

4025

Viani

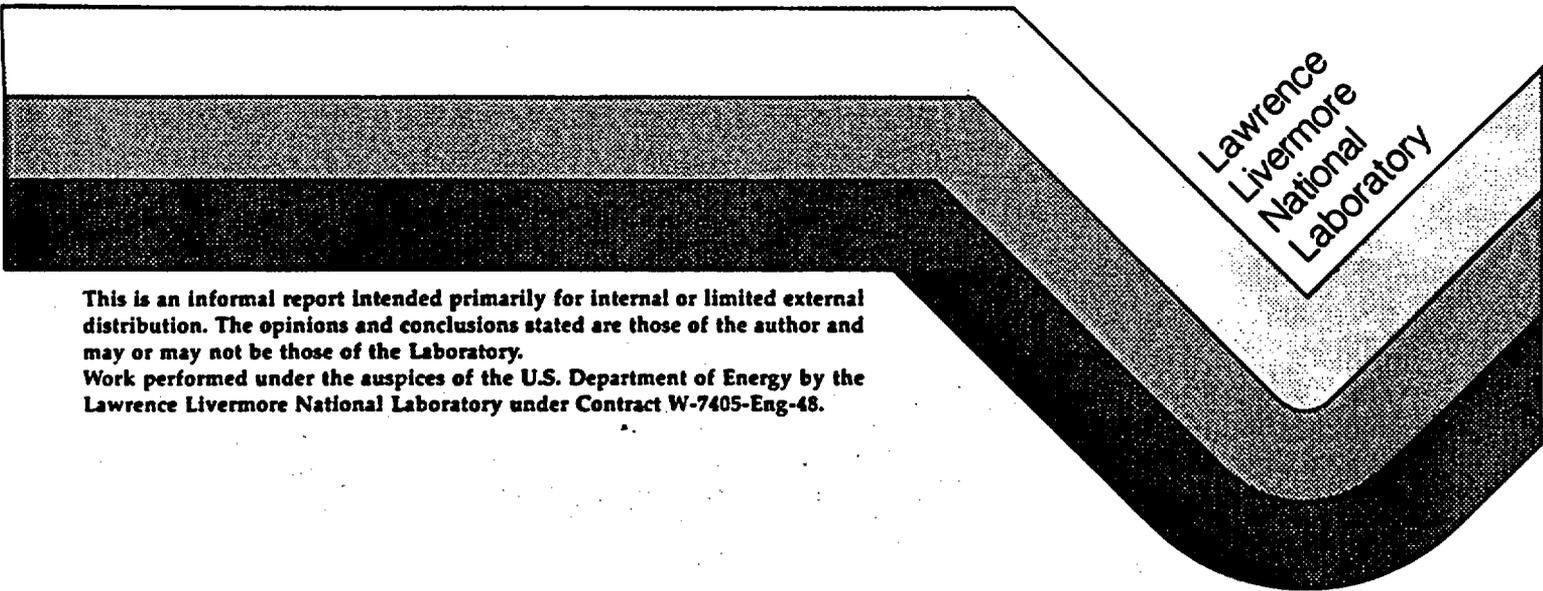
UCID- 21308  
Revision 1

INTERIM REPORT  
ON MODELING SORPTION  
WITH EQ3/6

Brian Viani

HYDROLOGY DOCUMENT NUMBER 608

January 1988



This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.  
Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

**DISCLAIMER**

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Printed in the United States of America  
Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road  
Springfield, VA 22161

<u>Price Code</u>	<u>Page Range</u>
A01	Microfiche
<u>Papercopy Prices</u>	
A02	001-050
A03	051-100
A04	101-200
A05	201-300
A06	301-400
A07	401-500
A08	501-600
A09	601

Prepared by Yucca Mountain Project (YMP) participants as part of the Civilian Radioactive Waste Management Program. The YMP project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. YMP Project work is sponsored by the DOE Office of Civilian Radioactive Waste Management.

## Interim Report on Modeling Sorption with EQ3/6

### SUMMARY

Reversible, equilibrium models of sorption to be incorporated into the EQ3/6 geochemical modeling package are summarized. Empirical sorption models as formulated in linear, Langmuir, and Freundlich isotherms will be developed as options to EQ3/6. This work will be done at LLNL. Options for modeling sorption using surface-complexation constructs (diffuse, constant capacitance, and triple-layer models) will also be developed. Development of the surface-complexation options will require part of the work be done under contract.

### INTRODUCTION

To predict the movement of radionuclides through rocks and other materials within and surrounding proposed nuclear waste repositories it is necessary to be able to predict the partitioning of radionuclides between solution, solid, and surface-adsorbed phases. The EQ3/6 package of geochemical modeling codes does not have the capability of partitioning elements between solution and surface-adsorbed phases, i.e. it cannot be used to model sorption. The first stages of the plan to rectify this shortcoming will be the implementation of reversible, equilibrium models into EQ3/6 (McKenzie et al., 1986). This report deals with the first stages of our sorption modeling plans and does not, therefore, address models in which rate (kinetic) and/or hysteretic dependent phenomena are considered. A summary of the equilibrium sorption models and our plans to incorporate them into EQ3/6 follow.

