September 15, 1986

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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 August 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

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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 transferred to the NRC under Task V.

ACTIVITIES DURING AUGUST 1986

Task I. Uncertainty in Integrated Radionuclide Discharge

Subtask 1A. Conceptual Models for Repository Sites.

Work on formulation of a conceptual model for a basalt site continued during August. The review and synthesis of ground-water composition data was completed. The sorption data obtained from a review of the open literature as well as ORNL, RHO, and PNL reports was entered into the dBASE III Plus data base. Additional features were added to the user-friendly menus which will simplify searches of the data and statistical and graphical processing of desired subsets of the data base. The data are currently being sorted and subsetted to define ranges of sorption ratios to be used in the parametric calculations for the basalt site. Sorption data tables which match the format of the original reports used as source for the data were generated as part of our QA/QC procedure.

A sequence of computer codes will be used to carry out the scoping calculations of integrated radionuclide discharges. These include the Latin Hypercube Sample (LHS) program to produce sets of input data for replicate simulations, the Network Flow and Transport code (NEFTRAN,

formerly NWFT/DVM) to calculate radionuclide discharges, and the TINTDIS program to calculate integrated dicharges both in curies and relative to the EPA cumulative release limits. The results will be presented as Complementary Cumulative Distribution Functions (CCDF). Sensitivity analysis will be carried out with the Partial Correlation Coefficient/Standardized Regression Coefficient programs. During August, the work required to link these codes was initiated.

Subtask 1B. Solubility/Speciation Effects.

A semi-annual progress report summarizing modifications to the Aqueous Solutions Database developed at Lawrence Berkeley Laboratory in support of this project was received during August. Important activities include improved documentation of sources of thermochemical data and additional critical evaluation of the internal consistency and validation of data for Sr, Se, Si, Pd, Al, and C. Copies of tables of thermochemical data for these elements are attached to this monthly report as Attachment 1.

Work was initiated on the compilation of the best available data for parameters (Pitzer and extended Debye Huckel equations) to calculate equilibrium concentrations of solute species in brines that might be expected at the proposed Deaf Smith repository site. The computer code PHRQPITZ will be used for these calculations.

Work on statistical pre- and post-processors for the ASD continued during August at LBL and SNLA. A BASIC version of LHS, the Monte Carlo Sampling program was written for an IBM PC to allow efficient investigation of the propagation of uncertainty in small systems of stoichiometric reaction equations. An abstract describing this work (see Attachment 2) was submitted to the International Conference on Thermodynamics of Aqueous Systems With Industrial Applications.

Task 1C. Sorption Effects.

As described under Task 1A above, available sorption data for the BWIP site have been compiled in a dBASE III Plus data base.

Subtask 1E. Coupled/Dynamic Effects

Evaluation of the computer code TRANQL continued during August. The stability of the solution techniques with respect to the criteria of Meyers (velocity and time and distance steps) and Courant (velocity, dispersivity, time and distance steps) was evaluated. In addition, the ability of the code to model large changes in solute concentration was examined. These calculations are needed to determine if the code can be used to model scenarios of interest to HLW management. A report summarizing the evaluations carried out at SNLA and Stanford University is in preparation.

Allocation of Resources

Task 1.....100%

Attachment 1

Aqueous Solutions Database	Lawrence Berkeley Laboratory	SILICON Critically Evaluated August 1986

PROPERTIES OF ELEMENTAL SILICON:

Atomic Number: 14
Formula Mass: 28.0855
Electronic Configuration: 3s2 3p2
Electronegativity: 1.8
Hydration Number:
Ionic Radius: 1.17 angstrom covalent
Selected Average for Soils: 320,000 mg/kg
Concentration in Natural Waters: 11-92 mg/L in tuff, basalt, granite waters

