W. KELLY WINGT

Trip Report for Workshop On

Geochemical Sensitivity Analysis Project

FIN A-1756

April 23-24, 1984

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ABSTRACT

A workshop for the Geochemical Sensitivity Analysis project carried out by Sandia National Laboratories (SNLA) for the Nuclear Regulatory Commission (FIN A-1756) was held at Lawrence Berkeley Laboratories on April 23 to 24, 1984. The purpose of the meeting was twofold: 1) to introduce geochemical modelers from several research institutions to the Performance Assessment Methodology developed at SNLA for the NRC, and 2) to provide an opportunity for the geochemical modelers to critique the methods used to represent geochemical processes. The presentations by NRC and SNLA staff were designed to illustrate the regulatory, schedular and computational framework within which performance assessment modeling is carried out. The talks presented by the geochemical modelers described the conceptual framework within which geochemical models must be constructed to be theoretically sound. It became clear during the discussions that available chemical transport simulators which explicitly model geochemical processes are not suitable for performance assessment studies. The lack of site binding constants for sorbing radionuclide species and the computing requirements of these codes are their most important deficiencies. At the same time, it became clear that available K_d, isotherm data and retardation factors are insufficient to describe radionuclide retardation under many conditions. Under FIN A-1756, SNLA will identify those conditions and scenarios where chemical speciation and colloidal transport of radionuclides must be considered in nuclear waste repository risk assessments. The geochemical modelers present at the workshop (see Attachment 1) will provide technical assistance to SNLA in support of this objective. The nature of this support and summaries of the workshop presentations (see Attachment 2) and individual discussions held after the meeting are found in the next section.

WORKSHOP PRESENTATIONS AND DISCUSSIONS

Regulatory Framework

The purpose of the talks presented by SNLA and NRC staff on the first day of the workshop was to introduce the other workshop participants to the regulatory framework of high level nuclear waste disposal and to the SNLA Performance Assessment Methodology. Walton Kelley (NRC) discussed the relationship between the DOE and the NRC as defined by the National Waste Policy Act of 1982. The interactions between the two organizations are highlighted by a series of site characterization plans, analyses and license applications. These activities of the DOE and NRC are supported by a Nuclear Waste Fund, composed of payments by the generators and owners of nuclear waste. The utilities are currently assessed a charge of 1 mill per kilowatt generated

power. This fee currently generates approximately 500 million dollars per year. Ongoing activities in waste management are approximately 5 years behind the milestone schedule that was drafted at the time of enactment of the Nuclear Waste Policy Act.

SNLA Performance Assessment Methodology

Robert Cranwell (SNLA) gave an overview of the SNLA Performance Assessment Methodology. The major components of the methodology are: 1) statistical sampling techniques (Latin Hypercube Sampling), 2) flow and transport codes (SWIFT and NWFT/DVM), and 3) sensitivity techniques (Stepwise Regression). These models have been described in numerous SNLA publications. The methods by which geochemical processes are represented in these codes were of primary concern at the workshop. NWFT/DVM (Network Flow and Transport/Distributed Velocity Method) is a quasi-multi-dimensional, semi-analytic code which models fluid flow and radionuclide transport. The current version allows for a generalized network of 1-D transport segments, single or dual porosity flow and transport, leach or solubility-limited source models, user-specified retardation factors for each radioelement in each leg and time/temperature-dependent leach and canister failure rates. The code easily models transport of multiple branching decay chains. DVM is a direct simulation technique which tracks the movement of particle distributions. Retardation of radionuclides is approximated by assumption of a linear equilibrium sorption isotherm (Eq. 1 below) . Matrix diffusion is represented by a linear driving force proportional to the difference between the concentrations of radionuclides in the fracture and the matrix (Eq. 2).

$$R = 1 + K_d \rho/\phi \qquad (1)$$

$$\partial C_F/\partial t = \beta[C_M(x,t) - C_F(x,t)] \qquad (2)$$

where R = retardation factor
K_d = sorption ratio
ρ = bulk density of matrix
ϕ = porosity of matrix
C_F = concentration in fracture
C_M = concentration in matrix
β = proportionality factor

The value of the proportionality factor β is user-specified and is a function of the diffusion constant, tortuosity, constrictivity and radionuclide retardation factor. NWFT/DVM is a very efficient code and is used primarily for multiple runs in sensitivity studies. Typical simulations cost tens of dollars in computing time.

E. J. Bonano (SNLA) described the capabilities of SWIFT II, the newest version of the Sandia Waste Isolation Flow and Transport code. SWIFT is a 3-dimensional, finite difference code which models fluid/heat flow, brine migration and radionuclide transport (see Attachment 3). Non-linear conservation equations are considered for each of the processes listed in the attachment. In fractured media, equations for fractures and rock matrix are coupled through matrix diffusion terms. A linear equilibrium sorption isotherm is assumed for the rock matrix-radionuclide interactions. A Freundlich (concentration dependent) isotherm is assumed for sorption in the fractures. Global equations used in the SWIFT model are shown in Attachment 4. Local equations for local interactions between matrix and fracture are shown in Attachment 5. SWIFT describes a greater number of processes with greater accuracy than NWFT/DVM. It is rarely used for multiple runs in sensitivity studies, however, due to the high computing costs. A typical simulation using SWIFT may cost over $1,000.

R. M. Cranwell (SNLA) discussed parameter correlations in the SNLA Performance Assessment Methodology. At present, only a simple correlation matrix can be specified to describe relationships between input variables. E. Bonano suggested that important relationships may exist between hydrodynamics and retardation and cited matrix diffusion as an example.

Sorption Data Base Management Systems

Prior to the meeting, it was felt that the ISIRS (International Sorption Information Retrieval System) might be used to examine relationships between sorption ratios, concentrations, groundwater compositions, rock surface: fluid volume ratio and substrate composition. J. Serne (PNL) described the current data base and software of the ISIRS. The majority of the data currently in the ISIRS are for granite or sediments. There are very few data available for tuff or basalt formations. There are approximately 2500 K_d measurements, 250 K_A values and 50 direct measurements of retardation factors for laboratory columns. A large fraction of the data are for strontium and cesium; relatively few data for uranium reside in the data bank. The final version of the data entry software will be completed by summer 1984 and the system will be usable on VAX computers. On the basis of Serne's presentation, and subsequent discussions, it was felt that the current data base of ISIRS is of limited use to the Geochemical Sensitivity Analyses project. The versatile software and quality assurance procedures, however, suggest that with additional data for tuff and basalt, this data management system could be of considerable use to the NRC.

NRC-funded Geochemistry Programs at LBL

C. Carnahan (LBL) described the results of investigations at LBL aimed at examining coupled geochemical-hydrological and thermodynamic transport processes. The computer code CHEMTRN was developed by LBL for the NRC to simulate 1-D transport of

aqueous species in porous media. The results to date show that simple retardation factors obtained from constant K_d's cannot be used to accurately predict radionuclide travel times or elution curves when the concentration of the element is high enough to significantly affect the ground-water composition. The error introduced in the calculation of travel time and concentration depends upon a number of factors including the site-binding constant, ground-water composition and identity of the radioelement. When the radioelement is present at trace levels and major species concentrations are constant a simple K_d will accurately predict transport. As demonstrated previously by several other researchers, systems which are undergoing dynamic chemical changes cannot be described by simple K_d's or retardation factors even if sorption is linear. Systems at steady state can be represented by K_d's if sorption is linear.

The current version of CHEMTRN is not usable for performance assessment calculations. Integrated discharge (as regulated by 40 CFR 191) could be calculated with a modified version of the code. Radionuclide decay and production are not considered in the model. Simulation of transport of 15 basis species for time periods of tens of years taxes the capability of LBL's CDC 7600 computer. Multiple calculations of integrated discharge of all radionuclides over 10,000 years for sensitivity analyses would be prohibitively expensive.

Geochemical Sensitivity Analysis

On the second day of the workshop, M. Siegel and K. Erickson (SNLA) presented results of geochemical sensitivity analyses carried out under FIN A-1158. M. Siegel summarized calculations that have been described in a recent letter report to the NRC (letter report to P. Ornstein, December 20, 1983) and at the Waste Management '84 conference ("Radionuclide Releases From a Hypothetical Nuclear Waste Repository: Potential Violations of the Proposed EPA Standard by Radionuclide With Multiple Aqueous Species"). Copies of viewgraphs presented during this talk are included in Attachment 6. These calculations describe the critical combinations of retardation factors, source terms and ground-water travel times that may lead to violations of the EPA release limit for neptunium-237 when a sorbing aqueous species reacts with ground-water ligands and converts irreversibly to a nonsorbing complex during transport. Radioactive production and decay were not considered in these calculations. This omission is reasonable for neptunium-237 if the initial containment period of the waste lasts 1000 years. After 1000 years, production of neptunium-237 by radioactive decay will be negligible; decay of this isotope will be insignificant during the 10,000 year EPA regulatory period due to its long half-life. Curves similar to those presented in Attachment 6 can be used by the NRC to prioritize the geochemical information that is needed to demonstrate compliance of repositories with 10 CFR 60. At present there are no species-specific sorption data for neptuniun. A con-

servative analysis can be made by assuming that any species (B) produced during transport will be unretarded ($R_B = 0$) and that the species release from the repository (A) will have a retardation factor (R_A) similar to those measured in the laboratory or calculated from experimental sorption data. Combinations of ground-water travel time, source term, R_A and reaction rate k when $R_B = 1$ which lead to violation of the EPA standard can be plotted. Through a review of available sorption data, it is possible to obtain media-specific ranges of R_A which represent the uncertainty in our current ability to characterize the ability of different rock formations to retard radionuclide migration. A range of chemical stabilities ($1/k_m$) required to ensure compliance with the EPA standard can be calculated for each range of R_A values. This information can be used to design future experiments which will yield definitive results for the purposes of nuclear waste management.

Ken Erickson (SNLA) provided an example of the application of the aforementioned approach to the design of batch sorption experiments. The equations, parameter values and plots used in this example are shown in Attachment 7. In this example, it is assumed that all of the radionuclide in the batch experiment is initially present as species A. A solution-phase speciation reaction irreversibly converts the sorbing species A to a nonsorbing species B at rate kC_A (Equation 3). The concentration of species A in solution changes due to sorption of A by the solid phase and conversion to species B (Equation 1). The rate of reversible sorption of species A by the solid phase is controlled by a linear concentration difference (Equation 2). Solution of these coupled equations by the technique of Laplace transforms yields Equation (4) which describes the ratio of the total concentration of the nuclide to the initial concentration as a function of time. The parameter values on page 3 of the attachment were used to produce the plot on page 4. In this calculation, the half-life of uptake of species A by sorption was 1 day and the half-life of conversion to species B (0.69/k) was 30 days. It can be seen that the value of C/Co drops rapidly due to the uptake of species A by the solid phase and slowly rises due to the conversion of A to B in solution (as C_A drops, the value of $Kd_AC_A - q_A$ (Equation 2) decreases to a negative value and the nuclide is desorbed). This reaction will continue until all of species A has been converted to species B and q_A is equal to zero. This effect cannot be observed during the first 35 days of the experiment in this example. The increase of C/Co during that time is within the uncertainty of the experimental data. Thus, if the duration of batch experiment is 30 days or less, a high and non-conservative K_d value would be assigned to the radionuclide under study. The experiment must be run for a time period longer than 30 days to detect important effects. This minimum run period is a function of the speciation reaction rate constant. Critical reaction rate constants can be

identified for nuclear waste management using the techniques described in Attachment 6. These rate constants, in turn, will determine the minimum run times of experiments needed to identify speciation effects that could disguise potential violation of the EPA standard.

The preceding discussions by Siegel and Erickson involved the irreversible conversion of species A to B. Erickson discussed a hypothetical chemical scenario in which the conversion of A to B is reversible and sufficiently fast so that local chemical equilibrium is a reasonable approximation. Thus, although species B migrates faster than species A, the conversion of species B back to A leads to the migration of A at a rate faster than that predicted by K_{dA} and R_A. Under these conditions, it can be shown that the average migration rate of the radionuclide can be described by an average retardation factor R (Attachment 8). This general expression (Equation 7, Attachment 8) applies to both linear and nonlinear isotherms. When the isotherm is linear, the expression reduces to Equation 8 and the corresponding material balance equations for species A and B are given by Equations 9 and 10 respectively in Attachment B.

Simulation of Transport and Solid/Solution Partitioning of Trace Elements

Dr. J. Leckie (Stanford University) discussed simulation of the transport and partitioning of trace metals between solids and solutions (see Attachment 9). He described a thermodynamic approach to the modeling of interactions between aqueous complexes and substrates. Table 1 of Attachment 9 defines several classes of surface reactions within a framework that is analogous to that used to describe coordination reactions of aqueous species. Figure 1 schematically illustrates the types of interactions that may occur between the solid particles and aqueous metal complexes. The complexity of the possible interactions suggest that a simple expression for K_d (Eq. 1) will not adequately describe the partitioning of metal between the solution and solid phases. A more general expression for K_d may be written (Eq. 2) that takes into account the thermodynamic equilibrium constant K' for the sorption reaction, (SOH_x) the concentration of available sites, β_{ij} and (L_i), the stoichiometric coefficient and aqueous concentration of any ligands involved in the reaction and x and (H), the stoichiometric coefficient and concentration of hydrogen ions. The parameter C_2 is a constant which rectifies units. Figure 2 shows the strong dependence of K_d on pH for a given value of (SOH).

TRANQL is a coupled transport-speciation code developed for the EPA at Stanford University. A flow chart for the TRANQL model is shown in Figure 3 of Attachment 9. The speciation code MICROQL is used in the calculation of the concentrations of sorbed and aqueous species in the system. The aqueous species

are transported by the code TRANSPORT into adjacent grid blocks and then MICROQL recalculates the equilibrium concentrations of sorbed and aqueous species in each block.

TRANQL was used to simulate transport of Cd in a laboratory column of sand. Both EDTA and Cd were assumed to be introduced as a pulse at the inlet boundary. EDTA is a nonretarded complex which binds reversibly and strongly with Cd. While bound to the EDTA, the Cd is relatively unretarded; when uncomplexed, the Cd binds strongly to the sand and is strongly retarded. In this system, the behavior of Cd is complex and cannot be modeled with a single value of K_d. Figure 4 in Attachment 9 shows profiles of species of Cd (total, adsorbed, aqueous-complexed). It can be seen that at locations where the concentration of EDTA is high, most of the Cd is present as an aqueous species ($Cd_T \approx Cd_{aq}$). At points where the concentration of EDTA is low, most of the Cd is bound to the solid substrate ($Cd_T \approx Cd_{ads}$). This variation in the Cd_{ads}/Cd_{aq} ratio is reflected in the change of K_d as a function of time and distance (Figure 5). During Leckie presentation and at a subsequent meeting at Stanford, the relevance of these results and the applicability of the TRANQL code to HLW performance assessment calculations were discussed. Many of the effects (especially the variation of K_d with time) described in Leckie's talk were a direct result of the introduction of the Cd and a nonsorbing species (EDTA) that complexed with the Cd together as a pulse input. Under conditions previously modeled in SNLA performance assessment studies, the radionuclides are released as a step-function and no complexing species similar to EDTA are considered. If it can be shown that a scenario similar to the one envisioned by Leckie is plausible for HLW repositories then it should not be modeled using a constant K_d value. The potential for such a scenario should be examined under FIN A-1756 or in other NRC-sponsored projects.

The present version of TRANQL cannot be used in HLW performance assessment calculations. It currently models transport of only non-radioactive species over distances and for time periods that are both short compared to the time-space domain regulated by the EPA and NRC regulations. At present, it is unclear if the code can be modified to model problems that are relevant to HLW management. These questions will be examined under FIN A-1756.

Availability of Thermochemical Data for Solubility/Speciation Calculations

Dr. S. Phillips (LBL) described the thermochemical data base that he has compiled for HLW management studies. Attachment 10 contains viewgraphs used in his presentation. At present two data bases are available. Critically-assessed data are available for a few elements. The data content and data evaluation criteria are described in Attachment 10. A draft copy of a data compilation for iodine is also shown. Critically-evaluated equilibrium constants, thermodynamic

properties (ΔG_f°, ΔH_f°, C_p), Nernstian potentials, solubility products and diffusion coefficients are tabulated for known species. All available data are considered in the compilation; an estimate of the uncertainties are included. The effects of temperature (to 200°C) and ionic strength (to I = 3.0) are evaluated using the Clark-Glew equations for K(T) and the Pitzer equations for K(I). The extended Debye-Huckel and Davies equations are also used to model changes in equilibrium constants as a function of salinity.

