

FINAL REPORT

Models of Geothermal Brine Chemistry

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PROJECT BACKGROUND: Many significant expenses encountered by the geothermal energy industry are related to chemical effects. When the composition, temperature or pressure of the fluids in the geological formation are changed, during reservoir evolution, well production, energy extraction or injection processes, the fluids that were originally at equilibrium with the formation minerals come to a new equilibrium composition, temperature and pressure. As a result, solid material can be precipitated, dissolved gases released and/or heat lost. Most geothermal energy operations experience these phenomena. For some resources, they create only minor problems. For others, they can have serious results, such as major scaling or corrosion of wells and plant equipment, reservoir permeability losses and toxic gas emission, that can significantly increase the costs of energy production and sometimes lead to site abandonment. In future operations that exploit deep heat sources and low permeability reservoirs, new chemical problems involving very high T, P rock/water interactions and unknown injection effects will arise.

The ability to predict chemical behavior and heat content for wide ranges of composition, temperature and pressure would enable the design of optimal operating strategies to minimize or avoid these adverse chemical effects. Predicting reservoir and energy production chemistry will become even more important as deeper, higher temperature geothermal resources, with very high development costs, are utilized to meet future energy needs. Unfortunately, predicting the chemistry of geothermal systems is difficult because of the variability and complexity of the solid-liquid-gas equilibria controlling chemical behavior. These equilibria are complicated functions of the system's composition, temperature and pressure (XTP). These variables are different for different resources and can vary over time and from well to well in a single resource. Marked changes in XTP variables also occur during energy extraction from a specific site. Reliance on experimental data for estimating behavior is generally inadequate because the data pertain to a given set of variables and are often for relatively low temperature ($\sim 100^{\circ}\text{C}$) and pressure (≈ 1 bar). The chemical complexity of geothermal systems makes the extrapolation of data to different conditions problematic. New laboratory simulations are time-consuming and costly, particularly at high temperature and pressure. Moreover, the very high temperatures and pressures of deep crustal and magma resources, where the bulk of the earth's heat is stored, are difficult or impossible to duplicate by current experimental methods.

Computer modeling technologies present the means to resolve these difficulties. Well-constructed models, based on sound thermodynamic principles, can handle the complicated chemical reactions determining the behavior of geothermal energy production processes. They provide a means of succinctly summarizing large amounts of experimental data and of

extrapolating to desired XTP conditions. Molecular level simulations can provide thermodynamic information in temperature and pressure regions inaccessible to present experimental methods. Incorporated into easy to use software, computer models can inexpensively provide reliable predictive capabilities for the industry.

With support from the DOE Geothermal Program, the UCSD Chemical Geology Group has carried out a research program to construct chemical models that accurately predict the chemical behavior of reservoirs, geothermal brines and their associated phases over wide ranges of composition, temperature and pressure. Our models are based on advances in physical chemistry theory that allow description of the thermodynamics of solids, liquids and gases via their free energy. These models can be used to improve the understanding of current ($T = 300^{\circ}\text{C}$) geothermal energy production processes (e.g., Møller et al., 1998) as well as future energy extraction operations from deep, high temperature and pressure (e.g., Duan et al., 1995b) and low permeability heat sources. By providing important assessment tools for predicting heat content, scaling, breakout, steam fractions, gas emission, phase co-existence, miscibility, pH, formation temperatures, etc., they can be used to significantly improve the productivity of geothermal operations. The free energy descriptions in both our subcritical ($T = 300^{\circ}\text{C}$) and supercritical models can be differentiated to produce models of heat properties for both regions. Since flexible computer models can easily and quickly simulate behavior under varying PVTX conditions, testing strategies to control unwanted behavior in active operations as well as forecasting the value of geothermal reservoirs as potential production sites is possible with this technology.

Parameterizing our phenomenological equations using experimental data provides a highly reliable representation of the equilibrium properties of complicated natural systems. To insure reliability, model construction and validation involves extensive comparison with experimental data. Model validation involves comparison of model predictions with data not used in parameter evaluation. Although these processes can be time-consuming, the benefits of having large amounts of experimental data summarized in a concise, easily transferable, equation format are considerable. In addition, the modeling process increases the applicability of many experimental data by providing a means to extrapolate information from limited composition, temperature, pressure experiments (e.g., boiling data in binary systems) to the more complex situations typical of natural fluids (e.g., boiling in multi-component systems).

For high T-P conditions where few data are available, we have developed new molecular based simulation technology (Duan et al., 1995a,c; 1996a) to generate reliable PVTX data. As we develop more theoretically based phenomenologies and better extrapolation techniques in the future, the amount of required data in model construction will be reduced and the region of extrapolation increased.

To facilitate the transfer of our modeling technologies, we have developed extensive user interface software so that our models can be bundled into easy-to-use application packages: TEQUIL (predicts scaling and reservoir chemistry as a function of composition for temperatures below 300°C); GEOFLUIDS (predicts processes, such as flashing and miscibility, to high temperature, pressure conditions) and GEOHEAT (predicts enthalpies of complex mixtures). We have also developed an interactive Internet website: geotherm.ucsd.edu. The geothermal

community and many researchers in other areas of interest access our modeling technology via this website.

PROJECT TECHNICAL OBJECTIVES: 1) To construct thermodynamic models for accurately predicting brine energetic and chemical behaviors and reservoir chemistry encountered in the extraction of energy from geothermal resources under a wide range of PTX conditions. (2) To develop new theoretically based modeling technologies that reduce the dependency on experimental data and increase the fundamental understanding of geothermal rock/water interactions. (3) To develop user interfaces and application software that facilitate the transfer and use of our model technologies. Specific project objectives are given in Table 1 below.

