Geothermal Chemical Modeling Project

DOE
Advanced Brine Chemistry
Program

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I. BACKGROUND

A primary goal of the DOE geothermal program is to lessen the risks and promote the more economical development of the Nation's geothermal energy resources. The development of a geothermal resource requires a considerable financial commitment. As in other energy extraction ventures, the security of this investment can be jeopardized by the uncertain behavior of the resource under operating conditions. Many of the most significant problems limiting the economical development of geothermal power are related to the chemical properties of the high temperature and high pressure formation fluids from which the energy is extracted. When the pressure and temperature conditions on these fluids are changed, either during the production phase or during the energy extraction phase of the operation, the fluids, which were originally in equilibrium with formation minerals, return to chemical equilibrium under new conditions. During this process, they may precipitate solid material (scaling) and/or release dissolved gases (breakout) in the formation and well bores and/or in the plant equipment. Additional problems may arise when these gases are toxic or corrosive. Handling of the spent brines may introduce a new set of chemical problems. For example, storage may concentrate toxic materials and reinjection may result in chemical problems such as decreased porosity in the injection formation.

Chemical problems, such as scaling and gas breakout, occur during energy extraction operations for essentially all geothermal resources. For some operations, these problems are only minor and can be handled with simple procedures and routine maintenance. However, for many large and important resources the control of problems associated with brine chemistry may determine whether or not energy production operations are successful. In some cases, scaling problems have been so severe that a resource has been abandoned even after considerable capital investment.

The costs related to increased maintenance needs and equipment losses due to scaling in geothermal operations can be high. Although various strategies (e.g., binary cycles, crystallizers, scale inhibitors) are available to help control scaling problems, these strategies generally require substantial additional costs either in terms of disposable materials (e.g., scale inhibitors),

additional equipment (e.g., crystallizers) or downtime (e.g., well cleanup). Because of these expenses, it is important to fully assess both the nature and magnitude of the scaling problems encountered during geothermal energy production and the effectiveness of strategies to relieve them. In addition, prediction of potential scaling problems before the development of a resource would significantly lessen the financial burden of the industry by reducing the risks of reservoir site selection.

**Table 1. SOME USES OF A CHEMICAL MODEL FOR
GEOTHERMAL ENERGY PRODUCTION OPERATIONS**

- Prediction of brine behavior under a variety of field conditions (temperature, pressure, composition)
- Prediction of well and plant damage due to mineral scaling
- Prediction of gas breakout and flashing as a function of brine composition, temperature and pressure
- Testing of strategies to decrease effect of mineral scaling and to maximize energy production
- Prediction of history and evolution of operating and potential resources
- Support of laboratory simulation programs
- Prediction of chemical incompatibilities during the reinjection of spent brines or mixing of spent brines at the surface
- Prediction of chemical evolution of evaporated brines during reservoir storage of spent brines
- Prediction of partial fugacities in mixed gas systems
- Prediction of liquid-vapor equilibria
- Design of optimal reaction pathways for ancillary mineral recovery programs

DOE funding to the University of California, San Diego (UCSD) Chemical Modeling Group supports research to provide computer models which will reliably characterize the equilibrium chemistry of geothermal brines (solution, solid and gas phases) under variable thermodynamic conditions. With this technology, it will be possible to rapidly and inexpensively predict the chemical behavior of geothermal brines during various resource recovery stages: exploration, production, plant energy extraction and reinjection as well as in ancillary programs such as mineral recovery (see Table 1).

Our computer models help meet the objectives (listed in Table 2) which have been established for the Advanced Brine Chemistry projects in the Geothermal Program of the Department of Energy. In addition, this technology will be useful in other programs supported by DOE as well as by other agencies and industries.

Table 2. OBJECTIVES DOE ADVANCED BRINE CHEMISTRY PROGRAM	
i.	Reduce geothermal production well maintenance costs related to scale deposition.
ii.	Reduce geothermal field surface equipment costs related to scale deposition.
iii.	Reduce geothermal power plant maintenance and equipment replacement costs related to scale deposition.

Accurately characterizing the chemistry of geothermal brines is difficult because brine behavior is a function of many variables. Furthermore, geothermal brine composition, temperature, and pressure characteristics are not only site specific but also may change at a particular site during various stages of operation. For computer models to reliably describe the complex chemical behavior of geothermal brines for the wide range of conditions found in various geothermal energy production operations, these models must be very accurate even to high concentration. They must be flexible, handling large variations in composition, temperature and pressure, as

well as be convenient to use.

Our modeling technology is based on recent progress in the physical chemistry of concentrated aqueous solutions. The behavior of these fluids has not been predicted from first principle theories. However, because of the importance of concentrated brines to many industrial and natural processes, there have been numerous efforts to develop accurate phenomenological expressions for predicting the chemical behavior of these brines. One of the most successful of these efforts is that of Pitzer and coworkers (see Pitzer (1987)). Incorporating the semiempirical equations of Pitzer, we have shown at UCSD that we can create highly accurate models of brine-solid-gas chemistry.

The construction of these models, which are parameterized by very careful fitting of experimental measurements, requires extensive data sets. However, the model framework (see below) is such that only relatively simple (e.g., binary and ternary) data are required to successfully predict the chemical behavior of very complicated geothermal systems. In many cases these data are readily available. Since the model framework is also highly flexible, new species and extended temperature and pressure ranges can be easily added to the models. Once the models have been parameterized, they are convenient to use and can be applied without further change to a wide variety of the chemical problems encountered in geothermal energy operations.