## SCOPE

The Nuclear Regulatory Commission (NRC) position on the determination of radionuclide sorption (NRC, 1987) stresses the need for careful experimentation using appropriately prepared and well characterized solids and solutions. The matrix of experiments carried out to measure sorption should reflect the range of solid and solution compositions expected in the repository. The NRC does not endorse any single experimental or modeling approach for assessing sorption. We propose to incorporate into the EQ3/6 code those empirical and surface-complexation models of adsorption that are relevant to repository site characterization, performance assessment, and modeling water-rock interactions and waste-form performance (Nevada Nuclear Waste Storage Investigations (NNWSI) Site Characterization Plan (Draft), 4.1.3.3, 8.3.1.3, 1987).

Sorption as defined by the NRC (NRC, 1986) is - "one or more physiochemical processes, including ion exchange, adsorption, and chemisorption, but excluding precipitation of stoichiometric (fixed radionuclide composition) solid phases, in which the radionuclide is removed from a liquid phase by interaction with a solid phase or phases." Although it is not stated explicitly, sorption as defined above could presumably also include "surface precipitation" (Farley et al., 1985) of non-stoichiometric phases or precipitation of any non-stoichiometric phase (solid-solution) of the radionuclide in question. Precipitation refers to the growth of a solid phase distinguished by the repetition of fundamental molecular entities in three dimensions (Sposito, 1986). In the following discussion, the terms sorption and adsorption will be used interchangeably and will refer to all the processes above with the exception of precipitation (surface or otherwise).

Empirical (linear, Langmuir, and Freundlich) and surface-complexation (diffuse-layer, constant-capacitance, double-layer (Stern), and triple-layer) models will be developed as EQ3/6 options and will allow modeling the combined processes of adsorption and chemisorption. Aside from the fact that relevant sorption data may be specific to a given model, a major reason for incorporating more than one sorption option is to develop the ability to test

the sensitivity of overall geochemical modeling results to the type of sorption model specified. Sorption models will be implemented with the assumption that partitioning between solution and surface will be both reversible (i.e. no hysteresis) and at equilibrium (i.e. instantaneous). While it is recognized that sorption models that explicitly include hysteresis and/or kinetics are sometimes necessary to describe natural systems (Honeyman and Santschi, 1987), such models and/or modifications of the equilibrium models will be considered only after the equilibrium case has been considered (McKenzie et al., 1986). For reasons stated below, surface precipitation and mass-action ion-exchange models will also be treated within the context of the solid solution options presently available within EQ3/6.

## ADSORPTION MODELS

### Empirical Models

Empirical models such as linear, Langmuir, and Freundlich isotherms have been successfully used to describe experimental and field data. Empirical models can be used to describe most experimental data sets without detailed characterization of the solution or the solid/solution interfacial region; thus, they are as easily applied to mixtures of solids as to single solid phases. The major shortcoming of these models is that their generality and predictive capability is often very limited (Kent et al., 1986; Serne and Relyea, 1982; Travis and Etnier, 1981). Therefore, for a given set of isotherm parameters, application of the model for predictive purposes is best restricted to problems for which the solid and solution components are unlikely to change (Reardon, 1981). No a priori description of the sorption process is necessary to apply an empirical model, though conformance of experimental data to a given isotherm may sometimes lead to a better understanding of the mechanism of sorption (Sposito, 1984).

While individual experiments to determine parameters defining empirical adsorption isotherms are relatively simple, many experiments are required to encompass variation in environmental and compositional variables appropriate

to the system of interest (NRC, 1987). The predictive ability of empirical models can be significantly improved by applying statistical methods to data collected from carefully controlled experiments that encompass a sufficiently broad test matrix (Serne and Relyea, 1982). Empirical models are readily incorporated into transport and performance codes and their incorporation into EQ3/6 should likewise be straightforward.

**Linear isotherm** - The sorption ratio,  $R$ , is the ratio of the concentration of an element adsorbed on a solid phase to that in the solution phase. For the linear case  $R$  is independent of both the concentration of adsorbate in solution and of the ratio of solid to solution. Thus;

$$R \equiv q/c_s \quad (1/kg) \quad (1)$$

where  $q$  is the concentration of adsorbed element (moles/kg of adsorbent) and  $c_s$  is the total molar concentration of the element in solution (the sum of all aqueous species of the element). At equilibrium the sorption ratio is identical to the partition coefficient. For implementation of adsorption models into EQ3/6,  $R$  will be assumed to measure the equilibrium partition coefficient.

If  $m/v$  is the ratio of the mass of adsorbent to the volume of solution (kg/l) then the concentration of the adsorbed element expressed in moles per liter of solution,  $c_a$ , is;

$$c_a = qm/v \quad (\text{mole/l}) \quad (2)$$

**Langmuir and Freundlich Isotherms** - These isotherms have been used to describe the adsorption of elements which do not obey the linear isotherm, i.e.  $R$  is not constant with respect to adsorbate or adsorbent concentration. For data obeying the Langmuir isotherm;

$$R = bk - kq \quad (3a)$$

or, solving for  $q$  in (1), substituting into (3a) and solving for  $R$ , yields,

$$R = bk/(1 + kc_s) \quad (3b)$$

where  $b$  and  $k$  are adjustable parameters. Substituting (1) into (3a) and solving for  $q$  yields;

$$q = bk/(1/c_s + k) \quad (4)$$

Thus, as the solution concentration,  $c_s$ , becomes large, the concentration sorbed,  $q$ , approaches a maximum, i.e.  $b$ .

