WM-RES
WM Record File A1756
SWL

WM Project 10, 11, 16
Docket No.
PDR ✓
LPDR B, N, S

WM DOCKET CONTROL CENTER

Distribution:
Kelly w/ nurse
Still
Joanne - ticket
(Return to WM, 623-SS)

November 15, 1986

'86 DEC -1 A11:42

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 October 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

8612220142 861115
PDR WMRES EXISANL
A-1756 PDR

3552

PROGRAM: Geochemical Sensitivity Analysis FIN#: A-1756

CONTRACTOR: Sandia National Laboratories BUDGET PERIOD: 10/86 - 9/87

NMSS PROGRAM MANAGER: W. Kelly BUDGET AMOUNT: 200K

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 OCTOBER 1986

Task I. Uncertainty in Integrated Radionuclide Discharge

Subtask 1A. Conceptual Models for Repository Sites.

Work needed to link the codes LHS, GENMIX and CCDPLT continued during October. GENMIX is the latest version of the NWFT/DVM code that has passed the QA program at SNLA. CCDPLT is an updated version of earlier codes used to calculate integrated radionuclide discharges and plot CCDF curves for comparison with the EPA standard.
The conceptual model of the basalt site was updated using information obtained from another SNLA/NRC project, A-1757: Technical Assistance in Numerical Modeling.

Subtask 1B. Solubility/Speciation Effects.

A procedure which allows users of the Aqueous Solutions Database to calculate log K values from basic thermodynamic data has been added to the DATATRIEVE system at Lawrence Berkeley Laboratory. The user can define any reaction based on tabulated GHS data and obtain a log K value with uncertainty values computed using sum of squares. The

implementation of this feature is the first step in the design of interfaces between the ASD and geochemical codes.
The list of KEY VALUES that will be used as basis species in speciation codes has been updated and is appended as Attachment 1.
Data for clays, zeolites and evaporite minerals have also been updated and added to the data base.

Subtask 1C. Sorption Effects.

Preliminary theoretical calculations designed to illustrate potential variations in the sorptive behavior of uranium in typical basalt ground waters have been completed. Future calculations will investigate the behavior of uranium and selenium in the presence of organics and changing redox state respectively.

Task 4. Short Term Technical Assistance.

A description of Quality Assurance procedures used in this project has been prepared at the request of the NRC program manager and is appended as Attachment 2 to this monthly report.

Task 5. Transfer of Sensitivity Analysis Tools

The ADDREACT and COMPLOGK procedures were added to the Aqueous Solutions Database during this month. The former can be used to enter new reactions into the ASD. ADDREACT automatically assigns a unique reaction number and merges thermodynamic data from the existing data base with the reactant and product information. The COMPLOGK procedure can be used to calculate equilibrium constants and uncertainty values from the free energies and associated uncertainties of substances in the ASD. The uncertainties in the log K values are calculated by propagation of error using the sum of squares technique.

Trips

M. Siegel met with research staff from Lawrence Berkeley Laboratory to discuss progress on development of interfaces between the Aqueous Solutions Database, geochemical speciation codes such as PHREEQE , and the sensitivity/uncertainty codes developed at SNLA.

OTHER ACTIVITIES

The writing of the annual report for FY86 was started during this month. Completion of the report has been postponed due to the delay in receipt of FY87 funds. Cessation of work on the report was chosen rather than cancellation of existing subcontracts to preserve momentum in the project until the new funding arrives at SNLA.

Allocation of Resources

Task 1..... 75%
Task 4..... 5%
Task 5.....20%

Attachment I

Aqueous Solutions Database	Lawrence Berkeley Laboratory	KEY VALUES Master Species October 1986

Key Values for Thermodynamic Properties at 298.15 K and Zero Ionic Strength, for Crystalline (s), Gaseous (g) and Aqueous (aq) Forms. Data obtained from CODATA, National Bureau of Standards, or as Noted. All Ions are in the Aqueous (aq) Form.

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
$O_2(g)$	0.000	0.000	205.04	29.36	5552
			0.03	0.0	
$O_2(aq)$	16.530	-12.138	108.90	224.00	9777
	0.2	0.8	0.80	25.0	
$H_2(g)$	0.000	0.000	130.57	28.82	9552
			0.03		
$H_2(aq)$	17.780	-4.040	57.37	175.00	9777
	0.9	0.8	2.50	25.0	
$H_2O(g)$	-228.572	-241.814	188.72	33.58	2552
	0.1	0.0	0.04		
$H_2O(l)$	-237.129	-285.830	69.95	75.29	9552
	0.1	0.0	0.08		
e^-,electron	0.000	0.000	65.28	14.42	0066
			0.01	0.1	
$Si(OH)_4(aq)$	-1308.000	-1460.100	180.00	215.00	9993
	1.7	1.7	4.20		
H^+	0.000	0.000	0.00	0.00	5555
NH_4^+	-79.310	-133.260	111.17	69.00	9557
	0.1	0.3	0.75	4.1	
Li^+	-292.620	-278.455	11.30	68.60	9552
	0.2	0.1	0.35		
Na^+	-261.905	-240.300	58.41	46.40	9552
	0.1	0.1	0.20		
K^+	-283.270	-252.170	101.04	21.80	9552
	0.1	0.1	0.25		