II. OVERVIEW OF THE MODELING APPROACH

Several phenomenological approaches, which have a basis in the current theory of electrolyte solutions, have recently been developed for describing complex brines. Phenomenological equations contain parameters which must be evaluated from experimental data. Therefore it is important to choose a modeling framework which will have the required generality and accuracy for geothermal applications while introducing a reasonable number of parameters. A variety of modeling approaches have been suggested in the literature (Bromley, 1973; Meissner and Kusik, 1972; Pitzer, 1987). Most of these approaches, while providing the necessary accuracy in binary

systems, have not been generalized to correctly treat the complex mixtures which are typical of natural and industrial brines. The approach introduced by Pitzer and co-workers (Pitzer, 1987) satisfies the complex mixing requirement, introduces a minimum of parameters and is highly accurate. In a number of articles (Harvie and Weare, 1980; Harvie et al., 1984; Felmy and Weare, 1986; Møller, 1988; Greenberg and Møller, 1989), we have demonstrated that these equations can be used in solubility models to describe complex brine behavior to high concentration and for a range of temperatures up to 250°C.

Our model development begins with the free energy minimum criterion. The equilibrium composition of a system at constant temperature and pressure is defined by the minimum of the Gibbs Free Energy function, G :

$$\min G = \sum_{i,p}^N \mu_i^p n_i^p , \quad (1)$$

subject to the constraints

$$\sum_{i,p}^N c_{ij}^p n_i^p = b_j \quad (2)$$

and

$$\sum_i z_i^p n_i^p = 0 \quad \text{for each phase } p .$$

In Eq. (1), n_i^p is the number of moles of species i in phase p , and μ_i^p is the chemical potential of species i in phase p . In Eq. (2), c_{ij}^p is the amount of component j in species i in phase p , b_j is the total amount of component j , N is the total number of species included in the model in all phases, and z_i^p is the charge of species i in phase p .

The method of solving the minimization problem, Eq's. (1) and (2), is an important aspect of a model. The algorithm chosen must be efficient and reliable. Problems with reliability become much more severe for highly concentrated, very nonideal systems. In our model, the free energy is minimized by an algorithm which has been developed to treat the special problems

of phase equilibrium calculations. This algorithm:

1. Incorporates stable numerical methods, providing not only rapid convergence but also guarding against failure because of a poorly conditioned problem or inadequate selection of initial concentrations.
2. Is capable of adding and removing mineral, gas, liquid, and solid-solution phases. It selects the correct phase assemblage for an arbitrary set of composition, temperature, and pressure conditions.
3. Generates its own stable reaction paths which are automatically chosen to emphasize major species.
4. Can precipitate and dissolve many phases simultaneously in systems constrained by mass balance. Again, it independently chooses the most stable phase assemblage.
5. Can handle nonconvex solution models with some instructions given by the user.

An article with an extensive description of this algorithm has been published (Harvie et al., 1987).

For aqueous phases, it is generally convenient to further express the chemical potential, μ_i , in a form related to that for ideal solutions. In order to do this, the activity, a_i , of solute species i is defined by the equation,

$$\mu_i = \mu_i^0(T) + RT \ln a_i \quad , \quad (3)$$

where μ_i^0 is the standard chemical potential of solute species i at infinite dilution and constant temperature and pressure. The relation to ideal solutions is further emphasized by defining the activity coefficient, γ_i , for the solute species by the equation,

$$a_i = \gamma_i m_i \quad . \quad (4)$$

In an ideal solution, $a_i = m_i$, the concentration in molality units.

For the solvent, water, the activity is written in terms of the osmotic coefficient, Φ , defined by,

$$\ln a_{\text{H}_2\text{O}} = \frac{-W}{1000} (\sum_i m_i) \Phi . \quad (5)$$

In Eq.(5), W is the molecular weight of water. The sum in Eq.(5) is over all solute species.

Given Equations 4 and 5, the free energy of the solution phase is defined, provided the dependence of the activity coefficients and osmotic coefficient are given as a function of concentration. The equations of Pitzer and co-workers (Pitzer, 1987), when parameterized using experimental data, provide the necessary concentration dependence to fully define the chemical potentials of all the species in an aqueous phase. Chemical potentials of the solid phases are a function of temperature and pressure only, since the compositions of all solid phases are assumed to be pure.

In an electrolyte solution the activity of a single ionic species cannot be measured. This would require the measurement of the change of free energy of the system when a single ionic species is added, *i.e.*, as the system becomes charged. In experiments which involve the addition of n_s moles of neutral salts, the free energy change can be measured and is written as:

$$\left(\frac{\partial G}{\partial n_s} \right)_{n_j, T, P} = \mu_s . \quad (6)$$

The derivative in Eq. (6) is taken with all the other species, n_j , held constant. The chemical potential of the salt, μ_s , is defined as:

$$\mu_s = v_a^s \mu_a + v_c^s \mu_c , \quad (7)$$

where the stoichiometric coefficient, v_a^s , is the number of anions in the particular salt (*e.g.*, 2 in CaCl_2) and v_c^s is the number of cations (*e.g.*, 1 in CaCl_2). Using the activity coefficient, γ_i , definition given in Eq's (3) and (4), Eq. (7) may be written in terms of ion activity coefficients as:

$$\mu_s = v_a^s \mu_a^o + v_c^s \mu_c^o + RT \ln m_a^{v_a^s} m_c^{v_c^s} + RT \ln \gamma_a^{v_a^s} \gamma_c^{v_c^s} . \quad (8)$$

The last term contains the non-ideal contributions to the salt chemical potential, μ_s . Because the single ion activity coefficients cannot be measured, the mean activity coefficient, $\gamma_{\pm}^v$, is defined as:

$$\gamma_{\pm}^v = \gamma_a^{v_a^s} \gamma_c^{v_c^s} \quad (9)$$

to distribute the non-ideality equally over the anions and cations. In Eq (9),

$$v = v_a^s + v_c^s . \quad (10)$$

The mean activity coefficient, $\gamma_{\pm}$, can be measured and is often reported.

