Sandia National Laboratories

Albuquerque, New Mexico 87185

May 15, 1985

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 April 1985.

A review of the letter report "Geochemical Sensitivity Analysis I. Radioelement Speciation" and a letter report containing recommendations on geochemical modeling were received in early May. We appreciate the comments by the Oak Ridge staff and will clarify those sections that led to any confusion. Although we recognize the limitations associated with calculations of radioelement speciation using available thermochemical data, we do not agree with the recommendations suggested by Jacobs. We do not feel they reflect the needs or methods of performance assessment or sensitivity analyses. Our response to these comments and recommendations will be sent to the NRC under a separate cover to prevent delay of the April progress report.
Please feel free to contact me if you have any questions or comments.

Sincerely,

R. M. Cranwell
Supervisor
Waste Management Systems
Division 6431

RMC:6431:jm

Enclosure

2075

Copy to:
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PROGRAM: Geochemical Sensitivity   FIN#:   A-1756
             Analysis

CONTRACTOR: Sandia National   BUDGET PERIOD: 10/01/84 -
             Laboratories   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 APRIL 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 continued this month.   A preliminary
list of hydrological variables that will be included in the
data base is shown in Table 1.   The data are being compiled
from BWIP reports (eg. SD-BWI-DP-035) and will be used for
scoping calculations of radionuclide discharge in Subtask IA
and for examination of rock properties important in sorption
and diffusion processes (eg. porosity, surface area/volume,
tortuosity etc.) in Subtasks 1B, 1C and 1D.

A meeting was held with Dr. S. Phillips of Lawrence Berkeley
Laboratory during April to review progress on the compilation
of thermochemical data for solids and aqueous species important
in high-level waste.   The major topic of discussion was the
revisions to the existing data base that has been published in

two reports, LBL-14966 (for BES) and LBID-977 (for NRC). An updated data base will be released during the first quarter of FY86 and will contain data compiled under both the Basic Energy Sciences (BES) and NRC (SNLA) contracts that support Dr. Phillips' work. This forthcoming publication will differ from the previous reports in several ways:

1. A new reference format will allow clear identification of the source of each datum. (See Attachment 1).

2. Extensive documentation in the "Comments" field of each table that will include the following types of information:

   a. The identity of technical reviewers for the data in the table.

   b. Identification of references that were consulted and contained data that were not included in the data base. Justification for the omission of these data will be given.

   c. Discussions of important approximations or questionable assumptions used to estimate data or interpret experimental results.

   d. Identification of alternative speciation models that could be used to interpret experimental data.

   e. Clear identification of data for species whose existences have been questioned in the literature (eg. $Np(OH)_5$, $Np(CO3)_5{}^{6-}$).

Another topic of discussion was the documentation of calculations that check the accuracy and internal self-consistency of the data in the data base. In general, this test is carried out by using the basic thermodynamic data (energy, enthalpy, and entropy of formation), activity coefficients, and the method of balanced-like-charges (Phillips and Silvester, 1983) to calculate the reaction quotients, $Q(I,T)$, for reactions that have been studied in laboratory experiments. The calculated values of the reaction quotients for a variety of ionic strengths and temperatures are tabulated in Format 2 of the data base (see Attachment 2.) However, the experimental values are not listed in this format and a direct comparison can not be made. Resources for the addition of experimental values ($Q(I,T)$) to the data base are not available in the FY85 budget and addition of this feature may have to be deferred until FY86.

Table 1

Preliminary List of Variables for Hydrogeologic Data Base

- Stratigraphic Data Files
  - Formation
  - Unit
  - Top contact depth
  - Bottom contact depth
  - Thickness

- Lithologic Data Files
  - Rock type
  - Top contact depth
  - Bottom contact depth
  - Thickness

- Fracture Data Files
  - Rock type
  - Test zone top depth
  - Test zone bottom depth
  - Fracture density
    - maximum
    - minimum
    - average
  - Aperture
    - maximum
    - minimum
    - average
  - Fracture filling material
  - Test type (lab or field)

- Porosity Data Files
  - Rock type
  - Test zone top depth
  - Test zone bottom depth
  - Total porosity
    - maximum
    - minimum
    - average
  - Matrix porosity
    - maximum
    - minimum
    - average
  - Fracture porosity
    - maximum
    - minimum
    - average
  - Test Type (lab or field)
  - Tortuosity/Constrictivity

