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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 December 1984.

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

Sincerely,

Malcolm

Malcolm D. Siegel
Waste Management Systems
Division 6431

MDS:6431:jm

Enclosure

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A-1756 PDR

1783

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: 267.6K

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 DECEMBER 1984

Task I Uncertainty in Integrated Radionuclide Discharge

Subtask IA. Speciation Effects
(M. Siegel, A. Trujillo, S. Phillips)

A meeting was held with staff of the Computing Division of Lawrence Berkeley Laboratories to review the status of the thermochemical data base. Details of this meeting are given in the trip report appended to this monthly report. Compilation of hydrogeological data for the systems calculations for bedded and dome salts was initiated this month.

Subtask IB. Equilibrium Sorption Effects
(M. Siegel, A. Trujillo)

Compilation of an initial sorption data base for tuff was completed this month using the dBase III system. A description of the variables and examples of the data format will be included in the first quarterly progress report for FY85.

Subtask 1D. Dynamic Effects
(M. Siegel, J. Leckie, K. Erickson)

A solution for the convective-dispersion-reaction equation for a system of multiple reacting species with radioactive decay and production was obtained. The solution yielded an expression for an effective retardation factor for a system of multiple rapid, reversible speciation reactions.

An initial evaluation of the applicability of the coupled speciation-transport code TRANQL to problems of interest in HLW management was completed. It was concluded that it is not feasible to make calculations over the required time (10,000 yr) and distance (10 km) with the current version of TRANQL on the Stanford University computers (DEC 20, VAX 11/750). Details of the evaluation will be provided in the first FY85 quarterly progress report.

A benchmarking calculation will be carried out at SNLA to determine if the calculations are more feasible on Sandia's CRAY computer. In the future, Stanford staff will suggest improvements to TRANQL to increase its efficiency.

A meeting was held at Stanford University to discuss the above topics on December 20, 1984 and is described in more detail in the attached trip report.

Task II Evaluation of Error Due to Organics and Colloids

No activity in December 1984.

Task IV Short Term Technical Assistance

No activity in December 1984.

Trips

Malcolm Siegel (6431) and Ken Erickson (1512) attended meetings with members of the Computing Division of Lawrence Berkeley Laboratory (LBL) and the Department of Civil Engineering of Stanford University on December 20-21, 1984, in Berkeley and Stanford, California, respectively. These two subcontractors are assisting Sandia Labs in two tasks of the Geochemical Sensitivity Analysis project: 1) compilation of a computerized up-to-date thermochemical data base and 2) comparison of values of integrated radionuclide discharge calculated by the simple geochemical algorithms used in the SNLA performance assessment methodology with values calculated with more complex coupled speciation-transport codes. Details of the discussions are included in the appended trip report.

Funding Breakdown for November

Task I - 100%

A-1756
1646.010
December 1984

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

	Month	Current Year-to-Date
I. Direct Manpower (man-months of charged effort)	1.2	5.0
II. Direct Loaded Labor Costs	9.0	50.0
Materials and Services	1.0	3.0
ADP Support (computer)	0.0	1.0
Subcontracts	7.0	38.0
Travel	0.0	3.0
Other	1.0	-2.0
TOTAL COSTS	18.0	93.0

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*	267.6K	200K	None

*Includes 40K of committed funds (purchases) that have not been invoiced.

Attachment 1

TRIP REPORT FOR PROJECT REVIEW MEETINGS FOR GEOCHEMICAL SENSITIVITY ANALYSIS

Stanford University

December 20, 1984

Lawrence Berkeley Laboratory

December 21, 1984

FIN A-1756

Malcolm Siegel

January 7, 1985

Sandia National Laboratories
Waste Management Systems Division
Albuquerque, NM 87185

MEETING WITH STANFORD UNIVERSITY SUBCONTRACTORS

December 20, 1984; Stanford University

Participants

M. D. Siegel (SNLA)
K. L. Erickson (SNLA)
J. O. Leckie (Stanford)
V. Tripathi (Stanford)
D. Kent (Stanford)

Summary

Two major topics were discussed at this meeting: 1. evaluation of the feasibility of using the coupled speciation/transport code TRANQL in sensitivity studies or performance assessment calculations and 2. compilation of sorption ratios, site-binding constants, and site density data of natural materials for use in theoretical calculations of radionuclide/solid substrate interactions.