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 °C; I=0

Substance	$\Delta_f G°$	$\Delta_f H°$	$S°$	$Cp°$	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
SiO_2(s),α-quartz	-856.288	-910.700	41.46	44.59	1111
	1.1	1.0	0.20		
SiO_2(s),cristobalite	-854.512	-908.346	43.40	44.18	1111
	2.1	2.0	0.13		
SiO_2(s),tridyamite	-853.812	-907.488	43.93	44.60	1111
	2.4	2.4	0.42		
SiO_2(s),stishovite	-802.827	-861.318	27.78	42.97	1111
	2.1	2.1	0.42		
SiO_2(am)	-850.700	-903.490	46.90	44.40	3333
SiO_2(s),silica glass	-850.559	-903.200	47.40	37.94	1111
	2.1	2.1	0.21		
SiO_2(s),coesite	-850.850	-905.584	40.38	45.40	1111
	2.1	2.1	0.42		
SiO_2(soil)	-851.438				*000
H_2SiO_3(aq)	-1079.400	-1182.800	109.00		3330
$Si(OH)_4$(aq)	-1316.600	-1468.600	180.00	215.00	3332
	1.7	1.7	4.20		
$SiO(OH)_3^-$	-1260.600	-1443.000	120.80	51.10	5555
	1.7	1.7	4.00	11.0	
$SiO_2(OH)_2^{--}$	-1187.000	-1420.000	-48.90	-280.30	2992
SiO_4^{----}	-1027.200	-1370.000	-459.00	-500.00	2999

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
$Si_4O_6(OH)_6^{--}$	-4207.447				4000
$Si_4O_8(OH)_4^{----}$	-4081.820				4000
NaAlSiO4(s),nepheline	-1977.498	-2092.110	124.35	115.81	1111
	2.5	2.4	1.30		
NaAlSi2O6.H2O(s),analcime	-3091.730	-3309.840	234.43		1110
	3.7	3.6	2.50		
NaAlSi3O8(s),low albite	-3711.723	-3935.120	207.40	205.10	1111
	3.4	3.4	0.40		
KAlSiO3O8(s),microcline	-3742.330	-3967.690	214.20	202.40	1111
	3.4	3.4	0.44		
CaAl2Si4O12.4H2O(s),laumonite	-6657.200				6000
	8.7				
CaAl2Si4O12.2H2O,wairakite	-6183.100				6000
	8.0				
CaAl2Si10O24.8H2O,clinop.	-12743.600				6000
	13.0				
MgAl2Si10O24.8H2O,clinop.	-12654.500				6000
	13.2				
Na2Al2Si10O24.8H2O,clinop.	-12720.200				6000
	15.8				
K2Al2Si10O24.8H2O,clinop.	-12827.300				6000
	12.9				
CaAl2Si7O18.6H2O,heulandite	-9700.200				6000
	11.6				
NaAlSi5O12.3H2O,mordenite	-6122.000				6000
	6.6				
KAlSi5O12.3H2O,mordenite	-6176.400				6000
	5.1				

Comments:

Reference 1 is Robie et al.,1978; 2=Naumov et al.,1974;3=Wagman et al.,1982; 5=R.H.Busey;R.E.Mesmer: Inorg.Chem. 1977, v.16, 2444; Data for SiO2,soil is from W.L.Lindsay: "Chemical Equilibria in Soils", John Wiley & Sons,Inc. New York (1979). Reference 6 is J.F.Kerrisk:"Free Energy of Formation of Some Minerals in Nevada Tuff",LA-9225-PR, Los Alamos National Laboratory Los Alamos, NM 87545 (April 1982),p.75. Note that clinop. is abbreviation for clinoptilolite.

Note Si(OH)4(aq) = H2SiO3(aq) + H2O, when calculating property values. Values for ^fH and S of SiO2(OH)2-- and SiO4---- calculated here to be consistent with data for Si(OH)4(aq) from the NBS Tables; and for

Comments:

SiO(OH)3- from Ref. 5. Heat capacity of the ionization forms of Si(OH)4(aq) calculated assuming a linear change with loss of H+. Uncertainties for zeolites calculated from average deviation of values given in Kerrisk, Table A-XI.

Reference 4 is Baes and Mesmer: "The Hydrolysis of Cations" (1976).

