized, and data from borehole tests can be used to predict the response in alcove tests, thus increasing confidence in our ability to characterize the given mass of rock. The length of time of the tests will vary as a function of the permeability of the porous medium. For the complete sequence,

tests are expected to last between five and ten years; because of the time span, the water content of the rock will have to be increased, particularly for the alcove-to-alcove tests.

To design and carry out these tests, we have identified the following tasks :

- **Prepare study plan.** The study plan requires information from quantitative experimental design, laboratory studies, field development, and modeling and inversion (see below).
- **Prepare quantitative experimental design.** To determine the type of data and sampling frequency for each phase of the field test, this activity will use the best available data and simulation models for the Calico Hills
- **Measure physical and chemical properties of the rock in the laboratory.** This task will determine procedures and define equipment to measure parameters and properties required for hydrologic, geochemical, and geophysical models. (In order to ensure consistency, the procedures will be based on procedures used by other site characterization studies in the Project as much as possible.)
- **Model flow and transport response and perform inversion analysis of these data.** This task will provide algorithms to analyze hydrological, chemical, and geophysical responses from the experiment.
- **Design field equipment and write procedures for its use.** Field equipment, including packer strings, water and tracer application and monitoring systems, and geophysical instruments will be designed, fabricated, and tested before the field tests begin. This task will provide the necessary quality assurance for deployment.
- **Use geological reconnaissance to locate potential sites for field testing.** Once the drifts to the Calico Hills are constructed and available, we will use geological reconnaissance to locate potential sites for the field application.
- **Implement test in the field.** This task will provide on-site support for the ongoing tests.
- **Evaluate field test.** This task will analyze the data using codes developed in the modeling and inversion task.

This study, which will be coordinated with other Project laboratory site characterization studies and computer simulations of radionuclide transport, addresses a key question: With regard to radionuclide transport, what is the efficacy of data collected by the Project in making predictions about site performance? In view of the fact that many the site characterization studies are now at capacity, this study will include the capability to determine properties and/or parameters in the field or laboratory if other resources within the Project are not available to support us.

## Summary and Conclusions

During FY92, we prepared a conceptual design to test radionuclide transport concepts in the unsaturated zone, and a resource-loaded schedule was completed.

The importance of this field test has been questioned in various forums this year. It is relatively easy to respond to questions by stating that the test described above is important, and a license will not be achieve without it; however, this statement is entirely not true. We believe confidence in the computer-generated models and laboratory studies will only be achieved when field tests can demonstrate that they adequately predict behavior at Yucca Mountain.

The importance of a study is determined by licensing strategies employed at Yucca Mountain, and because of its hydrologic and geochemical properties, the Calico Hills is considered a primary barrier to radionuclide transport. To confirm this, it is very important that fields tests are used to supplement laboratory tests of flow and transport.

Emphasis has been placed on the Calico Hills because of knowledge of its ambient conditions obtained from measurements made by previous and ongoing Yucca Mountain studies. A shift by the Project away from an emphasis on the Calico Hills because of an increased emphasis on thermal loading, waste package design, or the saturated zone could reduce the need to conduct an extensive series of field tests there. Field-testing is necessary to gain confidence in the models and parameters used at Yucca Mountain, but the scope and location of these tests should not be determined until some fundamental issues are resolved.