Table 1: RESEARCH OBJECTIVES

CONSTRUCT MODELS FOR GEOTHERMAL ENERGY APPLICATIONS:

- Predict the chemical behavior of complex brine-gas-solid systems for wide PTX ranges
- Predict heat properties of complex brines
- Develop molecular simulation technology to provide thermodynamic information for PTX conditions with poor data availability
- Analyze theoretical extrapolation techniques to reduce the dependence on experimental data
- Simulate energy production chemistry
- Predict gas emission and scale formation
- Predict breakout and steam fractions
- Predict phase coexistence
- Understand injectate/rock chemistry
- Predict reservoir mineralogical reactions
- Predict behavior of deep hydrothermal fluids (supercritical conditions)
- Test strategies for abating chemical problems
- Characterize downhole thermodynamics
- Predict pH
- Utilize computer capabilities to visualize chemical behavior

EXTEND USEFULNESS OF EXPERIMENTAL DATA WITH MODELS

- Identify and evaluate large amounts of experimental data in model parameterizations
- Provide standard for comparison of laboratory and field data
- Provide means of extrapolating data
- Summarize data in an easy to use and easily transferable format

EXPAND TECHNOLOGY TRANSFER

- Develop ancillary user interface software to facilitate use of modeling codes
- Incorporate models into application packages for PC use
- Provide a web site for interactive online use of modeling packages
- Develop visualization code that aids in the interpretation of model results
- Prepare modeling use instruction manuals
- Provide direct assistance to industry and geochemical research groups

APPROACH: Utilizing advances in physical chemistry, we develop equation of state (EOS) descriptions of the thermodynamics of mixed natural fluid systems. This approach allows the construction of chemical models that yield highly useful information (e.g., solubilities, phase equilibria and heat properties) about geothermal reservoir behavior and energy production processes as a function of PTX. Our modeling approaches, based on fundamental theory of the liquid state, support accurate extrapolation and interpolation of the data used in the model parameterization.

For current, relatively near surface, geothermal operations ($P \sim 1$ atm), the principal variation of the liquid density phase free energy is due to concentration changes of the solutes. For these conditions, we use modified Pitzer equations (1987) (see Solution Activity Equations, below) and laboratory measurements to construct models of complex rock-water-gas equilibria accurate to high concentration and temperature (Harvie and Weare, 1980; Harvie et al., 1984; Moller, 1988; Greenberg and Moller, 1989; Moller et al., 1998). In these equations, the coefficients, B , Z , β , γ , etc., are parameters to be evaluated from data. In this approach, only binary and ternary data are necessary to fully parameterize a model for complicated higher component systems. Gas phases are easy to add because they act nearly ideally near 1 atm. Pressure corrections for low concentration applications can be calculated from the limiting partial molal volumes. These data are available. For higher concentrations, partial molal volumes as a function of composition are needed.

Solution Activity Equations

$$\ln \bar{g}_i = z_M^2 F + S_a m_a (2B_{Ma} + ZC_{Ma}) + S_c m_c (2F_{Mc} + S_a m_a \gamma_{Mca})$$

$$+ S_a S_{a<a'} m_a m_{a'} \gamma_{aa'M} + |z_M| S_c S_a m_c m_a C_{ca}$$

$$+ S_n m_n (2I_{nM}) + S_n S_a m_n m_a z_{naM}$$

$$F = -A^f \left\{ I^{1/2} / (1 + 1.2I^{1/2}) + (2/1.2) \ln(1 + 1.2I^{1/2}) \right\}$$

$$+ S_c S_a m_c m_a B'_{ca} + S_c S_{c<c'} m_c m_{c'} F'_{cc'} + S_a S_{a<a'} m_a m_{a'} F'_{aa'}$$

$$B_{ma} = B_{Ma}^{(0)} + B_{Ma}^{(1)} g(a, I^{1/2}) + B_{Ma}^{(2)} g(12I^{1/2})$$

$$g(x) = 2(1 - (1+x)e^{-x})/x^2$$

$$F_{cc'} = F_{cc'} + E F_{cc'}(I)$$

$$C_{ca} = C_{ca}^f / 2 |z_c z_a|^{1/2}$$

$$Z = S_i |z_i| m_i$$

EOS for Compressible Phases

$$Z = \frac{PV}{RT} = Z^{hd} + Z^{dip} + Z^{per}$$

$$Z^{hd} = \frac{1 + \left[\frac{3DE}{F} - 2 \right] h + \left[\frac{3E^3}{F^2} - \frac{3DE}{F} + 1 \right] h^2 - \frac{E^3}{F^2} h^3}{(1-h)^3}$$

$$Z^{dip} = h \frac{\left[1 - \frac{2A_3}{A_2} \right] \frac{\partial A_2}{\partial h} + \frac{\partial A_3}{\partial h}}{\left[1 - \frac{A_3}{A_2} \right]^2}$$

$$Z^{per} = -\frac{1}{RT} \left[\frac{a}{v} + \frac{acb}{2v^2} + \frac{3adb^2}{16v^3} + \frac{aeb^3}{16v^4} \right]$$

New problems are expected to arise in the future development of higher temperature, pressure reservoirs. Densities in the supercritical region are a strong function of pressure. To treat these systems and problems requiring density variation (e.g., miscibility, flashing, fluid inclusion studies, 2-phase flow in reservoirs), we have developed more advanced equations of state (EOS) that are able to describe systems with compressible phases. One of the approaches used is based on thermodynamic perturbation theory (Duan et al., 1995b) (see EOS for Compressible Phases, above). In these equations the parameters, A , B , D , a , etc, are established from data and polynomial mixing rules. β and γ are functions of the molar volume. These new EOS descriptions

yield free energies that are correct at liquid and vapor densities and can describe the large changes in composition and very high solute mole fractions that can occur during phase separation.

Semiempirical models, even when based on physical chemistry theory, require thermodynamic data for parameterization. Since there are much fewer experimental data available for model parameterization of high T, P systems, we have turned to molecular level approaches (e.g., molecular dynamics and Monte Carlo simulations) to meet this challenge and to generate needed thermodynamic information in other T-P ranges. We have shown (Duan et al., 1992d; 1995a,c; 1996a) that these approaches can be used successfully to generate the accurate thermodynamic information needed to model brine behavior to very high temperatures and pressures.