PROPERTIES OF ELEMENTAL STRONTIUM:

Atomic Number: 38
Formula Mass: 87.62
Electronic Configuration: 5s2
Electronegativity: 1.0
Hydration Number:
Ionic Radius: 1.27 angstrom (Sr++)
Selected Average for Soils: 200 mg/kg
Concentration in Natural Waters: 5-15 mg/L in brines; 0.05 mg/L (Tuff)

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 °C; I=0

Substance	$\Delta_f G°$	$\Delta_f H°$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
α-Sr(s)	0.000	0.000	55.70	26.40	0012
			0.21		
SrO(s)	-559.960	-590.600	55.44	45.02	1112
	1.0	0.9	0.50		
$Sr(OH)_2$(s)	-882.175	-968.889	97.07	74.90	5555
		9.2	8.40		
SrF_2(s)	-1164.800	-1216.300	82.13	70.00	2222
α-$SrCl_2$(s)	-785.000	-833.850	114.85	75.60	1112
	0.8	1.0	0.42		
$SrCl_2$(aq)	-826.321	-885.060	81.70		9110
	1.0	1.0	0.50		
$SrSO_4$(s),celestite	-1340.700	-1453.100	118.00	100.00	4444
	4.0	4.2	4.20		
$SrSO_4$(aq)	-1320.300	-1449.970	60.90		9990
	5.0				
$SrCO_3$(s),strontianite	-1144.730	-1225.770	97.20	81.42	1113
	1.0	1.0	1.70		
$SrCO_3$(aq)	-1107.820	-1204.300	45.40		1110
	1.0	1.0	4.20		
SrSe(s)		-385.800			0200
$SrSeO_3$(s)	-969.400	-1047.700			3200
	4.0				

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
$SrSeO_4(s)$	-1039.100	-1156.210	112.90		3330
	7.0	6.3			
$SrSiO_3(s)$	-1561.640	-1645.980	96.70	88.53	3333
			0.84		
$Sr_2SiO_4(s)$	-2215.090	-2328.980	153.10	134.26	3333
		2.1	1.30		
Sr^{++}	-563.830	-550.900	-31.50	-20.90	1113
	0.8	0.5	2.00		
$SrOH^+$	-726.040	-775.900	-8.74		9990
	0.8	4.2			
SrF^+	-851.500				9000
	0.8				
$SrHCO_3{}^+$	-1157.520	-1215.560	174.40		1110
	1.0	1.0	4.20		
$Sr(HCO_3)_2(aq)$		-1928.000			0900

Comments:

Heat capacity of $SrSO_4(s)$ calculated from trends in other divalent metal sulfates, e.g. Ca,Sr,Ba,Ra. Values for Sr(s), Sr^{++}, $SrCl_2(s)$ selected from E.Busenberg;L.N.Plummer;V.B.Parker: Geochim.Cosmochim.Acta 1984, v.48, 2021.

Reference 1= E.Busenberg;L.Niel Plummer;V.B.Parker:Geochim.Cosmochim.Acta 1984,v.48,2021.

Reference 2=Wagman et al.,1982; 3=Naumov et al.,1974;4=Robie et al.,1978; 5 = JANAF Tables; 9 = This work.

^fGo[SrCl2,aq] recalculated to -826.21 for consistency with H-TS. Ref. 1 recommends -826.33 for ^fGo[SrCl2,aq]. NBS Tables [2] for SrSO4(aq) give inconsistent ^rG = ^rH - 298.15 ^rS; also, logK calculated from ref. [2] data is -0.76 for reaction Sr++ + SO4--= SrSO4(aq), in disagreement with range 2.1 - 2.55 given in Smith and Martell; and Millero and Schreiber: Am.J.Sci. 1982, v.282, 1508.