A large compilation of data also exists for many elements of interest to HLW studies. This second data base, however, has not undergone a critical review like that of the smaller critically-assessed data base. Examples of this compilation are also included in Attachment 10. SNLA is currently considering placement of a contract with Dr. Phillips to obtain a critically-assessed data base for elements of interest to HLW studies. This state-of-the-art data base would be the product of compilation and critique by Dr. Phillips and peer review by leading chemists involved in aqueous thermochemistry such as Pitzer, Baes and White. The data base would be accessible by computer and would be in format compatible with the PHREEQE geochemical code.

Attachment 1

Participants in Workshop
for
for Sandia Geochemical Sensitivity Analysis Program

Name	Affiliation	Phone	Expertise
E. Bonano	SNLA	8-844-5503	Chem. Engineering
R. Cranwell	SNLA	8-844-8368	Performance Assessment
K. Erickson	SNLA	8-844-4133	Chem. Engineering
M. Siegel	SNLA	8-846-5448	Geochemistry
C. Carnahan	LBL	8-451-6770	Transport Models
S. Phillips	LBL	8-451-6865	Thermochemistry
J. Leckie	LBL	415-497-2524	Surface Chemistry
J. Serne	PNL	8-509-376-8429	Geochemistry
W. Kelly	NRC	8-427-4571	Program Manager/ Geochemistry

Attachment 2

AGENDA

Sandia Geochemical Sensitivity Analysis Program

Room 50-D Conference Room
Lawrence Berkeley Laboratories
April 23-24, 1984

Monday, April 23

12:30pm	Introduction and Overview	M. Siegel/SNLA
1:00pm	Regulatory Framework	W. Kelley/US. NRC
1:30pm	SNLA Performance Assessment Methodology - Overview and Applications	R. Cranwell, M. Siegel/SNLA
2:15pm	Geochemical Processes in SNLA PA Methodology - Transport, Decay, Matrix Diffusion, Retardation, Solubility	R. Cranwell, E. Bonano M. Siegel/SNLA
3:00pm	Break	
3:10pm	Parameter Correlations and Relationships Between Hydrodynamic and Geochemical Variables	R. Cranwell, E. Bonano/SNLA
3:35pm	Description of ISIRS	J. Serne/PNL
4:45pm	NRC-Funded Geochemistry Programs at Lawrence Berkeley Laboratory	C. Carnahan/LBL
5:30pm	Adjourn	

Tuesday, April 24

8:15am	Introductory Remarks	M. Siegel/SNLA
8:20am	Geochemical Sensitivity Analysis I.	M. Siegel/SNLA
8:50am	Geochemical Sensitivity Analysis II. Experimental Design	K. L. Erickson/ SNLA
9:20am	Simulation of Transport and Solid/ Partitioning of Trace Elements	J. Leckie/Stanford
10:00am	Coffee/Donuts Break	

10:15am	Availability of Thermochemical Data for Solubility/Speciation Calculations	S. Phillips/LBL
11:00am	Overview of Geochemical Sensitivity Project	M. Siegel/SNLA
11:30am	Discussion	
12:00pm	Lunch (LBL Cafeteria)	
1:00pm	NRC-funded Geochemical Programs at Oak Ridge National Laboratories	W. Kelley/US NRC
1:30pm	General Discussion and Project Plan	
3:00pm	Adjournment	

ATTACHMENT 3

CHARACTERISTICS OF THE SWIFT II MODEL

PROCESSES:

- fluid flow
- heat transport
- brine migration
- radionuclide-chain transport

MEDIA:

- porous media
- fractured media

SUBMODELS:

- variable density
- variable viscosity
- salt dissolution
- waste leach
- well
- wellbore
- aquifer-influence functions
- over/underburden heat dissipation
- radiation
- free-water surface
- extended boundary conditions

GLOBAL EQUATIONS

Fluid:

$$\underbrace{-\nabla\cdot(\rho\underline{u})}_{\text{conduction}} - \underbrace{q}_{\text{production}} - \underbrace{q_W}_{\text{sink/source}} + \underbrace{R_C'}_{\text{salt dissolution}} - \underbrace{\Gamma_W}_{\text{loss to matrix}} = \frac{\partial}{\partial t}(\phi\rho) \qquad (2\text{-}1)$$

Heat:

$$\underbrace{-\nabla\cdot(\rho H\underline{u})}_{\text{convection}} + \underbrace{\nabla\cdot(\underline{\underline{E}}_H\cdot\nabla T)}_{\text{conduction/dispersion}} - \underbrace{H_I q}_{\text{injected enthalpy}} - \underbrace{Hq}_{\text{produced enthalpy}} - \underbrace{q_E}_{\text{sink/source}}$$

$$\underbrace{-(H\Gamma_W + \Gamma_H)}_{\text{loss to matrix}} = \underbrace{\frac{\partial}{\partial t}\left[\phi\rho U + (1-\phi)\rho_R U_R\right]}_{\text{accumulation in fluid and rock}} \qquad (2\text{-}2)$$

Brine:

$$\underbrace{-\nabla\cdot(\rho\hat{C}\underline{u})}_{\text{convection}} + \underbrace{\nabla\cdot(\rho\underline{\underline{E}}_C\cdot\nabla\hat{C})}_{\text{dispersion/diffusion}} - \underbrace{\hat{C}_I q}_{\text{injected brine}} - \underbrace{\hat{C}q}_{\text{produced brine}}$$

$$+ \underbrace{R_C}_{\text{salt dissolution}} - \underbrace{(\hat{C}\Gamma_W + \Gamma_C)}_{\text{loss to matrix}} = \underbrace{\frac{\partial}{\partial t}(\phi\rho\hat{C})}_{\text{accumulation}} \qquad (2\text{-}3)$$

Radionuclide r:

$$\underbrace{-\nabla\cdot(\rho C_r\underline{u})}_{\text{convection}} + \underbrace{\nabla\cdot(\rho\underline{\underline{E}}_C\cdot\nabla C_r)}_{\text{dispersion/diffusion}} - \underbrace{C_r q}_{\text{produced component}} - \underbrace{q_r}_{\text{sink/source}} + \underbrace{q_{Wr}}_{\text{waste leach}}$$

$$\underbrace{-(C_r\Gamma_W + \Gamma_r)}_{\text{loss to matrix}} + \underbrace{\sum_{s=1}^{N} k_{rs}\lambda_s\left[\phi\rho C_s + (1-\phi)\rho_R W_s\right]}_{\text{generation of component r by decay of s}} \qquad (2\text{-}4)$$

$$\underbrace{\lambda_r\left[\phi\rho C_r + (1-\phi)\rho_R W_r\right]}_{\text{decay of component r}} = \underbrace{\frac{\partial}{\partial t}\left[\phi\rho C_r + (1-\phi)\rho_R W_r\right]}_{\text{accumulation}}$$

LOCAL EQUATIONS

Fluid (matrix):

$$\underbrace{-\nabla\cdot(\rho'\underline{u}')}_{\text{conduction}} + \underbrace{\Gamma'_W}_{\text{gain from fracture}} = \underbrace{\frac{\partial}{\partial t}(\phi'\rho')}_{\text{accumulation}} \qquad (2\text{-}19)$$

Heat (matrix):

$$\underbrace{-\nabla\cdot(\rho'H'\underline{u}')}_{\text{convection}} + \underbrace{\nabla\cdot(\rho'E'_H\nabla H')}_{\text{conduction/dispersion}} \underbrace{(H'\Gamma'_W + \Gamma'_H)}_{\text{gain from fracture}}$$

$$= \underbrace{\frac{\partial}{\partial t}\left[\phi'\rho'U' + (1-\phi)\rho_R U'_R\right]}_{\text{accumulation in fluid and rock}} \qquad (2\text{-}20)$$

Brine (matrix):

$$\underbrace{-\nabla\cdot(\rho'\bar{C}'\underline{u}')}_{\text{convection}} + \underbrace{\nabla\cdot(\rho'E'_C\nabla\bar{C}')}_{\text{dispersion/diffusion}} + \underbrace{(\bar{C}'\Gamma'_W + \Gamma'_C)}_{\text{gain from fracture}}$$

$$= \underbrace{\frac{\partial}{\partial t}(\phi'\rho'\bar{C}')}_{\text{accumulation}} \qquad (2\text{-}21)$$

Radionuclide r (matrix):

$$\underbrace{-\nabla\cdot(\rho'C'_r\underline{u}')}_{\text{convection}} + \underbrace{\nabla\cdot(\rho'E'_C\nabla C'_r)}_{\text{dispersion/diffusion}} + \underbrace{\sum_s k_{rs}\lambda_s K'_s\phi'\rho'C'_s}_{\text{generation of component r by decay of s}}$$

$$\underbrace{-\lambda_r K'_r\phi'\rho'C'_r}_{\text{decay of component r}} + \underbrace{(C'_r\Gamma'_W + \Gamma'_r)}_{\text{gain from fracture}} = \underbrace{\frac{\partial}{\partial t}(K'_r\phi'\rho'C'_r)}_{\text{accumulation}} \qquad (2\text{-}22)$$

Attachment 6

Geochemical Sensitivity Analysis I. Speciation, Kinetics and Retardation

Dr. M. Siegel

Attachment 6

INTRODUCTION

- High-level waste repository performance-assessment calculations require simple algorithms to simulate radionuclide transport

- Use of retardation factors calculated from batch sorption data can cause underestimations of radionuclide discharge and disguise possible violations of proposed EPA Standard (40 CFR 191).

OBJECTIVE

- Develop method to identify physicochemical conditions where speciation reactions must be considered in risk assessments to ensure compliance with EPA Standard.

METHOD

- For purpose of calculating upper bound to radionuclide discharge, reactions among multiple dissolved species of a radionuclide can be represented by expressions of form:

$$\left\{\begin{array}{l}\text{net rate of}\\ \text{production by}\\ \text{homogeneous}\\ \text{reactions}\end{array}\right\} \lesssim \sum_{n,\,i} k_n c_i \qquad (1)$$

where k_n = reaction rate constant for n^{th} reaction
C_i = concentration of ith species of radionuclide

- Steps

1. Incorporate reaction terms into transport equation for each species.

2. Solve equations and integrate to obtain expression for discharge over 10,000 year EPA regulatory period.

3. Sum discharges of chemical species of radionuclide and set equal to EPA release limit.

4. Solve equation to determine combinations of parameters which cause violations of EPA Standard.

EXAMPLE: ^{237}Np

- Assume ^{237}Np is released entirely as species A from engineered facility at rate QC_A^o and converts irreversibly to species B during transport, at rate:

$$\frac{dC_A}{dt} = -k^* C_A = -\frac{dC_B}{dt} \qquad (2)$$

- Let retardation factor for A (R_A) >> retardation factor for B (R_B). Include above rate expressions in transport equations for species A and B to bound discharge of neptunium.

- Set sum of integrated discharges of A and B equal to W_{Np}, the EPA release limit for $^{237}N_P$ (20 C_i/1000 MTHM):

$t = 10{,}000$ yr.

$$Q \int (C_A + C_B)dt = f(R_A, R_B, k^*, \lambda, tg, t_0, C_A^o) = W_{Np} \qquad (3)$$

$t_o = 1000$ yr.

where t_o = initial containment period
tg = ground-water travel time
Q = volumetric water flux through facility
C_A^o = concentration of A in facility

- If $t_o = 1000$ yr, then radiocative decay and production of neptunium will be insignificant during the remainder of the 10,000 year EPA regulatory period. Eq. (3) becomes:

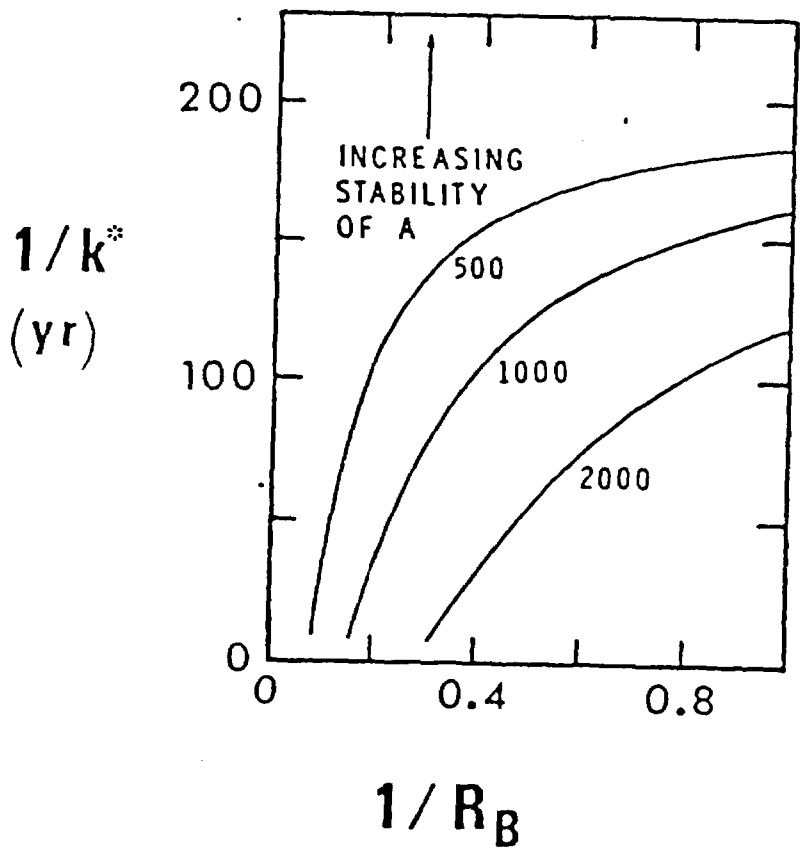
$$W_{Np} = QC_A^{\circ} \left[9000 - R_B tg + \frac{R_A - R_B}{k^*} \left[\exp\left(\frac{-k^*(9000 - R_B tg)}{R_A - R_B} \right) - 1 \right] \right]$$

$$+ QC_A^{\circ} \exp(-k^* tg) \left[\frac{(R_A - R_B)}{k^*} \right] \left[1 - \exp\left(\frac{-k^*(9000 - R_A tg)}{R_A - R_B} \right) \right]$$

- For constant QC_A°, R_A and tg determine combinations of R_B and k^* which lead to violation of EPA standard.

RESULTS

- Solutions of Eq. (4) for $R_A = 100$ for different ground-water travel times (tg) and release rates (QC_A^o) are plotted below. $W_{Np} = 20$ Ci/1000 metric tons heavy metal (MTHM) Areas above curves comply with EPA release limit.



