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August 15, 1986

Mr. Walton Kelly
Geotechnical Branch
Division of Waste Management
U.S. Nuclear Regulatory Commission
7915 Eastern Avenue
Silver Spring, MD 20910

Dear Mr. Kelly:

Enclosed is the monthly report on FIN A-1756, Geochemistry Sensitivity Analysis for July 1986. Please feel free to contact me if you have any questions or comments.

Sincerely,

Robert M. Cranwell

Robert M. Cranwell, Supervisor
Waste Management Systems
Division 6431

RMC:6431

Enclosure

Copy to:
Office of the Director, NMSS
Attn: Program Support
Robert Browning, Director
Division of Waste Management
Phillip Justus
Division of Waste Management
Malcolm R. Knapp
Low Level Waste and Uranium Recovery Branch
Kenneth Jackson
Division of Waste Management
Branch Chief
Health, Siting and Waste Management
Document Control Center
6430 N. R. Ortiz
6431 R. M. Cranwell
6431 M. D. Siegel
6431 R. Rechard
1500 W. Herrmann
1510 J. W. Nunziato
1512 J. C. Cummings
1512 K. L. Erickson

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A-1756 PDR

PROGRAM: Geochemical Sensitivity Analysis FIN#: A-1756

CONTRACTOR: Sandia National Laboratories BUDGET PERIOD: 10/85 - 9/86

NMSS PROGRAM MANAGER: W. Kelly BUDGET AMOUNT: 365K

CONTRACT PROGRAM MANAGER: R. M. Cranwell FTS PHONE: 844-8368

PRINCIPAL INVESTIGATORS: M. D. Siegel FTS PHONE: 846-5448

PROJECT OBJECTIVE

The objective of this project is to provide technical assistance to the NRC in determining the sensitivity of performance assessment calculations to uncertainties in geochemical data and in the representation of geochemical processes in transport models. In Task I, the error in model calculations of integrated radionuclide discharge due to speciation, sorption and kinetic effects will be evaluated. In Task II, the potential importance of organic molecules and colloids will be examined. SNLA will assist the NRC in determining how geochemical processes should be represented in transport models in Task III. Short-term technical assistance will be carried out under Task IV and the codes and data bases developed under this project will be transfered to the NRC under Task V.

ACTIVITIES DURING JULY 1986

Task I. Uncertainty in Integrated Radionuclide Discharge

Subtask 1A. Conceptual Models for Repository Sites.

A meeting was held with M. Logsdon and A. Brown to compare the conceptual flow models for the basalt and bedded salt sites developed at SNLA and by Nuclear Waste Consultants and its subcontractors. It was agreed that further meetings would be productive. Of particular interest is the diversity of opinions concerning the possible significance of thermally-driven convection at the BWIP site. The results of hydrologic modeling of BWIP by other SNLA staff will be available in the near future. The preliminary conceptual model presented to the NRC will be refined when these results are available. During July, a review of scenarios that may significantly alter the ground-water chemistry at the BWIP site was initiated.

Subtask 1B. Solubility/Speciation Effects.

Nothing to report for July.

Subtask 1C. Sorption Effects.

Data describing batch sorption tests for minerals along potential flow paths at the BWIP site was reviewed and entered into a dBASE III+ data base. Several user-friendly command files were written to allow researchers unfamiliar with dBASE III to carry out searches of the basalt and tuff data bases.

A final version of the report "Surface-complexation Models of Radionuclide Adsorption in Sub-surface Environments" was received from Stanford University. The report will be sent to the NRC under a separate cover for review before publication as a SAND document.

Subtask 1E. Coupled/Dynamic Effects

An interactive search and graphics program to plot TRANQL output data was made operational during July. The graphics program TRAGPH searches for the data necessary to make plots of concentration versus time or distance and calculates the integrated discharge for simple geometries. Reciept of the final versions of the interactive preprocessor TRANIN and user's manuals from Stanford University completes the suite of tools required to effectively evaluate the use of TRANQL in geochemical sensitivity analyses. Evaluation of the sensitivity of the code to hydrological and chemical parameters is underway.

Task 4. Short-Term Technical Assistance.

