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DEVELOPMENT OF MODELS FOR USE
IN THE ASSESSMENT OF WASTE REPOSITORY PERFORMANCE

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ANNUAL PROGRESS REPORT

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INTRODUCTION

Any repository suitable for the disposal of radioactive waste comprises a combination of various man-made and natural barriers which aim to prevent transfer of the radionuclides from the canister to the external environment. Our group has developed the techniques needed to model the equilibrium chemistry of complex multicomponent rock/water systems over a range of ionic strengths and temperatures (HARVIE and WEARE, 1980; HARVIE *et al.*, 1980; FELMY and WEARE, 1986; MØLLER *et al.*, in prep.). These models, which are based on the virial expansion proposed by PITZER (1972; 1987) show remarkable agreement with field measurements when applied to natural systems. They have been applied successfully to interpret a variety of geochemical processes: studies of ancient (Zechstein II — HARVIE *et al.*, 1980; EUGSTER *et al.*, 1980) and modern (Bocana de Virrillá — BRANTLEY *et al.*, 1984) marine evaporite systems, studies of the solar evaporation of seawater (MØLLER *et al.*, in prep.), studies of mineral formation in lakes (Great Salt Lake — SPENCER *et al.*, 1985; Searles Lake with borate species added — FELMY and WEARE, 1984), and in fluid inclusions (collaboration with B. Lazar and H. D. Holland). For a review of some of these applications see the recent article by WEARE (1987). For a discussion of the application of these models to site assessment see WEARE *et al.* (1986). *These models are now accepted as giving the highest reliability and have been included in a number of modeling packages (EQ3/6, PHREEQ)*

At present our models are limited to the components of the seawater system (Na^+ , Mg^{2+} , Ca^{2+} , H^+ , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , CO_2), together with the borate species and SiO_2 . While this model is of sufficient generality to be of use in many assessment problems and has been incorporated in the generally available computer codes developed by DOE (EQ3/6) for site assessment, the chemistry of a number of important natural water processes of interest in repository development fall outside the range of components included in the model and therefore cannot be treated. Certainly an important example is

aluminium. Al is one of the most abundant elements in the earth's crust. Yet its aqueous chemistry is poorly understood. Because of its small ionic size and high charge, it tends to form strong complexes with some anions in solution. In particular, a variety of hydroxide and fluoride complexes have been identified and a number of attempts have been made to measure their stability.

Table 1. Examples of typical weathering reactions
(STUMM and MORGAN, 1981)

Incongruent Dissolution Reactions	
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{s}) + 5 \text{H}_2\text{O} = 2 \text{Si}(\text{OH})_4 + \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} (\text{s})$	
kaolinite	gibbsite
$\text{NaAlSi}_3\text{O}_8 (\text{s}) + 5\frac{1}{2} \text{H}_2\text{O} = \text{Na}^+ + \text{OH}^- + 2 \text{Si}(\text{OH})_4 + \frac{1}{2} \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{s})$	
albite	kaolinite
$\text{CaAl}_2\text{Si}_2\text{O}_8 (\text{s}) + 3 \text{H}_2\text{O} = \text{Ca}^{2+} + 2 \text{OH}^- + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{s})$	
anorthite	kaolinite
$7 \text{NaAlSi}_3\text{O}_8 (\text{s}) + 6 \text{H}^+ + 20 \text{H}_2\text{O} = 6 \text{Na}^+ + 10 \text{Si}(\text{OH})_4 + 3 \text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 (\text{s})$	
albite	Na ⁺ -montmorillonite

Al is present in many minerals in repository formations and backfills. The solubilities of such minerals are determined by the activity of Al species in solution. A list of typical weathering reactions that might effect the integrity of a waste formation are given in Table 1. The activity of an ion in solution is a strong function of the hydrolysis and formation of other complexing species in solution which bind the ion and decrease its concentration in the free form. Therefore, an accurate knowledge of the stability of the complexing species of aluminum in solution is essential to the prediction of the chemical behavior of aluminum bearing minerals. Because Al is such an important constituent of common minerals in waste formations and backfills, a well defined model will be useful for repository site assessment. With the exception of Al highly accurate models exist for the

activity of all the species in these equations (WEARE, 1987; MØLLER, 1988). However, even the low concentration behavior for the Al system is controversial (see APPS *et al.*, 1986).