For data obeying the Freundlich isotherm  $R$  varies as;

$$R = a(c_s)^{B-1} \quad (5)$$

where  $a$  and  $B$  ( $0 < B < 1$ ) are adjustable parameters. In contrast to the Langmuir isotherm, the Freundlich isotherm does not show an adsorption maximum as  $c_s$  becomes large since  $q$  is proportional to  $c_s^B$ .

Solving an aqueous speciation problem (EQ3NR) or a reaction path problem (EQ6) with an accounting of adsorption will require additional mass balance and mass action constraints. For every adsorbate/adsorbent pair which is governed by one of the above relationships, a mass balance expression;

$$c_t = c_s + c_a \quad (6)$$

and a 'mass action' equation;

$$c_a = Rc_s(m/v) \quad (7)$$

apply. Equation (6) is simply an extension of the mass balance constraint that applies to solute species in EQ3NR (Wolery, 1983), where  $c_t$  is the sum of the concentrations of adsorbed and soluble species, and  $c_s$  is the sum of the concentrations of soluble species of the element in question. A separate

$c_a$  term will be required for each adsorbate/adsorbent pair. Equation (7) is analogous to a mass action equation, except it is not written in terms of a specific aqueous species but in terms of the sum of all aqueous species, i.e.  $c_s$ . In addition,  $R$  is not equivalent to an equilibrium 'constant' since, depending on the model, it may be a function of  $c_s$ . Each adsorbate/adsorbent pair will require one equation as in (7), and solution of the partition problem will require adjusting the mass balance constraints in EQ3/6. For any given problem, input of  $m/v$ ,  $b$ ,  $k$ ,  $a$ ,  $B$  (or  $R$  for the linear isotherm) will be necessary, and options for fixing  $c_t$  or  $c_a$  will be provided. The empirical models do not explicitly treat the stoichiometry of sorption/desorption. Consequently, the user will be given the option of specifying the charge of the adsorbed species, thus effectively defining a reaction stoichiometry. The adsorbed species would then be included in the overall electrical balance equation for the solution, subject to the electrical balancing options already implemented in EQ3/6 (Wolery, 1983).

### Surface-Complexation Models

In contrast to empirical isotherms, the surface-complexation approach is based on explicit models of the solid/liquid interfacial region. The advantages of this approach, in comparison to empirical models, are: the stoichiometry of adsorption is explicitly treated; the thermodynamic formalism embodied in the model is conceptually and computationally compatible with thermodynamic based geochemical modeling codes, and; surface-complexation models may be more accurate than empirical models because they explicitly treat adsorbate speciation in solution and in the interfacial region.

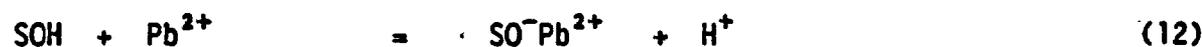
Description of the solid/liquid interface in terms of electrical-chemical double-layer models (i.e. Gouy-Chapman-Stern-Grahame-models) is well developed (Dzombak and Morel, 1987; Westall, 1986). Combination of double-layer models with site-binding mass action equations (Yates et al., 1974) has resulted in a variety of quasi-thermodynamic adsorption models that simultaneously describe the charge, potential, and surface excesses at solid/liquid interfaces (Westall and Hohl, 1980). Although the models are complex and their use in

transport codes is not well developed, they have been incorporated into geochemical modeling codes (Westall, 1980), and should prove amenable to incorporation into the EQ3/6 package.

Experimental determination of surface-complexation model parameters is more laborious than for empirical isotherms because both the solution and the solid must be well characterized. Solution phase species and their thermodynamic data for the adsorbate element must be known; the electrical properties of the solid/liquid interface must be known as a function of pH and ionic strength; and adsorption isotherms (from which site-binding constants are determined) must be measured under varying pH and ionic strength regimes appropriate to the solid/liquid system of interest. Application of surface-complexation models to predicting adsorption by mixtures of solid phases will require either characterization of all important solid phases in the mixture, or application of the models directly to mixtures as is done for empirical isotherms. The former approach requires the surface properties of the specimen minerals used to generate model parameters to be equivalent to those in the natural mixture, and that the 'aggregate' surface chemical behavior of a mixture be predictable from a knowledge of the behavior of each of the solids separately (Kent et al., 1986). Determination of model parameters for natural mixtures of solid phases may be a feasible alternative (Leckie, 1987), and this approach has been successful in modeling sorption in a multimineralic system such as soil (Charlet and Sposito, 1987). It is probable that the experimental effort required to determine parameters for surface-complexation models would be similar to that required to determine parameters for empirical isotherms collected over a realistically wide test matrix.

Each surface-complexation model is based on a different model of the geometry of the 'compact layer' or diffuse layer at the solid/liquid interface and/or a different set of surface complexes (Sposito, 1984; Dzombak and Morel, 1987). The number of parameters required to describe adsorption data is model dependent. In general, surface sites, e.g. surface hydroxyls (SOH), are presumed to bind protons,  $H^+$ , adsorbate species, and in some models background electrolyte ions, e.g.  $Na^+$  and  $Cl^-$ . Adsorption is assumed to occur at model-defined planes adjacent to the surface of the solid (Figure 1).