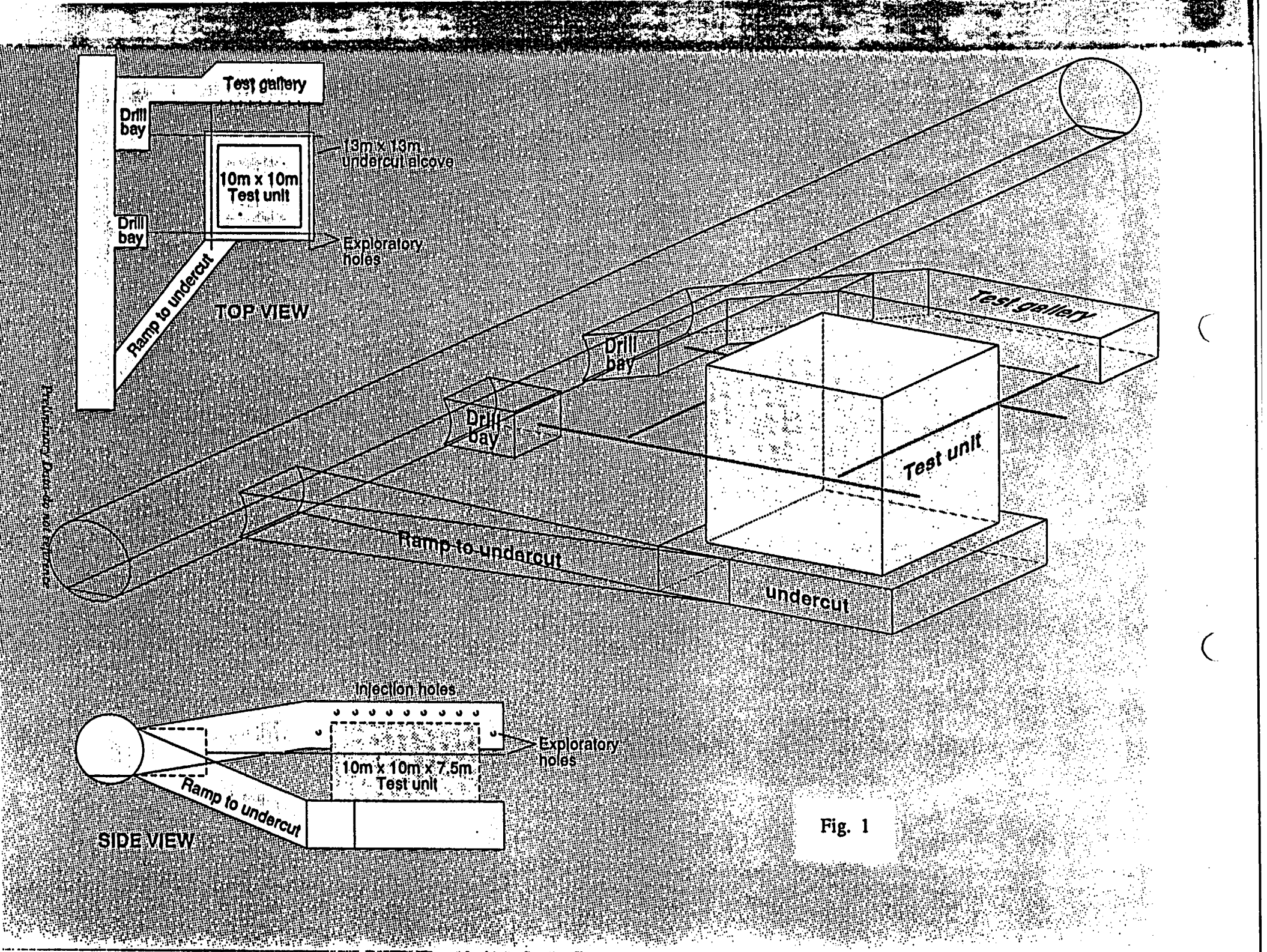


Fig. 1

LA-UR-92-3278

Title: FAR-FIELD TRANSPORT OF CARBON DIOXIDE: RETARDATION MECHANISMS AND POSSIBLE VALIDATION EXPERIMENTS

Author(s): Arend Meijer, INC-9

Submitted to: Milestone Report submitted to Yucca Mountain Project

# FAR-FIELD TRANSPORT OF CARBON DIOXIDE: RETARDATION MECHANISMS AND POSSIBLE VALIDATION EXPERIMENTS

By Arend Meijer, INC-9, Los Alamos National Laboratory

## A. INTRODUCTION

According to preliminary performance assessment calculations for the potential repository at Yucca Mountain (Barnard et al., 1992), gas phase releases of $^{14}C$ may exceed the regulatory limits specified by the NRC in 10CFR60 for the engineered barrier system and by the EPA in 40CFR191 for the accessible environment. The calculations presented in Barnard et al. (1992) include various assumptions about waste inventories, failure mechanisms and rates for engineered barriers, hydrologic models for Yucca Mountain, transport mechanisms for radionuclides in Yucca Mountain, and other pertinent parameters. They conclude that the 1985 EPA limit for release of $^{14}C$ may be exceeded in a limited number of cases given the assumptions of their models.