This proposal outlines a program of research designed to expand the Harvie-Møller-Weare model to include a portion of the aluminum system and to acquire data necessary to model the chemical behavior of iron and copper species which also may effect the integrity of the containment vessel. The work of Harvie, Møller and Weare has shown that even for relatively simple solutes such as NaCl, which show little evidence for association, the accurate description of their activity as a function of solution composition may be very complicated particularly at high concentration.

Fortunately, however, for systems at very low concentrations, such as are expected to be encountered in the Nevada repository site, it can be shown that the free energy of the system may be represented as a simple sum of ideal mixing terms for the solute species. For electrolytes, non-ideality at low concentrations can be treated by the usual Debye-Hückel expression for the activity coefficients of ions, which is also nearly additive. This expression is a universal function of ionic strength, adding no new parameters to be evaluated from experimental data apart from the Debye-Hückel limiting slope which depends solely on solvent properties. Because of these simplifications at low concentration, the parameters needed for a dilute natural water model are the standard chemical potentials for each species in the solution. It is important to note, however, that because data can never be taken at infinite dilution these standard chemical potential determinations must be consistent with the models in which they are to be used. For example, to be consistent with the present DOE Harvie, Møller, Weare model, the data must be analyzed with a similar extrapolation to zero concentration.

It is the purpose of the research discussed here to provide a consistent set of chemical potentials for systems important to the objectives of the DOE waste disposal program. For simple solutes these thermodynamic constants can be found from simple binary measurements (e.g. the solubility of quartz in H_2O). For more chemically

complicated systems such as Al in H_2O which form complex species (e.g. the hydrolysis product of Al, $\text{Al}(\text{OH})^{2+}$), it is more involved to obtain standard chemical potential values from thermodynamic measurements even at low concentrations, since it is necessary to obtain chemical potential values for each of the species in solution (e.g. for the reaction: $\text{Al}(\text{OH})^{2+} + \text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + \text{H}^+$). And it is difficult to obtain data in solutions in which there is only a single solute species. In such cases, it is necessary to take data over a range of compositions and to use complex data reduction schemes to extract the desired standard chemical potential values (see for example the LETAGROP program — BRAUNER and SILLÉN, 1968). Approximate values of the association equilibrium for the Al species have been incorporated into the data base for general equilibrium codes such as EQ3/6 (WOLERY, 1979a;b); however they do not represent a carefully evaluated set of experimental data and thus are often inaccurate (see for example the recent review by Apps — APPS *et al.*, 1986).

Because of the great importance of standard chemical potentials to the thermodynamics of dilute natural water chemistry, there has been a major effort by HELGESON and co-workers (e.g. HELGESON *et al.*, 1970) and others to use existing thermodynamic data and theoretical extrapolations to provide estimates of standard chemical potentials for a wide range of species, temperature, and pressure — see SVERJENSKY (1987) for a recent review. While these approaches may provide an important guide to phase equilibria in complex settings, particularly at high temperature and pressure, there are many applications for which they are not sufficiently accurate. In addition for some elements of considerable importance such as Al the chemical behavior even at low concentration and at 25 °C is somewhat controversial (APPS *et al.*, 1986; FELMY and WEARE, 1986). In such systems extrapolations cannot be expected to yield reliable results. In Table 2 we present the hydrolysis constants for aluminum hydroxide species, and the solubility of gibbsite, taken from several sources. More extensive comparisons are contained in Apps *et al.* Note that not only do different models of Al in solution have different equilibrium constants, they

contain different sets of species. The inconsistency of these data evaluations indicates the lack of a thorough understanding of this important system.