**Triple-layer model** - Important features of surface-complexation models are illustrated below using an example in which protons ( $H^+$ ), monovalent background electrolyte ions ( $M^+$ ,  $X^-$ ), and adsorbate species (in this case,  $Pb^{2+}$  and  $Pb(OH)^+$ ) are assumed to form surface complexes according to the triple-layer model. The proton is constrained to bind or dissociate from the o plane resulting in  $SOH$ ,  $SOH_2^+$ , and  $SO^-$  adsorption sites, while  $X^-$ ,  $M^+$ ,  $Pb^{2+}$ , and  $SO^-PbOH^+$  are constrained to bind at the b plane, resulting in  $SOH_2^+X^-$ ,  $SO^-M^+$ ,  $SO^-Pb^{2+}$ , and  $SO^-PbOH^+$  complexes, respectively. Note that the charges on the o and b plane are separately identified in this notation. The site-binding reactions are:



Explicit effects of diffuse and compact layers are taken into account in the formulation of intrinsic equilibrium constants defining the above site-binding reactions. Thus;

$$K_8 = \frac{\{SOH_2^+\} \exp[e\psi_o/kT]}{\{SOH\} \{H^+\}} \quad (14)$$

$$K_9 = \frac{\{SO^-\} \{H^+\} \exp[-e\psi_o/kT]}{\{SOH\}} \quad (15)$$

$$K_{10} = \frac{\{SOH_2^+X^-\} \exp[e(\psi_o - \psi_b)/kT]}{\{SOH\} \{X^-\} \{H^+\}} \quad (16)$$

$$K_{11} = \frac{\{SO-M^+\} \{H^+\} \exp[e(\psi_b - \psi_o)/kT]}{\{SOH\} \{M^+\}} \quad (17)$$

$$K_{12} = \frac{\{SO-Pb^{2+}\} \{H^+\} \exp[e(2\psi_b - \psi_o)/kT]}{\{SOH\} \{Pb^{2+}\}} \quad (18)$$

$$K_{13} = \frac{\{SO-PbOH^+\} \{H^+\} \exp[e(2\psi_b - \psi_o)/kT]}{\{SOH\} \{Pb^{2+}\} \{H_2O\}} \quad (19)$$

where { } signify activities of solution and surface species;  $\psi_o$  and  $\psi_b$  are the potentials (volts; relative to the potential in the bulk solution) at the o and b binding planes, respectively (Figure 1); e is the charge on the electron (coulombs); k is Boltzmann's constant (joule/deg K), and T is the absolute temperature.

The exponential terms in equations 14 - 19 are the coulombic contribution to the free energy of interaction for the site binding reactions. This treatment assumes that electrical (long range) and chemical (short range) components to the energy of interaction between ion and surface are separable (Hayes and Leckie, 1986; Sposito, 1983). In practice, activity coefficients of surface species are not determined, and are assumed to be unity. Some workers choose not to separate chemical and electrical interactions and identify the exponential term with activity coefficient ratios of surface species (Sposito, 1984) or a combination of surface and solution species (Hayes and Leckie, 1986). The type of surface complexation reactions considered and the planes at which species bind to the surface are model dependent, hence, the exponential terms in each model are different.

Assuming only one type of adsorption site is present, the total adsorption site density,  $N_s$  (mole/m<sup>2</sup>), constrains the concentration (moles/l) of model-defined surface species according to;

$$N_s = (1/A)[\{SOH\frac{1}{2}\} + \{SOH\} + \{SO^-\} + \{SO-M^+\} + \{SOH\frac{1}{2}X^-\} + \{SO-Pb^{2+}\} + \{SO-PbOH^+\}] \quad (20)$$

where A is the surface-to-volume ratio (m<sup>2</sup>/l).

The density of charge (coulomb/m<sup>2</sup>) at the two binding planes ( $\sigma_o$  and  $\sigma_b$ ), and in the diffuse layer ( $\sigma_d$ ) is constrained by electrical neutrality,

$$\sigma_d + \sigma_o + \sigma_b = 0 \quad (21)$$

by surface speciation,

$$\sigma_o = (F/A)[(\text{SOH}\frac{1}{2}) + (\text{SOH}\frac{1}{2}\text{X}^-) - (\text{SO}^-) - (\text{SO}^-\text{M}^+) - (\text{SO}^-\text{Pb}^{2+}) - (\text{SO}^-\text{PbOH}^+)] \quad (22)$$

$$\sigma_b = (F/A)[(\text{SO}^-\text{M}^+) + 2(\text{SO}^-\text{Pb}^{2+}) + (\text{SO}^-\text{PbOH}^+) - (\text{SOH}\frac{1}{2}\text{X}^-)] \quad (23)$$

and by the charge-potential relationships specific to the model used; for the triple-layer case these are:

$$\sigma_o = C1(\psi_o - \psi_b) \quad (24)$$

$$\sigma_d = C2(\psi_d - \psi_b) \quad (25)$$

$$\sigma_d = -0.1174 c^{1/2} \sinh[z e \psi_d / 2kT] \quad (26)$$

where F is the Faraday constant (coulomb/mole), C1 and C2 are integral capacitances (coulomb/volt m<sup>2</sup>) of the compact part of the double-layer (Figure 1) and c and z are the molar concentration and valence of a symmetrical background electrolyte, respectively.