At sufficiently low concentrations, the activities of ions in an aqueous solution obey universal behavior, which is not specific to the identity of the ions. This is the well known Debye-Hückel limiting region. At higher concentrations, however, the chemical identity of the species begins to play an important role in the thermodynamics of the system. Some of this behavior can be described by an ionic strength,

$$I = \frac{1}{2} (\sum_i m_i z_i^2) , \quad (11)$$

dependent phenomenological extension of the Debye-Hückel equation (e.g., the Davies equation). However, important contributions which are specific to the chemistry of each species are evident in measurements even at fairly low ionic strength. For example, for $I = 0.01$, the mean activity coefficient of CaCl_2 is 0.727 and for Ca(OH)_2 , it is 0.671. At higher concentrations these differences between species become much larger. To correctly predict solubilities in complex systems, phenomenologies must be able to treat these specific interactions. For the complex, concentrated brine systems often encountered in geothermal operations, a large number of minerals or combinations of minerals may be candidates for the equilibrium assemblage coexisting with the brine. Since in a typical situation, various potential mineral associations have simi-

lar stabilities, highly accurate models of the solution phase are required to correctly select among alternatives (Weare, 1987). Even small errors in the solution free energy may yield qualitatively incorrect prediction of equilibrium mineral assemblages.

In our models, the Pitzer equations describe the concentration dependence of the specific interaction behavior of the ions. These equations express the osmotic coefficient and the activity coefficients of the aqueous species in the virial expansion form:

$$\ln \gamma_i = \ln \gamma_i^{\text{DH}} + \sum_j D_{ij}(I) m_j + \sum_{jk} E_{ijk} m_j m_k \dots \quad (12)$$

γ_i^{DH} is a modified Debye-Hückel coefficient. The second and third virial coefficient terms (in $D_{ij}(I)$ and E_{ijk} , respectively) are specific for each ion interaction. As indicated, D is a function of ionic strength. The form given by Pitzer for $D_{ij}(I)$ is different for like-like (e.g., $i = \text{K}^+$, $j = \text{Na}^+$), like-unlike (e.g., $i = \text{K}^+$, $j = \text{Cl}^-$), and ion-neutral [e.g., $i = \text{Na}^+$, $j = \text{CO}_2(\text{aq})$] interactions. This reflects the expected differences between these interactions in solution. The ionic strength dependent form in D for like-unlike (single electrolyte) interactions contains various parameters, $\beta^{(0)}$, $\beta^{(1)}$ and $\beta^{(2)}$ (see Pitzer (1987)). The parameters in the D_{ij} expressions for like-like (mixed electrolyte) interactions, all the parameters in the E_{ijk} terms (θ , C and ψ , see Pitzer (1987)) and the λ parameters in the expressions for ion-neutral interactions are constants at constant temperature and pressure. All the parameters are evaluated by comparison with experimental data.

The most important contributions to the concentration behavior of the model come from the single electrolyte (like-unlike) terms. These terms may be determined from binary thermodynamic measurements. For example, in the system $\text{CaSO}_4\text{--NaCl--H}_2\text{O}$, the Ca-Cl parameters contained in both the second and third virial coefficient expressions can be evaluated from binary osmotic data in the $\text{CaCl}_2\text{--H}_2\text{O}$ system. Once these parameter values have been determined, they are fixed. For moderately concentrated systems ($I < 1\text{m}$), a model of a complex brine using only binary information gives quite reliable solubility predictions.

The solubility calculations that we have performed have shown that for geothermal applications, the series represented by Eq. (12) may be terminated at the triplet interaction (m^2) terms. For highest reliability in the moderately concentrated systems and for more concentrated systems, it is necessary to evaluate both the binary and the ternary parameters to high concentration. This is because the binary third virial coefficient terms (C) and the ternary second and third virial coefficient terms (θ and ψ) are insensitive to low concentration data. Evaluating them even from highly accurate low concentration measurements will provide a poor extrapolation to high concentration. The ternary parameters are evaluated from ternary thermodynamic measurements. For example, $\theta_{Ca,Na}$ in D(I) can be determined from NaCl solubility measurements in $CaCl_2$ brines. Once all the binary and ternary interaction parameters have been evaluated, any more complicated system containing these species may be treated. This results in a significant simplification when considering complex systems.

In constructing our variable temperature solubility models, the approach of Møller (1988) is used to model solubilities as a function of temperature. The temperature dependence of the solid phase chemical potentials and of the Pitzer parameters used to calculate the activity and osmotic coefficients is described by the equation:

$$\begin{aligned} \text{Parameter (T)} = & a_1 + a_2 T + a_3/T + a_4 \ln T + a_5/(T-263.) + a_6 T^2 \\ & + a_7/(680.-T) + a_8/(T-227.) \end{aligned} \quad (13)$$

and by the values of the constants, $a_1 - a_8$. This fitting equation is consistent with both thermal and activity data (Rogers and Pitzer (1981); Pitzer *et al.* (1984)). The temperature dependent constants ($a_1 - a_8$) in Eq. (13) are evaluated by comparing predicted activity values with activity (osmotic, emf and/or solubility) measurements using a non-linear least squares optimization algorithm which incorporates free energy minimization. (See Harvie, Greenberg and Weare (1987) for a complete description of this algorithm.)

For gas phases, the approach to modeling must be somewhat more general. For systems in which there may be more than one phase and it is desired to model transitions between phases, a

free energy equation must be defined which can describe both phases. For gases the fugacity, f , is defined via the equation,

$$\mu_i = \mu_i^0 + RT \ln f_i . \quad (14)$$

The fugacity must then be defined as a function of gas phase composition, pressure, and temperature. Since gas phases are very compressible, the equations describing their behavior must allow for variation of the density with pressure. For low total pressure applications in geochemistry, it is often sufficient to assume that the fugacity of species i is equal to the partial pressure of the gas phase species i . However for complex gas mixtures at high pressure, such as that found in geopressured systems, this assumption is not adequate. To model these systems, we begin by defining an empirical equation for the volume as a function of pressure. The form for this equation is found by analogy with the low density virial expansion. Various terms are added to describe high density behavior and the transition to the liquid state. We have shown that with sufficient care, an equation can be developed which describes both the liquid and the gas phases of a system with an accuracy close to that of the experimental measurements (Duan, Møller, and Weare). When this equation and Eq. (12) have been completely parameterized all the quantities in Eq. (1) have been defined and the distribution of species may be found by minimization.