1. Evaluation of TRANQL

Computations with TRANQL were carried out on Stanford's Dec 20 and VAX 11/750 computers. It was concluded that it is not feasible to use the current version of TRANQL on these computers to carry out chemical transport simulations over the time (10,000 yr) and distances (10 km) required for HLW repository risk assessment calculations. Two studies were described: 1. evaluation of TRANQL run-time as a function of simulation time and mean flow (interstitial velocity) and 2. evaluation of the effect of chemical complexity on the run-time of MINEQL (the geochemical equilibrium model in TRANQL). Calculations carried out in support of the first evaluation showed that TRANQL was very slow and that many months of CPU time would be required for 10,000 year simulations for most realistic flow velocities. For example, for a mean flow velocity of 0.08 cm/day over 5 minutes of CPU was required on the DEC 20 for a 1 week simulation. A 1 year simulation on the VAX 11/750 would require over 11 hours of CPU time. These calculations were for very simple geochemical and hydrological systems where no precipitation, dissolution, or changes in pH were allowed. A one-dimensional version of TRANQL was used and was represented by 45 finite elements and 92 nodes. The Stanford staff suggested that calculations for geochemically realistic 3-D systems will be nearly infeasible or extremely expensive even for the fastest available computers such as CRAY.

Nearly 88-98% of the CPU time spent in the simulations was used in MICRQL, the chemical equilibrium calculation module of TRANQL (see Fig. 1). The effect of chemical complexity on the run-time of MINEQL (the superset of MICRQL) was evaluated by comparing calculations on the DEC 20 for a simple geochemical system (11 aqueous species) with those for a more complex, realistic system (183 aqueous species, 73 possible solids). A single calculation when pH and speciation were calculated required 2 seconds of CPU time for the simple system and 50 seconds of CPU time for the more complex problem. This suggests that for the complex system, 1.25 hours of CPU time would be required per time step for the 45 element/92 node grid modeled in the TRANQL calculations described above.

The Stanford staff suggested that improvements to the efficiency of MINEQL/MICROQL would be the key step in reducing the execution time of TRANQL. The degree of improved efficiency cannot be estimated a priori; however, an improvement of 1 to 2 orders of magnitude is not unreasonable.

The relative speeds of the CRAY, DEC 20 and VAX 11/750 computers are not well known. A short (47 lines) benchmarking code was written at Stanford to compare the speeds that these computers carry out the most time-consuming part of MINEQL. This code will be run on the SNLA CRAY and the run-time will be compared to that of the Stanford computers. A report describing the calculations carried out at Stanford will be included in the forthcoming quarterly progress report.

2. Data Base of Sorption Data

The compilation of a data base of thermochemical data for use in MINEQL and TRANQL was also discussed. The Stanford staff have completed their review of available literature and have contacted researchers in the field of surface chemistry to obtain unpublished reports. The planned data base will include general reaction stoichiometries, site binding constants and descriptions of experimental conditions for each study that is considered to be acceptable. The criteria for data selection will be described in detail and should provide guidance to the NRC and SNLA in future critical evaluations of sorption data. A version of the data base will be formatted for use in MINEQL and will be compatible with the data base being developed at Lawrence Berkeley Laboratory for Sandia Labs.

The final topic discussed at this meeting was a plan to carry out a proposed comparison of values of radionuclide discharge calculated by TRANQL and by the analytic solutions to the convective-dispersion-reaction equation developed at SNLA. The calculation will require reformulation of expressions for retardation factors in terms of equilibrium constants for sorption reactions. The results of the calculation should allow formulation of more defensible expressions for radionuclide retardation factors in performance assessment calculations and provide a more accurate estimate of uncertainties in model calculations of radionuclide discharges.

MEETING WITH S. PHILLIPS OF LAWRENCE BERKELEY LABORATORY

December 21, 1984; Lawrence Berkeley Laboratory

Summary

S Phillips of the Computing Division of Lawrence Berkeley Laboratory (LBL) is assisting SNLA in the compilation of a critically-reviewed, state-of-the-art data base of thermochemical properties of actinides and fission products. At this meeting, a demonstration of the capabilities of the computer software associated with the data base was given. The data base currently resides on the central LBL VAX computer on the DATATRIEVE data management system. Several data formats are currently available. For example, the user may ask for a particular element (see Table 1) or a specific reaction (see Table 2) and obtain reaction stoichiometries, values of thermochemical constants, uncertainties and sources of data. In the future, other data formats will be added to the system. These include input files in a PHREEQE-compatible format and possibly input files compatible with format requirements for the codes MINEQL and EQ3/6. It is planned to make the data accessible to any NRC-supported researcher via a telecommunications net such as MILLNET. The data base will be continually up-dated at LBL, therefore, users of the system will be assured of the best available data at all times for their calculations.