Acid-base titration of solid/solution mixtures at a series of concentrations of the background electrolyte together with adsorption isotherms determined over a range of pH and ionic strength are used to estimate surface-complexation model parameters using extrapolation and/or minimization techniques (Kent et al., 1986). The parameters  $N_s$  and A are generally measured, C2 is normally fixed at a convenient value (Dzombak and Morel, 1987), while C1 and the intrinsic site-binding constants are used as fitting parameters. For the same experimental data set, different models often fit

the data equally well and yield different values for analogous parameters, a reflection of the purely formal description of the solid/solution interface that the models embody (Westall and Hohl, 1980).

The approach used to solve solution speciation problems is applicable to surface complexation as well (Westall, 1980). Governing equations which are used to solve surface speciation problems include: adsorbent site density constraint(s), adsorbate mass balance constraint(s), surface charge density constraints, site binding mass action equations, and the functional relationship between potential, solution composition, and surface charge density. Surface complexes will formally be treated as "fictive" solution species and will be handled by the solution speciation model in EQ3/6. In order to provide feed back between surface complexation and dissolution/precipitation, the surface-to-volume-ratio, A, will be updated each time the mass of the adsorbent is altered by precipitation or dissolution. A summary of the features of surface-complexation models to be incorporated into EQ3/6 is given in Table 1.

#### Other Models

Mass Action Ion Exchange Models - Mass action models have commonly been used to describe ion-exchange of alkali and alkaline earth cations on layer silicates, zeolites and other materials possessing a permanent charge (Sposito, 1984). These models do not require description of the solid/solution interface and can often be applied to multimineralic systems. Ion exchange models may be appropriate for modeling adsorption of radionuclides on layer silicates and zeolites (e.g. Silva et al., 1979; NNWSI Site Characterization Plan (Draft), 4.1.3.3, 8.3.1.3, 1987). Ion-exchange on permanently charged phases can also be treated as a solid-solution (e.g. Truesdell and Christ, 1968). Ion-exchange equilibrium can be expressed as:



where M and N refer to ions of valence  $m^+$  and  $n^+$ , respectively, and the superscript bar identifies ions on the exchanger phase. The equilibrium exchange constant,  $K_{ex}$ , is given by:

$$K_{ex} = \frac{\{M^{m+}\}^n \{\bar{N}\}^m}{\{N^{n+}\}^m \{\bar{M}\}^n} \quad (28)$$

where  $\{N^{n+}\}$  and  $\{\bar{N}\}$  refer to activities of ion N in solution and on the exchanger, respectively. Two concentration scales are commonly used to describe ion-exchange. If the concentration of ions on the exchanger is expressed as a mole fraction, then;

$$\{\bar{N}\} = fX_N \quad (29)$$

where  $X_N$  is the mole fraction of ion N on the exchanger, and  $f$  is the rational activity coefficient. If the concentration of ions on the exchanger is expressed as an equivalent fraction, then;

$$\{\bar{N}\} = gE_N \quad (30)$$

where  $E_N$  is the equivalent fraction of ion N on the exchanger and  $g$  is the appropriate activity coefficient.

An essential feature of mass-action ion-exchange models is that they are based solely on exchange equilibrium, i.e. there is no explicit consideration of the overall equilibrium of the exchanger phase with the solution. For many systems, e.g. soils, sediments, this is an appropriate way to describe solid/solution interaction. We intend to incorporate this approach into EQ3/6

by defining fictive aqueous exchange species, i.e. cation/exchanger "complexes", as defined by the reactions:



where S refers to the exchanger phase. The corresponding equilibrium relationships are:

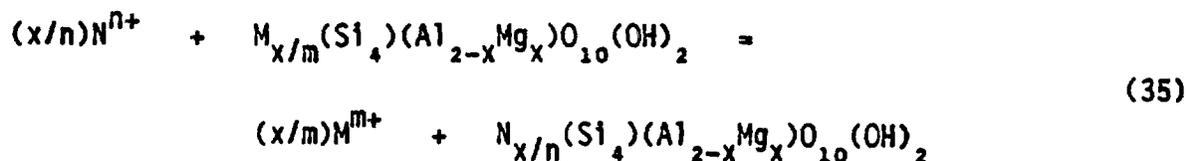
$$K_N = \frac{\{N_m S\}}{\{N^{n+}\}^m \{S^{mn-}\}} \quad (33)$$