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
Rb^+	-283.980	-251.120	120.46	6.70	9553
	0.2	0.1	0.40		
Cs^+	-292.020	-258.040	132.84	-10.50	9552
	0.2	0.1	0.40		
Tl^+	-32.430	5.360	125.50	4.20	2223
	0.2	1.2	4.00		
Cu^+	49.980	71.670	40.60	59.80	2223
	0.1	0.1	0.40		
Ag^+	77.107	105.750	73.38	21.80	9552
	0.1	0.1	0.40		
NpO_2^+	-915.000	-978.200	-21.00	92.00	4448
	5.4	4.6	8.00		
Hg_2^{++}	153.607	166.820	65.52		9550
	0.1	0.2	0.80		
Hg^{++}	164.700	170.160	-36.32		9550
	0.1	0.2	0.80		
Fe^{++}	-91.550	-92.730	-107.00	33.00	***3
	1.0	0.8	2.50	3.0	
Mg^{++}	-454.800	-466.850	-138.10	38.50	2223
	1.7	1.3	1.70	8.0	
Ca^{++}	-552.870	-543.100	-56.40	0.84	9553
	0.8	0.8	0.40		
Sr^{++}	-563.830	-550.900	-31.50	-20.90	***3
	0.8	0.5	2.00		
Ba^{++}	-560.740	-537.640	9.60	-34.70	1113
	0.1	0.1	0.85		
Ra^{++}	-561.500	-527.600	54.00	-69.94	2229
	10.0				
Cu^{++}	65.520	65.690	-97.10	23.40	9553
	0.1	0.8	1.20		
Pb^{++}	-23.970	0.920	17.70	-52.70	9553
	0.1	0.3	0.80		
Ni^{++}	-45.600	-54.000	-128.90	5.86	2223
	0.9	0.9	0.90		
Mn^{++}	-228.000	-220.700	-73.60	50.00	1112
	0.9	0.1	0.85	3.0	
UO_2^{++}	-952.700	-1019.200	-98.30	5.00	9558
	2.1	2.5	4.00		

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
PuO_2^{++}	-756.900	-822.200	-88.00	11.00	4448
	7.1	6.7	8.00		
Zn^{++}	-147.060	-153.390	-109.60	46.00	9552
	0.2	0.2	0.70		
Al^{+++}	-489.400	-531.000	-308.00	-119.30	111*
	1.4	1.4	15.00	10.0	
Fe^{+++}	-17.280	-50.110	-279.00	24.70	*933
	1.0	0.8	4.10	0.1	
Th^{++++}	-704.600	-769.000	-423.00	-1.00	444*
	5.4	2.5	17.00		
Pa^{++++}	-565.000	-619.700	-397.00		4440
	17.0	13.0	42.00		
F^-	-281.750	-335.350	-13.18	-122.00	9558
	0.7	0.7	0.54		
Cl^-	-131.228	-167.080	56.73	-136.40	9553
	0.1	0.1	0.16		
Br^-	-103.960	-121.500	82.84	-132.20	9557
	0.2	0.2	0.20	4.2	
I^-	-51.570	-56.900	106.70	-120.50	9557
	0.8	0.8	0.20	4.2	
OH^-	-157.244	-230.025	-10.71	-138.00	955*
	0.1	0.1	0.20	4.0	
NO_3^-	-108.740	-205.000	146.94	-86.60	2252
	0.0	0.0	0.85	0.0	
SO_4^{--}	-744.530	-909.600	18.83	-278.00	955*
	0.4	0.4	0.50		
CO_3^{--}	-527.810	-675.150	-49.96	-273.50	9777
	0.4	0.3	0.80	4.0	

Comments:

Reference 0 = no data; 1 = Robie et al.,1978; 2 = Wagman et al.,1982;
3 = Naumov et al.,1974; 4 = Fuger and Oetting,1976; 5 = CODATA,-1978;
6 = Ryabukhin, 1977,1980; 7 = L.Brewer,1981; 8 = Lemire and Tremaine,1980, and Lemire 1984
9 = This work.

For O2(aq) and H2(aq), we calculate ^fG using ^fH and S values from L.Brewer:"Thermodynamic Data for Flue-Gas Desulfurization",in"Flue Gas Desulfurization",LBL-12342, Lawrence Berkeley Laboratory (Sept.1981).

Heat capacity of O2(aq),H2(aq),NH4+ are from L.Brewer,1981.