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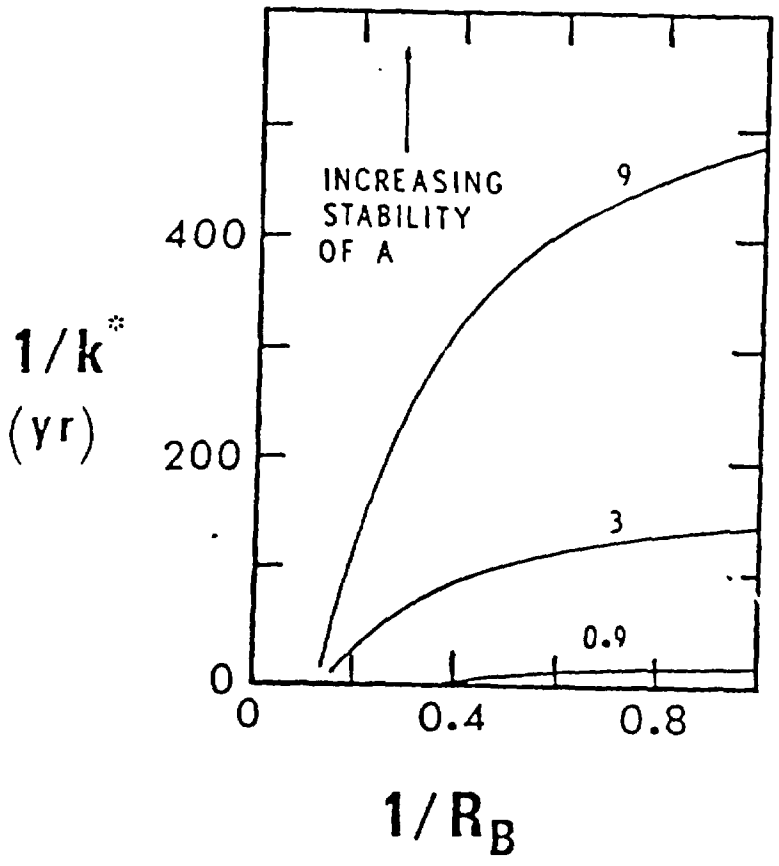
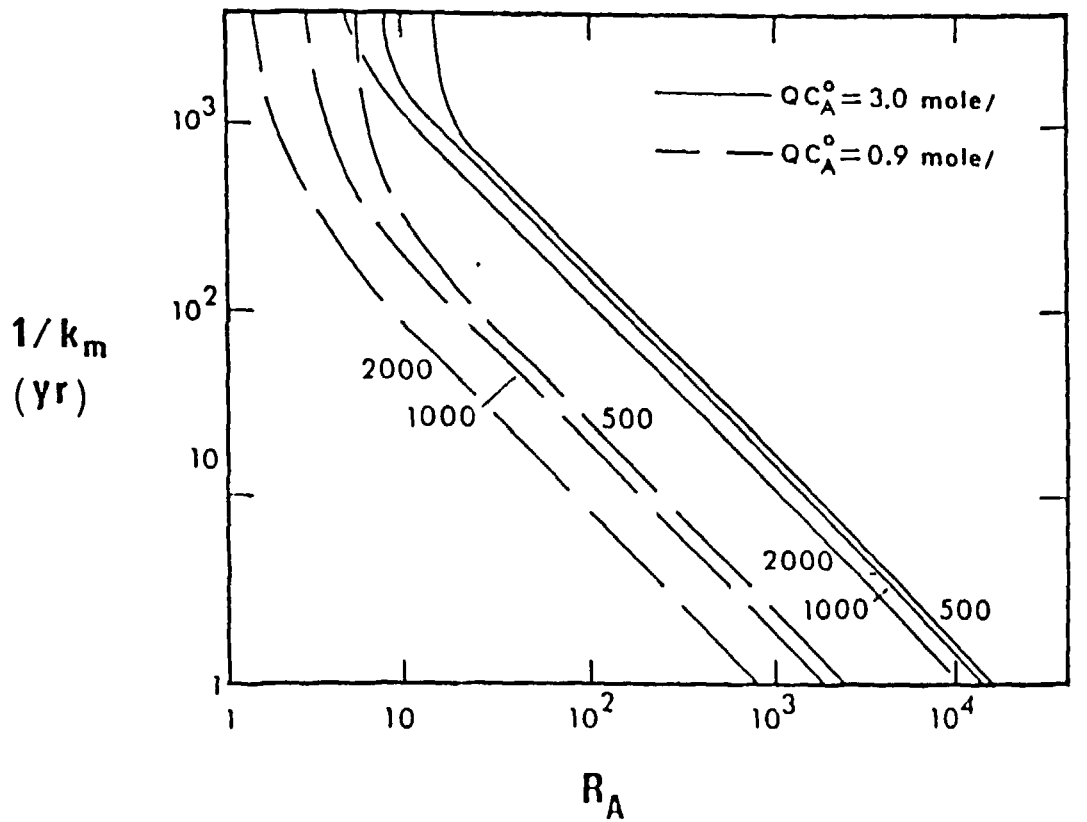
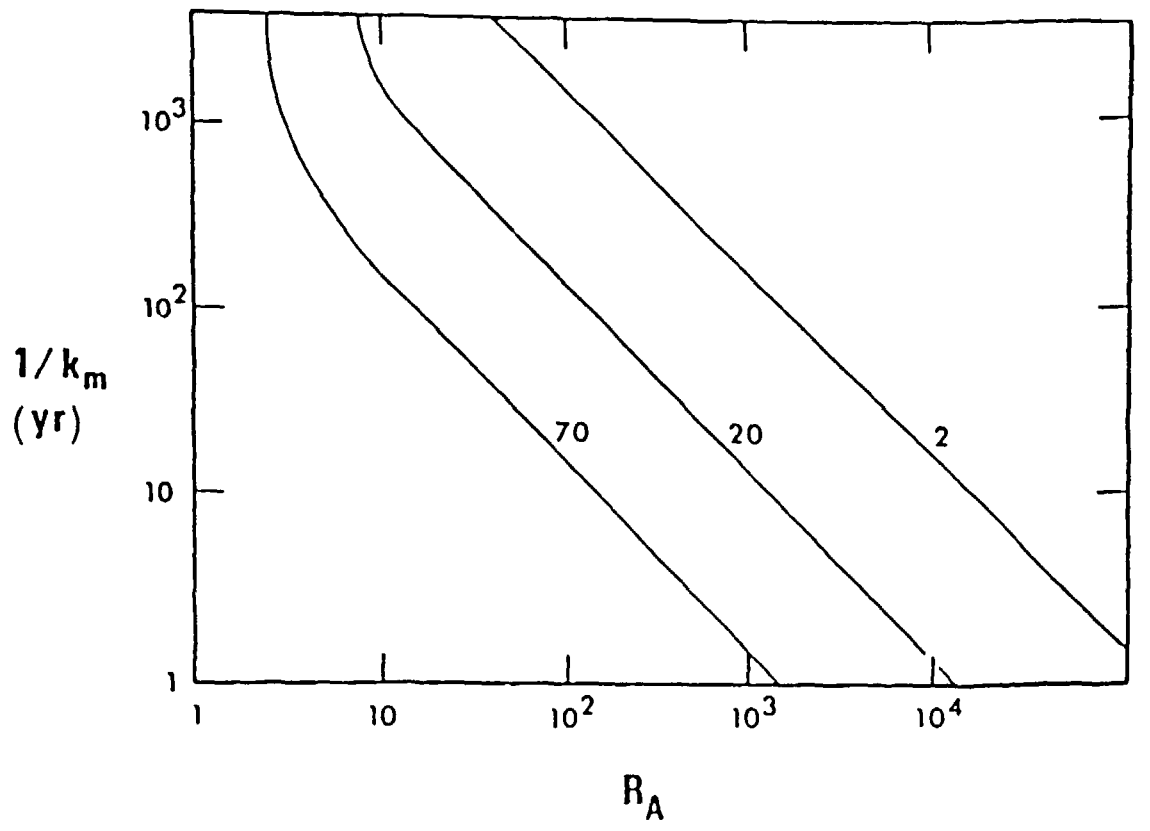


- Relationship between R_A and k_m for different release rates and ground-water travel times when species B is unretarded (k_m is value of k^* when $R_B = 1$). Areas above curves comply with EPA release limit (20 Ci/1000 MTHM).



- If other radionuclides are released from repository, then release of ^{237}Np must be less than 20 Ci/1000 MTHM. Relationships between k_m and R_A for different values of W_{Np} when $R_B = 1$, $tg = 1000$ yr, $QC_A^o = 3$ mole/yr are shown below.



CONCLUSIONS

- A conservative analysis can be made by calculating values of R_A from available Np sorption data. Minimum and mean R_A values have been compiled for several geologic media. Figure below shows corresponding chemical stability ($1/k_m$) for sorbing species A that is required for compliance with EPA Standard and 10 CFR 60 ($t_0 = 1000$ yr; tg = 1000 yr; $QC_A^o = 2.6$ mole/yr corresponding to annual fractional release rate of 10^{-5}).

- Potential radionuclide speciation introduces uncertainty in assessing compliance of HLW repositories with EPA Standard (40 CFR 191) and NRC Regulation (10 CFR 60).

- Methodology demonstrated above can be used to prioritize information needed to identify scenarios and physicochemical conditions where speciation must be considered.

- A minimum necessary chemical stability can be described for radionuclide species examined in laboratory or field studies which will ensure compliance with EPA Standard.

Attachment 7

Geochemical Sensitivity Analysis II. Experimental Design

Dr. K. Erickson

Batch Experiment

Material balances for species A :

(1) $$\frac{dC_A}{dt} = -\left(\frac{m}{V}\right)\frac{dq_A}{dt} - kC_A$$

$$C_A(0) = C_o = \text{a constant}$$

(2) $$\frac{dq_A}{dt} = \rho h a\left(K_{d_A} C_A - q_A\right)$$

$$q_A(0) = 0$$

Material balances for species B

(3) $$\frac{dC_3}{dt} = kC_A$$

$$C_B(0) = 0$$

$$q_B(t) \equiv 0$$

$$(4) \qquad \frac{C_A + C_B}{C_o} = 1 - A e^{-b_1 t}\left(1 - e^{-\sqrt{b^2 - 4c}\, t}\right)$$

where $$A = \frac{A_1}{\left[(1 + A_1 + A_2)^2 - 4A_2\right]^{1/2}}$$

$$A_1 = \frac{m K_{d_A}}{V}$$

$$A_2 = \frac{K}{\rho h a}$$

$$b = \rho h a (1 + A_1) + K$$

$$c = \rho h a K$$

$$b_1 = \frac{b - \sqrt{b^2 - 4c}}{2}$$

Parameter values

$m = 1$ gm

$V = 100$ ml

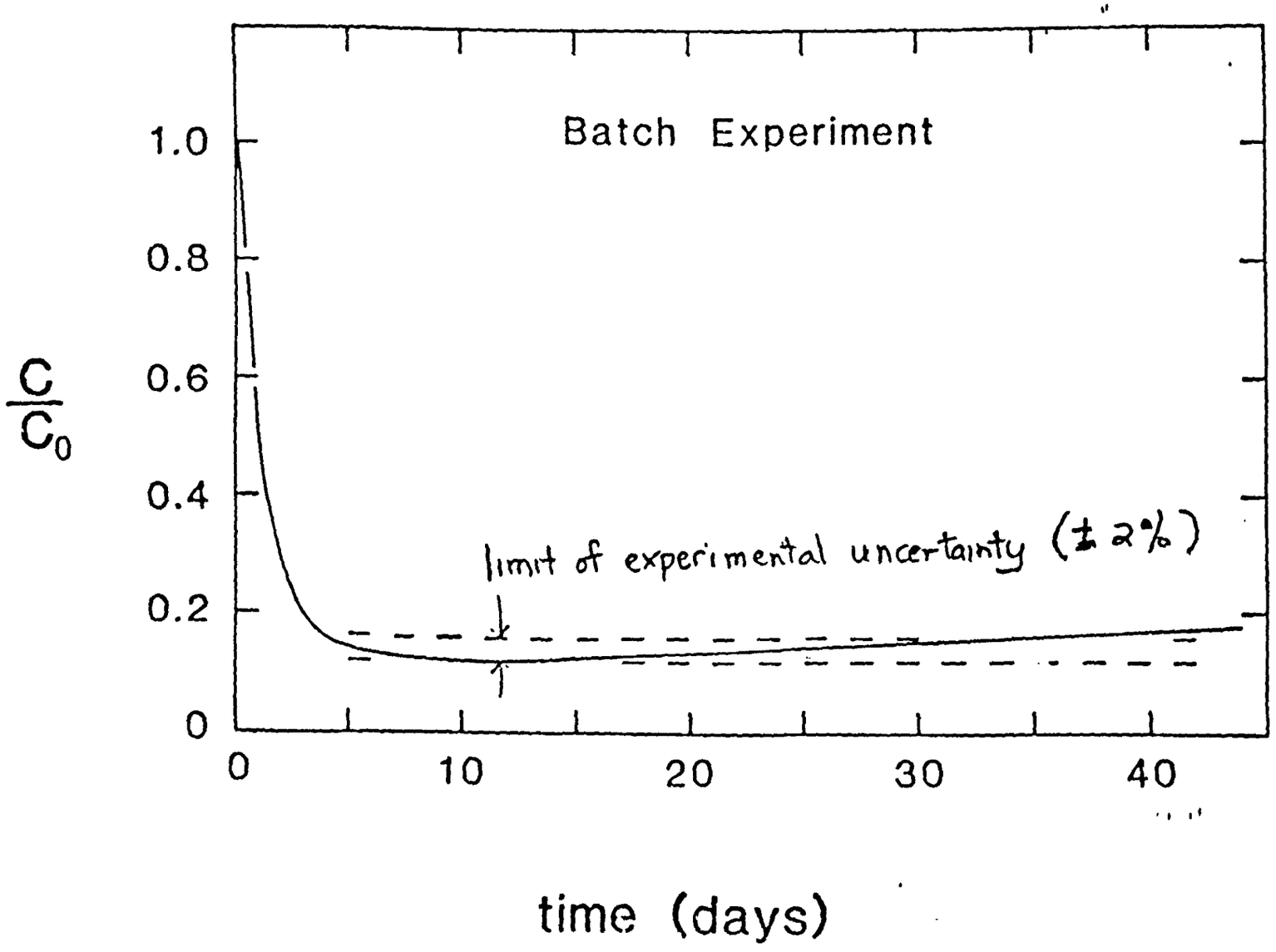
$K_{d_A} = 10^3$ ml gm^{-1} $\approx$ a constant

$\rho h a = 0.07$ day^{-1} ($t_{1/2} \approx 1$ day)

$k = 0.02$ day^{-1} ($t_{1/2} \approx 30$ day)

$C = C_A + C_B$

$C_0 = C_A^\circ$


Batch Experiment
limit of experimental uncertainty (± 2%)
C/C0
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
time (days)

(1) $$A + \ell L \rightleftharpoons b B$$

(2) $$\frac{\partial C_A}{\partial t} = -\frac{\vec{V}}{R}\cdot\vec{\nabla}C_A + \frac{b}{a^* R}\vec{\nabla}\cdot D\frac{a^*}{b}\vec{\nabla}C_A - \frac{P}{R}\frac{\lambda}{b}C_A$$

(3) $$\frac{\partial C_B}{\partial t} = -\frac{\vec{V}}{R}\cdot\vec{\nabla}C_B + \frac{1}{a R}\vec{\nabla}\cdot D a\vec{\nabla}C_B - \frac{P}{R}\lambda C_B$$

(4) $$a = \frac{1}{\left(\frac{b^2}{K_e^*}C_B^{b-1} + 1\right)} \qquad a^* = a\left(\frac{K_e^*}{C_B^{b-1}}\right)$$

(5) $$K_e^* = \frac{C_B^b}{C_A} = \frac{K_e C_L^\ell}{\left(\frac{\gamma_B^b}{\gamma_A \gamma_L^\ell}\right)} \qquad K_e = \frac{C_B^b}{C_A C_L^\ell}\frac{\gamma_B^b}{\gamma_A \gamma_L^\ell}$$

(6) $$P = 1 + \frac{\left(\frac{1-\phi}{\phi}\right)\rho\left(\frac{b C_B^{b-1}}{K_e^*}\frac{F_A}{C_A} + \frac{F_B}{C_B}\right)}{a}$$

(7) $$R = 1 + \frac{\left(\frac{1-\phi}{\phi}\right)\rho\left[\frac{b}{K_e^*}C_B^{b-1}\frac{\partial}{\partial C_A}(b F_A + F_B) + \frac{\partial}{\partial C_B}(b F_A + F_B)\right]}{a}$$

For $F_A = K_{D_A} C_A$

$F_B = K_{D_B} C_B$

$b = 1$

$$a = \left(\frac{1}{K_e^*} + 1\right) \qquad a^* = K_e^* a$$

(8) $$P = R = 1 + \frac{\left(\frac{1-\phi}{\phi}\right)\rho\left(\frac{K_{D_A}}{K_e^*} + K_{D_B}\right)}{a}$$

---

(9) $$\frac{\partial C_A}{\partial t} = -\frac{\vec{V}}{R}\cdot\vec{\nabla}C_A + \vec{\nabla}\cdot\frac{D}{R}\vec{\nabla}C_A - \lambda C_A$$

(10) $$\frac{\partial C_B}{\partial t} = -\frac{\vec{V}}{R}\vec{\nabla}C_B + \vec{\nabla}\cdot\frac{D}{R}\vec{\nabla}C_B - \lambda C_B$$

Attachment 9

Simulation of Transport and Solid/Solution Partitioning of Trace Elements

Dr. J. O. Leckie

TABLE 1 - Possible surface species which may form between oxide functional groups and solutes. Current analytical techniques do not allow direct confirmation of surface speciation.