III. PROJECT OBJECTIVES

The project objectives (see Table 3) of the UCSD Chemical Modeling Group support the DOE goal to decrease the financial risks of geothermal energy production by reducing the costs associated with scaling and other chemical problems. The technology which we are developing and disseminating to the geothermal energy industry are computer models capable of accurately predicting and analyzing critical aspects of the chemical behavior of geothermal brines. Our goal is to have these models retain the reliability of the experimental data on which they are based and to make these models flexible enough (variable composition and phases, temperature,

pressure, ionic strength and pH, P_{CO_2}) to simulate the thermodynamic conditions under which scaling problems and other chemical problems can occur. These criteria are difficult to achieve. However they are necessary characteristics to successfully predict the chemical behavior of geothermal brines and rock-brine interactions as well as to test and optimize modifications of powerplant design, operation and/or material selection aimed at abating chemical problems such as scaling. High reliability in geothermal scaling models is particularly important because even relatively small amounts of scaling per unit of brine can cause significant scaling problems when large quantities of brine are produced.

Table 3. PROJECT OBJECTIVES
<ul style="list-style-type: none">• DEVELOP TECHNOLOGY TO IMPROVE UNDERSTANDING AND PREDICTION OF NATURAL AND INDUSTRIAL BRINE CHEMISTRY• DEVELOP TECHNOLOGY SUPPORTING DOE GOAL TO REDUCE GEOTHERMAL ENERGY PRODUCTION COSTS ASSOCIATED WITH SCALING AND OTHER CHEMICAL PROBLEMS• COMPILE, EVALUATE AND SUMMARIZE BRINE SOLUBILITY DATA• APPLY TECHNOLOGY TO INTERPRET, PREDICT AND SIMULATE NATURAL AND INDUSTRIAL GEOCHEMICAL PROCESSES• PROMOTE TECHNOLOGY TRANSFER• PROMOTE COLLABORATIONS (ACADEMIC, AGENCY, INDUSTRY)• TRAIN STUDENTS IN BRINE CHEMISTRY

We have shown that using our solubility modeling approach, which incorporates the Pitzer thermodynamic equations, it is possible to achieve this high degree of accuracy and flexibility. However, this effort requires considerable data evaluation, careful model parameterization and rigorous model validation. For liquid phases, problems such as the identification of the

chemically important complex species in natural waters containing strongly associating components (e.g., boron and aluminum) and the accurate description of the activities of these species as a function of composition, pressure and temperature must be solved. For liquid-vapor models, equations of state which allow reliable prediction of the nonideal behavior of the gases and correct characterization of the liquid-gas equilibrium behavior must be established.

The technology we are developing will improve the understanding and prediction of natural and industrial brine chemistry. Therefore it will have application to many projects in the DOE Geothermal Energy Program. To most effectively meet the needs of the geothermal energy industry, our project development includes continued cooperation with the industry (through workshops and personal communication) in order to transmit technology, exchange ideas for model and documentation improvements, and to test and apply the models to geothermal problems.

The models will also be useful to other research programs such as those involving geothermal waste disposal, nuclear waste disposal, petroleum production, mineral recovery, water pollution, acid rain effects, *etc.* Since our methodology requires the collection and validation of a great deal of solubility data under a variety of PVT conditions, it provides an effective means of analyzing, summarizing and making more accessible brine chemistry data presently available and those being collected in programs supported by DOE and other agencies. Collaborations with academic, agency and industrial research groups as well as the training of students will help increase the understanding of our methodology and promote the transfer of our technology.

IV. PROJECT SIGNIFICANCE

Table 4 below summarizes the scientific importance of the technology being developed by the UCSD Chemical Modeling Group.

Table 4. SCIENTIFIC IMPORTANCE
UCSD GEOTHERMAL CHEMICAL MODELING PROJECT

- INCORPORATES RECENT HIGHLY SUCCESSFUL ADVANCES IN CHEMICAL THEORY INTO USEABLE TECHNOLOGY WITH MANY APPLICATIONS
- DEVELOPS TECHNOLOGY FOR RELIABLY PREDICTING THE CHEMICAL BEHAVIOR OF COMPLEX BRINE-MINERAL-GAS SYSTEMS UNDER A WIDE RANGE OF CONDITIONS (I,T, P)
- PROVIDES MODELS WHICH PREDICT THE BEHAVIOR OF MANY IMPORTANT GEOCHEMICAL SYSTEMS WITH AN ACCURACY SIMILAR TO LABORATORY SIMULATIONS
- PROVIDES A FAST, FLEXIBLE AND EASILY ACCESSIBLE TOOL TO RELIABLY PREDICT SCALING AND GAS BREAKOUT IN GEOTHERMAL BRINES AND THEREBY HELP REDUCE THE COSTS OF GEOTHERMAL ENERGY PRODUCTION (RESOURCE ASSESSMENT, ENERGY EXTRACTION, WASTE DISPOSAL)
- PROVIDES TECHNOLOGY THAT CAN HELP IMPROVE THE UNDERSTANDING OF FUNDAMENTAL PROBLEMS IN GEO-CHEMISTRY (EVAPORITE MINERAL FORMATION; FLUID INCLUSIONS)
- COMPILES, SUMMARIZES AND VALIDATES MANY THERMODYNAMIC DATA TAKEN IN DOE AND OTHER PROGRAMS INTO A USEABLE AND EASILY ACCESSIBLE PACKAGE
- PROVIDES A STANDARD OF COMPARISON FOR CHECKING MANY THERMODYNAMIC FIELD AND LABORATORY DATA

V. PROJECT PROGRESS

The capabilities of the geothermal brine models we have developed at UCSD to date are summarized in Table 5. These models will predict saturation ratios, scaling behavior, pH, formation porosity changes and gas breakout in production wells, throughout various brine flow and heat extraction systems and during reinjection procedures.