M. Siegel reviewed a draft of a letter report describing the NRC/ORNL workshop on Radionuclide Sorption Modeling Related to High Level Nuclear Waste Repository Performance Assessment. A copy of the review comments is appended as Attachment 1.

M. Siegel contributed to a report describing the results of the LANL/NRC Workshop on Comparative Modeling of Tracer Migration in the Unsaturated Zone that was held on June 18-19. A copy of this section is appended as Attachment 2. Calculations of the aqueous speciation of the system Sr-Ca-CO3-H2O were carried out using the MINEQL computer code in support of this work. A letter report describing the calculations will be prepared for the NRC in the future.

Allocation of Resources

Task 1........ 60%
Task 4.........35%

Attachment 1

July 24, 1986

Dr. A. D. Kelmers
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Dear Don:

I have completed a review of the draft letter report (6/30/86) describing the NRC/ORNL workshop Radionuclide Sorption Modeling Related to High-Level Nuclear Waste Repository Performance Assessment. I have discussed the report with R. Rechard and he concurs with the comments that appear below. E. Bonano has provided me with his comments; they are enclosed with this letter. In general, we felt that the discussion of specific experimental needs was good. Several comments and suggestions concerning the overall organization and conclusions of the draft report follow below.

1. The SUMMARY does not accurately reflect the multiplicity of views or aprroaches presented at the workshop. Emphasis is entirely on a 'classical' geochemical experimental approach with little mention of the role that system analyses or sensitivity studies will have in showing compliance with the regulations or setting research priorities. There is indirect mention of system studies in the main body of the paper. It does represent an approach that is fundamentally different than the experimental method emphasized in the summary and deserves a separate 'bullet' in the SUMMARY.

2. The report fails to adequately address the fundamental controversy surrounding the level of understanding required to bound radionuclide discharges. The term 'understanding of sorption processes' is used repeatedly throughout the letter report, yet there was little consensus at the workshop as to the operational definition of this term. It is very easy to agree that a greater degree of understanding of sorption processes is required (there was consensus at the workshop on this point), however, the important and unresolved issues deal with how to identify the information required to show compliance with the regulations. DOE should demonstrate that they have done this before the licensing activities are completed.

The two above issues could be addressed by including a paragraph in the SUMMARY similar to the following:

" There was a general recognition of the experimental and theoretical difficulties in gaining an accurate understanding of sorptionprocesses. Uncertainty/sensitivity analyses on radionuclide/site release scenarios are needed to specify the required degree of understanding and to set research priorities."

3. The division of essential and non-essential parameters is unclear on pages 6-12. Many of the 'parameters' described in section 2.2.2 are in essential, in my opinion, if they are evaluated for site-specific materials and conditions.

4. The discussion of Kd's on pages 15 to 16 combines the subjects of uncertainy and conservatism and may lead to the impression that areas of uncertainty necessarily coincide with non-conservative estimates of radionuclide discharge. I don't believe that this has been demonstrated yet for conditions relevant to the repositories. I would suggest breaking out separate sections for 'uncertain' and 'non-conservative' aspects of Kd models or avoid using the term 'non-conservative' as indicated in the marked copy enclosed with this letter. Again, the relationship between uncertainty and non-conservatism will depend on the particular site, radionuclide, release scenario, chemical process, flow regime and performance measure.

5. I have made some additional comments in the margins and on the text in the marked-up copy enclosed with this letter.

I hope that these comments will be useful to you in drafting the final version of your report.

Sincerely,

Malcolm Siegel
Waste Management Systems
Sandia National Laboratories

cc J. Bradbury, USNRC
W. Kelly, USNRC
G. Jacobs, ORNL

Attachment 2

M E M O R A N D U M

INSERTS FOR PANEL REPORT

Insert 1. (for 'SUMMARY OF APPROACHES')

Cederberg's approach involves the coupling of a 1-2 dimensional finite element transport code (ISOQUAD) with a chemical equilibrium code (MICROQL). Whereas the other approaches described in this report use an empirical retardation factor to describe the partitioning of solute between fluid and solid, the TRANQL code calculates the speciation of the contaminant based on the chemical composition of the system and thermodynamic equilibrium constants. Once the distribution of the solute between the solution and the substrate has been calculated, the transport of dissolved constituents is simulated by solution of the classical advection-dispersion equation for porous media. The spatial derivatives of the equation are approximated with the Galerkin finite element method using linear or quadratic, isoparametric basis functions (Cederberg,1985).

