Sandia National Laboratories
Albuquerque, New Mexico 87185

April 9, 1985

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Mr. Walton Kelly
U.S. Nuclear Regulatory Commission
Mail Stop 623-SS
Washington, DC 20555

Dear Mr. Kelly:

Enclosed is the monthly report for FIN A-1756, Geochemical Sensitivity Analysis for March 1985.

Please feel free to contact me if you have any questions or comments.

Sincerely,
Margaret Chu for
R.M. Cranwell

R. M. Cranwell
Supervisor
Waste Management Systems
Division 6431

RMC:6431:jm

Enclosure

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1993

PROGRAM: Geochemical Sensitivity Analysis FIN#: A-1756

CONTRACTOR: Sandia National Laboratories BUDGET PERIOD: 10/01/84 - 9/30/85

DRA PROGRAM MANAGER: W. R. Kelly BUDGET AMOUNT: 235K

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

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

PROJECT OBJECTIVES

The objective of this project is to provide technical assistance to the NRC in determining the sensitivity of far-field performance assessment calculations to uncertainties in geochemical and hydrological input 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, kinetic and sorption 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 under Task III. Short-term technical assistance will be carried out under Task IV.

ACTIVITIES DURING MARCH 1985

Task I Uncertainty in Integrated Radionuclide Discharge

Subtask IA. Speciation Effects
(M. Siegel, R. Guzowski, S. Phillips)

Compilation of hydrogeological data for the Hanford Site onto the dBase III system was started this month. A pilot file consisting of data for drill holes DDH-3 and DC-15 was constructed. The objective of this effort is the construction of compatible geochemical and hydrogeological files that can be used as sources of data for system scoping calculations and sensitivity studies.

Data for reactions of neptunium in aqueous solutions are being compiled in a format that is compatible with the computer code PHREEQE. The equilibrium quotients (K(T)) for the formation reactions of aqueous species and solids of neptunium have been

calculated from thermochemical data (ΔG_f°, ΔH_f°, ΔS_f° and Cp) compiled in LBL-14996 (Phillips and others, 1985). Table 1 lists the species and solids included in the data base. A copy of LBL-14996: (Hydrolysis, Formation and Ionization Constants at 25°C, and at High Temperature-High Ionic Strength.) is being sent to the NRC program manager under a separate cover. This compilation is largely a product of the DOE Basic Energy Sciences project that has been at Lawrence Berkeley Labs for the last few years and contains a minor amount of input from the NRC program A-1756. This report complements the information contained in LBID-977 (Thermodynamic Data for Nuclear Waste Disposal, Overview of Available Data and Criteria for Selection of Data) which was included in the first quarterly report of FIN A-1756 for FY 1985. Both of these works are under review, and together, they will form the nucleus of the data base for aqueous species that will be used in calculations carried out under FIN A-1756. Data for surface-complexation reactions are being compiled under Subtask IB and will be described in next month's progress report.

Subtask IB. Sorption Effects.

A quality-control procedure for the sorption data that is being entered into the dBase III system was designed and implemented during March. Under this procedure, a notebook containing copies of data from the original sources of data (e.g. LANL or BWIP reports) and print-outs of the data from the data base system is being prepared. The FORMAT and REPORT capabilities of dBase III are being used to print the data from each table in a format that is similar to that of the original source of information. This will allow rapid and accurate checking of the data for typographical errors.

A copy of an enhanced version of MINEQL (Westall and others, 1976), was obtained from Stanford University and transferred to the central Sandia computer (CDC) and to an IBM PC/AT. Conversion of the code to make it compatible with these systems is currently underway. This version includes the capability to model surface adsorption/complexation reactions using a site-binding, electrical, double-layer model; a user-friendly interactive input subroutine, and more complete error message documentation. Documentation of the changes to the original published code (Westall and others, 1976) is planned during the current fiscal year.

TABLE I

SOLIDS AND SPECIES INCLUDED IN DATA BASE FOR NEPTUNIUM

Solids	Complexes	
Np	NpO_2OH^+	NpO_2SO_4
$NpO_3 \cdot H_2O$	$(NpO_2)_2(OH)_2^{+2}$	$NpO_2SO_4^-$
Np_2O_5		$NpSO_4^{+2}$
NpO_2	$(NpO_2)_5(OH)_5^+$	$Np(SO_4)_2$
$NpO_2(OH)_2$		
$NpO_2\ OH_{(am)}$	NpO_2OH	$NpO_2(CO_3)_2^{-2}$
$Np(OH)_4$	$NpOH^{+3}$	$NpO_2(CO_3)_3^{-4}$
NpF_4	$Np(OH)_2^{+2}$	$NpO_2CO_3^-$
NpF_3	$Np(OH)_3^+$	$Np(CO_3)_5^{-6}$
$NpCl_4$	$Np(OH)_4$	
$NpCl_3$	$Np(OH)_5^-$	$NpO_2(CO_3)_2^{-3}$
$NaNpO_2CO_{3.3} \cdot 5H_2O$		
$NpBr_4$	NpO_2F^+	$NpO_2(CO_3)_3^{-5}$
$NpBr_3$	NpO_2F_2	
	NpO_2F	
Ions	NpF^{+3}	
Np^{+3}	NpF_2^{+2}	
NpO_2^{+2}	NpO_2Cl^+	
NpO_2^+	NpO_2Cl	
Np^{+4}	$NpCl^{+3}$	