Table 5. PROJECT PROGRESS
CAPABILITIES OF PRESENT MODELS

- Predict Behavior of Calcium Carbonate Scale Formation in NaCl and CaCl_2 Brines for $T = 0^\circ$ to 250°C (PC Version Available)
- Predict Solubility of CO_2 and CH_4 in NaCl Brines for $T = 0^\circ$ to 250°C (PC Version Available)
- Predict Solubility of Amorphous Silica Scale in Seawater-Type Brines for $T = 0^\circ$ to 250°C
- Predict Solubilities of Marine Scaling Minerals (NaCl, CaSO_4 , etc.) to 250°C
- Calculate Precipitation Characteristics of Rock-Water Systems Containing Na, K, Ca, Cl, and SO_4 for $T = 0^\circ$ to 250°C
- Predict Onset of Two Phase Behavior (Gas Breakout) in NaCl Brines
- Predict Solubility of Hydrogen Sulfide ($\text{H}_2\text{O}-\text{H}_2\text{S}-\text{HS}^-$) System (preliminary, $0^\circ - 90^\circ\text{C}$; 0 - 60 atm)
- Predict Partial Fugacity in Mixed Gas System ($\text{CO}_2-\text{CH}_4-\text{H}_2\text{O}$) $T = 0^\circ$ to 1000°C and $P = 0$ to 1000 bars
- Predict Gas-Liquid Equilibrium in the $\text{CO}_2 - \text{CH}_4 - \text{H}_2\text{O}$ system

The high degree of flexibility (variable composition and phases, temperature, pressure, pH, ionic strength and P_{CO_2}) represented in the modeling capabilities listed in Table 5 allows the

prediction and simulation of scaling and other important aspects of complex brine chemistry under a wide variety of thermodynamic conditions. Scaling abatement strategies, more efficient energy production procedures and site performance assessments can therefore be engineered and tested rapidly and cost-effectively. The models will also be useful to predict the scaling behavior of storage and reinjection systems and to investigate the effectiveness of well cleanup strategies, such as acid treatment.

The original brine models we developed were applicable to surface problems (near standard conditions). We demonstrated that the predictions of these models are sufficiently accurate to obtain important information about various geological and low temperature industrial processes. Model calculations are in excellent agreement with both laboratory and field measurements.

With the support of the DOE geothermal program, the low temperature brine models have been extended to the high temperatures characteristic of many geothermal fluids. We have implemented a model of the $\text{CaCO}_3\text{-SiO}_2\text{-CaSO}_4\text{-NaCl-CO}_2\text{-H-H}_2\text{O}$ system over a temperature range of 0°C to 250°C and to high ionic strength. This system contains most of the important carbonate, sulfate and silica scale-forming minerals. Parameterization of the seawater system, $\text{Na-K-Ca-Mg-Cl-SO}_4\text{-H}_2\text{O}$, is also complete to high temperature (0°C - 250°C) with the exception of the Ca-Mg interactions. With the inclusion of these interactions, these models will treat all the major components of seawater-type brines in addition to carbonate, CO_2 and silica solubilities.

Model calculations compare well with both laboratory and field data. Our models typically retain the reliability of the experimental data on which they are based. For example, the present calcite and silica scaling model predicts all the laboratory data we could find for calcite, amorphous silica, and CO_2 solubility for a temperature range from $0^\circ\text{-}250^\circ\text{C}$ within the accuracy of the measurements. Therefore, our models provide an effective means of summarizing, comparing and validating the brine chemistry data presently available. They also provide a reliable standard of comparison for both field and laboratory measurements being collected in programs supported by DOE and other agencies.

To illustrate the importance of our model validation by comparison with both laboratory and field data, it is important to note that it was necessary to reparameterize our initial calcite scale model. We discovered that our initial model of calcite scale formation exhibited unexpected behavior when compared to brines of unusual composition (e.g., high calcium concentration brines from the Gulf Coast Hulin well). After finding data which better defined the model in this composition range, we changed important parameter values and markedly improved the model's predictive reliability in such high calcium systems.

The brine modeling technology provides tools for accurately predicting the state of equilibrium of a geothermal brine and mineral precipitation at any point in the well bore, the power plant, or the reinjection system. In the design of a new power plant they can also be used to track the possible precipitation of scale through the potential plant operation, thus enabling optimal cycles to be designed consistent with scale control strategies.

As well as providing an important design tool for geothermal energy production, these brine models represent a very significant advance in our ability to interpret general problems in geochemistry. They have been used successfully to investigate a number of problems of general geochemical interest by our group (see PAPERS and REFERENCES) and by visitors to this group.

In a related program, the seawater brine model has been parameterized to temperatures down to the eutectic point of the seawater system. This model is presently being used to noninvasively interpret the composition of fluid inclusions via mineral coexistence in a cooling cycle. This information is useful in investigations of reservoir properties.

As Table 5 indicates, we have made significant breakthroughs in modeling the behavior of the gas phases associated with geothermal formations. During this funding period a model of the ternary system, $\text{CO}_2\text{--CH}_4\text{--H}_2\text{O}$, was completed. The nonideal behavior of these gases is important to the prediction of the scaling tendency of highly pressured geothermal (geopressured) systems. The prediction of two phase liquid-vapor equilibrium in this system is also useful for the analysis of reservoir characteristics via fluid inclusion studies.

We began the gas modeling program by testing the large number of published equations of state for the pure systems and binaries against laboratory PVT measurements. Results showed that the published equations, including those recommended by the International Union of Pure and Applied Chemistry, were inadequate for use in our geothermal models.

After extensive testing we have found a new equation of state which can predict the thermodynamic properties of this ternary within experimental accuracy. This equation for the pure end members is similar to the Benedict Webb Rubin (BWR) equation for pure systems.