In their transport model for $^{14}C$, Barnard et al. (1992) included a retardation factor that reflects only the equilibration of $^{14}CO_2$ with natural carbon species present in waters in the pore space of the volcanic units between the repository and the surface of Yucca Mountain. Barnard et. al. (1992) note that other mechanisms exist that may additionally retard the migration of $^{14}CO_2$ including calcite precipitation and sorption of $^{14}C$ species onto mineral surfaces in Yucca Mountain. This paper provides a discussion of these mechanisms and suggests experiments that could be carried out to help quantify them.

## B. RETARDATION MECHANISMS FOR $^{14}CO_2$ IN YUCCA MOUNTAIN

The main chemical retardation mechanisms for $^{14}CO_2$ in the unsaturated zone of Yucca Mountain include:

(1) equilibration with carbonate species in ground water (+/- precipitation of carbonates)

(2) isotope exchange with carbonate minerals (near-surface and bulk)

(3) sorption on non-carbonate minerals

### (1) Equilibration of $^{14}CO_2$ with Carbonate Species in Ground Water (+/- Precipitation of Carbonates)

Models for the equilibration of $^{14}CO_2$ with natural carbon dioxide in ground waters in the unsaturated zone at Yucca Mountain have been formulated by Knapp (1990), Light et al. (1990), Ross et al. (1992), and Codell and Murphy (1992). These models basically involve the isotopic equilibration of waste derived $^{14}CO_2$ with carbonate species in unsaturated zone ground waters. Therefore, the retardation factors are a function of the concentrations of carbon (chemical) species in the gas and fluid phases. The concentrations of the carbonate species in solution are derived either by (1) specifying or calculating the alkalinity of the ground waters, or (2) assuming equilibrium with calcite. Light et al. (1990) calculate the solubility of $CO_2$ in distilled water based

on known equilibrium constants. Because the alkalinity of distilled water is low, they calculate a very conservative value for the $^{14}CO_2$ retardation factor. Using a more realistic approach, Knapp (1990) and Ross et al. (1992) calculated retardation factors on the basis of the measured or calculated alkalinities of the ground waters found in the saturated and unsaturated zones of Yucca Mountain. Knapp (1990) used the measured alkalinity for well J-13 and varied the pH from 7-9 while Ross et al. (1992) calculated the alkalinity based on the calcium concentrations of unsaturated zone waters (Yang et al., 1988) and the assumption that these waters were saturated with calcite. The latter approach results in retardation factors in the range of 30-75. Although these values are large relative to the retardation factor used by Light et al. (1990), even this range of retardation factors still causes the EPA release limit to be exceeded in some of the calculations (Barnard et al., 1992).

Codell and Murphy (1992) presented a model in which $^{14}CO_2$ is retarded both by exchange with carbonate species in ground water and by calcite precipitation. Unfortunately, their calculations were intended only to demonstrate the approach and not to assess the performance of the Yucca Mountain site in relation to the EPA regulations. Interestingly, these authors note that the amount of $^{14}CO_2$ bound up in calcite is small compared to the amount dissolved in ground water.

According to Kerrisk (1987, Fig. 10), most waters from the saturated zone at Yucca Mountain are undersaturated with respect to calcite. Although complete water compositions from the unsaturated zone at Yucca Mountain are not available at the present time, the partial analyses of unsaturated zone waters presented by Yang et al. (1988) can be used to estimate the calcite saturation index for these waters. By assuming the charge imbalance calculated from these analyses is due to unreported bicarbonate concentrations, estimates of bicarbonate concentrations can be derived for these waters. Calculation of the calcite saturation index based on these estimates indicates these waters are undersaturated with respect to calcite. Taken together, these observations suggest that the measured alkalinities of Yucca Mountain ground waters likely provide a more conservative estimate of $^{14}CO_2$ retardation potential than alkalinity values calculated assuming saturation with calcite.

The alkalinity of waters in the saturated zone beneath Yucca Mountain ranges from approximately 1.8 to 11.4 milliequivalents/liter. If the water from the carbonate aquifer is excluded, the range is 1.8-4.7 meq/l. The calculated alkalinity of unsaturated zone water compositions reported by Yang et al. (1988), ranges from 1.1-5.0 meq/l. On the basis of these data, a likely range of alkalinity in Yucca Mountain ground waters would be 1.0-5.0 meq/l. With this range in alkalinity, the retardation factors for $^{14}CO_2$ in unsaturated zone waters range from 50-80. This is similar to the range (at 20 degrees C) used by Barnard et al. (1992).