SURFACE SPECIATION REACTIONS	SURFACE SPECIES
Proton/Surface Reactions	
$SOH_2^+ = SOH + H^+$	
$SOH = SO^- + H^+$	
Metal/Surface Reactions (Inner Sphere)	
$SOH_2^+ + M = SOM + 2H^+$	
$SOH + M = SOM + H^+$	
$SO^- + M = SOM$	
$SOH + H_2O + M = SOMOH + 2H^+$	
$SOH + 2H_2O + M = SOM(OH)_2 + 3H^+$	
$(SOH)_2 + M = (SO)_2M + 2H^+$	
$(SOH)_2 + M = S_2OOHM + H^+$	
Ligand/Surface Reactions (Inner Sphere)	
$SOH_2^+ + L = SL + H_2O$	
$SOH + H^+ + L = SL + H_2O$	
$SOH + 2H + L = SLH + H_2O$	
$(SOH)_2 + 2H^+ + L = S_2L + 2H_2O$	
$(SOH)_3 + 3H^+ + L = S_3L + 3H_2O$	
Mixed Ligand (Ternary) Reactions (Inner Sphere)	
$SOH + ML = SOML + H^+$	
$SOH + ML = SLM + OH^-$	
$(SOH)_2 + ML = SOMLS + H_2O$	
Ion Pair Reactions (Outer Sphere)	
$SOH + M = SO^-{-}M + H^+$	
$SOH + H_2O + M = SO^-{-}MOH + 2H^+$	
$SOH + H^+ + L = SOH_2^+{-}L$	
$SOH + 2H^+ + L = SOH_2^+{-}LH$	
Exchange Reactions	
$SO^-{-}Na^+ + M = SO^-{-}M + Na^+$	
$SO^-{-}Na^+ + M = SOM + Na^+$	
$SOH_2^+{-}SO_4^{2-} + L = SOH_2^+{-}L + SO_4^{2-}$	
$SOH_2^+{-}SO_4^{2-} + L = SL + SO_4^{2-} + H_2O$	

(1) $$K_d = \frac{C_{solid}}{C_{solution}} \frac{mg/g}{mg/l}$$

(2) $$K_d = \frac{K'(SOH_x)\ C_2}{(H)^x[1 + \sum_i^m \sum_j^n (\beta_{ij}(L_i)_j)]}$$

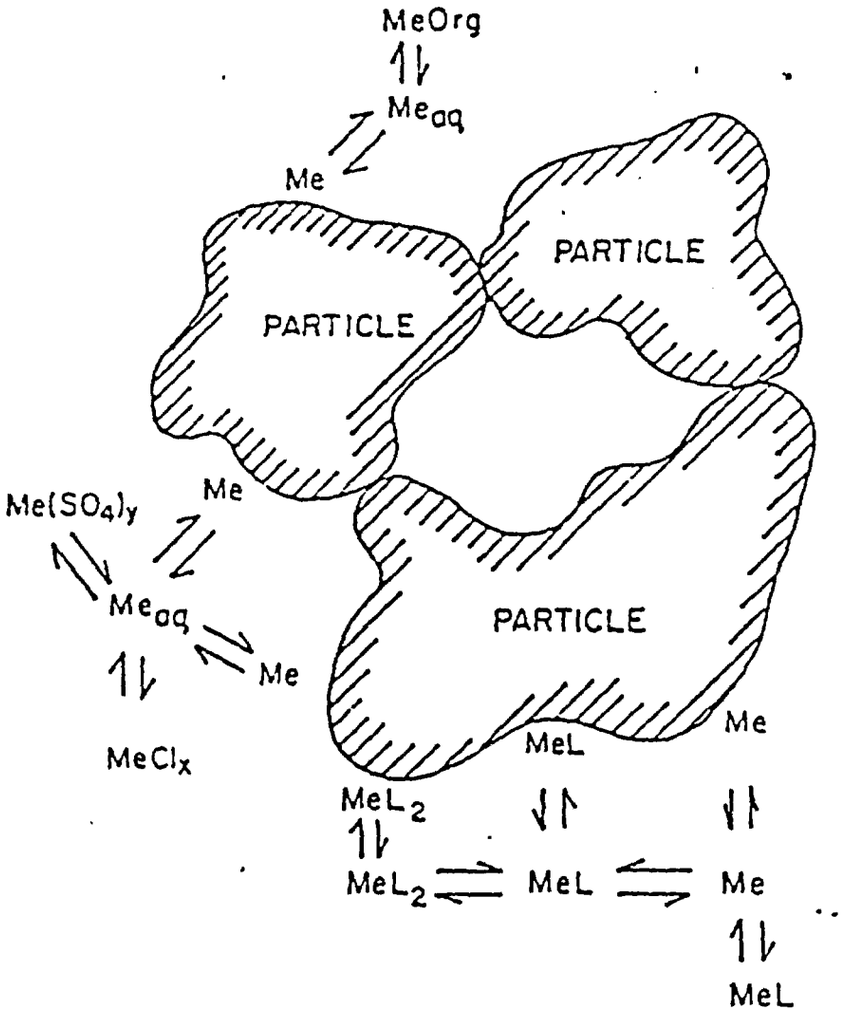


Figure 18. Schematic illustrating complexity of reactions between solution species and surface complexes.

Figure 1.

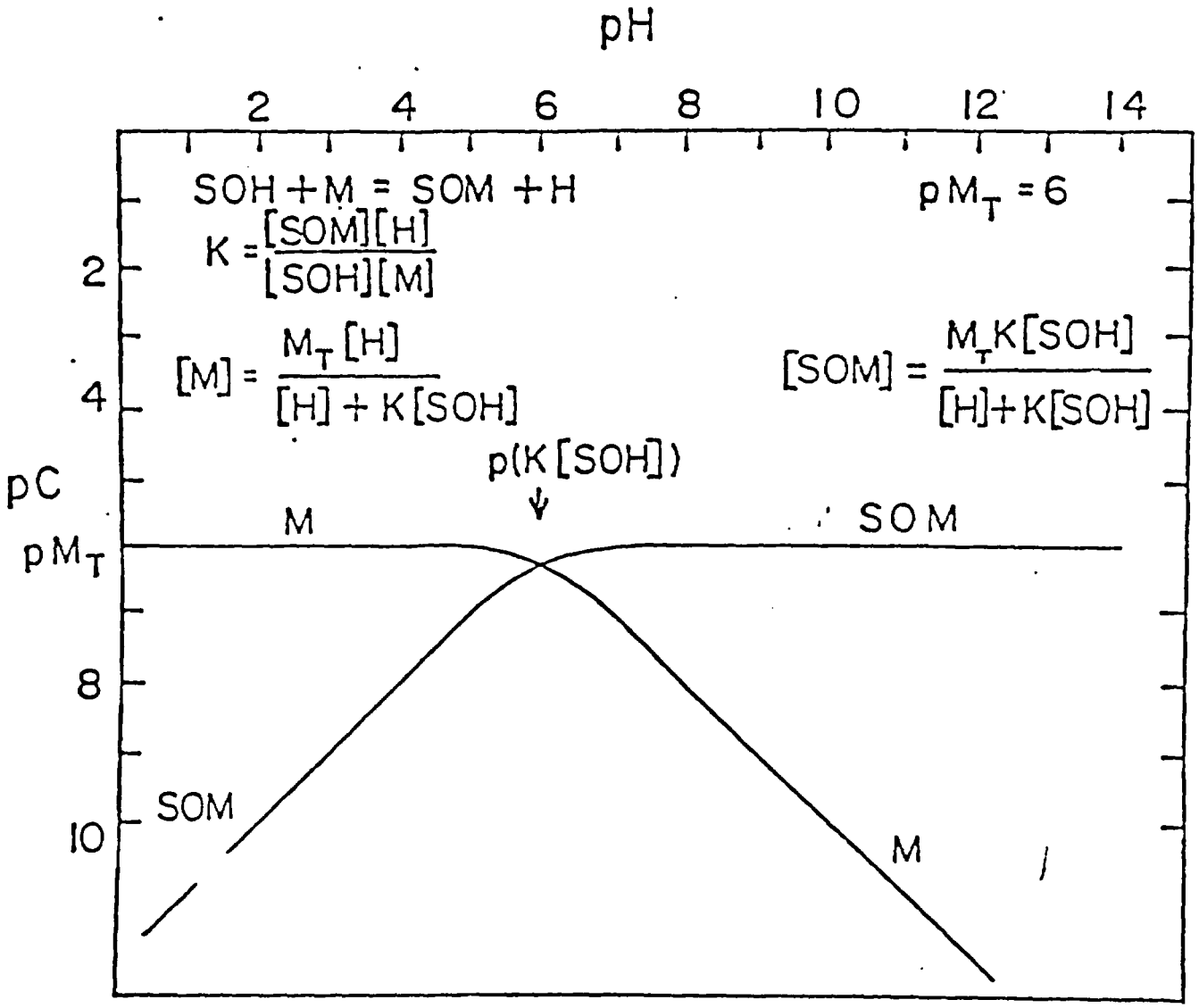


Figure 19. pC-pH diagram showing speciation dependence on available surface binding sites (SOH).

Note: $K_d \propto \frac{[SOM]}{[M]}$

Figure 2.

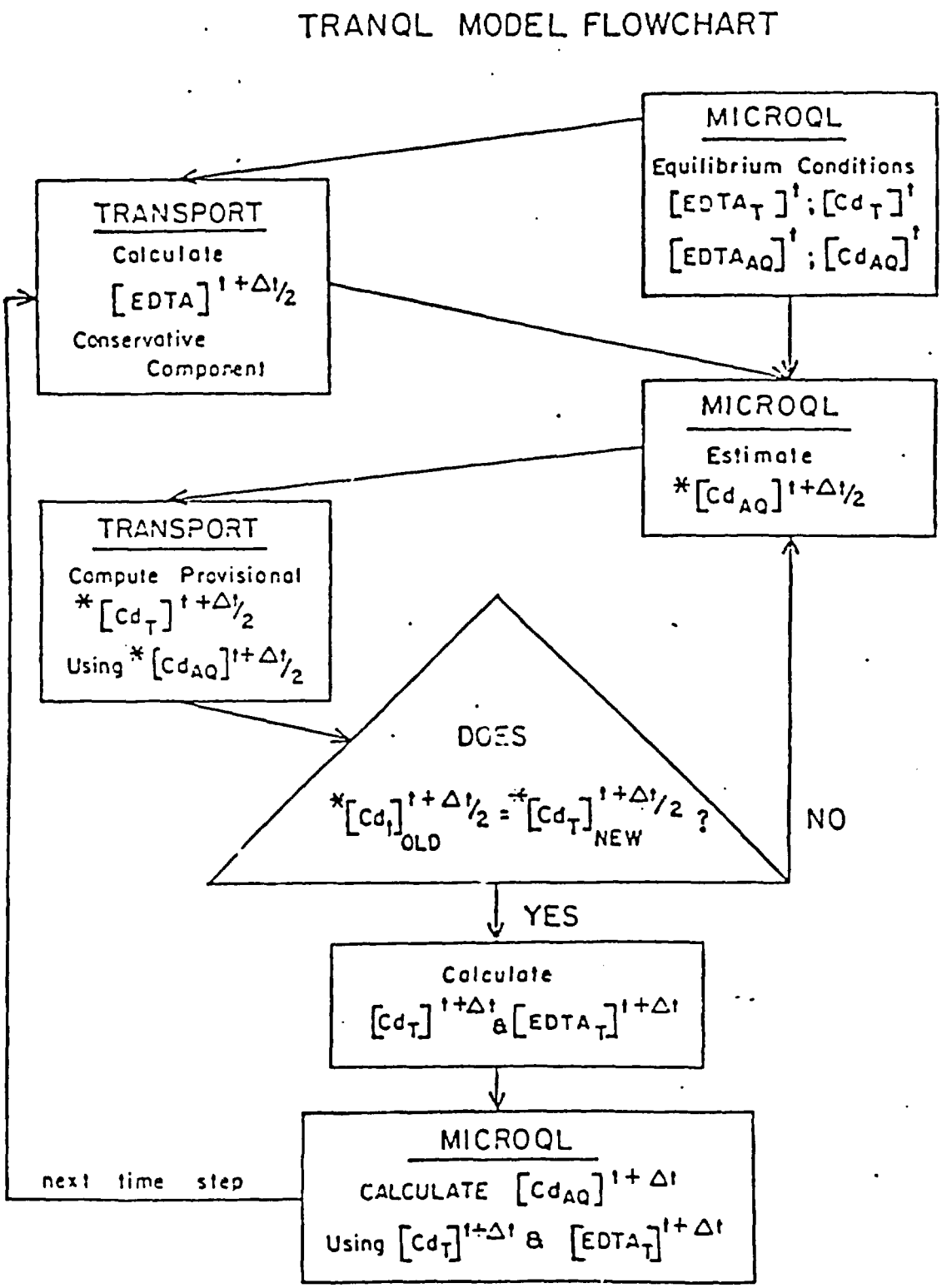
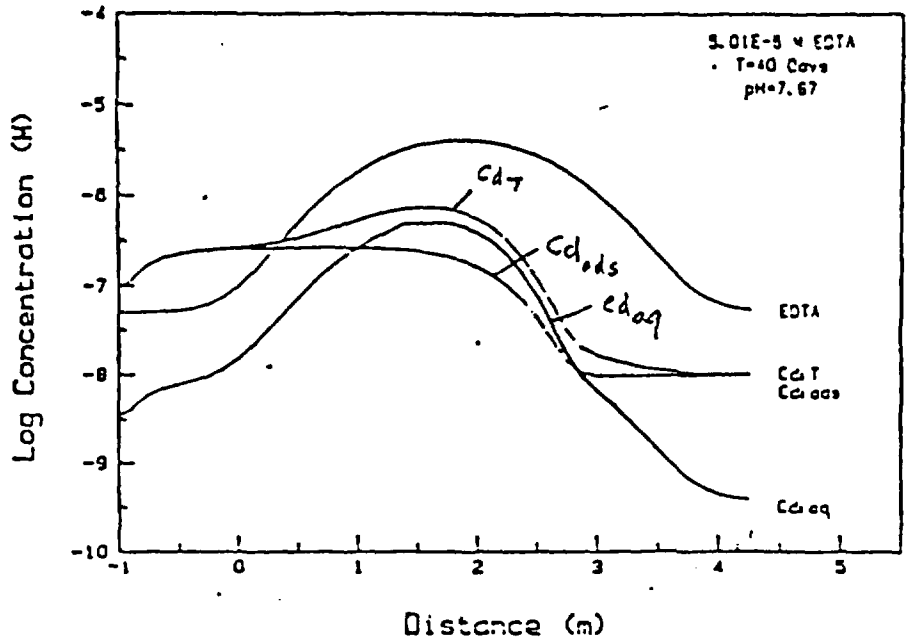
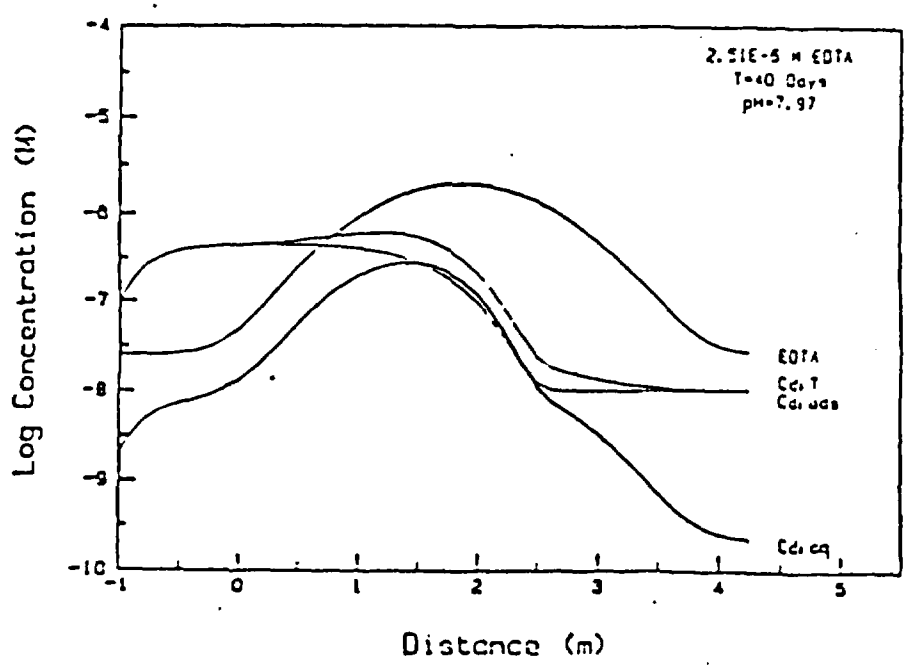


Figure 22. Flow chart for the TRANQL transport-speciation model.