We have also developed a method to include mixing behavior. A simple mixing rule yields results which are adequate above the critical temperatures of the binaries even to quite high pressures. In the liquid coexistence ranges, binary mixing becomes very nonideal, and a more complex mixing relation is required. We have found that it is necessary to use phase coexistence data (solvus data) and a relatively complicated mixing rule in order to accurately predict the thermodynamic behavior below the critical point.

Our final equation of state is the first, of which we are aware, that can model a system from the two phase region through the critical point to the homogeneous region. We consider this to be a breakthrough in thermodynamic modeling of natural processes. We have shown that our new technology (equation of state and mixing rules) allows us to successfully model the behavior of gas-liquid systems of the compositions associated with geothermal operations as a function of temperature and pressure. The temperature (0°C to 1000°C) and pressure (0 to 1000 bars) dependent model of the $\text{CO}_2\text{--CH}_4\text{--H}_2\text{O}$ system which we have developed can simulate both the single and two phase behavior of gas mixtures within experimental accuracy. We will use these models to improve our predictions of gas breakout in highly pressurized formations, where a major part of the extracted energy in these systems is in the dissolved gases. These models will also be used for predicting reservoir performance characteristics (fluid inclusion studies) and carbonate scale -gas breakout inter-relationships.

We have compared predictions of the models described in Table 5 with geothermal field measurements and have found very good agreement. They have, for example, successfully

predicted breakout conditions for the East Mesa brine and the scaling behavior of Dixie Valley geothermal brines. Excellent agreement between model calculations and down hole samples from high pressured oil formations has also shown that the models can accurately predict brine behavior near formation conditions. We have also completed a brine-gas model for the $\text{CO}_2\text{-CH}_4\text{-NaCl-H}_2\text{O}$ system to 250°C which can be used in gas breakout calculations (see Table 5). These models have been included in the EQUIL software package and are now being distributed (see below).

A preliminary model of the important $\text{H}_2\text{S-H}_2\text{O}$ system has been prepared for the 0°C to 90°C temperature range (0 - 60 atm). When a model of the $\text{H}_2\text{S-NaCl-H}_2\text{O}$ system is complete to high temperature (T_{max} will depend on data availability) we will be able to begin the development of models of sulfide scale formation.

We have carried out efforts to transfer our modeling technology to the geothermal energy community. Versions of the modeling code have been adapted for use on both MacIntosh and IBM personal computers. A manual for describing the models and their application to geothermal problems has been prepared. A workshop for the industry was conducted at the Lawrence-Berkeley Laboratory (University of California, Berkeley) in September, 1991. We have also continued to apply our models to geothermal problems.

Transfer of technology to other industries (e.g., mineral recovery, petroleum) academic institutions and agencies (e.g., INEL, LLL, LBL, Battelle, USGS) (see Table 6 below) continues to take place. The models we have developed have been incorporated in model codes (e.g., EQ3/6; PHREEQ; SOLMINEQ; GMIN) which have been supported and widely distributed by other agencies (e.g., USGS). Applications to interpret important aspects of the geochemistry of natural brine-rock interactions have been highly successful (see, for example, PAPERS and REFERENCES listed below).

VI. RELATED INTERFACE/CONTACTS (FUNDING PERIOD)

The technology we have developed (Table 5) and continue to develop will improve the understanding and prediction of natural and industrial brine chemistry. Therefore it will have application to many of the projects included in the DOE Geothermal Program. In September, 1991, we conducted a workshop for the geothermal community at Lawrence-Berkeley Laboratory (U.C., Berkeley). The purpose of this workshop was to demonstrate the use of our modeling technology in geothermal energy applications and to promote the exchange of information between our modeling group and the industry.

Our models may also be applied to a number of important problems in other energy technologies (e.g., oil production problems, solar pond thermodynamics, waste cleanup, etc.), in industrial process chemistry and in nuclear waste isolation (see Table 6). We have already demonstrated their usefulness in many of these applications. For example, the isothermal models developed by our group have become the standard models of the nuclear waste program for studying moderately concentrated aqueous solutions. Recently our program was used by members of the Canadian potash industry in studies of mine stability. After a survey of the various programs available for thermodynamic predictions, they reported that our model is the only program giving satisfactory agreement with experimental measurements of mineral solubility.

Our programs are used by many industrial and research organizations. We collaborate with investigators in many countries. A number of these investigators visit our group regularly and have taken research level versions of the code back to their home institutions. As a result, our models have been validated by comparison with many types of laboratory and field data involving both natural and industrial brines.

Table 6. TECHNOLOGY TRANSFER OF CHEMICAL MODELS

- Mineral yields in mineral production processes
- Scaling potentials in industrial evaporation systems
- Solar pond thermodynamics
- Scale formation in oil wells
- Prediction of outcome of programs for scaling abatement
- Injection water incompatibilities in oil formations
- Site performance assessment in nuclear waste disposal programs
- Prediction of methane content in geopressured systems
- Yield and performance assessment of processes in the aluminum industry
- Atmospheric studies of CO₂ (e.g., global warming)
- Interpretation of natural and industrial geochemical processes
- Validation of laboratory data

VII. RELATED MEETINGS/REVIEWS (FUNDING PERIOD)

September 26-29, 1988, *Invited talk*: "Solubility Predictions in Complex Mineral Systems," Los Angeles, American Chemical Society Conference.

February 9, 1989, *Invited presentation*, Washington, D.C., Geothermal Technical Program Review.

March 21-23, 1989, *Invited presentation*, San Francisco, Geothermal Program Review VII: DOE R&D for the Geothermal Market Place.

September 25-26, 1989, *Invited speaker*, SIAM Conference on Mathematical and Computational Issues in Geophysical Fluid and Solid Mechanics.

September 28, 1989, *Invited speaker*, Houston, Texas, British Petroleum.

April 18-20, 1990, *Invited presentation*, San Francisco, Geothermal Program Review VIII: The National Energy Strategy---The Role of Geothermal Technology Development.