$$K_M = \frac{\{M_n S\}}{\{M^{m+}\}^n \{S^{mn-}\}} \quad (34)$$

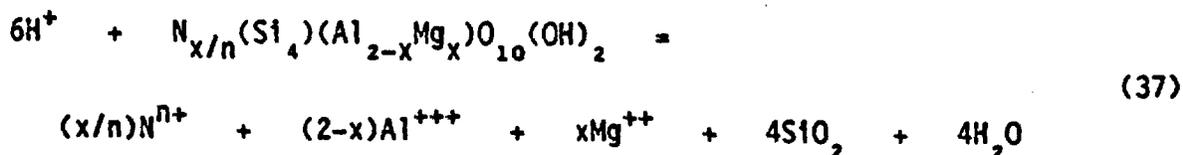
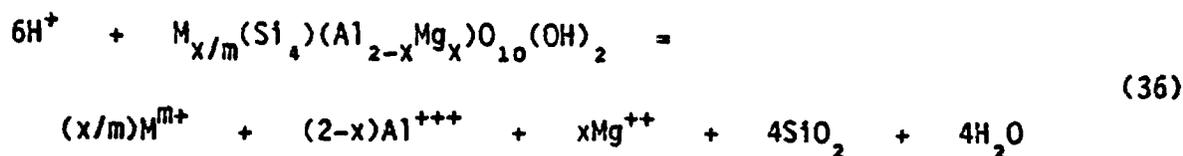
The ratio  $K_N/K_M$  is numerically equal to  $K_{ex}$  defined by equation 28 if the exchanger composition is described by the equivalent fraction and the exchange is ideal, i.e.  $g = 1.0$  (eq. 30) for all exchanger compositions. Reactions 31 and 32 can also be written in a way to make the ratio  $K_N/K_M$  equal  $K_{ex}$  if exchange is ideal and mole fraction is the composition variable. The values of  $K_N$  and  $K_M$  will be adjusted to insure that the concentration of  $S^{mn-}$  is vanishingly small. The ratio  $K_N/K_M$  will be constrained to equal published values of  $K_{ex}$ .

Ion-exchange can also be treated as a solid-solution. Exchange is represented by equilibrium between the solid-solution components. Using this approach, exchange is allowed only when the exchanger phase is in overall equilibrium

with the solution. Using montmorillonite as an example, the exchange reaction is;



where x is the negative charge per formula unit. The endmembers are in equilibrium with the solution, thus:



The composition of a solid-solution (i.e. the mole fractions of the components making up the solid-solution) can be computed from a knowledge of the equilibrium solution composition (Bourcier, 1985). The smectite solid-solution option to be incorporated into EQ3/6 will utilize an ideal site-mixing model (Aagaard and Helgeson, 1983). For ions on the exchange sites this is numerically equivalent to assuming ideal exchange using equivalent fraction as the composition variable.

**Surface Precipitation - Adsorption isotherms** obtained under constant pH and ionic strength conditions sometimes do not show an adsorption maximum (i.e. are not Langmuir type isotherms) as predicted by surface-complexation models based on a single type of adsorption site. To explain this observation,

precipitation of solid-solutions of the adsorbate-adsorbent has been postulated (for oxide systems), and a surface-complexation model incorporating surface precipitation of mixed hydroxides has been developed (Farley et al., 1985). This hypothesis has not been proven and it may be premature to infer a precipitation mechanism on the basis of solution and/or sorption data in the absence of direct observation of a precipitate (Sposito, 1986). To explain this observation without postulating surface precipitation, i.e. within the framework of surface-complexation models, multiple types of adsorption sites having differing binding constants have been postulated (Benjamin and Leckie, 1981). Either approach can fit the observed data. If it is necessary to model surface precipitation using EQ3/6, it would best be treated within the framework of the current solid-solution option. The surface precipitation model that has been developed (Farley et al., 1985) could easily be applied now using EQ3/6 given appropriate estimates of the necessary solid-solution parameters.

#### PLANS

**Empirical models** - Incorporation of the empirical models into EQ3/6 will take place at LLNL by members of the EQ3/6 group. This will be started first quarter of FY 89 and completed mid FY 89, and will include: amending data input routines; coding required computational subroutines; writing user documentation to supplement EQ3/6 user's guides; developing test input data sets and verifying outputs for each of the models. There will be no attempt to develop, review, or incorporate a data base of empirical isotherm parameters. Approximately 0.5 FTE will be allocated for this task.

**Surface-complexation models** - Because of the complexity of surface-complexation models and the varied forms they can take, incorporation of these models and options into EQ3/6 will comprise two steps. First a series of surface complexation models will be developed and incorporated into a geochemical modeling code (MINEQL) by experts in adsorption modeling (James Leckie and colleagues at Stanford University). Leckie will develop the code for MINEQL in such a way as to make its incorporation into EQ3/6 straightforward. Leckie will also deliver: documents summarizing surface-complexation model theory,

experimental and parameter estimation methodology; a sensitivity analysis of the various models; and a critical compilation of surface chemical model parameters for selected adsorbates and adsorbents. We expect to work closely with him during the code development period to maximize the compatibility of his final product with the EQ3/6 code package.

Incorporation of the coded adsorption models and associated input data preprocessors will be undertaken at LLNL under software quality assurance protocol, for example, NNWSI Quality Assurance Program Plan, 033-NWMP-R 19.3, 1986. The MINEQL code and the test input/output runs supplied by Leckie will be used in verifying and benchmarking the sorption options.

A two-year contract with Leckie is planned, tentatively starting in FY 1988-89, subject to funding levels. As Leckie develops and codes adsorption model subprograms, incorporation into EQ3/6 will begin at LLNL. This task will require approximately 1.5 FTE at LLNL.

#### REFERENCES

- Aagaard, P. and Helgeson, H. 1983. Activity composition relations among silicates and aqueous solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites, and mixed-layer clays. *Clays & Clay Miner.* 31:207-217.
- Benjamin, M. M., and Leckie, J. O. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *J. Coll. Inter. Sci.* 79:209-221.
- Bourcier, W. L. 1985. Improvements in the Solid Solution Modeling Capabilities of the EQ3/6 Geochemical Code. LLNL UCID 20587.