Table 2. Hydrolysis constants at 25 °C for aluminum hydroxide species, and the solubility product of gibbsite.

Species	$\ln K_H^\dagger$		
	MAY <i>et al.</i> (1979)	BAES and MESMER (1976)	EQ3
$\text{Al}(\text{OH})^{2+}$	-11.49	-11.44	-10.91
$\text{Al}(\text{OH})_2^+$	-23.33	-21.41	-
$\text{Al}(\text{OH})_3(\text{aq})$	-	-34.54	-
$\text{Al}(\text{OH})_4^-$	-51.02	-52.96	-51.02
$\text{Al}_2(\text{OH})_7^{4+}$	-	-17.73	-
$\text{Al}_3(\text{OH})_{10}^{3+}$	-	-32.10	-
$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	-	-227.33	-
		$\ln K_{\text{sol}}^\ddagger$	
$\text{Al}(\text{OH})_3(\text{s})$	18.675	19.572	18.328

[†] Reactions are of the form: $\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al}(\text{OH})^{2+} + \text{H}^+$.

[‡] The reaction is: $\text{Al}(\text{OH})_3(\text{s}) + 3 \text{H}^+ = \text{Al}^{3+} + 3 \text{H}_2\text{O}$.

In this proposal we discuss the continuation of our program aimed at providing data and model parameters for subsystems such as those needed to describe the processes in Table 1. This research will extend the application of our present model to important assessment problems which cannot yet be treated. A program is also proposed which is aimed at the prediction of the reactions between canister materials such as iron and copper and formation brines. Apart from the establishment of the parameters for the Al, Fe, and Cu species proposed here, we believe that the collaboration of our group with the other researchers in the LLL waste program will lead to an improved consistency between modeling efforts.

OVERVIEW OF THE MODEL

In this section we discuss briefly the method we have developed to generate models of the chemical behavior of aqueous solutions. Our models are based on the usual expression for the free energy:

$$G = \sum_i \mu_i n_i \quad (1)$$

where μ_i is the chemical potential for species i , and n_i is the number of moles of species i . μ_i can be written in a form that emphasizes the theoretical behavior at low concentration:

$$\mu_i = \mu_i^\circ + RT \ln m_i + RT \ln \gamma_i^{\text{DH}} + RT \ln \gamma_i^{\text{exc}} \quad (2)$$

The first term on the right hand side is the standard chemical potential, the second term represents ideal mixing, the third represents corrections for long range electrostatic behavior (Debye-Hückel), and the fourth term represents further non-ideal corrections. As the first three terms have some basis in theory, we will call the sum of these terms the 'ideal' electrolyte behavior.

Two steps are needed to define a model. First, the species in solution which appear in the sum in equation (1) must be identified. Once this choice has been made, the ideal electrolyte behavior for the chemical potential of each species is given by the sum of the first three terms in (2), and can be included in equation (1). However, for systems of even moderate concentration additional 'non-ideal' thermodynamic behavior is evident in the experimental data. To include this behavior in the phenomenological description of the system, an equation must be given for the chemical potential of each species as a function of the concentration of all the other species in the solution. These contributions are lumped into the fourth term of equation (2).

Actually for most systems of geochemical interest even the choice of species to be included must be considered to be part of the modeling procedure. In an ideal situation each species would be identified by direct measurement (e.g. spectroscopy). However for many

systems of interest to site assessment problems there is not sufficient evidence to determine them uniquely. The choice of species then becomes part of the modeling decision.

The first step in developing a model is choosing which species are to be included in equation (1). Generally the choice of species is made on the basis of fitting a low concentration model to low concentration data. Once the species have been chosen, the model may be extended to higher concentrations by choosing an appropriate phenomenology with which to describe the fourth term in equation (2).