September 4-6, 1990, *Invited lecturer*, University of Saskatchewan, Canada, Taught short course on optimizing brine process chemistry.

September 27, 1990, *Invited speaker*, Lawrence-Berkeley Laboratory, University of California.

October 21-26, 1990, *Invited presentation*, 1990 Annual Meeting of the Soil Science Society of America, San Antonio, Texas.

December 10-12, 1990, *Invited presentation*, Washington, D.C., Geothermal Technical Program Review.

February 6-8, 1991, *Invited speaker*, Alcoa Aluminum Company, Alcoa Tech Center, Pittsburgh, Pennsylvania.

March 19-21, 1991, *Invited speaker*, Department of Energy's Geothermal Program Review IX, "The Geothermal Partnership... Industry, Utilities and Government Meeting the Challenges of the 90's," Lecture: "Models of Geothermal Brine Chemistry for Optimizing Resource Performance," San Francisco, California.

September 26-27, 1991, *Presented workshop*, "Modeling Workshop on Scale Prediction in Geothermal Power Production Systems," Lawrence-Berkeley Laboratory, U.C., Berkeley (California).

December 3-4, 1991, *Presentation*, Department of Energy Geothermal Program Technical Review, Salt Lake City, Utah.

Reviewed numerous articles for technical journals.

Reviewed proposals for numerous agencies (e.g., AOR, NSF, DOE).

VIII. RELATED PAPERS (FUNDING PERIOD)

The Prediction of Mineral Solubilities in Natural Waters: A Chemical Equilibrium Model for the Na–Ca–Cl–SO₄–H₂O System to High Temperature and Concentration, Nancy Møller, *Geochim. Cosmochim. Acta* **52**, 821-837 (1988).

The Prediction of Chemical Scaling in Geothermal Power Plants, John H. Weare and Nancy Møller, Proceedings of the Geothermal Program Review VI: Beyond Goals and Objectives (CONF-880477) April 19-21, 71-75 (1988).

Above paper also in: Proceedings of the Technical Review on the Advances in Geothermal Reservoir Technology---Research in Progress June 14-15, 23-27 (1988).

The Prediction of Mineral Solubilities in Natural Waters: A Chemical Equilibrium Model for the Na–K–Ca–Cl–SO₄–H₂O System to High Concentration from 0°C to 250°C, Jerry P. Greenberg and N. Møller, *Geochim. Cosmochim. Acta* **53**, 2503-2518 (1989).

Anhydrite Saturation Index in the Red Sea Brines, Cristophe Monnin and N. Møller, Societe de Mineralogie Workshop on the Thermodynamic Properties of Hydrothermal Solutions Feb. 16 (1989).

Prediction of Scaling in Geothermal Systems, John H. Weare and N. Møller, Proceedings of the Geothermal Program Review VII: DOE Research and Development for the Geothermal Marketplace (1989).

Chemical Models for Optimizing Geothermal Power Production, J. Weare, N. Møller, Z. Duan and J. Greenberg, Proceedings of the Geothermal Program Review VIII, National Energy

Strategy--The Role of Geothermal Technology Development, CONF-9004131, 49-53 (1990).

The Development and Application of Aqueous Thermodynamic Models: The Specific Interaction Approach, Andrew Felmy and John H. Weare, In press: Proceedings of the Soil Science Society in America.

Fluid Inclusions in Messian Halite from the Red Sea: Clues to the Composition of Miocene Seawater, Boaz Lazar, Heinrich D. Holland and John H. Weare, Submitted to: *Geochim. Cosmochim. Acta*.

Calculation of Multi-Component Ionic Diffusion from Zero to High Concentration: I. The System Na-K-Ca-Mg-Cl-SO₄-H₂O at 25°C, A.R. Felmy and J.H. Weare, *Geochim. Cosmochim. Acta*, **55**, 113-131 (1991).

Calculation of Multi-Component Ionic Diffusion from Zero to High Concentration: II. Inclusion of Associated Ion Species, A.R. Felmy and J.H. Weare, *Geochim. Cosmochim. Acta*, **55**, 133-144 (1991).

An Equation of State for the CH₄-CO₂-H₂O system. I. Pure systems from 0 to 1000 °C and 0 to 8000 bar, Z. Duan, N. Møller and J.H. Weare, *Geochim. Cosmochim. Acta*, **56**, 2605-2617 (1992).

An Equation of State for the CH₄-CO₂-H₂O system. II. Mixtures from 50 to 1000 °C and 0 to 1000 bar, Z. Duan, N. Møller and J.H. Weare, *Geochim. Cosmochim. Acta*, **56**, 2619-2631 (1992).

The Prediction of Methane Solubility in Natural Waters to High Ionic Strength from 0°C to 250°C and from 1 to 1600 bar, Z. Duan, N. Møller, J. Greenberg and J.H. Weare, *Geochim. Cosmochim. Acta*, **56**, 1451-1460 (1992).

Models of Geothermal Brine Chemistry for Optimizing Resource Performance, Z. Duan, N. Møller, J. Greenberg and John H. Weare, Proceedings of the Department of Energy Geothermal Program Review IX, The Geothermal Partnership---Industry, Utilities and Government Meeting the Challenges of the 90's (CONF-913105), 91-95 (1991).

Prediction of solubility and first dissociation constant of H_2S in natural waters: A chemical equilibrium model for the H_2S - HS - OH - Cl - H - Na - H_2O system (0° - $90^\circ C$; 0-60 atm; 0-6 m NaCl), Z. Duan, J.P. Greenberg, N. Møller and J.H. Weare, In preparation.

IX. END OF FUNDING PERIOD STATUS

The brine-calcite-anhydrite-silica scale model program is ready to be used by the industry at a research level. Versions are already in use in studies of scaling in geothermal and oil production systems. A set of short course notes has been prepared to help perspective users. IBM and Macintosh versions of the model are available. The gas phase models have been incorporated in the general package for distribution. Both mainframe (SUN) and PC versions (MacIntosh and IBM) of the code have been distributed.