As our models are developed, they are incorporated into interactive software packages that facilitate their application to problems encountered by the geothermal community. Our present technology can be divided into four general modeling packages. (1) Aqueous solution models, based on the semiempirical electrolyte equations of Pitzer (see Pitzer (1987)), which can be used to predict liquid-solid-gas equilibria in dilute to concentrated brines up to high temperature ($T = 300^{\circ}\text{C}$). These models are incorporated into the application software package, TEQUIL. (2) Equation of state (EOS) models which can be used to calculate the PTX properties and vapor-liquid equilibria of natural fluids from subcritical to supercritical temperatures and pressures. These models are incorporated into the GEOFLUIDS application package. (3) First principle models, based on molecular dynamics (MD) and Monte Carlo (MC) simulations. These are particularly useful to generate the accurate thermodynamic data needed for developing EOS models which treat conditions that are difficult or impossible to simulate experimentally. (4) Heat content models, incorporating the aqueous solution and EOS technologies, which calculate specific heats and enthalpies for complex liquid-gas mixtures and allow predictions of such information as steam ratios, available heat and work. These models are incorporated into the GEOHEAT application package. Our software packages are available at no cost to the geothermal community to run on PCs and UNIX based computers.

We are also developing an interactive website which will expand the transfer of our technology. Even when summarized by models, the chemistry of geothermal systems is complicated. However, utilizing the interactive capabilities available over the Web, innovative visualization methods can be developed that will help users understand the complicated thermodynamic relationships that are responsible for brine behavior. A test website is now being prepared which has some of the TEQUIL models implemented (see Table 2). A TEQUIL User Manual, accessible from the site, is available.

RESULTS/VARIANCES:

TEQUIL Models: We have made considerable progress building a comprehensive suite of models for application to current, near surface geothermal operations ($T < 300^{\circ}\text{C}$) up to high brine

Table 2. TEQUIL MODELS (3/99)

MODEL	DESCRIPTION	IMP ^a	REF.
Model: SiO ₂ -NaCl-KCl-MgCl ₂ -CaCl ₂ -H ₂ O	Solubility of silica in brines, 0°C to 250°C, 1 atm - sat. pressure. Pitzer eq's.	yes	MGW 1998
Model: Na-K-Ca-HCO ₃ -CO ₃ -HCl-CO ₂ -H ₂ O	Solubility of calcite in brines, sat. ratios, CO ₂ vapor/liquid equilibria, pH, 0°C to 250°C; 1 atm-sat pressure. Pitzer eq's.	yes	MGW 1998
EOS: NH ₃ -H ₂ O	Densities 0-400°C, 1-1200 bar Mixture: 50°C and 1bar to near critical T,P PVTX and phase equilibria	no	DMW 1996b
Model: Na-K-H-Ca-Mg-Cl-HCO ₃ -CO ₃ -SO ₄ -H ₂ O-CO ₂	Solubility of salts in brines at 25°C, 1 atm. saturation ratios, activities, variable pCO ₂ , pH. Pitzer eq's.	yes	HMW 1984
Model: Na-K-Ca-Mg-Cl-SO ₄ -H ₂ O	Low temperature solubility model, 25° to -54°C, saturation ratios, phase equilibria. Pitzer eq's.	yes	SMW 1990
Model: Na-K-Ca-Mg-Cl-SO ₄ -H ₂ O	Water-solid equilibria, 0° to 250°C, saturation ratios, phase transitions. Pitzer eq's.	no	M in prep.

a. Implemented in TEQUIL

concentrations. These TEQUIL models, which predict liquid/solid/gas equilibria as a function of brine composition and temperature, provide important tools for performance assessment (e.g., potential for flashing and scaling in power plants and well bores), predicting downhole chemistry and testing problem abatement strategies. Table 2 summarizes the status of the TEQUIL model package as of March 1999. The TEQUIL models implemented on the web site (see Table 2) include our 0-250°C model for calcite and amorphous silica scale and CO₂ exchange, the Harvey-Møller-Weare 25°C model (1984) of the complete seawater system, Na-K-H-Ca-Mg-Cl-OH-SO₄-HCO₃-CO₃-H₂O-CO₂, and the Spencer-Møller-Weare (1990) low temperature (-55° to 25°C) model of solid/liquid equilibria within the carbonate-free seawater system. The carbonate-free seawater system has also been modeled from 0° - 250°C (Møller, in prep). Application of the present TEQUIL package is illustrated below via solutions to selected problems encountered in the production of geothermal energy.

The calcite scaling model in TEQUIL (see Table 2) predicts $\text{CaCO}_3(\text{s})$ solubility as a function of brine composition to high ionic strength and to 250°C . Table 3 compares geothermal well data for steam fractions and downhole calcium compositions (Ted DeRocher, personal communication; see also Duan et al., 1996d) with predictions of the model (together with results of the GEOFLUIDS and GEOHEAT models, see below).

Table 3. Calcite Scale Prediction in a Geothermal Well					
	Steam Fraction	CaCO_3 SR ^a Wellhead T=171°C	CaCO_3 SR ^a Wellhead T=227°C	CaCO_3 SR ^b Wellhead T=227°C	Ca Concentration (m) ^c Well Bottom
Measured	9%	---	---	---	.000243
Prediction	12%	0.39	2.2	0.3	.000201

a) Brine-CO₂; b) Brine+3183 ppm CO₂(aq); c) Antiscalent Conditions

The predicted steam fraction is calculated with the assumption of constant enthalpy expansion using GEOFLUIDS and GEOHEAT. The measured value is lower than predicted from this assumption, indicating a possible loss in heat to the formation. Using measured wellhead compositions and temperature (171°C), we predict calcite undersaturation at the wellhead (SR = 0.39). At 227°C (the well bottom temperature), the wellhead brine would be supersaturated (SR = 2.2) with respect to calcite due to the loss of CO₂. In order to replicate the downhole conditions, we recombine the reported CO₂ in the gas phase at the wellhead into the brine component. Now the brine is predicted to be undersaturated (SR = 0.3) at the downhole temperature. To reproduce downhole conditions in the presence of antiscalent, this brine was then re-equilibrated with the formation calcite. This results in a predicted well bottom Ca value of .000201. In Table 3, this value is compared to the measured value of .000243 taken in the presence of antiscalent. The higher measured concentration can be accounted for by the slightly elevated well bottom pressure (87 bars) which increases calcite solubility. The close agreement of observed and predicted results provides additional confidence in the application of the model to field geothermal problems.