PROPERTIES OF ELEMENTAL OXYGEN:

Atomic Number: 8
Formula Mass: 15.9994 for 0
Electronic Configuration: 1s2 2s2 2p4
Electronegativity: 3.5
Hydration Number: 6.1 for OH-
Ionic Radius:
Selected Average for Soils: 490,000 mg/kg
Concentration in Natural Waters:

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 °C; I=0

Substance	$\Delta_f G°$	$\Delta_f H°$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
O_2(g)	0.000	0.000	205.04	29.36	5551
			0.03		
O_2(aq)	16.530	-12.138	108.90	224.00	9***
	0.2	0.2	0.80	25.0	
H_2O(g)	-228.572	-241.814	188.72	33.58	1551
	0.1	0.0	0.04		
H_2O(l)	-237.129	-285.830	69.95	75.29	1551
	0.1	0.1	0.08		
OH^-	-157.244	-230.025	-10.71	-138.00	155*
	0.1	0.0	0.20	4.0	
OH(aq),radical	13.900	-4.990	64.80		***0
		2.5	8.00		
O^-(aq)	81.600	37.400	-16.60	-116.40	****
		8.3	17.00	2.5	
O_2^-(aq)		-53.400	41.60		0**0
		8.3	33.00		
O_3^-(aq)	48.900				*000

Comments:

Reference 1 = Wagman et al.,1982; 5 = CODATA, 1976. Data for O_2(aq) are from L.Brewer, 1981. O2(g)/O2(aq) equilibrium data published by N.E.Khomutov;A.Sh.Groisman: Russ.J.Phys.Chem. 1984, v.58, 1078. ^fG for .OH(aq), O-(aq) and O3-(aq) from W.H.Koppenol;J.F.Liebman:

Comments:

J.Phys.Chem. 1984, v.88, 99.

^fH, S and Cp data on OH(aq), O-(aq), O3-(aq), and all data for O2-(aq) are from L. Brewer, 1981.

PROPERTIES OF ELEMENTAL CARBON:

Atomic Number: 6
Formula Mass: 12.011
Electronic Configuration: 1s2 2s2 2p2
Electronegativity: 2.5
Hydration Number: 2(HCO3-); 15(CO3--)
Ionic Radius: 0.77 angstrom covalent radius
Selected Average for Soils: 20,000 mg/kg
Concentration in Natural Waters: < 10 mg/L CO2 (surface waters);

THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 °C; I=0

Substance	$\Delta_f G°$	$\Delta_f H°$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1} K^{-1}		
CO_2(g)	-394.359	-393.510	213.68	37.11	2552
	0.1	0.1	0.04		
CO_2(aq)	-385.980	-413.800	117.60	212.00	222*
	0.2	0.2	0.90	17.0	
CS_2(g)	67.120	116.970	237.85	45.66	2***
CS_2(l)	65.270	89.700	151.34	75.70	2222
CSe_2(l)		164.800	165.30	88.70	02**
CH_4(aq)	-34.330	-89.040	83.70		2220
CH_4(g),methane	-50.720	-74.810	186.26	35.31	2222
CH_2N_2(g),diazirine			238.05	42.63	0022
CH_2N_2(g),diazomethane			242.87	52.51	0022
NH_2CN(s),cyanamide		59.000			0200
$(CH_3)_2S$(g)	7.300	-37.240	285.96	74.10	2222
$(CH_3)_2S_2$(g)	15.300	-23.600	336.75	94.31	2222
$(CH_3)_2SO_2$(g)	-272.700	-371.100	310.60	100.00	2222
CH_3SH(g)	-9.300	-22.340	255.17	50.25	2222
$CaHCO_3^+$	-1241.100		67.40	173.30	****
	1.0				
$MgHCO_3^+$	-1219.900	-1155.600	-110.00	160.80	****
$CaCO_3$(aq)	-1081.390	-1219.970	-110.00		***0
$MgCO_3$(aq)	-1002.500				*000