There are a number of phenomenological expressions for $\ln \gamma_i^{\text{exc}}$ in the literature (BROMLEY, 1973; MEISSNER and KUSIK, 1972; PITZER, 1987). These expressions contain parameters which must be evaluated from experiments. Because of this, it is important to choose an approach which has the required generality and accuracy while introducing a minimum number of parameters. All the approaches referred to above can describe data for simple binary systems with accuracy (e.g. osmotic data in the system $\text{NaCl-H}_2\text{O}$). However, the equations proposed by Bromley and by Meissner have not been generalized to treat mixtures. Since most natural water systems are complex mixtures, this is a significant limitation to the application of these approaches. While it would not be difficult to modify the Bromley and Meissner equations, a phenomenological approach which does treat mixing consistently has been given by Pitzer and co-workers. This theory and its application to natural water problems have been reviewed by PITZER (1987) and by WEARE (1987). This approach appears to have the accuracy required while introducing a minimum of parameters.

In this phenomenology the activity coefficients of the species in solution are represented by an equation of the form

$$\ln \gamma_i = \ln \gamma_i^{\text{DH}} + \sum_j D_{ij}(I)m_j + \sum_j \sum_k E_{ijk} m_j m_k + \dots$$

where γ_i^{DH} is the Debye-Hückel limiting law value, and m is the molality. The coefficient D_{ij} for oppositely charged species is a function of ionic strength and contains the so called

Pitzer parameters: $\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$, D_{ij} for similarly charged species, and all E_{ijk} are constants (see PITZER, 1987 ; WEARE, 1987). All of these parameters must be evaluated from experimental data.

The major limitation to the wide-spread application of the Pitzer phenomenology is the evaluation of the parameters it contains. On the other hand our results seem to indicate that no other approach that has fewer parameters has the accuracy required to predict the correct mineralogy of a formation. We note that the number of adjusted parameters is roughly the same as in a typical ion-pairing model for the same system, because a smaller number of species are typically included in our models (HARVIE and WEARE, 1980).

The objective of this research is to provide a model of the solution behavior of solute species necessary for the assessment of the performance of the nuclear waste repository in Nevada. For this application the concentrations of the ground water is not expected to be high and therefore the primary objective will be to obtain the relevant chemical potentials at infinite dilution (the first contribution in Eq.(2)). We note, however, that fall data must be taken at finite concentration and therefore the extrapolation to zero concentration is a function of the phenomenological equations used. Therefore, it is important to use programs for data analysis which are consistent with the rest of the Harvie-Møller-Weare model.

Since data is scarce in the systems to be discussed, this will require both a modeling effort and new measurements. We believe that more efficient modeling will result from close collaboration between the experimental and modeling aspects of the program. Consider for example the Al^{3+} - H_2O system. As was discussed above Al^{3+} in aqueous solutions forms a variety of hydration species. These species tend to co-exist over a range of compositions. However, there may be regions in which one species may dominate. In such a situation it is important to identify those experiments which best yield the required parameters. This can be done efficiently using a model.

On the other hand it may not be possible to isolate regions of particular parameter sensitivity. In this case it is important to treat the data using data fitting routines which have the complete model phenomenology built in. We have developed a software package that evaluates standard chemical parameters and parameters in the non ideal contributions to the free energy simultaneously, and as a function of temperature. Our program has capabilities similar to other data-fitting programs (LEGGETT, 1985). However, because the Pitzer model is built into the program it is not limited to the treatment of constant ionic strength media. This allows simultaneous evaluation of data from media with widely different compositions and insures the consistency of the derived potential parameters with the Harvie Møller Weare phenomenology.

The software is written in a way that allows the inclusion of new species with a minimum of effort. A variety of species (e.g. $\text{Al}(\text{OH})_4^-$ species) may be evaluated as to their effectiveness in reducing the difference between model estimates and measurements for all compositions. Thus providing an efficient strategy for selecting the optimal speciation scheme. We believe such a capability is essential for treating the complex aqueous chemistry of elements such as Al. The canister materials iron and copper which are also part of the program also show considerable complex formation in solution and therefore require similar techniques for model building.