Dissolved SiO₂ concentration can be used as a silica geothermometer to estimate the downhole temperatures of geothermal formations. This technique, which is widely used in exploration, depends on the facts that the solubility of quartz is a function of temperature and that the residence time of formation waters is long enough to assume chemical equilibrium.

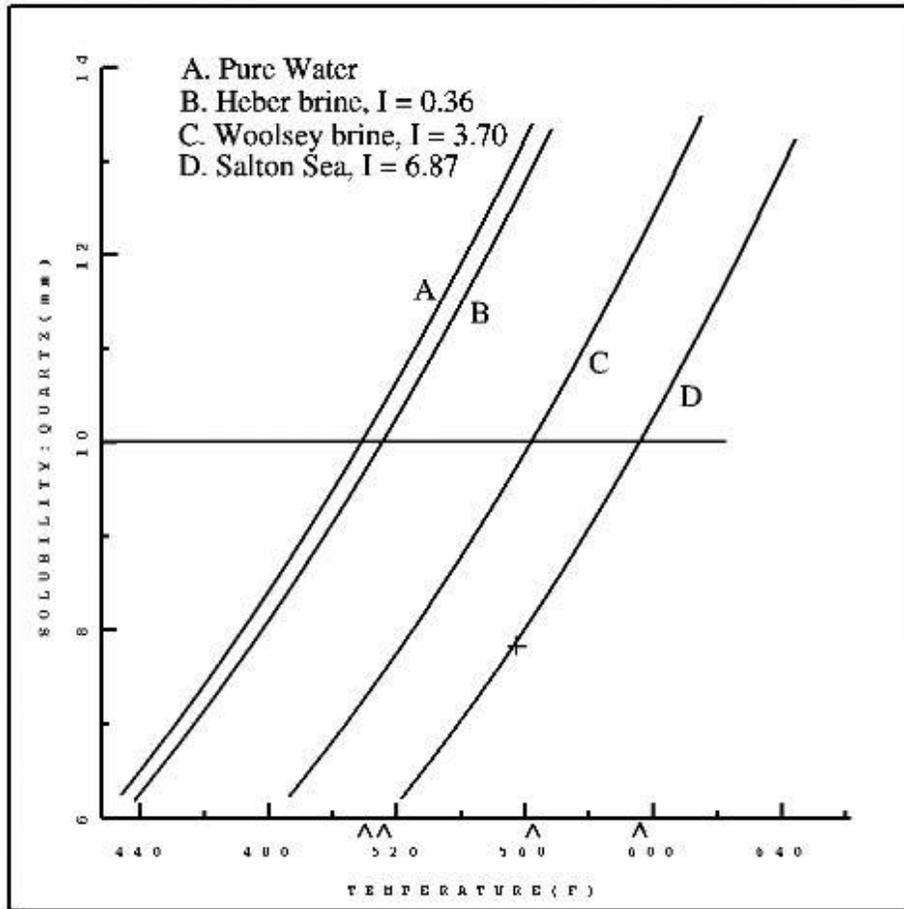


Figure 1: Solubility of quartz in brine.

The stable form of silica in most high temperature formations is quartz. Dissolution of quartz in water, according to the reaction:



yields H_4SiO_4 , a very weak acid. Quartz solubility, like that of many minerals, decreases as the temperature is lowered. As a well is produced, the downhole fluid rises to the surface and undergoes a decrease in temperature and pressure. A significant temperature decrease would be expected to cause quartz to precipitate and lower the concentration of H_4SiO_4 in the brine. However, this does not occur for the SiO_2 system because the rate of nucleation and precipitation of quartz is very slow. This feature makes the silica system an attractive candidate as a geothermometer.

The fact that the solubility of quartz is also a function of brine composition creates a problem for the prediction of downhole temperatures from H_4SiO_4 concentrations at the wellhead.

Generally, neutral species are “salted out”; that is, they become less soluble as the salt concentration increases in the solution. This effect can be appreciable for concentrated brines (such as those found in the Salton Sea geothermal area). From the equilibrium relation for the solubility, Eq. (1), the effects of dissolved salt concentration can be expressed in terms of the activity coefficient for the H_4SiO_4 species in the solution. Assuming that H_4SiO_4 does not dissociate, these coefficients can be calculated for a wide range of brine conditions using the TEQUIL software. Results of such calculations are given in Fig. 1, above. In this figure, the horizontal line represents a hypothetical measured H_4SiO_4 concentration in a geothermal brine. The curves represent the calculated quartz solubility as a function of temperature for different brine compositions: A. in pure water; B. in the low concentration East Mesa brine; C. in the higher concentration Heber brine; and D. in the high concentration Salton Sea brine. From the figure, it can be seen that an error of 86°C would result if the pure water solubility curve was used instead of the Salton Sea curve to relate the SiO_2 concentrations in the Salton Sea geothermal area to formation temperatures.

An additional compositional effect on the silica geothermometer reliability is the fact that boiling (breakout), caused by the pressure decrease as the brine moves up the well bore to the surface, also increases the concentrations of the dissolved species. This problem can be treated by the GEOHEAT software program and is discussed below.

