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Dr. D. J. Brooks
Geotechnical Branch
Office of Nuclear Materials
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Room 623-SS
Washington, D.C. 20555

WM-RES
WM Record File B0287 ORNL

WM Project 10, 11, 16
Docket No.
PDR ✓
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Distribution:
Brooks, D. | Joan-Ticket
(Return to WM, 623-SS)

Dear Dave:

Enclosed are the following:

(1) Progress Report for March 1987

(2) Descriptions of Supplemental Work Tasks. These are in response to your request for brief descriptions of additional tasks which we could initiate this fiscal year.

- Determination of Diffusion Coefficients, Gary K. Jacobs
- Geochemical Model Validation, Gary K. Jacobs
- Application of Sensitivity Analysis and Error Propagation to Simulation of Far-field Behavior of Radionuclide Transport, Vijay S. Tripathi

If you need further information, please call me at FTS 624-6870.

Sincerely,

A. D. Kelmers /cj

A. D. Kelmers, Project Manager
B0287 Technical Assistance in Geochemistry
Chemical Technology Division

ADK:cj

Enclosures (2)

cc w/encl (1): Office of the Director, NMSS, (Attn: Program Support Branch)
Division Director, NMSS Division of Waste Management (2)
Branch Chief, Waste Management Branch, RES
P. S. Justus, Chief, Geotechnical Branch, NMSS
A. P. Malinauskas, ORNL Director, NRC Programs
J. W. Bradbury, Geotechnical Branch, NMSS

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PROGRESS REPORT FOR MARCH 1987

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT STAFF: J. G. Blencoe, R. M. Gove, G. K. Jacobs, R. E. Meyer, V. S. Tripathi, and K. L. Von Damm

PROJECT MANAGER: A. D. Kelmers
Chemical Development Section
Chemical Technology Division
OAK RIDGE NATIONAL LABORATORY, Operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

OBJECTIVE:

The objective of this project is to provide technical assistance to the NRC in the evaluation of geochemical information pertinent to the candidate HLW geologic repository sites. The project emphasizes the collection and review of key information to provide input to the NRC analysis of technical issues regarding the geochemical aspects of HLW isolation.

TECHNICAL HIGHLIGHTS:

Geochemical Modeling:

A comparison of the K_D method of modeling radionuclide retardation in groundwater is being conducted *vs* comprehensive modeling approaches to explore the applicability and compare the accuracy of these methods for the modeling prediction of high-level nuclear waste repository performance. We have developed a model, HYDROGEOCHEM, which simulates complexation, dissolution, precipitation, and adsorption processes. The model is being used to analyze scenarios of varying geochemical complexity, and to examine variabilities in K_D predictions. The results to date showed that, even in simple systems, K_D values displayed a considerable variability (over several orders of magnitude) with only moderate changes in solution composition.

These results prompted us to investigate complex systems which more closesly mimic natural systems. The computations were being performed on a VAX 8600. However, more realistic computations could be more easily done on a faster machine. In March, we implemented HYDROGEOCHEM on a CRAY X-MP. On the CRAY, HYDROGEOCHEM runs 30 to 50 times faster, and costs 5 to 50 times less than on the VAX (depending on priorities). These improvements mean a sharp increase in our ability to simulate more realistic natural systems. We have constructed a two-dimensional finite element representation for this purpose. We will use this representation in addition to the earlier one-dimension system to document and substantiate our earlier findings of K_D variability.

Geochemistry Issues:

Draft Letter Reports analyzing the geochemistry issues for the Yucca Mountain site and The Hanford Site are being prepared. Six issues have been defined that cover all aspects of site characterization and selection, and of repository construction, operation, and closure. Major report sections for the six issues at each site will be: (i) Regulatory Rationale, (ii) Data and Information Needed to Analyze the Issue, (iii) Methods, Strategies, and Approaches Available to Acquire the Needed Data and Information, and (iv) Precision and Accuracy Necessary, or Uncertainty Acceptable, for the Data and Information Needed to Analyze the Issue. A draft of the Regulatory Rationale has been completed and we are working on the various Data and Information Needed sections. A draft of the Yucca Mountain report containing these two sections for all six issues is expected to be completed on schedule and forwarded to the NRC Project Manager with the April Progress Report.