Figure 3.



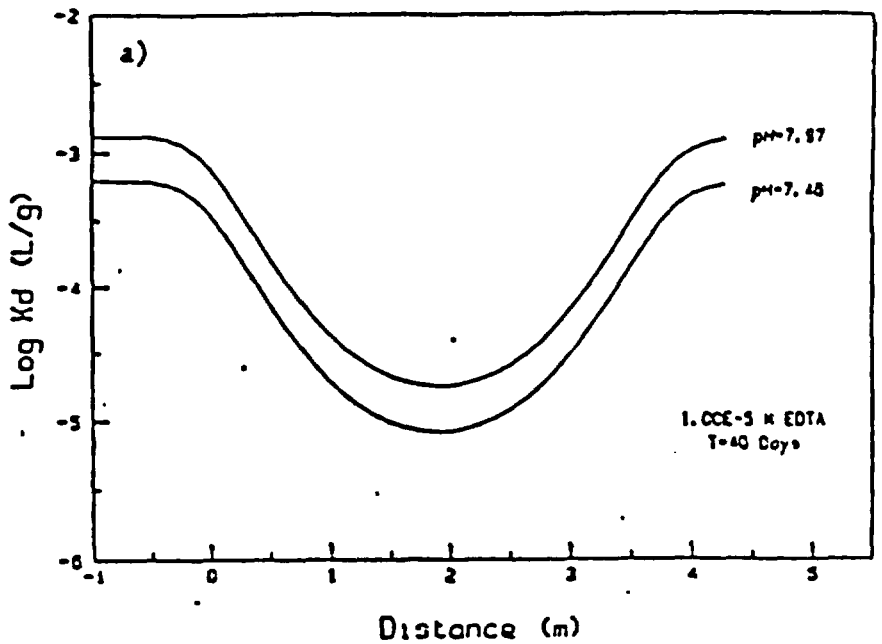
c. EDTA concentration = 5.0×10^{-6}M.



d. EDTA concentration = 2.5×10^{-6}M.

Figure 23 (cont). Simulation of transport of Cd and EDTA at pH 7.97 for four different EDTA concentrations. Simulation of distance at 40 days and $Cd_T = 10^{-6}$M.

Figure 4



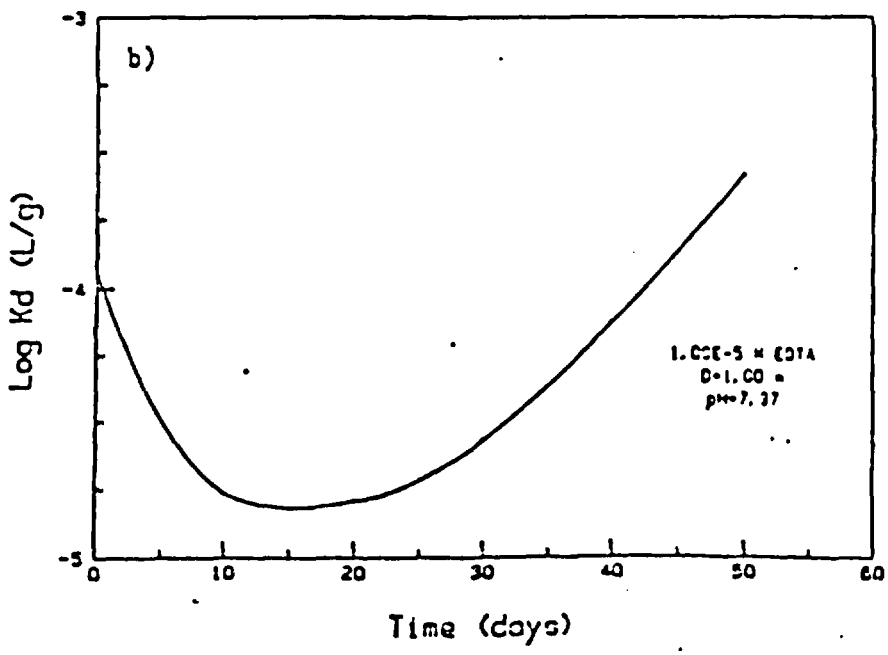


Figure 26. a. Changes in computed K_d with distance at two pH values and at 40 days; b. Changes in computed K_d values with time at 1 m distance and pH 7.97.

Attachment 10

Availability of Thermochemical Data for Solubility/Speciation Calculations

Dr. S. Phillips

Focus on Equilibria for Nuclear Waste Disposal

$$U^{4+} + H_2O = UOH^{3+} + H^+$$

$$UO_2^{2+} + e = UO_2^+$$

Fórmat for Selected Code(s)

$$U^{4+} + 2H_2O = UO_2^{2+} + 4H^+ + 2e$$

Ranges

0 - 200, 350°C

0 - 3, 6 ionic strength

Thermochemical data content

(1) Select most reliable measurements

(2) Tabulate values which reproduce most reliable measurements

(3) Assign uncertainty

(4) Use other compilations (NBS; CODATA; JANAF; Cobble et al.; deBethune et al.; Naumov et al.; Fuger,Oetting)

(5) Clark - Glew for log K(T)

(6) Pitzer for log K(I)

Data Evaluation Criteria Include

- °Purity of materials
- °Details given on experimental procedure
- °Uncertainty assigned by researcher
- °Number of replicate measurements
- °Publication in refereed journal
- °Previous publications by researcher
- °Temperature, pressure, concentration range covered

Critically Evaluated Thermochemical Data

(25 °C; I = 0)

- °Equilibrium constants
- °Thermodynamic properties
- °Nernstian potentials
- °Solubility product
- °Diffusion coefficient
- °Other (e.g.,solubility)

Hubi; Ans

Aqueous Solutions Database

DRAFT COPY

IODINE
Element
Data Compilation
March 1984

SUBSTANCES: I2(aq);I2(s);I2(g)

PROPERTIES OF ELEMENTAL IODINE:

Atomic Number: 53
Formula Mass: 126.9044 for I
Electronic Configuration: [Kr]4d10 5s2 5p5
Electronegativity: 2.55(17)
Hydration Number: 2 (25 C;K+ or Cl- reference ions) (19)
Ionic Radius (I-): 0.222 nanometer (3)
Common range for soils: 0.1 to 40 mg/L(25)
Concentration in natural waters: ug/L range(29).
Concentration in brine (I-): 10 mg/L(30).
Half-life: I-129 = 1.57 E+7 year;beta- 0.15 and gamma 0.03958 (7.50% A) decay modes (27).

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

Substance	ΔfGo kJ mol-1	ΔfHo kJ mol-1	So J mol-1 K-1	Cp J mol-1 K-1
I2(g)	19.327*	62.421±.080	260.567±.063	36.90*
I2(s)	0	0	116.135*	54.438*
I2(aq)	16.40*	22.6*	137.2*	330.5±?

*Uncertainty lies between 8 and 80 units of last (right-most) digit (10).

B. CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	logK
I2(s) = I2(aq)	- 2.87
I2(s) = I2(g)	- 3.39
I2(g) = I2(aq)	0.51
I2(aq) + I- = I3-	2.84
I2(aq) + H2O = HIO(aq) + H+ + I-	-12.27
I2(aq) + H2O = H2IO+ +I-	-10.95
3I2(aq) + 3H2O = IO3- + 5I- + 6H+	-48.41
3I2(aq) + 6OH- = IO3- + 5I- + 3H2O	35.56
I2(g) = I2(sorbed;Ag on alumina)*	>3 retention factor

*See Trevorrow et al. for detailed data on distribution ratio

C. THERMODYNAMIC PROPERTIES OF CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	ΔrH kJ mol-1	ΔS J mol-1 K-1	ΔCp
I2(s) = I2(aq)	22.6	21.1	276.1
I2(s) = I2(g)	62.42	144.432	- 17.54
I2(g) = I2(aq)	- 39.82	-123.4	293.6
I2(aq) + I- = I3-	- 17.59	- 4.6	138*
I2(aq) + H2O = HIO(aq) + H+ + I-	68.23	- 5.05	- 414.2
3I2(aq) + 3H2O = IO3- + 5I- + 6H+	283.89	30.45	-2008.4
3I2(aq) + 6OH- = IO3- + 5I- + 3H2O	- 50.94	514.41	- 665.6

* Cp estimated from reference (20).

D. ELECTRODE POTENTIAL: 25 C; I=0

Electrochemical Equation	Eo,volt
I3- + 2e = 3I-	+0.536
I2(s) + 2e = 2I-	+0.5355
I2(aq) + 2e = 2I-	+0.5355

E. DIFFUSION COEFFICIENT:25 C. I2(aq) = 2.25±0.02 E-5 cm2/sec.(23).

F. SOLUBILITY IN WATER:25 C. 0.335 gI2/1000g H2O. Reference (12) tabulates solubility from 0 to 110 C. Katzin and Gebert find (13):

Solution	Solubility(in units of 1.00 E-3 M) 20 C	25 C	30 C
H2O	1.127	1.320	1.526
0.01M HClO4	1.129	1.310	1.520
1.0 M HClO4	1.053	1.27	1.465
0.09M NaClO4 + 0.01M HClO4	1.093	1.269	1.36
0.1 M NaClO4	1.126	1.275	1.46
1.0M NaClO4	0.834	1.039	1.15
0.99M NaClO4 + 0.01M HClO4		0.965	

Uncertainty ±0.007

SUBSTANCES: I-;I3-;CH3I(g);HgI(s);HgI(aq);AgI(s)

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

Substance	ΔfGo kJ mol-1	ΔfHo kJ mol-1	So J mol-1 K-1	Cp J mol-1 K-1
I-	- 51.57*	-56.90±0.84	106.70±0.20	-142.3*
I3-	- 51.4*	-51.89±0.3	239.3*	326.2±?
CH3I(g)	14.7*	13.0*	254.12*	44.10*
HgI2(s)	-101.7*	-105.4*	180*	82.0(100 C)
HgI2(aq)	- 75.3*	-79.5*	176*	
AgI(s)	- 66.19*	-61.84*	115.5*	56.82*

*Uncertainty lies between 8 and 80 units of last digit (10).

B. CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	logK
I- + IO- + H2O = I2OH- + OH-	- 0.89
I- + IO- = I2O--	- 1.34
I- + I2(aq) = I3-	2.84
I- + H+ + HIO3(aq) = I2(aq) + H2O	12.27
5I- + IO3- + 6H+ = 3I2(aq) + 3H2O	48.41
I- = I(sorbed);PbS(s)	FR = 0.94±0.05*

*FR = fraction of activity sorbed (26).

C. THERMODYNAMIC PROPERTIES OF CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	$\Delta_r H$ kJ mol-1	ΔS J mol-1 K-1	ΔCp
I- + IO- + H2O = I2OH- + OH-			
I- + IO- = I2O--			
I- + I2(aq) = I3-	- 17.59	- 4.6	138
I- + H+ + HIO3(aq) = I2(aq) + H2O	- 68.23	5.05	414.3
5I- + IO3- + 6H+ = 3I2(aq) + 3H2O	-283.89	- 30.45	2008.4

D. DIFFUSION COEFFICIENT:25C. I- = 1.765±0.035 E-5 cm2/sec. in 1M NaCl (22).

SUBSTANCES: IO3-;IO-;I2O--;I2OH-;HIO3(aq);HIO(aq);HIO(g)

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

Substance	ΔfGo	ΔfHo	So	Cp
	kJ mol-1		J mol-1 K-1	
IO3-	-128.0*	-221.3*	118.4*	- 79.5±? **
IO-	- 38.5*	-107.5*	- 5.4*	
I2O--	- 82.4*			
H2IO+	-106.7*			
I2OH-	-165.0±?			
HIO(g)	- 85.8±1.4	- 98.3±11.8	187.4±47	
HIO(aq)	- 99.1*	-138.1*	95.4*	(133.9)±? ***
HIO3(aq)	-132.6*	-211.3*	166.9*	

*Uncertainty lies between 8 and 80 units of last (right-most) digit (10).
**From Naumov et al.(9).
***From Cobble et al.(5).
COMMENT: Data for HIO(g) from Lin (31).

B. CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	logK
HIO3(aq) = IO3- + H+	- 0.81
3I2(aq) + 3H2O = IO3- + 5I- +6H+	-48.41
3I2(aq) + 6OH- = IO3- + 5I- + 3H2O	35.56
HIO(aq) = IO- + H+	-10.62
IO- + I- + H2O = I2OH- + OH-	- 0.89
IO- + I- = I2O--	- 1.34
H2IO+ = HIO(aq) + H+	- 1.33
I2(aq) + H2O = HIO(aq) + H+ + I-	-12.27
IO3- = IO3(sorbed);PbS(s)	FR = 0.95±0.04(26)
IO- + 2I- + H2O = I3- + 2OH-	- 2.26
I2OH- = I2O-- + H+	-14.47

C. THERMODYNAMIC PROPERTIES OF CHEMICAL EQUILIBRIA: 25 C; I=0

Chemical Equation	$\Delta_r H$ kJ mol-1	ΔS J mol-1 K-1	ΔC_p
HIO3(aq) = IO3- + H+	- 2.76*	- 24.7*	
3I2(aq) + 3H2O = IO3- + 5I- +6H+	-283.09	30.45	-2008.4
3I2(aq) + 6OH- = IO3- + 5I- + 3H2O	- 50.94	514.41	- 665.6
HIO(aq) = IO- + H+	30.6	-100.8	
IO- + I- + H2O = I2OH- + OH-			
I[illegible] + [illegible]- = I2O--			
H2IO+ = HIO(aq) + H+			
I2(aq) + H2O = HIO(aq) + H+ + I-	68.23	- 5.05	-414.3

*From Woolley et al.(15).

D. ELECTRODE POTENTIAL: 25 C; I=0

Electrochemical Equation	Eo,volt
2HIO(aq) + 2H+ + 2e = I2(aq) + 2H2O	+1.439
IO- + 2H+ + 2e = I- + H2O	+1.31
2IO3- + 12H+ + 10e = I2(aq) + 6H2O	+1.195
IO3- + 6H+ + 6e = I- + 3H2O	+1.085
HIO3(aq) + 5H+ + 6e = I- + 3H2O	+1.08
HIO(aq) + H+ + 2e= I- + H2O	+0.987
IO3- + 2H2O + 4e = IO- + 4OH-	+0.56
IO- + H2O + 2e = I- + 2OH-	+0.485
IO3- + 3H2O + 6e = I- + 6OH-	+0.26

E. DIFFUSION COEFFICIENT:

F. COMMENT: Palmer and Lietzke (1) list 31 references to publications on chemistry of iodine. Barner and Scheuerman (8) tabulate thermodynamic properties of IO3-,I-,IO-,HIO(aq),HIO3(aq) from 25 to 300 C. Data on ionization of HIO3(aq) are from Woolley et al.(15).

Summary of Effect of Ionic Strength and Temperature on Equilibria

A. CHANGE IN logK(I) WITH IONIC STRENGTH: 25 C

Chemical Equation	logK(I) at ionic strength indicated logK(I)	Ref.
I2(aq) + I- = I3-	2.84(0);2.86(0.1);2.86(1.0)	2,13,20
I2(aq) + H2O = HIO(aq) + H+ + I-	-12.27(0.01);-13.31(0.01,1.6 C)	2,35
3I2(aq) + 3H2O = IO3- + 5I- 6H+	-48.41(0);-46.90;-47.23	1,31,38
IO- + I- + H2O = I2OH- + OH-	- 0.89	2
IO- + I- = I2O--	- 1.34(0)	2
HIO(aq) = IO- + H+	-10.61(0);-12.35	2,31,38
HIO3(aq) = IO3- + H+	-0.81(0);-0.68(.179);-0.62(.274) -0.48(.445);-0.74(.110);-0.64(.195) -0.57(.295);-0.59(.178)	2,16
H2IO+ = HIO(aq) + H+	-1.33(0);-1.35(0.01);-1.52	1,35
I2(aq) + H2O = H2IO+ +I-	-10.9(0.01)	35
IO - + 2I- + H2O = I3- + 2OH-	- 2.29	2
I2OH- = I2O-- + H+	-14.48	2

A1. ACTIVITY COEFFICIENTS; 25 C

Substance	Activity coefficient,at ionic strength shown	Ref.
IO3-		
IO-		
I2O--		
I2OH-		
H2IO-		
I3-		
I-	0.702(0.1);0.7~~3~~2(.2);0.707(0.41);~~1.630~~ 0.693(0.62);0.687(0.83)	34

COMMENT: Ionic strength of seawater = 0.723, ionic strength of river water is 0.00209 (34).