GEOFLUIDS Models: Fluids containing NaCl , H_2O , CO_2 and CH_4 as major components are commonly encountered in geothermal systems. The CH_4 and CO_2 species represent two of the most important insoluble gases in geothermal fluids, their presence greatly influencing the behavior of energy extraction processes (e.g., breakout characteristics of geothermal wells). Therefore, analysis of many problems associated with geothermal energy production operations requires the ability to predict the thermodynamic properties of this 4-component system as a function of composition, temperature and pressure. A major research goal for this grant period was to make substantial progress developing models for the $\text{NaCl-H}_2\text{O-CO}_2\text{-CH}_4$ system that can treat a wide range of compositions, temperatures and pressures.

Previously, we constructed a model for predicting methane solubility in multicomponent geothermal brines (0 - 6 m) from 0° to 250°C and from 0 to 1600 bar (see Table 4, Duan et al., 1992c). This model incorporates Pitzer specific interaction phenomenology, parameterized by solubility data, to describe the liquid phase. The vapor phase is described by our EOS developed earlier (Duan et al., 1992a) for the pure CH_4 , CO_2 and H_2O species (Table 4) and by assuming ideal mixing of H_2O and CH_4 . In this grant period, using a similar approach, we developed a model for the $\text{H}_2\text{O-CO}_2\text{-NaCl}$ system that is applicable to temperatures from 50° to 300°C and for pressures from 0 to 1000 bar. A low temperature (50° - 300°C) model for the 4-component $\text{NaCl-H}_2\text{O-CO}_2\text{-CH}_4$ system was then constructed using the model we developed for mixtures in the $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ system (Table 4) (Duan et al. (1992b). Fig. 2 shows flashing pressures as a function of temperature calculated by this model for a typical geothermal fluid. Because these noncondensable gases are so insoluble, they make a large contribution to the flashing pressure even at low concentration. We note that for temperatures below 200°C their contribution is much larger than the contribution from the vapor pressure of water. Also note the strong effect of the presence of CH_4 in the brine. Since CH_4 is very insoluble, its contribution to the flashing pressure

is large even when its concentration is low. In this approximation, the chemistry of other electrolytes is lumped into the NaCl variable. Note that this model assumes that NaCl is completely dissociated in the liquid phase and absent from the vapor phase. It is therefore limited to temperatures below approximately 300°C.

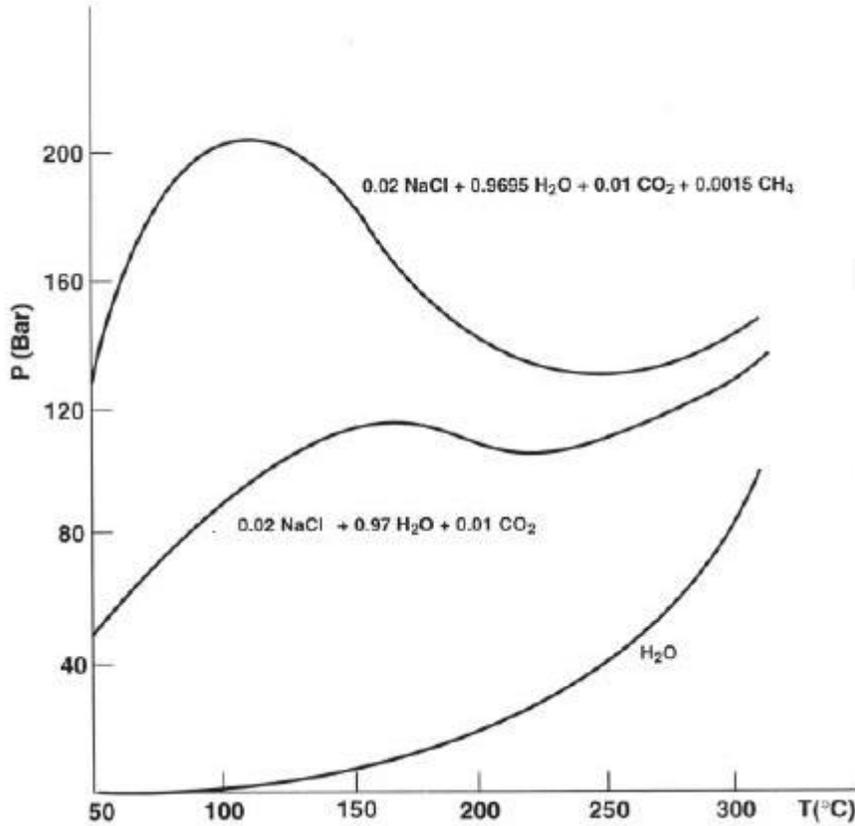


Figure 2: Breakout pressure for geothermal brines.

Our equation of state (EOS) modeling approach used for the low temperature NaCl-H₂O-CO₂-CH₄ model cannot be extended for temperature and pressure conditions above the critical point of water. The phenomenology used in the liquid density Pitzer-type models (discussed in the last section), cannot be generalized to arbitrary densities. Although the EOS for mixtures in the CO₂-CH₄-H₂O (0° - 1000°C; 0 - 8000 bar) (Duan et al., 1992b) handles variations in density, the addition of a salt end member, NaCl, seemed impractical using this approach. Therefore, to incorporate compositional complexity into variable density models we had to explore different approaches that take into consideration the unique properties of the various subsystems in the NaCl-H₂O-CO₂-CH₄ quaternary.