Substance	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S°	Cp°	Ref.
	kJ mol^{-1}		J mol^{-1}K^{-1}		
C(s)(graphite)	0.000	0.000	5.74	8.53	5552
			0.12		
$C_3H_7NO_2S$,L-cysteine	-344.176		169.90	162.30	*0**.
	2.0	2.0			
$C_3H_6NO_2S^-$	-325.970				*000
$CS(NH_2)_2$(s),thiourea		-88.300			0200
$CO(NH_2)_2$(s),urea	-197.300	-333.510	104.60	93.14	2222
$CSe(NH_2)_2$(s),selenourea		-63.800			0900
		10.0			
CO_3^{--}	-527.810	-675.150	-49.96	-273.50	****
	0.4	0.3	0.80	4.0	
HCO_3^-	-586.770	-689.860	98.43	-54.04	****
	0.4	0.2	0.60	4.0	
H_2CO_3(aq)	-623.080	-699.000	189.30	286.80	****
	0.4	0.2	0.60	17.0	

Comments:

Ref.1=Robie et al.,1978;2=Wagman et al.,1982;5=CODATA,1978;9=This work;0=No data. *Values for CO2(aq),HCO3-,CO3-- and H_2CO_3(aq) selected from L.Brewer:"Thermodynamic Data for Flue-Gas Desulfurization Processes",in,"Flue Gas Desulfurization",LBL-12342,Lawrence Berkeley Laboratory,p.303 (Sept.1981). Recommended values published by Larson et al.: Can.J.Chem. 1982,v.60,2141, and Barbero et al.: Can.J.Chem. 1983,v.61,2509 were also considered. C_p and S data for both CSe_2(l) and L-Cysteine are from Domalski et al.: J.Phys. Chem.Ref.Data 1984,v.23,Suppl.1. ^fG and S for L-cysteine(s) from Huffman and Ellis: J.Am.Chem.Soc. 1935,v.57,46 (Chem.Abstr.) Enthalpy of diazomethane calculated using Gibbs energy of reaction and enthalpy of following reaction:

$CSe(NH_2)_2(s) + H_2O(l) = H_2Se(g) + NH_2CN(s)$

where logK=-27.70,enthalpy = 351.04 kJmol as measured by Ostrovskaya et al.:Russ.J.Phys.Chem. 1976,v.50,956. Enthalpy of selenourea calculated using correlation between electronegativity of O^{--},S^{--} and Se^{--} with heats of formation of urea, thiourea,see A.F.Clifford: J.Phys.Chem. 1959,v.63,1227.

^fG of C3H6NO2S- calculated from ionization of l-cysteine measured by C.L.Sharma;S.S.Narvi:Thermochim.Acta 1985,v.90,1. We extrapolated their data to zero ionic strength using extended Debye-Huckel equation.

Attachment 2

DEVELOPMENT OF AN INTEGRATED GEOCHEMICAL DATA BASE FOR MODELING AND SENSITIVITY ANALYSIS IN NUCLEAR WASTE REPOSITORY PERFORMANCE ASSESSMENT STUDIES. S. L. Phillips and F. Hale, Lawrence Berkeley Laboratory, Berkeley, CA 94720; and M. D. Siegel, Sandia National Laboratories, Albuquerque, NM 87185. (SAND86-1342A)

The Aqueous Solutions Database is being developed as a national resource of high-quality, documented and critically-evaluated thermodynamic data. In this paper the contents, scope and quality assurance procedures employed in data evaluation will be described. When completed, the data base will contain thermodynamic property and process values for aqueous species, simple oxides and minerals important to understanding the migration of radionuclides in ground waters at HLW and LLW disposal sites. Pre- and post-processors are being written to generate files of stability constants that can be used by the PHREEQE geochemical speciation computer code and to carry out sensitivity/uncertainty analysis with the Latin Hypercube and Partial Correlation Coefficient/Standardized Regression Coefficients programs. The complete integrated data base system will be used to 1) estimate the overall uncertainty in radionuclide concentration and speciation due to the collective uncertainties in thermochemical data and ground-water composition at potential sites and 2) identify key variables which dominate the overall uncertainty of the calculated results. Potential uses of the integrated data base system will be illustrated with examples relevant to HLW and LLW disposal.

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