The consistency and accuracy of the data in the data base were also discussed. Dr. Phillips stressed that this data base is not merely a rote collection of data. Instead, it is a self-consistent compilation of the best values based on a critical evaluation of currently available data. Self-consistency of the data base is achieved by assigning a hierarchy to available data and calculating any missing theoretical constants from the best experimental data. The hierarchy assumed in the data base, in order of decreasing importance, is:

1. Critically-reviewed experimental data for actinides and fission products.

2. CODATA compilations (Committee on Data for Science and Technology)

3. NBS compilations (National Bureau of Standards)

4. IAEA compilations (International Atomic Energy Agency)

5. Other recognized authoritative compilations such as those by Baes and Mesmer, and by Lemire and Tremaine.

When new data that are superior to older values are published, the new values are included in the data base. All changes required to make the data base consistent with the new data are also made.

Equilibrium constants for reactions at high temperatures and salinities are calculated from the GHS data (ΔG_f°, ΔH_f°, S°) compiled for standard conditions (25°C, 1 atmos.). Salinity corrections for ionic strengths of up to 3.0 M are being made with the extended Debye-Huckel equation for activity coefficients. Pitzer-type equations should be used to calculate solubilities at ionic strengths above 3.0 M. Data for the coefficients of Pitzer-type equations, however, are sparse and are nearly non-existent for the actinides. Thus, although considerable uncertainty will result from extrapolation of the extended Debye-Huckel equation to an ionic strength of 3 molar, this approach may be the only option available at this time. In a future progress report, comparisons of values of activity coefficients calculated with the extended Debye-Huckel equation and Pitzer-type equations will be described. A suite of species which span typical chemical behaviors and for which viral coefficient data are available will be chosen for these calculations.

Table 1

****
* Aqueous *
* Solutions *
* Database *
****

URANIUM
Solids;
Aqueous Species
September 1984

PROPERTIES OF ELEMENTAL URANIUM:
Atomic Number: 92
Formula Mass: 238.0290 for U
Electronic Configuration: 5f3 6s2 6p6 6d1 7s2
Electronegativity: U++++ = 1.4; UO2++ = 1.9
Hydration Number: UO2++ = 7.35
Ionic Radius: 1.025 angstrom (U+++); 0.93 angstrom (U++++)
Selected Average for Soils:
Concentration in Natural Waters: 3.3 ug/L in sea water

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 C; I=0

Substance	¯fGo kJ mol-1	¯fHo kJ mol-1	So J mol-1 K-1	Cpo J mol-1 K-1	Ref.
U(s)	0.000	0.000	50.21	27.67	10,51
			0.13	0.0	
UO2(s)	-1031.700	-1084.900	77.03	63.60	10,18
	1.0	1.0	0.20		
alpha-U3O8(s)	-3396.700	-3574.800	282.59	238.36	10,18
	3.0	2.5	0.50		
gamma-UO3(s)	-1145.900	-1223.800	96.11	81.67	10,18
	2.0	2.0	0.40		
UO3.2H2O(s)	-1633.900	-1827.200	176.00	200.20	10,50
	2.9	2.1	8.00		
U4O9(s)	-4275.100	-4510.400	334.13	293.34	10
beta-UO2(OH)2(s)	-1394.000	-1534.700	141.80	85.79	4,9
	4.0	4.0			
UO2(OH)2.H2O(s)	-1633.400	-1825.900	178.20		12
UF6(s)	-2068.500	-2197.000	227.60	166.77	10,51
		1.7	1.30	0.2	
UF4(s)	-1823.300	-1914.200	151.67	116.02	10,51
		4.1	0.17	0.1	
UCl6(s)	- 962.000	-1092.000	285.80	175.70	10,51
		13.0	1.70	4.1	
UOCl2(s)	- 996.200	-1066.900	138.32	95.06	10,51
		2.5	0.20	0.4	
USiO4(s)	-1891.200	-1999.900	117.10	-	12
UO2CO3(s)	-1562.600	-1691.200	138.10	125.50	4,50
	2.0		8.00		
beta-UO2SO4(s)	-1685.915	-1845.100	163.17	144.90	50
(UO2)3(PO4)2(s)	-5167.000	-6008.200	406.00	357.00	4,9,12
	17.0	17.0	21.00		
(UO2)2(HPO4)2(s)	-4218.000	-4577.300	331.00	298.00	4,12
	13.0	13.0	17.00		

Table 2

****
* Aqueous *
* Solutions *
* Database *
****

URANIUM
OXIDES
rc = U46
November 1984

EQUILIBRIUM REACTION: $UO_3.2H_2O(s) + 2H^+ = UO_2^{++} + 3H_2O$

THERMOCHEMICAL PROPERTIES:

^rHo, J mol-1 : - 49890
^So, J mol-1 K-1 : - 63.37
^Cpo, J mol-1 K-1 : 30.67
Ay^z2, (kg mol-1) 1/2 :
b, kg mol-1 :
log Ko : 5.43

EQUILIBRIUM QUOTIENTS: I=ionic strength, mol kg-1

	log Q							
I/T	25 C	50 C	75 C	100 C	150 C	200 C	250 C	300 C
0.00	5.43	4.76	4.19	3.71	2.93	2.34	1.88	1.51
0.01								
0.10								
0.20								
0.50								
1.00								
2.00								
3.00								

REFERENCES: 4.