Table 4. GEOFLUIDS MODELS (3/99)

MODEL	DESCRIPTION	IMP ^a	REF.
EOS: CH ₄ -CO ₂ -H ₂ O (I) Modified Lee-Kesler approach	Pure species, 0-1000°C, 0-8000bar PVTX properties, phase equilibria	yes	DMW 1992a
EOS: CH ₄ -CO ₂ -H ₂ O (II) Modified Lee-Kesler approach	Mixtures, 50-1000°C, 0-1000bar PVTX properties, phase equilibria	yes	DMW 1992b
EOS: NH ₃ -H ₂ O	Densities 0-400°C, 1-1200 bar Mixture: 50°C and 1bar to near critical T,P PVTX and phase equilibria	no	DMW 1996b
Model: methane solubility in brines	Solubility 0-250°C, 0-1600bar, 0-6m; CH ₄ - CaCl ₂ -H ₂ O: 25°C-125°C; CH ₄ -Na-K-Mg-Ca- Cl-SO ₄ -HCO ₃ -CO ₃ -H ₂ O:25°C EOS for vapor phase chemical pot. and Pitzer eq's. for liquid phase chemical potential	no no	DMGW 1992c
Model: NaCl-H ₂ O-CO ₂ - CH ₄	Solubility 50-300°C; 0-1000 bar. Use DMGW 1992c approach and DMW1992b for CH ₄ - CO ₂ -H ₂ O mixtures		
Model: H ₂ S-NaCl-H ₂ O	Solubility of H ₂ S in NaCl aqueous systems, 0- 320°C, 1-300bar and 0-6m NaCl. EOS for vapor phase chemical potential and Pitzer eq's. for liquid phase chemical potential	no	DMW 1996c
EOS: CH ₄ CO ₂ CO N ₂ O ₂ Cl Lennard-Jones md sim. data and scaling	Pure nonpolar and weakly polar species, supercritical to 2000 K and 20,000 bar, PVTX properties, No phase equilibria	no	DMW 1992c
EOS: H ₂ O CH ₄ CO ₂ CO N ₂ O ₂ H ₂ H ₂ S Ar L-J MD sim and scaling	Extend above to polar H ₂ O and to binary mixtures, supercritical to 2000 K and 0-25,000 bar, PVTX , No phase equilibria	no	DMW 1996a
EOS: CH ₄ , N ₂ , O ₂ , CO ₂	Shows that 1992c EOS can be used to construct phase diagrams using MD simulated data in liquid/vapor coexistence range and Maxwell constructions	no	DMW 1995a
EOS: NaCl-H ₂ O-CO ₂	Pure systems and binary aqueous salt mixtures, 300-1000°C; 0-6000bar, PVTX, phase equilibria. Modified Anderko-Pitzer perturbation approach	yes	DMW 1995b
EOS: (preliminary)	Modified Anderko-Pitzer perturbation approach	no	

This grant period considerable effort was spent developing variable density models for the salt-containing ternaries: NaCl-H₂O-CO₂ (>300° - 1000 °C; 0 - 6000 bar) (Duan et al., 1995b) and NaCl-H₂O-CH₄. Our approach generalizes the model of the NaCl-H₂O system developed by Anderko and Pitzer (1993) that is related to the earlier approach of Dimitrelis and Prausnitz (1986). Extensive evaluation of the NaCl-H₂O system led us to the conclusion that the hard sphere and dipolar terms used by Anderko and Pitzer are needed for a reasonable description of the NaCl-H₂O data to high temperature and pressure. To treat mixtures in the NaCl-H₂O-CO₂ and NaCl-H₂O-CH₄ systems, this forced us to adopt a form similar to the Anderko-Pitzer EOS for the less polar binaries involving CO₂ and CH₄. Therefore, rather than incorporating our already tested EOS for the CO₂-CH₄-H₂O system (Duan, Møller and Weare (1992b), we used the formulism of Anderko and Pitzer to add CO₂ and CH₄ to the NaCl-H₂O model (see Duan et al., 1995b). A preliminary 4-component model is completed.

The development of the EOS is based on the Helmholtz free energy. The system is first idealized as a system of molecules (e.g., NaCl, H₂O, CO₂, CH₄) interacting with intermolecular potentials for which an approximate Helmholtz free energy can be calculated from statistical mechanics. The theoretical forms assumed for this “reference system” are then corrected to incorporate the behavior of the real system. The corrections are empirical, but chosen to retain the limiting behavior. The parameters in the resulting equations are evaluated from both PVXT data and phase equilibria data. The detailed equations describing the parameterization of these equations for the NaCl-H₂O system are very complicated and are given in Anderko and Pitzer (1993) and Duan, Møller and Weare (1995b). We point out that the NaCl-H₂O-CO₂ (Duan et al., 1995b) and NaCl-H₂O-CH₄ models are only applicable above 300°C because the NaCl species is assumed to be associated. Our earlier model of the salt-free CO₂-CH₄-H₂O system (1992b), which is also included in the GEOFLUIDS package, is applicable to lower temperature systems (50° to 1000°C and 0 to 1000 bar).

The ternary EOS models form the base for constructing an EOS for the quaternary NaCl-H₂O-CO₂-CH₄ system that can treat variable density. These models are very important for many geothermal calculations (e.g., boiling pressure (see Fig. 3), gas fugacity, solubility, volumetric properties, densities, etc.) in mixed gas-brine systems. We believe that our models are the only ones available that are able to predict phase equilibria and PVTX properties in these systems over such broad T-P ranges. These capabilities are essential to predict the behavior of geothermal systems undergoing phase separation and density and compositional changes due to significant alterations of temperature and pressure. These conditions can occur during brine extraction (e.g., flashing) and reinjection as well as during the evolution of the resource when brines are cycled through high temperature and pressure regions in the formation.

GEOHEAT Models: Accurate estimates of the available heat in the working fluid are essential for the economic exploitation of a geothermal resource. Unfortunately, with the exception of the pure water system, there are very few enthalpy data for the temperatures and pressures of geothermal operations. Therefore it is common in the industry to use pure water enthalpy information to predict fluid behavior (e.g., prediction of steam fractions). However geothermal fluids are typically solutions with high concentrations of ionic species and insoluble gases. The enthalpy of such solutions is a complex function of composition, temperature and pressure. As a result, predictions of important geothermal information from pure water enthalpies can have significant errors.