General:

The topical review on the solubility of radionuclides (NUREG/CR-4024) is in final preparation on mats. The topical review on matrix diffusion, being prepared in conjunction with Jerry Grisak of Intera Technologies Inc., is being revised and expanded to include a discussion of the relationship between performance measurement and matrix diffusion parameters. The topical review on the geochemical conditions at the Hanford Site will be revised when the review of the draft manuscript by the NRC is received.

MEETINGS AND TRIPS:

None

REPORTS AND PUBLICATIONS:

None

PROBLEM AREAS:

None

COST/BUDGET REPORT:

Expenditures for March were not available at this time. A detailed cost/budget report will be forwarded under separate cover.

DETERMINATION OF DIFFUSION COEFFICIENTS

Gary K. Jacobs
Oak Ridge National Laboratory

Evaluating the uncertainty in the values of diffusion coefficients currently used in performance assessment calculations is especially important in two areas. First, as shown by Pigford and coworkers, the steady-state release rate of a radionuclide from a waste form in contact with slow-moving groundwater is a direct function of its diffusion coefficient (D), its concentration at the waste form-water interface (C), the porosity of the surrounding medium (ϕ), and the physical characteristics of the waste package. The uncertainty in diffusion coefficients directly effects the predictions of radionuclide release rates. The second area of importance, especially for host rocks characterized by fracture-flow hydrology, is that the extent of contact between dissolved radionuclides being transported in fractures and the sorptive matrix of the host rock is a strong function of the diffusion coefficient. Thus, to properly assess the contribution that geochemical retardation may play in fracture-flow geohydrologic concepts, DOE must demonstrate that reasonable values for diffusion coefficients are used.

Diffusion coefficients in groundwaters with a high dissolved solids content may be many times larger or smaller than in dilute waters. Little direct information is available for relevant elements at elevated temperatures or within chemical gradients likely to occur within the disturbed zone and engineered barrier system of most repository concepts. It is proposed to measure diffusion coefficients for selected elements important to both waste package performance and radionuclide transport near the engineered barrier system. The elements to be studied initially include uranium, technetium, and carbon. Uranium is important because its rate of release from the waste form may control the release of other actinide elements (e.g., plutonium and americium). Carbon and technetium will be studied because they are anticipated to be quite soluble and relatively mobile — thus, careful evaluation of diffusion coefficients for these elements may be required to ensure that calculated release rates are within regulatory limits. The diffusion coefficients will be determined using simple diffusion cells. The tests will be conducted over a range of groundwater chemistry and temperature conditions so that the values will be applicable to calculations of both radionuclide release rates from waste packages and radionuclide migration within the disturbed zone and engineered barrier system of various repository concepts.

estimated cost: $90K per year.

GEOCHEMICAL MODEL VALIDATION

Gary K. Jacobs
Oak Ridge National Laboratory

Geochemical models are anticipated to be used to support performance assessments of high-level nuclear waste repositories. These computer codes (e.g., EQ3/6, PHREEQE, MINTEQ) are capable of simulating geochemical reactions that occur during processes such as: (1) groundwater/rock interactions, (2) waste form dissolution, (3) canister degradation, (4) groundwater mixing, and (5) radionuclide sorption. Simulations of these processes may be used to help interpret experimental results, perform sensitivity studies, and to act as detailed-process models within a system-level performance assessment model.