The relationship of temperature and the retardation factor is somewhat complicated because it depends on the time at which $^{14}CO_2$ is released from the waste package relative to the time of the thermal pulse. If $^{14}CO_2$ is released from the waste packages early (<200 yr), calcite precipitation in the near-field of the repository could fix a fraction of the $^{14}CO_2$ for a considerable period of time leading to an enhanced retardation factor. This possibility was addressed in the Codell and Murphy (1992) model. On the other hand, if the $^{14}CO_2$ is released after the peak in the thermal pulse, essentially none of it would be retarded by coprecipitation with calcite in the near-field. In this case, the alkalinity of the ground waters as a function of temperature would provide the most reliable retardation factors even if the waters are saturated with calcite. According to Barnard et al. (1992), the $^{14}CO_2$ retardation factor falls off by approximately a factor of two over the temperature range from 20-60 degrees Centigrade. Clearly, the calculations presented by Barnard et al. (1992) could be improved if a model was developed coupling the container failure times with the time of the thermal pulse as discussed by Codell and Murphy (1992).

(2) Isotope Exchange With Carbonate Minerals

Although evidence exists that indicates $^{14}C$ exchanges isotopically with carbon on the surfaces of carbonate minerals (Allard et al., 1981; Garnier, 1985), such exchange processes are relatively complicated in detail and are subject to various other chemical parameters (Mozeto et al., 1984). Because the abundance of natural calcite in the unsaturated zone of Yucca Mountain is small and distributed quite heterogeneously (Bish and Vaniman, 1985), it would be difficult to quantify the retardation potential of $^{14}CO_2$ associated with isotope exchange on calcite surfaces. Further, most of the available calcite above the proposed repository occurs near the surface in the soil zone. Because $^{14}CO_2$ would be readily accessible to plant roots in this zone, the calcite in this zone would not provide a reliable barrier.

According to the Codell and Murphy (1992) model, calcite could be precipitated in the near-field of the proposed repository prior to the peak in the thermal pulse. This calcite would be precipitated mainly as a result of drying-out of the near-field environment. As noted above, $^{14}CO_2$ could be coprecipitated with this calcite if $^{14}CO_2$ is released prior to the drying-out event. However, if the $^{14}CO_2$ is released after the drying-out event but prior to the rehydration of the near-field environment, it could be exchanged isotopically with the surface of the previously precipitated calcite crystals. In this case, $^{14}C$ would have to exchange with carbon on the calcite surface from the gas phase. Unfortunately, there are not sufficient data available at the present time to model this process. However, because the amount of calcite deposited in the near-field will likely be limited (Codell and Murphy, 1992), the amount of $^{14}CO_2$ retarded by this mechanism may be insignificant. For this reason, this mechanism is probably not worth pursuing. During the rehydration of the near-field environment, previously deposited calcite will be redissolved and alkalinity will again be the most reliable guide to the $^{14}CO_2$ retardation factor.

If isotope exchange of $^{14}C$ with carbon on the surface of calcite crystals is likely to have only a minor impact on the transport of $^{14}CO_2$ in the unsaturated zone of Yucca Mountain, bulk isotope exchange will be even less likely to have a significant impact.

(3) Sorption on Non-Carbonate Minerals

The adsorption of $^{14}CO_2$ onto non-carbonate mineral surfaces in Yucca Mountain tuffs may provide a significant retardation potential for $^{14}CO_2$. For instance, iron oxides and oxyhydroxides appear to have a high affinity for $CO_2$ (Russel et al., 1975) and these oxides appear to be fairly homogeneously distributed within any given unit in Yucca Mountain. Based on available data, preliminary calculations suggest the retardation factors for $^{14}CO_2$ which include surface adsorption may be as much as a factor of three higher than those calculated on the basis of alkalinity alone.