RESEARCH PROGRAM PHASE I: The Aluminum System

In this phase of the program, the primary objective will be to continue the development of an accurate model of the aluminum-water system over the range 25–95 °C, and for a range of background salt concentrations and compositions. As mentioned above, this system is characterized by the formation of complex hydroxy-aluminum species. At low aluminum concentration the species in solution appear to be of the form $\text{Al}(\text{OH})_n$. While there is general agreement as to the stoichiometry of these species at low concentrations of aluminum, there is considerable controversy as to their formation constants (see Table 2). There appears to be fairly general agreement as to the first and fourth equilibrium constants (for the species $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^-$). However, formation constants for the intermediate species are very poorly known. These remarks apply to systems at zero concentration of background salt with low concentrations of aluminum. The information needed to model the system in a mixed brine at any concentration does not exist. Furthermore if the concentration of Al is high (greater than $10^{-4} \text{ mol}\cdot\text{kg}^{-1}$) new hydration species (e.g. $\text{Al}_{13}(\text{OH})_{32}$) become important. The structural and thermal properties of these polymeric species are complicated and more controversial. Fortunately, for natural water systems near chemical equilibrium the aluminum concentration is kept very low (less than $10^{-5} \text{ mol}\cdot\text{kg}^{-1}$) by the presence of very insoluble hydroxide and oxy-hydroxide phases. Therefore polymeric species such as $\text{Al}_{13}(\text{OH})_{32}$ may not be important to the assessment of repository performance.

The long range goal of our program is to develop a highly accurate model of hydrolysis equilibria as a function of temperature, pressure and composition. This is an ambitious undertaking and will require the careful evaluation of a large data base much of which does not exist at present.

Current Experimental Progress

The primary emphasis during the first period of this contract has been placed on the acquisition of data to be used to build a high quality model of the Al system over a range of temperature from 25 °C to 100 °C. The first priority in studying the aluminum system was to obtain information about the behavior of the Al^{3+} ion in aqueous solution. This was studied by measurements on the following cell:

As the solutions in the cell are acidic, there is very little hydrolysis to form species such as $\text{Al}(\text{OH})^{2+}$. This cell has been used to measure the activity of HCl in AlCl_3 solutions, at various ionic strength ratios, over a range of ionic strengths ($0.1 - 3.0 \text{ mol}\cdot\text{kg}^{-1}$) and temperatures ($0 - 45^\circ\text{C}$). These data are currently being evaluated to assess their internal consistency.

A graduate student (Mr. Wei-Jun Cai) is currently developing methods which use a coulometric procedure to generate base in NaCl media. (This approach is discussed in greater detail below.) Once he has shown that this can be successfully achieved using our apparatus, this method will be used to investigate aluminum hydrolysis reactions at elevated temperatures (up to 90°C). As this data becomes available it will be input into our data fitting programs and the relevant parameters found.

Current Progress in Modeling

We have begun the development of our general model for Al by developing a model of the behavior of Al^{3+} at low pH. At pH values less than 3 the concentration of various hydrolysis species will be very low because hydroxide ion concentration is very low. This leaves the unassociated Al^{3+} and H^+ as the principal species in solution. In the initial period of this research the cell measurements discussed in the first part of this proposal have provided the necessary data to evaluate the parameters for the interactions between Al^{3+} , H^+ and Cl^- species. Basically these experiments measure the activity of HCl as a function of solution composition. In previous work we have developed an accurate model of H^+ Cl^- interactions. The small changes in the e.m.f. of the cell due to the addition of the Al^{3+} species provide information as to the interaction of the Al^{3+} with Cl^- ions and interactions between Al^{3+} and H^+ . Under other funding we have developed an extensive library of data reduction software. This software is especially designed to simultaneously treat a variety of measurements including e.m.f. measurements.