- Charlet, L. and Sposito, G. 1987. Monovalent ion adsorption by an Oxisol. *Soil Sci. Soc. Am. J.* 51:1155-1160.
- Dzombak, D. A., and Morel, F. M. 1987. Adsorption of inorganic pollutants in aquatic systems. *J. Hydrol. Eng.* 113:430-475.
- Farley, K. J., Dzombak, D. A., and Morel, F. M. 1985. A surface precipitation model for the sorption of cations on metal oxides. *J. Coll. Inter. Sci.* 106:226-242
- Hayes, K. F. and Leckie, J. O. 1986. Mechanism of lead ion adsorption at the goethite-water interface. p.114-141. In Davis, J. A. and Hayes, K. F. (eds) Geochemical Processes at Mineral Surfaces. Amer. Chem. Soc., Washington DC.
- Honeyman, B. D., and Santschi, P. 1987. Can we predict metal residence times in aquatic systems? *Environmental Science and Technology* (in press).
- Kent, D. B., Tripathi, V. S., Ball, N. B., and Leckie, J. O. 1986. Surface-Complexation Modeling of Radionuclide Adsorption in Sub-Surface Environments. Technical Rept. 294. Dept. Civil Engineering, Stanford University.
- Leckie, J. O. 1987. Personal communication.
- McKenzie, W.F., Wolery, T.J., Delany, J.M., Silva, R.J., Jackson, K.J., Bourcier, W.L., and Emerson, D.O. 1986. Geochemical Modeling (E03/6) Plan, Office of Civilian Radioactive Waste Management Program. LLNL UCID-20864
- NNWSI Quality Assurance Program Plan 1986. 033-NWMP-R
- NNWSI Site Characterization Plan (Draft) 1987.

- NRC. 1987. Generic Technical Position on Determination of Radionuclide Sorption for High-Level Nuclear Waste Repositories. Geochemistry Section, Geotechnical Branch Division of Waste Management. U.S. Nuclear Regulatory Commission.
- Reardon, E. J. 1981.  $K_d$ 's - Can they be used to describe reversible ion sorption reactions in contaminant migration. *Groundwater* 19:279.
- Serne, R. J., and Relyea, J. F. 1982. The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program. PNL-3997. Pacific Northwest Laboratory.
- Silva, R. J., Benson, L. V., and Yee, A. W. 1979. Waste Isolation Safety Assessment Program, Task 4: Collection and Generation of Transport Data, Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks. Ann. Progr. Rept. LBL-9945 UC-70.
- Sposito, G. 1983. On the surface complexation model of the oxide-aqueous solution interface. *J. Coll. Inter. Sci.* 91:329
- Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, NY 234 p.
- Sposito, G. 1986. Distinguishing adsorption from surface precipitation. p217 In Davis, J. A. and Hayes, K. F. (eds) Geochemical Processes at Mineral Surfaces. Amer. Chem. Soc., Washington DC.
- Travis, C.S., and Etnier, E. L. 1981. A survey of sorption relationships for reactive solutes in soil. *J. Env. Qual.* 10:8
- Truesdell, A. H., and Christ, C. L. 1968. Cation exchange in clays interpreted by regular solution theory: *Amer. J. Sci.* 266:402-412.

Westall, J. 1980. Chemical equilibrium including adsorption on charged surfaces. p. 33-44. In Kavanaugh, M. C. and Leckie, J. O. (eds) Particulates in Water. Amer. Chem. Soc., Washington DC

Westall, J. 1986. Reaction at the oxide-solution interface: Chemical and electrostatic models. p.54-78. In Davis, J. A. and Hayes, K. F. (eds) Geochemical Processes at Mineral Surfaces. Amer. Chem. Soc., Washington DC.

Westall, J. and Hohl, H. 1980. A comparison of electrostatic models for the oxide/solution interface. Adv. Coll. Inter. Sci. 12:265.

Wolery, T. J. 1983. EO3NR: A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation. UCRL-53414 Lawrence Livermore National Laboratory.

Yates, D. E., Levine, S., and Healy, T. W. 1974. Site-binding model of the electrical double layer at the oxide/water interface. J. Chem. Soc., Farad. Trans. I 70:1807

Table 1 Comparison of surface-complexation models to be implemented in the EQ3/6 geochemical modeling code.

MODEL	Binding Planes	Binding Species	Charge-Potential Constraints	Required Parameters <sup>+</sup>
Diffuse Layer	o	H, A*	$\sigma_0 + \sigma_d = 0$ $\sigma_d = -0.1174 c^{1/2} \sinh[ze\psi_d/2kT]$	$N_s, S, K_p$ 's, $K_A$ 's
Constant Capacitance	o	H, A	$\sigma_0 + \sigma_b = 0$ $\sigma_0 = C\psi_0$	$N_s, S; C, K_p$ 's, $K_A$ 's at each ionic strength
Double Layer	o b	H B, A	$\sigma_0 + \sigma_b + \sigma_d = 0$ $\sigma_d = -0.1174 c^{1/2} \sinh[ze\psi_d/2kT]$	$N_s, S, C1, K_p$ 's, $K_A$ 's, $K_B$ 's
Triple Layer	o b	H, A B, A	$\sigma_0 + \sigma_b + \sigma_d = 0$ $\sigma_d = -0.1174 c^{1/2} \sinh[ze\psi_d/2kT]$	$N_s, S, C1, C2, K_p$ 's, $K_A$ 's, $K_B$ 's

\* H, B, and A refer to protons, background electrolyte ions, and adsorbate species respectively.