C. EXPERIMENTAL EVALUATION OF SORPTION POTENTIAL FOR $^{14}CO_2$

Experimental evaluation of the sorption potential for $^{14}CO_2$ should include batch sorption experiments, column experiments and possibly field experiments. The batch sorption experiments could follow the same procedures as those used for the non-gaseous radionuclides (Daniels et. al., 1984). Allard et al. (1981) and Striegl (1988) have carried out batch adsorption experiments with $^{14}CO_2$ on minerals, glacial and eolian sediments. Their experimental procedures could also be used in the study of Yucca Mountain samples with minor revision. Column experiments with $^{14}CO_2$ will require more development because they must

be carried out under unsaturated conditions at near-atmospheric pressure. Perhaps existing column techniques could be modified to allow for low pressure gas transport. Alternatively, new techniques must be developed to carry out these experiments.

In order to select appropriate rock samples for the experimental work, it is critical that a set of experiments be carried out on pure separates of the mineral phases identified in Yucca Mountain. Although iron oxides and oxyhydroxides appear to have a high affinity for carbonate species (Russel et al., 1975), other materials are also known to have affinities for $CO_2$ including aluminum oxides (Schulthess and McCarthy, 1990), clays, and concrete (Allard et al., 1981). The pure mineral experiments should be carried out with water compositions representative of the unsaturated zone at Yucca Mountain, especially in terms of alkalinity.

## D. RECOMMENDATIONS FOR SITE CHARACTERIZATION ACTIVITIES

In order to allow more detailed modeling of $^{14}CO_2$ transport in Yucca Mountain, additional data will be required of the site characterization activities. These include:

(1) Additional data on unsaturated zone water chemistries (alkalinity distributions)

(2) Spatial distributions of matrix and fracture minerals critical to $^{14}CO_2$ transport

(3) Accessibility of $^{14}CO_2$ to critical minerals.

As noted above, alkalinity may be the best parameter to gauge the $^{14}CO_2$ retardation potential of hydrologic units in the unsaturated zone of Yucca Mountain. With the currently available database, an alkalinity range of 1-5 meq/l is suggested for both the unsaturated and saturated zone waters in Yucca Mountain. What is required of the site characterization activities is better definition of this range and a probability distribution of the values within this range. This probability distribution could be converted to a probability distribution for retardation factors which could in turn be used directly in performance assessment calculations.

In order to derive reliable estimates of retardation potential due to surface adsorption, site characterization activities must provide a reliable measure of the homogeneity in the distribution of key $^{14}C$ sorbing minerals such as iron oxides in each of the hydrologic units specified in the flow models. If the mineral distributions can be shown to be sufficiently homogeneous, representative sorption coefficients could be derived as a function of alkalinity and temperature using laboratory sorption data. If the distributions of key minerals are inhomogeneous, it will be difficult to derive representative sorption coefficients. In this case, taking credit for retardation due to sorption on mineral surfaces should be avoided.

An additional factor in the derivation of representative sorption coefficients for $^{14}C$ on key minerals concerns the accessibility of the mineral surfaces to unsaturated zone waters. Because secondary iron oxides represent the alteration of primary iron oxides by reaction with atmospheric oxygen, the existence of these secondary iron oxides in the rocks is evidence of their accessibility to atmospheric gases. However, it would be prudent to evaluate the accessibility of these oxides to fluids by performing acid leach experiments on representative samples. These experiments could be relatively straightforward for iron oxides but could be more difficult for other minerals that may be identified as $^{14}CO_2$ sorbers.

## E. RECOMMENDATIONS FOR MODELING STUDIES

Based on a review of published models, a more comprehensive chemical model for $^{14}CO_2$ transport in Yucca Mountain could be developed. This model should incorporate at least the following two items:

(1) probability distributions for $^{14}CO_2$ retardation factors based on probability distributions for alkalinity in Yucca Mountain waters,

(2) sorption potentials as measured in representative whole-rock samples.

and (3) a near-field calcite precipitation model coupled (Codell and Murphy, 1992) with a waste container failure model

## F. SUMMARY AND CONCLUSIONS

Existing models for $^{14}CO_2$ transport in Yucca Mountain are on the right track in basing retardation on alkalinity whether using measured values or values calculated from the calcite saturation assumption. Consideration of the potential for near-field calcite precipitation in these models may be worthwhile if coupled with a model for container failure rates. This would enhance the retardation potential of the near-field environment. The addition of a surface adsorption model to the transport calculations would further enhance the retardation potential. Based on the available data, it seems likely the site could meet the EPA release limits if (mineral)surface adsorption potential was included in the transport calculation.

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