- Hydraulic Properties Files
  - Drill hole
  - Hydraulic conductivity
    - minimum
    - maximum
    - average
    - best estimate
  - Type test
  - Test zone top depth
  - Test zone bottom depth
  - Hydraulic head

Subtask 1B. Sorption Effects
(M. Siegel, A. Trujillo, J. Leckie)

Review and correction of tuff sorption data compiled on the dBase III system continued during April. A number of errors and inconsistencies in the data reported in the report LA-9328-MS <u>Summary Report on the Geochemistry of Yucca Mountain and Environs</u> published by Los Alamos Laboratories were discovered during this review. These errors and data omissions in other reports will be summarized in a later progress report.

A meeting was held with staff at Stanford University (J. Leckie, D. Kent, V. Tripathi) to review progress in compilation of data for actinide site-binding constants and mineral site densities. These data will be used to examine the potential variation of radionuclide distribution coefficients due to variations in ground-water composition and mineralogy along possible flow paths in the far-field of repositories. A preliminary report which summarizes available data and describes the application of the triple-layer model for surface complexation is in preparation. Stanford staff will complete the first draft of their chapters during June; the final draft will be included in the FY85 annual progress report. A preliminary outline of the report is included as Attachment 3 to this monthly report.

Subtasks 1C, 1D Kinetic and Dynamic Effects

Additional calculations were carried out to evaluate the CPU time required by the code TRANQL to simulate radionuclide migration over a 10 km distance for a 10,000 year period. These calculations suggest that with the present form of TRANQL, a single simulation with a grid size of 10 meters for a geochemically simple system (14 complexes), would require approximately 40 hours of CPU time on the SNLA CRAY. Stanford staff suggest that improvements to the efficiency of the code could reduce the run-time by a factor of 100. One minute of CPU time on the SNLA CRAY costs approximately $16.80. Although it appears that it will not be feasible to use TRANQL to carry out full simulations of geochemically-realistic systems for HLW performance assessment, it may be possible to use the code in sensitivity studies. An interim report describing the code and the calculations performed to date is in preparation and will be sent to the NRC during the summer.

Task II Evaluation of Error Due to Organics and Colloids

No activity in April 1985.

Task IV Short Term Technical Assistance

No activity in April 1985.

Other Activities - Project Management

A revised schedule for this project has been requested by the NRC program manager. Significant revisions in the milestone chart will result from three changes in this project: 1. Funding in FY85 was decreased from $250K to $235K, resulting in delay of some activities. 2. As discussed previously with the NRC P.M., costs listed in the Schedule 189 for this project were reported in constant 1984 dollars. We have been informed by the NRC that there will be no adjustment for inflation in the budgets for FY86-87. Therefore, there is a discrepancy between the number of F.T.E.'s (staff years) and the associated costs in dollars listed in the 189. The magnitude of this difference will increase each year and must result in the postponement or changes in scope of some of the tasks for this project. 3. The NRC Program Manager and SNLA staff agree that the most useful product of this project will be a suite of user-friendly computer codes that will enable NRC staff to carry out geochemical sensitivity analyses. These analyses will become more important and meaningful in the future when many of the necessary data become available. It is anticipated that all of the above changes can be accommodated without an increase in the present level of funding. This can be accomplished by changing the scope of Tasks 2 and 3. This shift in emphasis in the project should be discussed in detail at the proposed meetings between M. Siegel and NRC staff in mid-June. A preliminary revised schedule reflecting these changes in the project is in preparation and will be presented to the NRC for comment prior to these meetings.

Trips

On April 8, M. Siegel met with Dr. S. Phillips at Lawrence Berkeley Laboratory to discuss revisions to the data base of thermodynamic properties of aqueous complexes and solids of actinides and fission products. The results of these discussions are described under Subtask 1A above.

On April 9-10, M. Siegel and K. L. Erickson met with Drs. J. Leckie, V. Tripathi and D. Kent at Stanford University to discuss: 1. progress towards compilation of a critically-reviewed data base of surface complexation and site density constants for use in triple-layer models of sorption of waste elements onto natural materials; 2. progress in the evaluation of the computer code TRANQL in performance assessment and sensitivity studies. Details of the discussions are included under Subtasks 1B, 1C and 1D above.