COMMENTS:

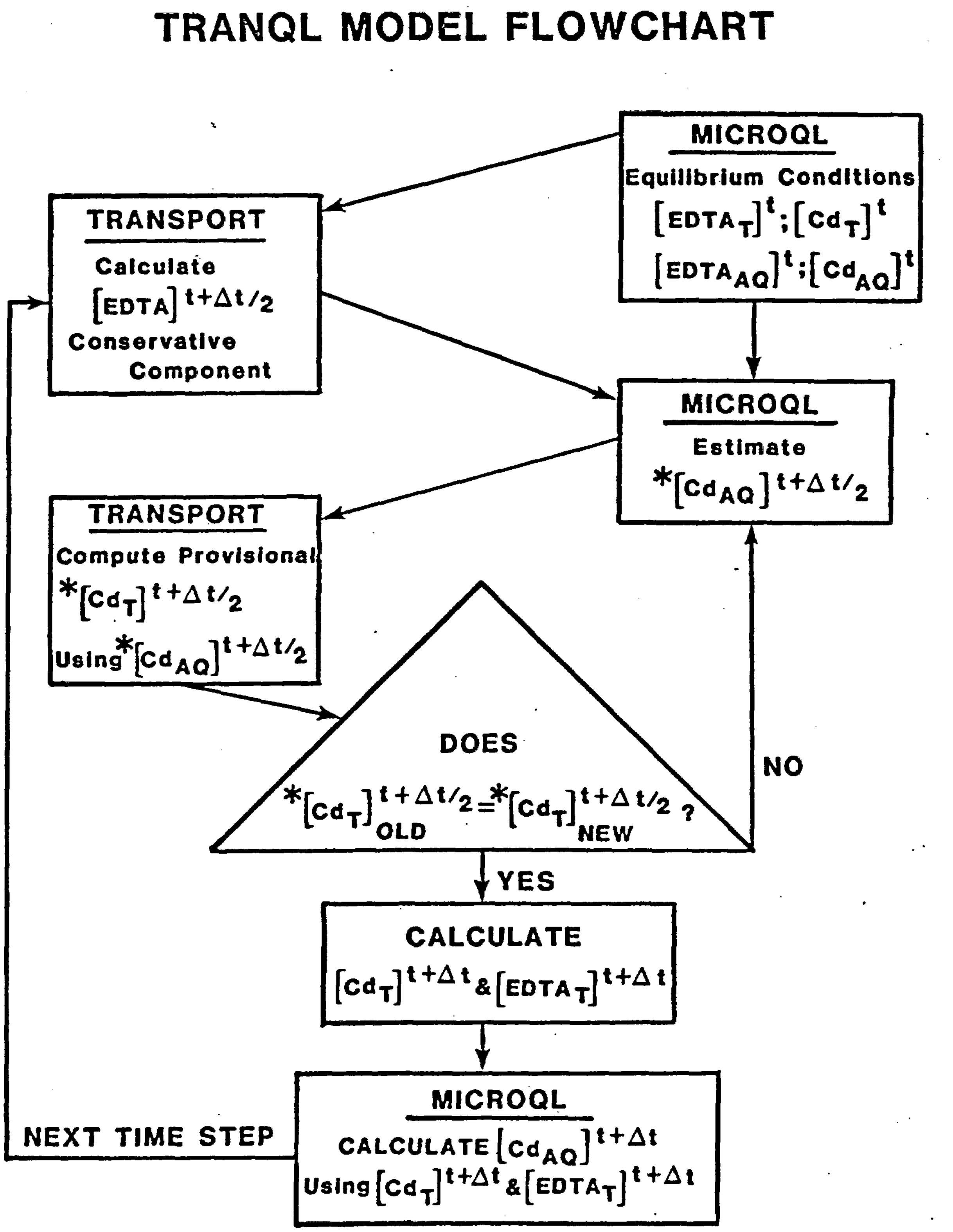

FIGURE 1. Flow Chart for the TRANQL Transport-Speciation Model Example given is for transport of Cd and EDTA.