A workshop for the industry was conducted at the Lawrence- Berkeley Laboratory (University of California, Berkeley) in September, 1991. We have also continued to apply our models to geothermal problems. The models we have developed have been incorporated in model codes (e.g., EQ3/6; PHREEQ; SOLMINEQ; GMIN) which have been supported and widely distributed by other agencies (e.g., USGS). Applications to interpret important aspects of the geochemistry of natural brine-rock interactions have been highly successful (see, for example, PAPERS and REFERENCES).

X. FUTURE PLANS

We will continue the development of the equilibrium modeling codes and the documentation that will facilitate their use by the geothermal energy industry. One of the first projects we will undertake is to make more user friendly the carbonate-sulfate-silica scaling models now available in codes documented at a research level. Parameterization of the seawater brine model is expected to be complete within this fiscal year. This model will then be included in the carbonate-silica scaling model program and documented for user distribution.

The modeling technology will be improved to include additional liquid and gas phase components and more mineral solubilities important to geothermal energy production operations. Our long range goal is to complete a comprehensive chemical equilibrium model which will predict scaling (gypsum-anhydrite, carbonate, silica, metal sulfides) and acid-base characteristics in the system, $\text{H-Na-K-Ca-Mg-Cl-HSO}_4\text{-SO}_4\text{-S-HCO}_3\text{-CO}_3\text{-SiO}_2$, as a function of brine composition, ionic strength, pH, P_{CO_2} and temperature (to 250°C). We plan to extend the carbonate scaling models into the carbonate-rich region (high pH) to 250°C as data allow. Pressure effects on scale solubilities (to $P \approx 400$ bars and above, if data allow) will be included in the model. After the model is completed to 250°C, the model will be parameterized to predict the near critical behavior of brines.

Recent new data for the $\text{SO}_4\text{-HSO}_4\text{-H}_2\text{O}$ system taken with DOE support will be used to parameterize the important acid-base interactions in sulfate brines to high temperature. This task, which will be initiated in this fiscal year, will allow pH prediction in these brines. Another immediate project is to improve the high concentration parameterization of the Mg-carbonate interactions to as high temperature as data allow.

A second major goal is to complete a variable temperature and pressure liquid-vapor model which includes the gas phases: CO_2 , CH_4 , N_2 , and H_2S . The development of a model of the solubility of these gases in brines will be continued.

We will soon initiate adding the aluminum silicate minerals to the high temperature brine

models by parameterizing a model of aluminum speciation in brines to high temperature ($T_{\max}$ will depend on data availability). Researchers at Oak Ridge are carrying out thermodynamic studies of the aluminum system. We hope to use these data for model parameterization as they become available. Inclusion of the aluminum species in our modeling technology will greatly broaden its application in reservoir studies.

We will continue the program just started to model fluids and solids under high temperature and pressure conditions using first principle methods. This approach to describing the chemistry of brines will be particularly useful for conditions where the availability of data is poor. We are now developing a model for the ternary gas system, $\text{CO}_2\text{--CH}_4\text{--H}_2\text{O}$, using the molecular dynamics techniques we have recently developed (different funding).

We will continue to validate the models and apply them to geothermal problems. We will continue to promote the transfer of our technology to the geothermal energy community through model documentation, workshops, publications, research collaborations and student training. Work will continue to develop personal computer versions (with documentation) of our models.

We will collaborate with research teams carrying out the needed measurements to meet our modeling objectives. Our collaborations with research groups in other areas and our transfer of technology to other industries will continue.

XI. REFERENCES

- Bromley L.A. (1973) Thermodynamic properties of strong electrolytes in aqueous solutions. *AICHE, B 10*, 313.
- Duan Z., Møller N. and Weare J.H. (1992) An Equation of State for the $\text{CH}_4\text{--CO}_2\text{--H}_2\text{O}$ system. I. Pure Systems from 0 to 1000°C and 0 to 8000 bar. *Geochim. Cosmochim. Acta* **56**, 2605-2617.
- Duan Z. Møller N. and Weare J.H. (1992) An Equation of State for the $\text{CH}_4\text{--CO}_2\text{--H}_2\text{O}$ system.

II. Mixtures from 50 to 1000°C and 0 to 1000 bar. *Geochim. Cosmochim. Acta* **56**, 2619-2631.

Felmy A. R. and Weare J. H. (1986) The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California. *Geochim. Cosmochim. Acta* **50**, 2771-2783.

Greenberg J.P and Møller N. (1989) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system from 0° to 250°C. *Geochim. Cosmochim. Acta* **53**, 2503-2518.

Harvie C. E., Greenberg, J. P. and Weare J. H. (1987) A chemical equilibrium algorithm for highly non-ideal multiphase systems: Free energy minimization. *Geochim. Cosmochim. Acta* **51**, 1045-1057.

Harvie C. E., Møller N., and Weare J. H. (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723-751.

Harvie C. E. and Weare J. H. (1980) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO₄-H₂O systems from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **44**, 981-997.

Meissner H.P. and Kusik C.L. (1972) Activity coefficients of strong electrolytes in aqueous solutions. *Ind. Eng. Chem. Process Des. Dev.* **11**, 128.

Møller N. (1988) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O system to high temperature and concentration. *Geochim. Cosmochim. Acta* **52**, 821-837.

Pitzer K.S. (1987) Thermodynamic model for aqueous solutions of liquid-like density. *Reviews in Mineralogy* **17**, 97-142.

Pitzer K.S., Peiper J.C. and Busey R.H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13**, 1-102.

- Rogers P.S.Z. and Pitzer K.S. (1981) High temperature thermodynamic properties of sodium sulfate solutions. *J. Phys. Chem.* **85**, 2886-2895.
- Weare, J.H. (1987) Models of mineral solubility in concentrated brines with application to field observations. *Reviews in Mineralogy* **17**, 143-176.