Insert 2. (for 'DATA USED')

The data requirements for the TRANQL code are quite different from those of other models of the workshop. In previously published applications of this code, (Cederberg,1985) the pore water velocity was assumed to be steady and independent of solution composition. Transport parameters such as fluid velocity, dispersivity, and porosity were assumed to be constant in time but may be spatially variable. Calculation of the chemical speciation of the solute requires specification of the concentrations of all major species which can complex with or compete with the solute in complexation reactions, the equilibrium constants for all important homogeneous and heterogeneous reactions, the specific surface areas of sorbing substrates,and the solution to solid ratio of the porous matrix. In addition, if electrostatic interactions between the solids and solution species are to modeled, the capacitances of the electrical double layers must be estimated. The chemical equilibrium model assumed in TRANQL requires that the thermodynamically stable (or important metastable) solids be identified and included in the data base.

Insert 3. (for 'ADVANTAGES/DISADVANTAGES OF EACH APPROACH')

The results of attempts to model the caisson data using TRANQL were not available in time to be included in this report. Therefore, a final evaluation of the comparative advantages and disadvantages of this approach could not be made. However, some general comments concerning the applications of TRANQL and other similar coupled reaction/transport codes to the caisson experiment can still be made and are summarised below.

The use of a retardation factor in a classical advection-disperion equation requires the following assumptions: 1. sorption is the dominant chemical interaction between the solute and the rock; 2. a single dominant aqueous species of each solute is present; 3. local chemical equilibrium between the solution and rock exists; 4. sorption isotherms have been obtained in solutions of the chemical compositions that exist along the solute flow path. If a Kd is used to describe the partitioning of solute between the rock and fluid, it also must be assumed that the degree of sorption is independent of solute concentration. The Kd values must be obtained with samples of the mineralogies that exist along the flow path.

The main advantage of the TRANQL code is its potential to describe solute transport under conditions in which the above assumptions are not valid. Previously, TRANQL has been used to model transport of a sorbing tracer in the presence of a conservative complexing ligand (Cederberg, 1985). In that study it was shown that the sorption of cadmium (expressed as a Kd) varied over several orders of magnitude due to complexation with EDTA. In its current form, TRANQL can be used to describe the transport of solute more accurately than codes using retardation factors when aqueous speciation and nonlinear sorption are important. The extensive chemical data required by the code, however, are a major disadvantage. For example, few of the data required for simulation of the transport of Sr are available. At present there are insufficient thermochemical data to adequately model sorption of Sr on tuff in the solutions used in the caisson.

In its current form, TRANQL cannot be used to model systems in which precipitation, coprecipitation or kinetic effects are important. As discussed in the next section, preliminary modeling of the chemical data from the caissons (Siegel, 1986) using the more comprehensive geochemical speciation code MINEQL suggest that these phenomena must be considered in simulations of this system. The thermochemical data required to accurately model these effects are also unavailable. In addition, modeling of these phenomena with either TRANQL or MINEQL requires detailed characterization of the mineralogy, surface area and site-binding capacity of the tuff within the caissons. The difficulty in obtaining these data for this type of experiment is another disadvantage of this modeling approach.

Insert 4. (for 'SUMMARY OF MODELING RESULTS')

As discussed above, the behavior of strontium in the caissson could not be described using a retardation factor in either the stochastic or deterministic models. The strontium concentration profiles do not show the expected decrease in peak height with distance from the tracer source.The curve at 36 cm has two peaks, the peaks at 119 and 271 cm are slightly asymmetrical and small, and the peaks at 194 and 347 cm are sharp with high concentrations. The strontium introduced during Unsteady State Pulse #1 had not eluted completely by the time the experiment had ended. The arrival of the strontium peak from the USS Pulse #1 at the 188 and 246 cm sampling points coincided with the appearance of the iodide peaks from the Steady State Pulse #1 and Unsteady State Pulse #2 respectively.