Entropy and Cp of electron(gas) are from A.G.Ryabukhin:Russ.J.Phys.Chem. 1977, v.51, 573; and Ibid., 1980, v.54, 1197. Gibbs energy of formation

Comments:

for Hg^{++},Hg_2^{++} compare well with Hepler;Olofsson:Chem.Rev.1975, v.75,585. * Gibbs energy and enthalpy of Fe^{++} from J.W.Cobble;R.C.Murray; P.J.Turner;K.Chen: "High-Temperature Thermodynamic Data for Species in Aqueous Solution",NP-2400, San Diego State Univ.,San Diego, CA (May 1982). GHS values for Sr++ from E.Busenberg;L.N.Plummer; V.B.Parker: Geochim.Cosmochim.Acta 1984, v.48, 2021. ^fG [UO2++] was calculated here using CODATA values of ^fH and S; Cp[UO2++] is from R.J.Lemire;P.R.Tremaine: J.Chem.Eng.Data 1980, v.25, 361. $\Delta_f H[Fe^{+++},aq]$ calculated from Gibbs energy and entropy, in Cobble. values from C.M.Flynn: Chem.Rev. 1984, v.84, 31. Heat capacity of OH- is from J.A.Barbero;L.G.Hepler;K.G.McCurdy;P.R.Tremaine: Can.J.Chem. 1983, v.61, 2509. Heat capacity of SO4-- from J.W.Larson;K.G.Zeeb; L.G.Hepler: Can.J.Chem. 1982, v.60, 2141. Heat capacity of Cl- and Br- are both from L.Brewer,1981. For Cl-, S.N.L'vov;Ya.D.Rakhmilevich; I.A.Dibrov: Russ.J.Phys.Chem. 1984, v.58, 1364 find from emf measurements, S = 75.6 J/mol/K, and Cp = -61 J/mol/K.
The Gibbs energy of formation, enthalpy of formation, entropy and heat capacity for CO3-- are from L.Brewer, 1981.
Heat capacity of Al+++(aq) from J.K.Hovey;P.R.Tremaine: Geochim. Cosmochim. Acta 1986, v. 50, 453.

ATTACHMENT 2

DATE: November 10, 1986

SUBJECT: Quality Assurance/Control Procedures for FIN A-1756

TO: Walt Kelley, USNRC

FROM: M. Siegel, SNLA

Quality Assurance procedures for computer software created and maintained by Sandia that will be transferred to the NRC are described in NUREG/CR-4369 (Quality Assurance Plan for Computer Software Supporting the U. S. Nuclear Regulatory Commission's High-Level Waste Management Program). In general, reports to the NRC and published papers use computer codes that conform to this QA plan. Thus for example, the versions of LHS, EPACDF and GENMIX used in the calculations carried out under Subtask 1A are the QA versions maintained by SNLA. It is unclear if available resources will allow the application of the QA program to research codes such as TRANQL, MINEQL, and PHRQPITZ; however, the NRC will be informed of the status of these codes at the close of the project.
Reports that will be published as SAND, NUREG reports or in the open literature are reviewed for technical content by two staff members and by management. Appendix 1 in NUREG/CR-4369 contains a sample of the review sheet used for technical review. The other quality control/assurance procedures for each subtask in FIN A1756 are described below.

Subtask 1A. Conceptual Models for Repository Sites.

The data used in support of the model calculations are all taken from published documents that have undergone some sort of peer review. The codes used in the calculations conform to the QA program outlined in NUREG/CR-4369.

Subtask 1B. Speciation Effects.

The Aqueous Solution Database is being used as the source of thermochemical data for this task. The QA/QC procedures for the ASD are being developed jointly by SNLA, LBL and the NRC. Procedures to ensure the internal consistency of the data have been described in previous annual and monthly progress reports. A technical peer review committee composed of recognized experts has been formed to review the content of the data base. Portions of the data base are sent out for review by other experts. A record is maintained of all comments and changes to the data that result from the review process. The data base incorporates recent critical compilations for many elements. In only a few cases has original experimental data been re-evaluated. Ground-water compositions used in speciation calculations are taken from DOE reports and the reliability of these data is limited by the DOE QA/QC procedures.

Subtask 1C. Sorption Effects.

Thermochemical data are obtained from the ASD and from recent critical evaluations carried out by researchers at Stanford University. A topical report containing the data has been reviewed at Stanford and is currently under review at SNLA.
Available empirical sorption data (sorption isotherm and Kd values) for ground waters and rocks from the BWIP and NTS sites have been compiled in a dBASE III+ data management system. The data are checked several times after being entered. The FORMAT and REPORT features of the dBASE system are used to print hard copies of the data in the data base in the same format that appears in the original reports. A QA notebook is maintained which contains photocopies of the original tables of data and the tables produced from the dBASE system.

Subtask 1D. Kinetic Effects.

A computer program, written to carry out calculations published in several peer-reviewed proceedings, conforms to QA procedures which preceeded the current QA program. The input values, equations and results of all calculations used in support of the publications are kept in a QA notebook.

Subtask 1E. Dynamic Effects.

Same as Subtask 1C.

A-1756
1646.010
October 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)	0.6	0.6
II. Direct Loaded Labor Costs	6	6
Materials and Services	10	10
ADP Support (computer)	0	0
Subcontracts	32	32
Travel	0	0
Other (computer roundoff)	0	0
TOTAL COSTS	48	48

III. Funding Status

Prior FY Carryover	FY 87 Projected Funding Level	FY 87 Funds Received to Date	FY 87 Funding Balance Needed
32K *	232K	0K	200K

* Represents unpaid invoices for work carried out in FY86.