For results from geochemical models to be acceptable in repository analyses they must be validated (i.e., it must be demonstrated that the model in question correctly simulates the processes of interest). Validation of a geochemical model will entail assessing the conceptual model within the code, as well as the thermodynamic and/or kinetic data bases that support the model. One effective approach for validating geochemical models is to use complementary laboratory studies and field (natural analog) investigations. The approach proposed here involves: (1) elucidating the dominant geochemical controls in a generic uranium-rock system via laboratory studies, (2) validating geochemical model simulations against this system, (3) characterizing a natural system with attributes analogous to, but more complex than, those of the laboratory system, and (4) perform calculations to validate the model against the natural system. The complete validation will document both agreements and inconsistencies between the predictions of the model and the laboratory and natural systems. It is essential that the reasons for the agreements and/or inconsistencies occur be established. Otherwise, simple coincidence could mask severe problems with the geochemical models.

It is proposed to initiate a laboratory-oriented validation study that will lead to the eventual field validation of typical geochemical models. The validation study will emphasize the system uranium - quartz - clay - calcite - Fe-oxide - feldspar. This system is amenable to experimental investigation and possesses several potential natural analogs that may be used for the eventual field validation. A systematic approach from the "simple" to the "complex" will allow the models to be validated in a step-wise manner. Thus, errors or inconsistencies that may need to be corrected before progressing to the next stage of complexity can be identified. The types of reactions to be validated include: (1) dissolution, (2) precipitation, (3) redox, (4) complexation, and (5) sorption. The general approach will be to react U(IV)- and U(VI)- bearing solids with "typical" groundwaters (several different systems will be tested so as to provide a broad base of validation data). The resulting fluids would then be allowed to react with selected mineral phases. The low-temperature (25-100°C) experimental system will consist of a series of mixed-flow cells that will allow fluids to be continuously sampled as a function of time from one cell so that the approach to steady state can be monitored. The system will also allow fluids to continuously flow from one cell to the next so that effects of fluid flow, groundwater mixing, and changing temperature may be investigated in a single experimental run.

The sequential progress of the reactions to be studied will allow much of the data to be used for some preliminary testing of the transport code, HYDROGEOCHEM, being developed by Tripathi and Yeh, and to assess the relative merits of K_d-based versus comprehensive transport models. The validation program will progress with the eventual goal in mind to use a natural analog to the laboratory system for a final field validation.

estimated cost: $150K per year.

Application of Sensitivity Analysis and Error Propagation to Simulation of Far-field Behavior of Radionuclide Transport

Vijay S. Tripathi
Oak Ridge National Laboratory

Performance assessment of high-level nuclear waste repositories requires an evaluation of the extent of radionuclide transport. Specifically, a demonstration of acceptable estimates of cumulative release and maximum concentration limits along the transport path are mandated by federal regulations. Coupled hydrologic and geochemical calculations are being used to estimate these concentrations by many groups at present. These geochemical calculations depend on the values of thermodynamic properties of radionuclides and their complexes and compounds. The uncertainties in the input values introduce *significant uncertainties* in calculated results. This in turn raises questions about the reliability of performance assessment and evaluations.

We are developing methods for error propagation in a geochemical model (MINEQL). We are in a position to investigate the effects of uncertain geochemical data on computed model response. We propose to apply the error-propagation and sensitivity analysis, in an exploratory fashion, to simulation of radionuclide behavior. The uncertainties in stability constants of radionuclides vary from a few tenths to upto several orders of magnitude (Sillen and Martell, 1964; Langmuir, 1978; Tripathi, 1983; Tripathi and Parks, 1987). Our preliminary computations have shown that such uncertainties, and their interactions can introduce *large* bands of uncertainties in computed radionuclide solubilities. We request approximately $ 10 K for the rest of FY 1987; virtually all of this will be used to cover computer costs chiefly on a CRAY-X MP computer.

The results of this work, if supported, will be promptly submitted for journal publication.

Langmuir, D., 1978, *Geochim. Cosmochim. Acta.*

Sillen, L.G. and Martell, A.E., 1964, *Stability Constants.* Chemical Society of London.

Tripathi, V.S., 1983, Ph.D. dissertation, Stanford University.

Tripathi, V.S. and Parks, G.A., 1987, Factors governing reliability of stability constants of complexes. In preparation.