Based on preliminary speciation calculations, Cederberg suggested that the precipitation of strontianite, $SrCO_3$ might be occuring in the caisson. Additional calculations using the MINEQL computer code

(Siegel, 1986) suggest that several other phenomena must also be considered in any attempt to model transport of strontium in this system. These include: 1. coprecipitation of strontium in calcite, 2. the consumption of acetate and production of bicarbonate by bacteria, and 3. dissolution of the tuff, concomitant release of silica and consumption of protons. The preliminary calculations suggest that if the chemical system was open to the atmospheric carbon dioxide, then saturation with respect to $SrCO_3$ was not achieved. The observed concentrations of strontium, however, are consistent with coprecipitation of Sr with calcite when reasonable distribution coefficients are assumed (Stumm and Morgan, 1981). Additional mineralogical and compositional data for the tuff within the caisson must be obtained in order to test this hypothesis. If the system was closed with respect to CO_2, then saturation of strontianite occurred at the 188 cm depth. The sorption of Sr onto crushed tuff has been shown to be very sensitive to the presence of minor amounts of clay and clinoptilolite (see reviews by Guzowski and others, 1983; Tien and others, 1985). Thus anomalous behavior of the strontium in the caisson could also be due to variations of the strontium Kd within the crushed rock matrix.

Insert 5. (for 'CONCLUSIONS AND RECOMMENDATIONS' section)

There was a consensus among modelers and panelists that the caisson experiment had not been designed properly for the study of the transport of non-conservative (reactive) tracers. Several deficiencies in the chemical and mineralogical data obtained from the experiment prevented application of the chemical subroutines of TRANQL to this study. The required data include a continuous record of the alkalinity of the solutions at the sampler locations and mineralogical analyses of representative samples of the crushed tuff in the caisson. The use of crushed Bandelier Tuff with highly reactive mineral surfaces presents additional problems. The freshly exposed grain surfaces will release silica, calcium and magnesium and consume protons. A large number of heterogenous and homogeneous reactions are possible in such a reactive system and the use of a retardation factor to describe solute-rock interactions may be inappropriate. In future caisson experiments, mineralogical and chemical analyses of representative samples from different depths within the caisson should be taken before and after the experiment. If possible, the tuff in the caisson should be pre-equilibrated with the background electrolyte for a period of time sufficient to 'age' the solids and obtain a chemically stable system.

References

Cederberg, G., 1985, TRANQL: A Ground-Water Mass-Transport and Equilibrium Chemistry Model for Multicomponent Systems, Ph.D. Dissertation, Stanford University, Stanford, CA.

Guzowski, R. V., Nimick, F. B., Siegel, M. D., and Finley, N. C., 1983, Repository Site Data for Tuff: Yucca Mountain, Nevada, Sandia Nat. Labs., NUREG/CR-2937, 312 p.

Siegel, M.D., Chemical speciation calculations in support of the LANL low-level waste caisson study, Letter report to the N.R.C., August, 1986.

Stumm, W. and Morgan, J. J., 1981, Aquatic Chemistry, Wiley-Interscience, New York, pp 287-291.

Tien, P., Siegel, M. D., Updegraff, C. D., Wahi, K. K., and Guzowski, R. V., 1985, Repository Site Data Report for Unsaturated Tuff, Yucca Mountain, Nevada, Sandia Nat. Labs., NUREG/CR-4110, pp.103-114.

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July 1986

THIS IS AN ESTIMATE ONLY AND MAY NOT MATCH THE INVOICES SENT TO NRC BY SANDIA'S ACCOUNTING DEPARTMENT.

		Current Month	Year -to- Date
I.	Direct Manpower (man-months of charged effort)	1.1	11.8
II.	Direct Loaded Labor Costs	12	122
	Materials and Services	0	2
	ADP Support (computer)	1	1
	Subcontracts	64	124
	Travel	1	8
	Other (computer roundoff)	1	0
	TOTAL COSTS	77	258

III. Funding Status

Prior FY Carryover	FY 86 Projected Funding Level	FY 86 Funds Received to Date	FY 86 Funding Balance Needed
None	365K	365K	None