B. CHANGE IN logK(T) WITH TEMPERATURE: I=0

Chemical Equation	logK(T) 25	50	75	100	150	200
*I2(aq) + I- = I3-	2.84	2.63	2.48	2.39	2.33	2.46
I2(aq) + H2O = HIO(aq) + H+ + I-	-12.22	-11.36	-10.75	-10.32	- 9.87	- 9.78
**3I2(aq) + 3H2O = IO3- + 5I- 6H+	-48.14	-44.62	-42.19	-40.59	-39.19	-39.39
IO- + I- + H2O = I2OH- + OH-	- 0.87	- 0.74	-0.61	-0.50	-0.32	-0.18
IO- + I- = I2O--	- 1.34					
HIO(aq) = IO- + H+	-10.64	-10.36	-10.19	- 9.91	- 8.58	- 5.85
HIO3(aq) = IO3- + H+	- 0.78	- 0.91	- 0.98	- 0.99	- 0.91	- 0.71
H2IO+ = HIO(aq) + H+	- 1.52	- 0.79	- 0.23	0.21	0.83	1.17
*3I2(aq) + 6OH- = IO3- + 5I- + 3H2O	35.79	34.99	34.11	33.18	31.25	29.29
I2(g) = I2(aq)	0.53	0.04	-0.29	-0.51	-0.69	-0.64

COMMENT: Data for HIO(aq)=IO- + H+ calculated here from data in Barner and Scheuerman (8).

*Calculated using balanced like charges (5) and following equation:

$$2.303\ R\ \log K(T) = \Delta So - \Delta Ho/T + \Delta Cpo[298.15/T - 1 + \ln(T/298.15)] \quad (1)$$

**from eq(1) and 6(logKw).

C. SUMMARY OF SELECTED EXPERIMENTAL DATA

Substance	Method	Data	Reference
I2(aq)	Capillary cell	Diffusion Coefficient	23
HIO3(aq)	Calorimetry	ΔrH;ΔrG;ΔS;25 C	15
HIO3(aq)	Ion-exchange	Dissociation quotients 0.179(u(0.450;25 C	16
I3-	CCl4 extraction;	Equilibria quotients ΔCp;25-63 C	20
I3-	Calorimetry	KΔfH;ΔfG; S;25C	24
I2(aq)	I-131;diaphragm cell	Diffusion coeffient;25C 0.1-3.669M LiCl;NaCl;KCl	22
I2(s)	Calorimetry	ΔH(solution	24
I-	Calorimetry	ΔrH for IO3- + I- reaction;25 C	24
I2(aq)	Calorimetry	ΔfH;ΔfG;ΔS;25C	24
IO3-	Calorimetry	ΔfH;ΔfG;ΔS;25C	24
I-	Calorimetry	ΔfH;25 C	4
I-	Calorimetry	ΔfH;25 C	6
I3-	Solubility	I3- formation quotients;20-30 C	13
I2(aq)	Titration	Solubility 20-30 C	13
HIO(aq)	Spectroscopy	HIO(aq) ionization quotients;25 C	2
IO-	emf	standard potential;25C	2
IO-	Spectroscopic	Equilibria quotients for reactions with I-	2
	trap;I-13:	HIO(g) properties	
I-	Ag sorbents; gamma spectroscopy	Sorption of I-	32
HIO(g)	Ion-exchange;gas trap;I-131	HIO(g)/HIO(aq) partition; HIO(g) properties	31
I2(aq)	Conductivity	Hydrolysis	31
I2(aq)	Spectroscopy	Hydrolysis; thermodynamic properties	35

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	0.40	Smith 76
CuCl2	0.69±0.04(20,.691)	Morris 62;Sato 77
	0.40±0.05(1.0)	Bjerrum 77
	0.28(5.0)	Bjerrum 77
	0.16	Ball 81
CuCl3^-	0.55±0.03(20,.691)	Morris 62;Sato 77
	0.31(5.0)	Bjerrum 77
	-2.29	Ball 81
CuCl4^2-	0.00±.18(20,.691)	Morris 62;Sato 77
	0.32(5.0)	Bjerrum 77
	-4.59	Ball 81
CuSO4	2.36±0.03	Smith 76
	2.26±0.07	Izatt 69
CuHCO3^+	2.08±0.01	Bauman 81
	4.29	Mattigod 79
CuCO3	6.75±0.02	Smith 76
	6.73	Mattigod 79
	6.74	Sunda 79
	6.1(0.1)	Bilinski 76
Cu(CO3)2^2-	9.92±0.09	Smith 76
	10.24	Sunda 79
	10.01	Lu 77
	9.9(0.1)	Bilinski 76
CuHPO4	3.2(.1)	Smith 76
	4.09	Wolery 80
CuH2PO4^+	1.76	Mattigod 79
	1.3(37C,.15)	Smith 76
CuPO4^-	9.85	Mattigod 79
Curium		
Cm^3+		
CmOH^2+	-3.4±0.1(.005)	Shalinets 72
	-5.92(0.1)	Desire 69
Cm(OH)2^+	-9.1±0.3(.005)	Shalinets 72
CmF^2+	3.34(.5)	Smith 76
	2.61±0.02(1.0)	Choppin 76
CmF2^+	6.18(.5)	Smith 76
CmF3	9.1(.5)	Smith 76
CmCl^2+	1.15	Ward 56
	0.21±0.02(30,1.0)	Khopkar 80
CmCl2^+	-0.027±0.004(30,1.0)	Khopkar 80
CmSO4^+	1.86(0.5)	Smith 76
	1.51±0.2(30C,1.0)	Khopkar 80
	1.34(2.0)	Smith 76
Cm(SO4)2^-	2.7(.5)	Smith 76
	2.4±0.1(1.0,30C)	Khopkar 80
	1.84(2.0)	Smith 76
CmH2PO4^2+	1.48(20C,1.0)	Moskvin 71C
Cm(H2PO4)2^+	2.08(20C,1.0)	Moskvin 71C
Cm(H2PO4)3	2.84(20C,1.0)	Moskvin 71C
Cm(H2PO4)4^-	3.1(20C,1.0)	Moskvin 71C
CmPO4	17.5(20C,1.0)	Moskvin 71C
Cm(PO4)2^3-	34.1(20C,1.0)	Moskvin 71C

Pb6(OH)8^4+	-43.61±0.1	Baes 76
	-43.38±0.009(0.1)	Sylva 80
	-44.68±0.01(3.0)	Kogure 81
PbF^+	1.44±0.04(1.0)	Smith 76
	1.25	Ball 81
	2.09	Wolery 82
PbF2	2.54(1.0)	Smith 76
	2.56	Ball 81
	3.48	Wolery 82
PbF3^-	3.42	Ball 81
PbF4^2-	3.1	Ball 81
PbCl^+	1.59±0.02	Lu 77;Smith 76
	0.90±0.02(1.0)	Byrne 81B
PbCl2	1.8	Byrne 81;Smith 76
	1.21±0.02(1.0)	Byrne 81B
PbCl3^-	1.7	Smith 76
	1.16±0.05(1.0)	Byrne 81B
PbCl4^2-	1.7±0.2(4.0)	Smith 76
	1.4	Smith 76
PbSO4	2.75±0.1	Smith 76
Pb(SO4)2^2-	3.47	Hem 76
PbCO3	7.00	Turner 81
	6.4(0.1)	Bilinski 76
	5.75(0.3)	Petrie 78
	6.6±0.8(0.7)	Nurnberg 76
Pb(CO3)2^2-	10.36	Hem 76;Whitfield 80
	9.8(0.1)	Bilinski 76
	9.15(0.3)	Petrie 78
PbHCO3^+	5.43±0.31(0.7)	Nurnberg 76
Pb(HCO3)2	8.73±0.9(0.7)	Nurnberg 76
PbHPO4	3.1±0.8	Nriagu 72B
PbH2PO4^+	1.5±0.5	Nriagu 72B

Neptunium

NpO2^2+

NpO2OH^+	-5.15±0.09	Baes 76
NpO2(OH)2	(-10.2±0.8)	Allard 80
NpO2(OH)3^-	(-19±2)	Allard 80
(NpO2)2OH^3+	(-4±2)	Allard 80
(NpO2)2(OH)2^2+	-6.39±0.06	Baes 76
(NpO2)3(OH)4^2+	(-13±2)	Allard 80
(NpO2)3(OH)5^+	-17.49±0.06	Baes 76
NpO2F^+	4.6	Smith 76
NpO2F2	7.01(.1)	Smith 76
NpO2Cl^+	-0.3(.5)	Smith 76
NpO2Cl2	-0.8(10 C,3.0)	Smith 76
NpO2SO4	3.27	Smith 76
NpO2(SO4)2^2-	3.8(.1)	Smith 76

NpO2^+

NpO2OH	-8.85±?	Baes 76
	-8.88±0.02(20C,.02)	Sevost'yanova 76

NpO2(OH)2^-	(-18±2)	Allard 80
NpO2Cl	0.38±0.04(2.0)	Vasudeva Rao 79
NpO2F	0.28±0.06(2.0)	Vasudeva Rao 79
NpO2SO4^-	1.04±0.4(20C,1.5)	Moskvin 79
	2.8±0.3(2.0)	Vasudeva Rao 79
NpO2HCO3	2.15±0.05(20C,.25)	Moskvin 79
NpO2(HCO3)2^-	3.66±0.12(20C,.25)	Moskvin 79
NpO2CO3^-	5.9±0.5	Nitsche 82
NpO2(CO3)3^5-	16.3±0.5	Nitsche 82
NpO2HPO4^-	2.90±0.11(20C,.1)	Moskvin 79
NpO2PO4^2-	5.78±0.25(20C,1.0)	Moskvin 79
NpO2(C2O4)^-	3.38±0.11(20C,.5)	Moskvin 79
NpO2(C2O4)2^3-	5.65±0.12(20C,.5)	Moskvin 79
Np^4+		
NpOH^3+	-1.49±0.05	Baes 76
Np(OH)2^2+	(-2.8±0.7)	Allard 80
Np(OH)3^+	(-5.6±1.1)	Allard 80
Np(OH)4	(-9.9±1.4)	Allard 80
Np(OH)5^-	(-17±2)	Allard 80
Np2(OH)2^6+	(-2±3)	Allard 80
Np2(OH)3^5+	(-3±4)	Allard 80
Np2(OH)4^4+	(-5±5)	Allard 80
Np2(OH)5^3+	(-9±6)	Allard 80
NpF^3+	7.45±0.02(1.0)	Choppin 76
	8.3(20C,4.0)	Smith 76
NpF2^2+	14.5(20C,4.0)	Smith 76
NpF3^+	20.3(20C,4.0)	Smith 76
NpF4	25.1(20C,4.0)	Smith 76
NpCl^3+	-0.04(20C,1.0)	Smith 76
NpCl2^2+	-0.24(20C,1.0)	Smith 76
NpCl3^+	-0.5(20C,1.0)	Smith 76
NpSO4^2+	3.41(23C,3.0)	Smith 76
	3.46(2.0)	Fardy 74;Ahrland 68
Np(SO4)2	5.42(23C,3.0)	Smith 76
Np^3+		
NpOH^2+	(-7.4±0.5)	Allard 80;Mefod'eva 74
Np(OH)2^+	(-17±1)	Allard 80
Np(OH)3	(-27±2)	Allard 80
Np(OH)4^-	(-38±2)	Allard 80
Np2(OH)2^4+	(-13±2)	Allard 80
NpCl^2+	-2.4±0.1(11.7)	Shiloh 66
NpCl2^+	-4.96±0.04(11.7)	Shiloh 66
Nickel		
NiOH^+	-9.86±0.03	Baes 76
Ni(OH)2	-20.26±1.77	Tremaine 80
Ni(OH)3^-	-29.03±0.50	Tremaine 80
Ni(OH)4^2-	<-44	Baes 76

Pu(H2PO4)4^-	3.5(20C,1.0)	Moskvin 71C
PuPO4	19.3(20C,1.0)	Moskvin 71C
Samarium		
SmOH^2+	-7.9±0.2	Baes 76
Sm(OH)2^+	-16.6	Turner 81
Sm(OH)3	-25.8	Turner 81
Sm(OH)4^-	-35.7	Turner 81
SmF^2+	3.12(1.0)	Smith 76
	4.02	Turner 81
SmCl^2+	0.13(1.0)	Moulin 75
	0.80	Turner 81
SmCl2^+	-0.29	Turner 81
SmSO4^+	3.67±0.01	Smith 76
	3.52±0.09	Izatt 69
Sm(SO4)2^-	5.19	Turner 81
	5.20±0.10	Izatt 69
SmCO3^+	6.86	Turner 81
Strontium		
SrOH^+	-13.29±0.1	Baes 76
SrF^+	0.1±0.1(1.0)	Smith 76
SrF2	2.02	Rai 78
SrCl2	0.00	Rai 78
SrSO4	2.55	Smith 76
SrPO4^-	[illegible].2(20,.1)	Smith 76
SrHPO4	2.57	Wolery 80
SrH2PO4^+	0.75	Wolery 80
Technetium		
TcOOH^+	-1.4(20C,0.1)	Jensen 81;Smith 76
TcO(OH)2	-3.8(20C,0.1)	Jensen 81
Thorium		
ThOH^3+	-3.20±0.2	Baes 76
Th(OH)2^2+	-6.93±0.2	Baes 76
Th(OH)3^+	<-11.7	Baes 76
Th(OH)4	-15.9±0.3	Baes 76
Th2(OH)2^6+	-6.14±0.06	Baes 76
Th4(OH)8^8+	-21.1±0.1	Baes 76
Th6(OH)15^9+	-36.76±0.06	Baes 76
ThF^3+	8.03	Langmuir 80
	7.43±0.03(1.0)	Choppin 76
	7.62(0.5)	Shetty 77
	8.08(0.1)	Bauman 70
ThF2^2+	14.25	Langmuir 80
ThF3^+	18.93	Langmuir 80
ThF4	22.31	Langmuir 80
ThCl^3+	1.09	Langmuir 80
ThCl2^2+	0.80	Langmuir 80
ThCl3^+	1.65	Langmuir 80
ThCl4	1.26	Langmuir 80

U(HPO4)4^4-	39±4	Lemire 80
U^3+		
UOH^2+	(-7±1)	Allard 80
U(OH)2^+	(-17±2)	Allard 80
U(OH)3	(-27±3)	Allard 80
U(OH)4^-	(-39±4)	Allard 80
U2(OH)2^4+	(-13±2)	Allard 80
Zirconium		
ZrOH^3+	0.3±0.05	Baes 76
Zr(OH)2^2+	(-1.7±?)	Baes 76
Zr(OH)3^+	(-5.1±?)	Baes 76
Zr(OH)4	-9.7±1	Baes 76
Zr(OH)5^-	-16.0±?	Baes 76
Zr3(OH)4^8+	-0.6±0.1	Baes 76*
Zr3(OH)5^7+	3.70±0.1	Baes 76*
Zr4(OH)8^8+	6.0±0.1	Baes 76
ZrF^3+	9.80	Turner 81
ZrF2^2+	17.88	Turner 81
ZrF3^+	23.88	Turner 81
ZrF4	31.86	Turner 81
ZrF5^-	25.86	Turner 81
ZrF6^2-	29.83	Turner 81
ZrCl^3+	1.57	Turner 81
ZrCl2^2+	1.47	Turner 81
ZrCl3^+	0.80	Turner 81
ZrCl4	1.2(20,6.5M H^+)	Smith 76
ZrSO4^2+	7.79	Turner 81
Zr(SO4)2	12.59	Turner 81
Zr(SO4)3^2-	13.49	Turner 81