Funding Breakdown for April

Task I - 100%

Reference

Phillips, S. L., and Silvester, L. F., 1983, Use of balanced-like-charges approach for metal-bicarbonate reactions, Inorg. Chem. 22, 3848-3851.

A-1756
1646.010
April 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)	1.0	9.2
II.	Direct Loaded Labor Costs	10.0	92.0
	Materials and Services	0.0	3.0
	ADP Support (computer)	1.0	2.0
	Subcontracts	22.0	84.0
	Travel	1.1	5.0
	Other	1.0	-1.0
	TOTAL COSTS	35.0	184.0

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

############
Aqueous
Solutions
Database
############

‿‿tachment 1

1‿‿JETIUM
Solids;
Aqueous Species
February 1985

· PROPERTIES OF ELEMENTAL TECHNETIUM
    Atomic Number: 43
    Formula Mass: 98.9060 for Tc
    Electronic Configuration: 4s2 4p6 4d6 5s1
    Electronegativity:___ ___
    Hydration Number:
    Ionic Radius:
    Selected Average for Soils:
    Concentration in Natural Waters:

A. THERMODYNAMIC PROPERTIES OF SUBSTANCES: 25 C; I=0

Substance	ΔfGo kJ mol-1	ΔfHo	So J mol-1 K-1	Cpo	Ref. G,H,S,C
Tc(s)	0	0	30.9	24.3	1,1,2,3
Tc(g)		678	181.07	20.7	1,1,1,1
Tc207(s)	− 935.6 15	−1120.0 8	166.0 13		3,3,3,0
Tc207(g)	− 880.5 16	− 987.4 10	449.4 13		3,3,3,0
KTcO4(s)	− 917.34	−1014.8	164.8 0.3	123.3	2,2,5,5
HTcO4(s)	− 589.8 10.5	− 703.8 9.6	126.3		3,3,3,0
HTcO4(aq)	− 602.11	− 724.0	98.6		7,1,8,0
NaTcO4(s)	− 877.0 10.1				3,0,0,0
TcO3(s)	− 461.035	− 539.74	72.4		2,2,2,0
TcO2(s)	− 382.21	− 433.96	62.3		2,2,2,0
TcO2.2H2O(s)	− 836.3 7				3,0,0,0
Tc3O4(s am?)	− 863.8 3.8				3,0,0,0
Tc4O7(s am?)	−1324.0 21				3,0,0,0
Tc(OH)4(s)	− 833.41				6,0,0,0
Tc(OH)3(s)	− 657.84				6,0,0,0
Tc(OH)2(s)	− 460.36				6,0,0,0
Tc(OH)(s)	− 234.14				6,0,0,0
TcF6(s)			253.52 0.25		0,0,3,0
TcF6(g)			371.28 0.75		0,0,3,0
K2TcCl6(s)			333.0 4		0,0,3,0

TcO3Cl(s)			7 .6	0,0,3,0
TcO4-	- 623.8	716.3	179.0	3,3,3,0
	10	4.5	1.3	
TcO4--	- 564.9			3,0,0,0
	10			
HTcO4-	- 614.6			3,0,0,0
	10.5			
H2TcO4(aq)	- 616.3			3,0,0,0
	12.1			
TcO4---	- 508.0			3,0,0,0
	11.2			
TcO++	- 100.6			3,0,0,0
	10.5			
TcO(OH)+	- 331.3			3,0,0,0
	10.5			
TcO(OH)2(aq)	- 556.0			3,0,0,0
	10.5			
[TcO(OH)2(aq)]2	-1149.2			3,0,0,0
	21.3			
Tc+++	105.8			3,0,0,0
	10.5			
Tc++	77.19			6,0,0,0
	?			

B. COMMENTS:

1. Rard considers Tc(OH)4(s) is better formulated as TcO2.2H2O.

2. Rard does not include Tc++; concludes value for Eo estimated by Latimer is probably in error.

3. In Ref. column of Page 1, 0 means no reference because there are no data for the property.

REFERENCES:

1. D.D.Wagman;W.H.Evans;V.B.Parker;R.H.Schumm;I.Halow;S.M.Bailey;K.L.Churney; R.L.Nuttall: The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units, J.Phys. Chem.Ref.Data 1982,v.11,Suppl.No.2.