Since the models in TEQUIL and GEOFLUIDS are based on the free energy of a system, all other thermodynamic properties, including heat properties (specific heat, heat of solution and enthalpy) of complex brine/gas mixtures, can be derived by the appropriate derivatives. However, in order for heat model development to be successful it is generally necessary to include some heat data in the database for the parameterization of the free energy. We have developed models of brine and gas phase enthalpies using this approach. Because the relation between the free energy and the enthalpy is maintained, these models produce consistent predictions of heat properties and other temperature dependent properties related to the free energy (e.g., the solubility of scaling minerals, the temperature dependence of phase coexistence). Using this approach, an enthalpy model (50°C to about 2000°C) of the CO₂-CH₄-H₂O system was developed that is based on our free energy model for this system (Duan et al., 1992a,b).

There are very few enthalpy data for the complete NaCl-H₂O-CO₂-CH₄ system, and a single modeling approach that extends from low temperatures (50°C) to high temperatures (>300°C) is not yet available for the salt containing systems. Therefore, a method to calculate enthalpy in the NaCl-H₂O-CO₂-CH₄ system can be developed that is based on the assumptions:

1. for salt free systems, we can use the H₂O-CO₂-CH₄ enthalpy model to calculate the enthalpy for all temperatures above 50°C.
2. for the gas phases in salt containing systems, we can use the enthalpy calculated from our model of the H₂O-CO₂-CH₄ system for temperatures below 300°C.
3. for the liquid phase in salt containing systems, we can use the enthalpy calculated from the NaCl-H₂O model of Pitzer et al. (1984) for temperatures below 300°C.
4. for salt containing system above 300°C, we can *estimate* (due to the lack of heat data) the enthalpy by differentiating our perturbation theory EOS for the complete system. This model can be used both for the dense fluid and vapor phases.

Given the pressure, temperature and composition of a fluid in the NaCl-H₂O-CO₂-CH₄ system, for temperatures below 300°C we can use the GEOFLUIDS NaCl-H₂O-CO₂-CH₄ model (Table 4; EOS for vapor phase chemical potential and Pitzer eq's. for liquid phase chemical potential) to determine if there is a phase separation (liquid-vapor coexistence). If there is, this GEOFLUIDS model can calculate the amount of the phases (liquid and vapor) and their compositions. Above 300°C, we use the perturbation theory model for the NaCl-H₂O-CO₂-CH₄ system (Table 4; modified Anderko-Pitzer approach) for these calculations. With this information, we can estimate accurately the total enthalpy of the system using the enthalpy models for the separate phases as above. This information can be plotted on an enthalpy pressure diagram (with

enthalpy and pressure as variables). It is still difficult to determine the pressure for any given enthalpy but this can be done graphically. Presently, GEOHEAT includes the $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ model.

In Fig. 3, we have constructed an enthalpy/mol vs. pressure diagram for a brine similar in composition to that of the Salton Sea geothermal field. Note that the solid lines represent the isotherms. For a multicomponent system such a diagram is dependent on the total composition.

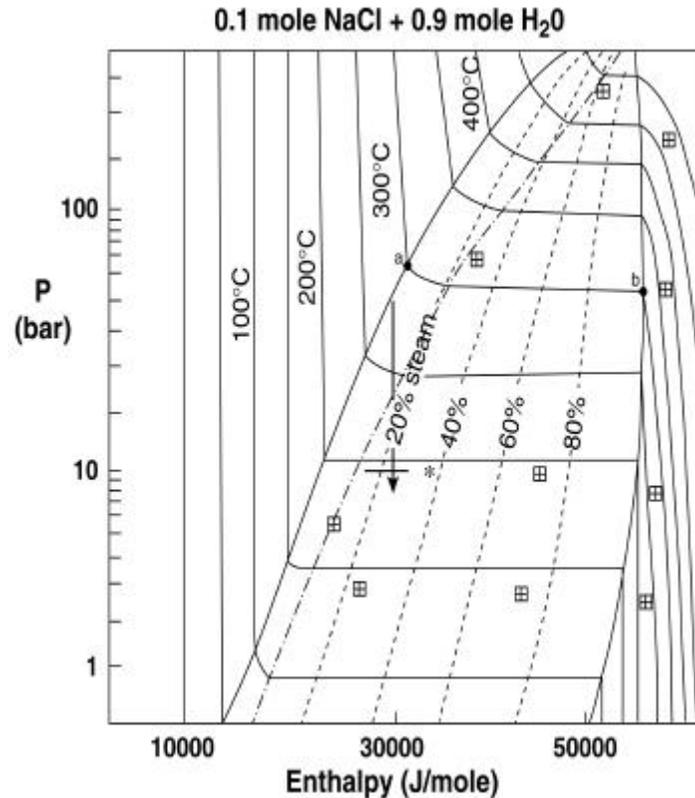


Figure 3: Enthalpy-Pressure diagram for a Salton Sea-like brine.

In this calculation, we have lumped the entire brine solute composition into the NaCl concentration. For subcritical systems, liquids (lower enthalpy systems) are present on the left of the diagram and gases (higher enthalpy systems) on the right. Considering the 300°C isotherm as an example, we can see that at high pressure the enthalpy is fairly constant with pressure drop. This is because the enthalpy change with pressure in a liquid density system at constant temperature is relatively small. At some pressure, the system will flash and the enthalpy change related to the formation of steam becomes large. For this temperature and composition, flashing occurs at 67 bars, point (a) in the 300°C isotherm. This pressure is a little lower than it would be for pure water (87 bars) because the vapor pressure of the fluid is lowered by the dissolved salt.