Subtasks IC and ID Kinetic and Dynamic Effects
(M. Siegel, K. Erickson, J. Leckie, V. Tripathi)

An abstract for a paper describing work performed under this subtask was prepared and submitted to the NRC/DOE HYDROCOIN conference to be held in May 1985. A copy of the abstract is included as Attachment 1. An abstract submitted to the 1985 annual meeting of the Materials Research Society (see February 1985 Progress Report) was accepted for presentation and publication.

Task II Evaluation of Error Due to Organics and Colloids

No activity in March 1985.

Task IV Short Term Technical Assistance

No activity in March 1985.

Meetings

Malcolm Siegel attended the sessions on performance assessment and radionuclide transport at the Waste Management '85 conference on March 27, 1985. Of particular interest were talks on kinetics and reversibility of the sorption of Cs, Ba and Co on tuff by W. Polzer and H. Fuentes. The authors describe the sorption data by two methods that have not been commonly used in the HLW literature: a modified Freundlich isotherm and Hill plots. These tools will be examined for potential use in FIN A-1756. On March 28-29, 1985, M. Siegel worked with contractors at Stanford University on the application of the code MINEQL to the problems involving the aqueous speciation and surface complexation of neptunium.

Funding Breakdown for March

Task I - 100%

Reference

Westall, J. C., Zachary, J. L., and Morel, F. M. M., 1976, MINEQL, a Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems, Technical Note No. 18, Water Quality Laboratory, Dept. of Civil Engineering, Mass. Institute of Technology, Cambridge, MA, 90 p.

Attachment 1

GEOCHEMICAL SENSITIVITY ANALYSIS FOR PERFORMANCE ASSESSMENT OF HLW REPOSITORIES: EFFECTS OF SPECIATION AND MATRIX DIFFUSION

M. D. Siegel and K. L. Erickson, Sandia National Laboratories, Albuquerque, NM 87185

Performance assessment requires calculating radionuclide discharge for many sets of conditions and scenarios. In general, such calculations use empirical retardation factors that describe the average effect of all radionuclide/fluid/rock interactions. This method, however, may underestimate radionuclide discharges and disguise potential violations of regulatory standards. An alternative approach, coupled reaction-transport models, can be used to obtain a detailed understanding of physicochemical phenomena but the general application of such rigorous models may be impractical in risk assessment.

The objective of this geochemical sensitivity analysis is to use simple, approximate models to calculate upper bounds for radionuclide discharges and to identify physicochemical conditions where more rigorous theoretical transport calculations must be done. An approximate model is given for bounding discharges of radionuclides in porous rock in scenarios where radioactive production is negligible but decay is appreciable, and several nuclides of an element migrate and undergo a speciation reaction. The model is incorporated into a methodology to determine critical combinations of hydrological and chemical parameter values that result in discharges that violate the HLW standard proposed by the U.S. Environmental Protection Agency (40CFR191). As an example, the methodology is applied to the discharges of ^{243}Am and ^{237}Np from a reference repository. It also is shown how results from the sensitivity analyses can be used to develop criteria for designing laboratory experiments so that effects of significant speciation reactions will be detected. Three approximate methods for calculating radionuclide discharge are evaluated for extending these analyses to transport in fractured rock where diffusion of radionuclides into the matrix may occur. These are (1) a porous medium approximation, (2) a linear driving-force approximation, and (3) a semi-infinite-medium approximation. Criteria for application of each method are derived from a general consideration of fluid residence times in the fractures and relaxation times for radionuclide concentration gradients in the matrix. In addition, the applicability of each method to performance assessment for repositories in granite and tuff is shown using media-specific hydrological and geochemical data.

*This work was supported by the United States Nuclear Regulatory Commission for the Office of Nuclear Material Safety and Safeguards and performed at Sandia National Laboratories which is operated by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

A-1756
1646.010
March 1985

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)	.8	8.2
II.	Direct Loaded Labor Costs	8.0	81.0
	Materials and Services	0.0	3.0
	ADP Support (computer)	0.0	1.0
	Subcontracts	5.0	61.0
	Travel	0.0	4.0
	Other	0.0	0.0
	TOTAL COSTS	13.0	150.0

Other = rounding approximation by computer

III. Funding Status

Prior FY Carryover	FY85 Projected Funding Level	FY85 Funds Received to Date	FY85 Funding Balance Needed
67.6K	302.60K	235K	None