* Select either species, but not both
Rem: JOSH 2

Table 2.Coefficients for calculating LogKxy vs. I using Eq 1 or Eq 2;25C

Species	LogKxy(0)	AΔz2	B	C	Ref.(equation)
Aluminum					
AlOH^2+	-4.98	-2.044	1.0	0.52	Baes 76,81(Eq 1)
Al(OH)2^+	-10.1	-3.07	1.0	0.55	Eq 1
Al(OH)3	-16.0	-3.07	1.0	0.45	Eq 1
Al(OH)4^-	-23.0	-2.044	1.0	0.36	Baes 76(Eq 1)
Al13O4(OH)24^7+	-98.73	-18.40	1.0	3.55	Baes 76(Eq 1)
Al2(OH)2^4+	-7.7	0	0	0	Baes 76(Eq 1)
Al3(OH)4^5+	-13.94	1.022	1.0	0	Baes 76(Eq 1)
AlF^2+	7.01	-3.07	1.71	0.20	Turner 81(Eq 1)
AlF2^+	12.73	-5.11	1.33	0.50	Turner 81(Eq 1)
AlF3	16.71	-6.14	1.57	0.70	Turner 81(Eq 1)
AlF4^-	19.67	-6.14	1.62	0.70	Turner 81(Eq 1)
AlF5^2-	20.73	-5.11	1.62	0.70	Turner 81(Eq 1)
AlF6^3-	20.46	-3.07	1.62	0.70	Turner 81(Eq 1)
AlSO4^+	3.02	-3.07	1.0	0.30	Eq 2
Al(SO4)2^-	4.92	-8.18	1.0	0.30	Eq 2
Americium					
AmO2^+					
AmO2HCO3	2.4	-1.02	1.0	0.3	Eq 2
AmO2C2O4^-	3.7	-2.04	1.0	0.3	Eq 2
AmO2(C2O4)2^3-	5.4	0	1.0	0.3	Eq 2
Am^3+					
AmOH^2+	-8.0	-2.04	3.22	-0.25	Eq 1
Am(OH)2^+	(-16.9)	-3.07	2.88	-0.25	Eq 1
Am(OH)3	(-26.5)	-3.07	3.02	-0.32	Eq 1
Am(OH)4^-	-37.1	-2.04	4.18	-0.54	Eq 1
Am2(OH)2^4+	-13.86	0	1.0	0	Eq 1
Am3(OH)5^4+	-28.5	-3.07	1.6	1.01	Eq 1
AmF^2+	4.3	-3.07	1.6	0.065	Eq 1
AmF2^+	7.4	-5.11	1.0	0.3	Eq 2
AmF3	10.6	-6.13	1.0	0.3	Eq 2
AmCl^2+	1.1	-3.07	1.0	0.3	Eq 2
AmSO4^+	3.6	-6.13	1.6	0.12	Eq 1
Am(SO4)2^-	5.0	-8.18	1.6	0.3	Eq 1
AmH2PO4^2+	2.73	-3.07	1.0	0.3	Eq 2
Am(H2PO4)^2+	3.72	-5.11	1.0	0.3	Eq 2
Cesium					
CsCl	-0.39	-1.02	0.78	0.06	Turner 81(Eq 1)
CsSO4^-	1.08	-3.07	1.0	0.3	Eq 2
Copper					
CuOH^+	-7.93	-1.02	1.6	0.38	Eq 1
Cu(OH)2	-16.24	-1.02	1.6	0.15	Eq 1
Cu(OH)3^-	(-27.8)	0	1.0	-0.04	Baes 76(Eq 1)
Cu(OH)4^2-	-39.6	+2.044	1.0	-0.16	Baes 76(Eq 1)
Cu2(OH)2^2+	-10.36	-1.022	1.0	0.08	Baes 76(Eq 1)
Cu3(OH)4^2+	-21.62	-2.04	1.0	0.3	Eq 2
Cu2OH^3+	-6.82	-1.02	1.0	0.3	Eq 2
CuF^+	1.52	-2.04	1.57	0.17	Turner 81(Eq 1)
CuCl^+	0.40	-2.05	1.6	0.14	Eq 1
CuCl2	0.16	-3.07	1.0	0.3	Eq 2
CuCl3^-	-2.29	-3.07	1.0	0.3	Eq 2
CuCl4^2-	-4.59	-2.04	1.0	0.3	Eq 2
CuSO4	2.36	-4.09	1.618	0.052	Freeman 81(Eq 1)
CuHCO3^+	4.29	-2.05	1.0	0.3	Eq 2
CuCO3	6.74	-4.09	1.63	0.05	Turner 81(Eq 1)
Cu(CO3)2^2-	10.2	-4.09	1.61	-0.22	Turner 81(Eq 1)
CuHPO4	4.1	-4.09	1.0	0.30	Eq 2
Curium					
Cm^3+					
CmF^2+	4.2	-3.07	1.0	0.3	Eq 2
CmF2^+	7.8	-5.11	1.0	0.3	Eq 2

CmF3	11.9	-6.14	1.0	0.3	Eq 2
CmCl^2+	1.15	-3.07	1.0	0.3	Eq 2
Europium					
EuOH^2+	-7.8	-2.04	3.22	-0.25	Turner 81(Eq 1)
Eu(OH)2^+	-16.6	-3.07	2.88	-0.25	Turner 81(Eq 1)
Eu(OH)3	-25.6	-3.07	3.02	-0.32	Turner 81(Eq 1)
Eu(OH)4^-	-35.3	-2.04	4.18	-0.54	Turner 81(Eq 1)
EuF^2+	4.09	-3.07	1.88	0.16	Turner 81(Eq 1)
EuCl^2+	0.80	-3.07	1.88	0.16	Turner 81(Eq 1)
EuCl2^+	0.99	-5.11	1.33	0.50	Turner 81(Eq 1)
EuSO4^+	3.61	-6.13	1.6	0.21	Eq 1
Eu(SO4)2^-	5.41	-8.18	1.62	0.03	Turner 81(Eq 1)
EuCO3^+	6.83	-6.14	1.85	0.14	Turner 81(Eq 1)
Iron					
Fe^3+					
FeOH^2+	-2.19	-2.04	2.71	-0.04	Turner 81(Eq 1)
Fe(OH)2^+	-5.67	-3.07	3.71	-0.16	Turner 81(Eq 1)
Fe(OH)3	-13.6	-3.07	3.81	-0.07	Eq 1
Fe(OH)4^-	-21.6	-2.04	8.40	-0.22	Turner 81(Eq 1)
Fe2(OH)2^4+	-2.95	0	1.6	0.29	Eq 1
Fe3(OH)4^5+	-6.3	-1.02	1.0	0	Eq 1
FeF^2+	6.0	-3.07	1.77	0.29	Turner 81(Eq 1)
FeF2^+	10.8	-5.11	1.33	0.50	Turner 81(Eq 1)
FeF3	13.8	-6.14	1.57	0.70	Turner 81(Eq 1)
FeCl^2+	1.48	-3.07	1.5	0.295	Rabinowitch42(Eq
FeCl2^+	2.44	-5.11	1.33	0.50	Turner 81(Eq 1)
FeCl3	1.06	-6.14	1.57	0.70	Turner 81(Eq 1)
FeSO4^+	4.04	-3.07	1.85	0.14	Turner 81(Eq 1)
Fe(SO4)2^2-	5.38	-8.18	2.35	-0.39	Turner 81(Eq 1)
FeCO3^+	9.72	-6.14	1.85	0.14	Turner 81(Eq 1)
FeHPO4^+	10.1	-6.13	1.0	0.3	Eq 2
FeH2PO4^2+	4.2	-3.07	1.0	0.3	Eq 2
Fe^2+					
FeOH^+	-9.50	-1.02	2.10	0.01	Turner 81(Eq 1)
Fe(OH)2	-20.6	-1.02	2.01	-0.12	Turner 81(Eq 1)
Fe(OH)3^-	-31	0	0	0.3	Eq 2
Fe(OH)4^2-	-46	-2.05	1.0	-0.34	Turner 81(Eq 1)
FeF^+	1.42	-2.05	1.57	0.17	Turner 81(Eq 1)
FeCl^+	0.32	-2.05	1.57	0.17	Turner 81(Eq 1)
FeCl2	0.81	-3.07	1.0	0.3	Eq 2
FeSO4	2.12	-4.09	1.63	0.05	Turner 81(Eq 1)
FeCO3	5.0	-4.09	1.63	0.05	Turner 81(Eq 1)
FeHCO3^+	2.72	-2.05	1.0	0.3	Eq 2
FeHPO4	3.6	-4.09	1.0	0.3	Eq 2
FeH2PO4^+	2.7	-2.05	1.0	0.3	Eq 2
Lead					
PbOH^+	-7.71	-1.02	17.71	-0.02	Turner 81(Eq 1)
Pb(OH)2	-17.12	-1.02	35.73	-0.09	Turner 81(Eq 1)
Pb(OH)3^-	-28.06	0	1.0	0.3	Eq 2
Pb2OH^3+	-6.36	-1.02	1.0	0.3	Eq 2
Pb3(OH)4^2+	-23.88	-2.04	1.0	0.3	Eq 2
Pb3(OH)5^+	-31.7	-3.07	1.0	0.3	Eq 2
Pb4(OH)4^4+	-20.88	-2.04	1.0	0.3	Eq 2
Pb6(OH)8^4+	-43.61	0	1.0	0.3	Eq 2
PbF^+	2.07	-2.05	1.57	0.17	Turner 81(Eq 1)
PbF2	3.42	-3.07	1.52	0.34	Turner 81(Eq 1)
PbCl^+	1.59	-2.05	1.29	0.22	Turner 81(Eq 1)
PbCl2	1.82	-3.07	2.90	0.26	Turner 81(Eq 1)
PbCl3^-	1.71	-3.07	3.13	0.35	Turner 81(Eq 1)

PbCl4^2-	1.40	-2.04	3.65	0.47	Turner 81(Eq 1)
PbSO4	2.75	-4.09	1.63	0.05	Turner 81(Eq 1)
Pb(SO4)2^2-	4.0	-4.09	1.61	-0.22	Turner 81(Eq 1)
PbCO3	7.00	-4.09	1.63	0.05	Turner 81(Eq 1)
Pb(CO3)2^2-	10.36	-4.09	1.61	-0.22	Turner 81(Eq 1)
PbHPO4	3.1	-4.09	1.0	0.3	Eq 2
PbH2PO4^+	1.5	-2.05	1.0	0.3	Eq 2
Neptunium					
NpO2^2+					
NpO2OH^+	-5.15	-1.02	1.6	0.32	Eq 1
NpO2(OH)2	(-10.2)	-1.02	1.0	0.3	Eq 2
NpO2(OH)3^-	(-19)	0	1.0	0.3	Eq 2
(NpO2)2OH^3+	(-4)	-1.02	1.0	0.3	Eq 2
(NpO2)2(OH)2^2+	-6.39	-1.02	1.6	0.014	Eq 1
(NpO2)3(OH)4^2+	(-13)	-3.07	1.0	0.3	Eq 2
(NpO2)3(OH)5^+	-17.49	-3.07	1.6	0.17	Eq 1
NpO2F^+	4.6	-2.05	1.6	0.43	Eq 1
NpO2F2	7.7	-3.07	1.6	0.93	Eq 1
NpO2Cl^+	0.3	-2.05	1.0	0.3	Eq 2
NpO2SO4	3.27	-4.09	1.0	0.3	Eq 2
NpO2^+					
NpO2OH	-8.85	0	1.0	0.3	Eq 2
NpO2(OH)2^-	(-18)	-1.02	1.0	0.3	Eq 2
NpO2HCO3	2.5	-1.02	1.0	0.3	Eq 2
NpO2(HCO3)2^-	3.9	-1.02	1.0	0.3	Eq 2
NpO2HPO4^-	3.3	-2.04	1.0	0.3	Eq 2
NpO2CO3^-	5.9	-1.02	1.0	0.3	Eq 2
NpO2(CO3)3^5-	16.3	+6.13	1.0	0.3	Eq 2
Np^4+					
NpOH^3+	-1.49	-3.07	1.6	0.12	Eq 1
Np(OH)2^2+	(-2.8)	-5.11	1.0	0.3	Eq 2
Np(OH)3^+	(-5.6)	-6.13	1.0	0.3	Eq 2
Np(OH)4	(-9.9)	-6.13	1.0	0.3	Eq 2
Np(OH)5^-	(-17)	-5.11	1.0	0.3	Eq 2
Np2(OH)2^6+	(-2)	+3.07	1.0	0.3	Eq 2
Np2(OH)3^5+	(-3)	-2.04	1.0	0.3	Eq 2
Np2(OH)4^4+	(-5)	-6.13	1.0	0.3	Eq 2
Np2(OH)5^3+	(-9)	-9.19	1.0	0.3	Eq 2
Np^3+					
NpOH^2+	(-7.4)	-2.04	1.0	0.3	Eq 2
Np(OH)2^+	(-17)	-3.07	1.0	0.3	Eq 2
Np(OH)3	(-27)	+3.07	1.0	0.3	Eq 2
Np(OH)4^-	(-38)	-2.04	1.0	0.3	Eq 2
Np2(OH)2^4+	(-13)	0	1.0	0.3	Eq 2
Nickel					
NiOH^+	-9.86	-1.02	2.02	-0.03	Turner 81(Eq 1)
Ni(OH)2	-20.63	-1.02	2.01	-0.12	Turner 81(Eq 1)
Ni(OH)3^-	-29.03	0	1.0	0.3	Eq 2
Ni(OH)4^2-	-44	+2.04	1.0	-0.34	Turner 81(Eq 1)
Ni2(OH)^3+	-10.7	+1.02	1.6	0	Eq 1
Ni4(OH)4^4+	-27.74	+2.05	1.0	0.3	Eq 2
NiF^+	1.2	-2.05	1.57	0.17	Turner 81(Eq 1)
NiCl^+	0.72	-2.05	1.57	0.17	Turner 81(Eq 1)
NiCl2	0.70	-3.07	1.0	0.3	Eq 2
NiSO4	2.29	-4.09	1.90	-0.06	Turner 81(Eq 1)
Ni(SO4)2^2+	3.2	-4.09	1.61	-0.22	Turner 81(Eq 1)
NiCO3	5.78	-4.09	1.63	0.05	Turner 81(Eq 1)
Ni(CO3)2^2-	10.11	-4.09	1.0	0.3	Eq 2
NiHCO3^+	3.08	-2.05	1.0	0.3	Eq 2
NiPO4^-	8.37	-6.13	1.0	0.3	Eq 2
Plutonium					