+  $N_s, S, C, C1, C2$  as described in text;  $K_p$ 's refer to the proton binding constants (i.e.  $K_8$  and  $K_9$  in text);  $K_B$ 's refer to the binding constants for background electrolyte ions (i.e.  $K_{10}$  and  $K_{11}$ ); and  $K_A$ 's refer to the binding constants for adsorbate species (e.g.  $K_{12}$  and  $K_{13}$ ).

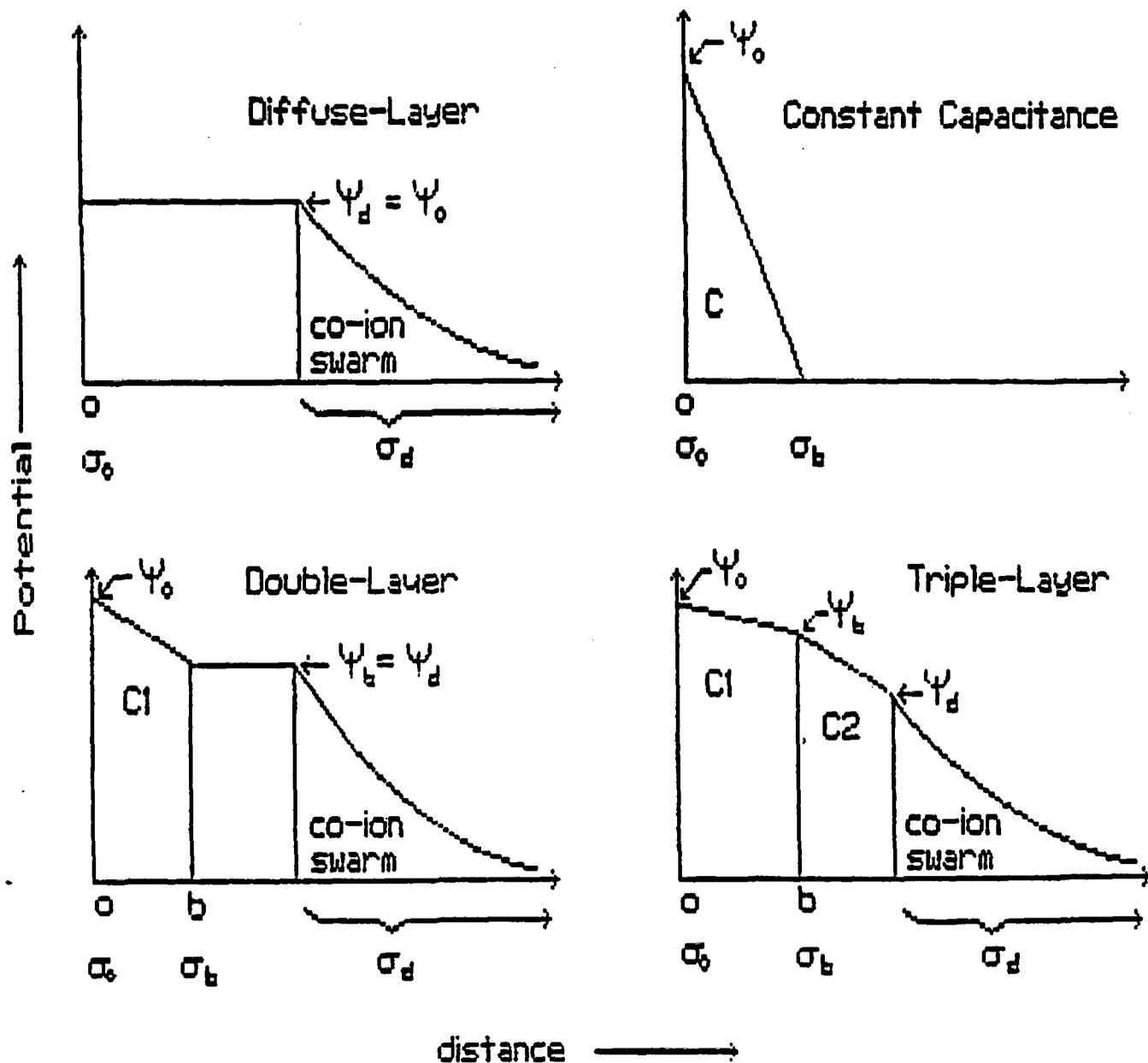


Figure 1. Schematic representation of solid/solution interface for diffuse-layer, constant capacitance, double-, and triple-layer models showing potential ( $\psi$ ) versus distance from the solid surface, position of binding planes (o,b) and their charge density ( $\sigma_0, \sigma_b$ ), the charge of the diffuse-layer ion-swarm ( $\sigma_d$ ), the capacitances of the inner (C1) and outer (C2) zones of the 'compact' layer, and the constant capacitance approximation (C) (after Westall, 1986). The relationship between charge and potential and model-specific binding features are discussed in the text and/or listed in Table 1.

**The following number is for Office of Civilian Radioactive  
Waste Management Records Management purposes only and  
should not be used when ordering this document:**

**Accession Number: NNA.881117.0005**

**Technical Information Department · Lawrence Livermore National Laboratory**  
**University of California · Livermore, California 94550**