2. J.W.Cobble;W.T.Smith;G.E.Boyd: Thermodynamic Properties of Technetium and Rhenium Compounds.II.Heats of Formation of Technetium Heptoxide and Pertechnic Acid,Potential of the Technetium(IV)-Technetium(VII)Couple, and a Potential Diagram for Technetium, J.Am.Chem.Soc. 1953,v.75,5777.

3. J.A.Rard: Critical Review of the Chemistry and Thermodynamics of Technetiu and Some of Its Inorganic Compounds and Aqueous Species, UCRL-53440, Lawrence Livermore National Laboratory,Livermore,CA 94550(Sept.15,1983).

4. K.H.Gayer;A.Y.Herell;R.H.Busey: The Enthalpies of Formation of Technetium Heptaoxide and Pertechnetate Ion,J.Chem.Thermodynamics 1976,v.8,959.

5. R.H.Busey;R.B.Bevan;R.A.Gilbert: The Heat Capacity of Potassium Pertechnetate from 10 to 310 K. Entropy and Gibbs Energy. Entropy of the Aqueous Pertechnetate Ion, J.Chem.Thermodynamics 1972,v.4,77.

6. R.J.Magee;T.J.Cardwell: Rhenium and Technetium,in Encyclopedia of Electrochemistry of the Elements,vol.II,Marcel Dekker,NY(1974).

7. A.S.Skotnikov;E.G.Teterin;A.M.Rozen: A Physicochemical Study of Aqueous Solutions of Permanganic, Pertechnetic, and Perrhenic Acids,Russ.J.Inorg. Chem. 1984,v.29,417.

8. This work. So calculated from $\Delta rGo = \Delta rHo - T\Delta rSo$ using ΔfGo from Ref.1. Note also that $So[HTcO4(aq)] = 99$ J mol-1 K-1 agrees reasonably well with predicted 125 ± 21: see Cobble:J.Am.Chem.Soc. 1953,v.21,1443 (his eq.4). Note also that HTcO4(aq) is a 'strong' acid.

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************       URANIUM
* Aqueous  *       FLUORIDES
* Solutions *      rc = 037
* Database  *      January 1985
************
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EQUILIBRIUM REACTION: $2UF4.2.5H2O = 2U^{++++} + 8F^- + 5H2O$

THERMOCHEMICAL PROPERTIES:

```
    ^rHo, J mol-1              : - 31863
    ^So, J mol-1 K-1           :
    ^Cpo, J mol-1 K-1          : -1955.00
    Ay^z2, (kg mol-1) 1/2      :
    b, kg mol-1                :
    log Ko                     : -55.10
```

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	-55.10	-55.86	-57.07	-58.61	-62.34	-66.56	-71.01	-75.53
0.01								
0.10								
0.20								
0.50								
1.00								
2.00								
3.00								

REFERENCES: 4

COMMENTS: ^So = -1161.89 J mol-1 K-1 for this rection. Formula for
          UF4.2.5H2O corrected; was UF.2.5H2O.

Attachment 3

Preliminary Outline of Report on Compilation
of Surface Complexation Data for HLW
Geochemical Sensitivity Analysis

1. Introduction

   1.1 Scope
   1.2 Organization
   1.3 Modeling Approach
   1.4 Conclusions

2. Properties of Oxide Adsorbents
   2.1 Criteria for Selection of Data
   2.2 Properties
         2.2.1 Oxide
         2.2.2 Source
         2.2.3 Specific Surface Area
         2.2.4 Density of Surface Sites
         2.2.5 pH(PZC)
         2.2.6 Temperature
         2.2.7 Triple Layer Parameters (TL)
   3.3 Estimating TL Parameters from Titration Data: Case Study

3. Sensitivity and Interdependence of TL Parameters: Case Study

   3.1 Introduction
   3.2 Stoichiometry of Surface Species
   3.3 Inner Layer Capacitance
   3.4 Sensitivity Analysis of Surface Coefficients

4. Evaluation of Adsorption of NpO_2^+ on am-Fe(OH)$_3$
   4.1 Introduction
   4.2 Np(V) Species of Interest
   4.3 Estimating Activity Coefficients
         4.3.1 H^+
         4.3.2 Carbonate Species
         4.3.3 Cl^-
         4.3.4 NO_3^-
         4.3.5 NpO_2^+
         4.3.6 Activity Coefficients of Ion Pairs

   4.4 Need for Further Research

   4.5 Comparison of Speciation of Np (V) Solutions Using
        Extrapolated and Uncorrected Constants