SmCO3^+	6.86	-6.14	1.85	0.14	Turner 81(Eq 1)
Strontium					
SrOH^+	-13.29	-1.02	1.0	0.3	Eq 2
SrCl2	0.00	-3.07	1.0	0.3	Eq 2
SrSO4	2.55	-4.09	1.0	0.3	Eq 2
SrPO4^-	5.6	-6.13	1.0	0.3	Eq 2
chnetium					
TcOOH^+	-1.0	-2.04	1.0	0.3	Eq 2
TcO(OH)2	-3.2	-3.07	1.0	0.3	Eq 2
Thorium					
ThOH^3+	-3.20	-3.07	2.02	0.09	Turner 81(Eq 1)
Th(OH)2^2+	-6.93	-5.11	4.84	0.19	Turner 81(Eq 1)
Th(OH)3^+	-11.7	-6.13	4.01	-0.11	Turner 81(Eq 1)
Th(OH)4	-15.9	-6.13	4.11	-0.17	Turner 81(Eq 1)
Th2(OH)2^6+	-6.14	+3.06	1.0	0.3	Eq 2
Th4(OH)8^8+	-21.1	+4.09	1.0	0.3	Eq 2
Th6(OH)15^9+	-36.76	0	1.0	0.3	Eq 2
ThF^3+	8.03	-4.09	2.55	0.25	Turner 81(Eq 1)
ThF2^2+	14.25	-7.16	2.07	0.55	Turner 81(Eq 1)
ThF3^+	18.93	-9.21	2.79	0.58	Turner 81(Eq 1)
ThF4	22.31	-10.23	1.62	0.70	Turner 81(Eq 1)
ThCl^3+	1.09	-4.09	2.16	0.08	Turner 81(Eq 1)
ThCl2^2+	0.80	-7.16	2.07	0.55	Turner 81(Eq 1)
ThCl3^+	1.65	-9.21	1.0	0.3	Eq 2
ThCl4	1.26	-10.23	1.0	0.3	Eq 2
ThSO4^2+	5.45	-8.18	1.0	0.3	Eq 2
Th(SO4)2	9.73	-12.28	1.0	0.3	Eq 2
Th(SO4)3^2-	10.50	-12.28	1.0	0.3	Eq 2
Th(SO4)4^4-	8.48	-8.18	1.0	0.3	Eq 2
ThHPO4^2+	12.9	-8.18	1.0	0.3	Eq 2
Th(HPO4)2	28.0	-12.28	1.0	0.3	Eq 2
Th(HPO4)3^2-	34.5	-12.28	1.0	0.3	Eq 2
ThH2PO4^3+	4.52	-4.09	1.0	0.3	Eq 2
Th(H2PO4)2^2+	8.88	-7.16	1.0	0.3	Eq 2
ThCO3^2+	11.03	-8.18	1.0	0.34	Turner 81(Eq 1)
Tin					
Sn^2+					
SnOH^+	-3.40	-1.02	1.0	0.06	Baes 76(Eq 1)
Sn(OH)2	-7.06	-1.022	1.0	0	Baes 76(Eq 1)
Sn(OH)3^-	-16.61	0	1.0	-0.11	Baes 76(Eq 1)
Sn2(OH)2^2+	-4.77	-1.022	1.0	0.3	Baes 76(Eq 1)
Sn3(OH)4^2+	-6.88	-2.044	1.0	0.45	Baes 76(Eq 1)
SnCl^+	1.51	-2.05	1.0	0.3	Eq 2
SnCl2	2.25	-3.07	1.0	0.3	Eq 2
SnCl3^-	2.0	-3.07	1.0	0.3	Eq 2
SnCl4^2-	1.5	-2.04	1.0	0.3	Eq 2
Uranium					
UO2^2+					
UO2OH^+	-5.1	-1.02	2.32	0.3	Turner 81(Eq 1)
UO2(OH)2	(-10.8)	0	1.0	0.3	Eq 2
UO2(OH)3^-	-21	0	1.0	0.3	Eq 2
(UO2)2(OH)2^2+	-5.62	-1.02	1.6	0.0166	Eq 1
(UO2)3(OH)4^2+	(-11.8)	-2.04	1.0	0.3	Eq 2
(UO2)3(OH)5^+	-15.6	-3.07	1.0	0.3	Eq 2
(UO2)3(OH)7^-	-31	-2.04	1.0	0.3	Eq 2
UO2F^+	5.16	-2.05	1.57	0.17	Turner 81(Eq 1)
UO2F2	8.85	-3.07	1.52	0.34	Turner 81(Eq 1)
UO2F3^-	11.42	-3.07	1.12	0.58	Turner 81(Eq 1)
UO2F4^2-	11.97	-1.02	3.65	0.47	Turner 81(Eq 1)
UO2Cl^+	0.21	-2.05	6.25	0.01	Turner 81(Eq 1)
UO2SO4	2.95	-4.09	2.63	-0.01	Turner 81(Eq 1)
UO2(SO4)2^2-	4.3	-4.09	1.61	-0.22	Turner 81(Eq 1)
UO2(SO4)3^4-	4.7	0	1.0	0.3	Eq 2
UO2CO3	9.9	-4.09	1.63	0.05	Turner 81(Eq 1)
UO2(CO3)2^2-	16.7	-4.09	1.61	-0.22	Turner 81(Eq 1)

Chemical Equilibrium

$$R \ln K = A + \frac{B}{T} + C \ln T + DT + ET^2 + FT^3 , \tag{5}$$

where

$$A = \Delta S^\circ_\Theta - \left(C_0 - \frac{\Theta^2}{4}C_2 + \frac{10\Theta^3}{72}C_3\right) - \ln\Theta\left(C_0 - \Theta C_1 + \frac{\Theta^2}{2}C_2 - \frac{\Theta^3}{6}C_3\right) ,$$

$$B = -\Delta H^\circ_\Theta + \Theta C_0 - \frac{\Theta^2}{2}C_1 + \frac{\Theta^3}{6}C_2 - \frac{\Theta^4}{24}C_3 ,$$

$$C = C_0 - \Theta C_1 + \frac{\Theta^2}{2}C_2 - \frac{\Theta^3}{6}C_3 ,$$

$$D = \frac{C_1}{2} - \frac{\Theta}{2}C_2 + \frac{\Theta^2}{4}C_3 ,$$

$$E = \frac{C_2}{12} - \frac{\Theta}{12}C_3 , \qquad F = \frac{C_3}{72} ;$$

and where

$$C_0 = \Delta C_{p\Theta} , \qquad C_1 = \left(\frac{d\Delta C_p}{dT}\right)_\Theta , \qquad C_2 = \left(\frac{d^2\Delta C_p}{dT^2}\right)_\Theta , \qquad C_3 = \left(\frac{d^3\Delta C_p}{dT^3}\right)_\Theta .$$

For a constant heat capacity over the temperature range considered, equation (5) becomes:

$$R \ln K = \Delta S^\circ_\Theta - \frac{\Delta H^\circ_\Theta}{T} + \Delta C_p \left(\frac{\Theta}{T} - 1 + \ln\frac{T}{\Theta}\right) . \tag{6}$$

a Debye-Hückel (extended)

$$\log K(I) = \log K^{\circ} + \frac{A \Delta Z^2 I^{1/2}}{1 + B I^{1/2}} + C I \qquad (1)$$

$$\log K(I) = \log K^{\circ} + 0.5 \Delta Z^2 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.31 \right] \qquad (2)$$

Davies eq

Table 19. Coefficients for an extended Debye-Huckel equation used to estimate the effect of ionic strength on dissociation and ionization constants of selected ligands, at 25 °C.

Ligand source	A	B	C	D	log K°
H_2O	1.02	1.30	-0.293	0	-13.997
HF	1.022	1.6	-0.2	0	-3.17
HSO_4^-	-1.687	1.0	0	0	1.981
$H_2PO_4^-$	2.05	1.78	0.021	0	-7.199
HPO_4^{2-}	3.06	1.6	0.047	0	-12.35
H_2CO_3	1.022	1.0	-0.12	-0.01	-6.352
HCO_3^-	1.644	1.4	-0.013	0	-10.33

Interpolating. equation:

$$\log K = \log K^\circ + A\, I^{1/2}/(1 + B\, I^{1/2}) + CI + DI^2$$

Table 20. Hydrolysis constants of Al^3+,25C

I	1,1	1,2	1,3	1,4
0.0	-4.90	-10.1	-16.0	-23.0
0.1	-5.42	-10.8	-16.7	-23.5
0.3	-5.55	-11.0	-17.0	-23.6
0.5	-5.57	-11.1	-17.0	-23.7
1.0	-5.48	-11.1	-17.1	-23.7
2.0	-5.14	-10.8	-16.9	-23.5
3.0	-4.72	-10.4	-16.6	-23.2

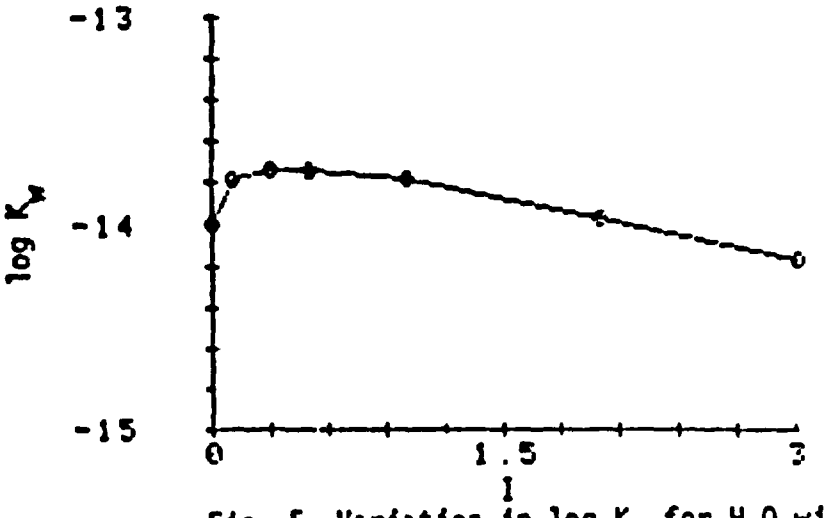

Fig. 5. Variation in log K_w for H_2O with I.

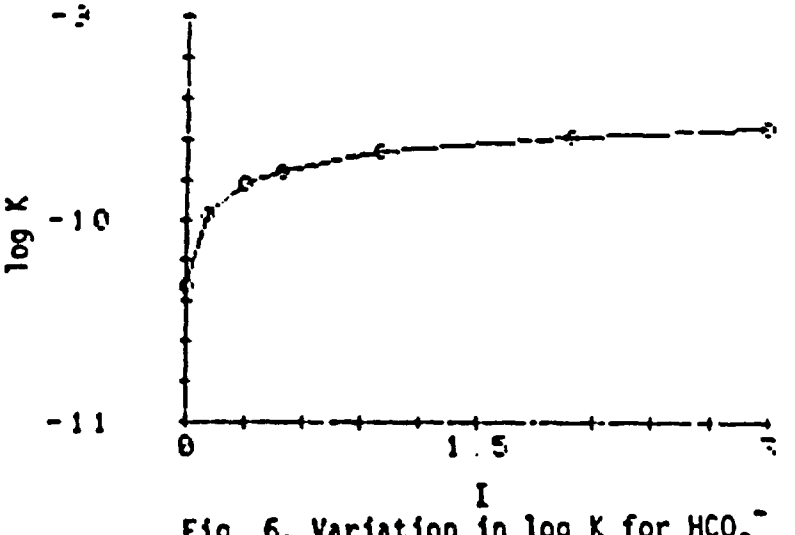

Fig. 6. Variation in log K for HCO_3^- with I.

Criteria for Code(s) Selection

- °Quality of database
- °Temperature range
- °Ionic strength range
- °Maintenance
- °Predictive capability
- °Other

Predictive Code(s) Selection

Selected Code	Advantages	Disadvantages
EQ3/EQ6		
PHREEQUE		
WATEQ( )		
MINEQL		
ENIVEL		
ECES		
SOLMNEQ		
OTHER		

Identify Significant Gaps

- °No experimental data
  - -Technetium; $U(OH)_2^{2+}$
- °Experimental data with "unacceptable" uncertainty
  - -9 ± 4; or, $\pm ?$
- °Experimental data are not reasonable, vis-a-vis theoretical expectations
  - NdOH for AmOH
- °Other
  - high temperature data: -3 ± 2

GEOCHEMICAL SENSITIVITY ANALYSIS FOR HLW REPOSITORY RISK ASSESSMENT: I. RADIOELEMENT SPECIATION. K. L. ERICKSON, M. D. SIEGEL, Sandia National Laboratories, Albuquerque, NM 87185.*

The purpose of this work is to identify physicochemical conditions where chemical speciation of radioelements must be considered in HLW repository risk assessments. Previous assessments of the compliance of hypothetical high-level waste repositories[1] with the EPA Standard 40CFR191 used distribution coefficients (K_d values) to calculate the retardation factors for radionuclides. Such expressions are strictly valid when only one species is present in solution and when the partitioning of radionuclides between solid and fluid is reversible, independent of radionuclide concentration, and rapid relative to the radionuclide travel times.

K_d values obtained by batch methods describe the "average" sorption behavior of all species of a radionuclide that are present in solution. When several species are present, it is likely that at least one complex will migrate at a rate faster than that predicted by the measured K_d value. The use of these K_d values in performance assessment calculations could cause underestimations of radionuclide discharges and disguise possible violations of the EPA Standard. In this paper a methodology to assess the impact of changes in radionuclide speciation on EPA compliance assessments is developed.

In general, transport of radionuclides involved in any number of homogeneous and heterogeneous chemical reactions is described by equations of the form

$$\left\{\begin{matrix}\text{rate}\\ \text{of}\\ \text{accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{net rate of}\\ \text{influx by}\\ \text{convection}\end{matrix}\right\} + \left\{\begin{matrix}\text{net rate of}\\ \text{influx by}\\ \text{dispersion}\end{matrix}\right\}$$

$$- \left\{\begin{matrix}\text{rate of}\\ \text{radioactive}\\ \text{decay}\end{matrix}\right\} + \left\{\begin{matrix}\text{rate of}\\ \text{radioactive}\\ \text{production}\end{matrix}\right\} \quad \{1\}$$

$$+ \left\{\begin{matrix}\text{net rate of}\\ \text{production}\\ \text{by heterogeneous}\\ \text{reactions}\end{matrix}\right\} + \left\{\begin{matrix}\text{net rate of}\\ \text{production}\\ \text{by homogeneous}\\ \text{reactions}\end{matrix}\right\}$$

where a separate equation is written for each species of each radionuclide.

The first five terms on the right hand side of the above expression are normally included in solute transport models. The fifth term is generally used to represent reversible first-order sorption reactions (adsorption and ion exchange). Similar terms also could be used to calculate upper bounds on radionuclide discharge when colloid retention and irreversible sorption must be considered.

The last term in the above expression represents reactions between dissolved constituents. These may include changes in radionuclide speciation, precipitation by homogeneous nucleation and colloid formation. For the purpose of calculating upper bounds to radionuclide discharge, these reactions can be represented by expressions of the form

$$\left\{\begin{matrix}\text{net rate of}\\ \text{production by}\\ \text{homogeneous}\\ \text{reactions}\end{matrix}\right\} = \sum_{m} k_m C_i \quad \{2\}$$

where k_m is the rate constant for the mth reaction involving the ith species of the radionuclide and C_i is the species concentration.

The EPA Standard 40CFR191 regulates the integrated discharge of radionuclides from a HLW repository to the accessible environment. Critical combinations of values of geochemical and hydrologic parameters which violate the EPA Standard can be identified in the following manner:

(1) terms for both homogeneous and heterogeneous reactions are incorporated into the radionuclide transport equations;

(2) the equations are solved and the integrated discharge is calculated for the 10,000 year regulatory period;

(3) the discharges of all chemical species of a radionuclide are summed and the resultant expression is set equal to the EPA radionuclide release limit W,

$$W = f(R_i, R_j \ldots, k_{ij} \ldots, C_i^{\circ}, \ldots C_j^{\circ}, \lambda_i \ldots \lambda_j, Q, t_g) \qquad \{3\}$$

where R_i, R_j, etc. are the retardation factors for the chemical species; k_{ij}, etc. are the reaction rate constants for speciation reactions; C_i°, C_j°, etc. are the initial concentrations of the chemical species in the engineered facility, Q is the annual volumetric flux of water through the engineered facility; and t_g is the ground-water travel time from the engineered facility to the accessible environment;

(4) equation {3} is solved numerically to determine combinations of the parameters which cause violations of the EPA Standard.

The results can be presented as bivariate curves in which critical combinations of the values of retardation factors for two species of a radionuclide and the rate constant of their interconversion are plotted for a specific source term and ground-water travel time.[2]

In a previous paper[2] this procedure was applied to the discharge of a long-lived radionuclide ^{237}Np ($t_{1/2} > 2x10^6$ yr) in a scenario in which radioactive production was negligible. The conversion of an immobile chemical species A to a mobile species B by irreversible reaction during transport was considered. In this second paper, the analyses are extended to elements such as ~~uranium,~~ plutonium, americium and curium. For such nuclides, terms for radioactive decay and production must be included in the ~~transport equations.~~ analysis Critical combinations of parameter values which lead to violations of the EPA Standard are identified for each radionuclide. Furthermore, based on these critical combinations, radionuclide-specific criteria are developed for designing laboratory and field experiments which will yield definitive results in cases where chemical speciation must be considered in HLW risk assessment studies. These results can be applied to each radionuclide on a site-specific basis and can be used by the NRC and DOE to prioritize the information that is needed to assure compliance of real repository sites with the EPA Standard.

REFERENCES

[1]M. D. Siegel et al., in Scientific Basis for Nuclear Waste Management, D. Brookins, Ed., North-Holland, NY, 6, 497 (1983).

[2]M. D. Siegel and K. L. Erickson, in Waste Management 84, to be published.

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