On the diagram, the two phase region is separated from the single phase region by a solid line. Point (a) on the diagram for the 300°C isotherm is the enthalpy of the liquid at the bubble point. As the pressure is lowered below that of point (a), more water is evaporated. Since the composition of the liquid and vapor are changing, the total enthalpy/mol in the coexistence region has a curvature. At some point in this system solid NaCl precipitates. When this occurs, the vapor pressure and the solubility (concentration in the liquid phase) of the system are fixed. With continued evaporation, the liquid is then removed from the system along the horizontal line. When the liquid disappears, the pressure again drops at constant T. The enthalpy/mol of the vapor coexisting with the liquid and the solid at 300°C (and along the coexisting liquid/vapor/solid line) is represented on the diagram by point (b).

Fig. 3 also includes mole % steam lines (dashed lines). These lines, which give the steam ratio for a particular isotherm, are especially useful for geothermal applications. All this information may be calculated from the GEOHEAT and GEOFLUIDS software.

As an application of the diagram shown in Fig. 3, reconsider Fig. 1. The measured well head brine silica composition in this figure is represented by the horizontal line. To use the silica geothermometer approach for estimating the downhole temperature, we must be able to reconstruct the downhole brine concentrations. Therefore, we need to correct this wellhead composition to compensate for the loss of water due to evaporation during production. An interactive process would be required to get a precise answer. Here, we will only look at one cycle. Suppose that the uncorrected composition gives a downhole temperature of 300°C (572°F) from the geothermometer (see Fig. 1 for a Salton Sea brine). Take that as an initial estimate of the temperature and assume that the fluid at the bottom of the well is at the bubble point (point (a) on the diagram in Fig. 3). We can now ask how much a fluid at 300°C evaporated while moving up the well bore, assuming that the motion of the fluid up the well bore is a constant enthalpy process (see the arrow in Fig. 3). Fixing the wellhead pressure at 10 bar, we see that the constant enthalpy line intersects the 10 bar line at a breakout of roughly 23% steam. We can now use this information to approximately correct the wellhead composition and recalculate the data of Fig. 1. Diluting the measured wellhead concentration of H_4SiO_4 to reflect the loss of water due to evaporation, we recalculate the bottom hole temperature (indicated on Fig. 1 by a cross). Note that the new temperature of (558°F) is 38°F less than the first estimate (Table 5, 596°F).

Table 5: Steam Separation Properties for Pure Water vs. the NaCl-H₂O System

System	SR	Wellhead T (F)	Wellhead P	Quartz T (F)
Pure Water	0.29	174 (345)	10 bar	453 (510)
Brine (6.87 m)	0.23	188 (370)	10 bar	558 (596)

Recalculated values for important well properties are summarized in Table 5. As expected, the wellhead steam ratio (SR) at fixed wellhead pressure is less for the brine than for pure water. This decrease in evaporation is also reflected in the higher wellhead temperature of the brine.

Molecular Simulation Studies: When possible our models are based on high quality laboratory measurements. However, the ranges of composition, temperature and pressure variables that can be encountered in present day and future geothermal applications are extremely large. It is unlikely that sufficient data to completely parameterize models covering these ranges will ever exist. Furthermore, while there has been progress in the development of appropriate equations to describe the thermodynamics of complex aqueous mixtures, there is still much we don't know about solutions at high temperatures and pressures. Therefore, one of our research goals is to develop first principles and molecular based technologies that can be used to generate both accurate thermodynamic data and equations that better represent behavior at high temperatures and pressures.

The results of our molecular dynamics (MD) and Monte Carlo (MC) simulations have been very positive (Duan et al. 1992d; 1995a,c; 1996a). Our EOS model of the CH₄-CO₂-N₂-H₂O system (1996a) for high temperatures and pressures was generated from PVT data (see Table 4). Recent comparisons of model predictions with new experimental data have shown it to be considerable more accurate than other competing EOS. Simulations are more difficult for brine systems. However, the results of our 1-1 electrolyte (NaCl and KCl) simulations, which use a simple parameterization of the intermolecular potentials, have accuracies close to that of experiments for a large range of T and P, both above and below the critical values for water.

We have also begun a study to quantify the accuracy of simulation-based water thermodynamics. The most important data for geological applications involve the free energy of aqueous systems (*e.g.*, phase equilibria). A system's free energy is very difficult to simulate because this involves integration over intensive variable changes from a known state (*e.g.*, ideal gas) to the state of interest. To do this requires many simulation points. Although a great deal of experimental thermodynamic data exist for the pure water system, few simulation studies have

focused on comparing free energy predictions. We have made good progress using our Watts water potential (Duan et al., 1995c). We have shown that this potential provides higher quality predictions of properties (such as enthalpy, liquid structures, *etc.*) than other models of water interactions. Preliminary calculations, however, suggest that there may be some problems in the prediction of liquid-vapor coexistence even with this highly accurate model. We are presently trying to solve these problems. When completed, this study will be highly valuable for estimating errors in the simulated properties of aqueous systems for geothermal applications.

Website Development: The calculations that have been reported above can all be done with the software available from our group. We will continue to offer diskette-based software. However, we are in the process of developing an interactive website that will incorporate the present models as well as provide new functionality. By having this software on the internet, updates of the models will immediately be available to users. In addition, we have initiated development of a postprocessing package called GEOPHASES, which will compile and process data from the other application packages.

In Fig. 4, we show a phase diagram for the 5-component system, Na-K-Mg-Cl-SO₄-H₂O, computed as a function of temperature with a preliminary version of GEOPHASES. Charge balance implies that there are four degrees of freedom when T and P are fixed. Obviously, the general phase relations for this system cannot be drawn on a three dimensional diagram. However, the dimensionality may be reduced by plotting only certain regions of the diagram. For example, in the projection shown in Fig. 4 all phases coexist with solid NaCl. To construct this figure, the TEQUIL solubility models are used to calculate brine compositions in equilibrium with all the invariant mineral assemblages throughout the 0° to 250°C temperature range. Obtaining this large number of calculated “data” points and then drawing the polythermal phase diagram by hand is a daunting task. GEOPHASES will automatize this process. The GEOPHASES software will both direct computations and construct the appropriate projections.

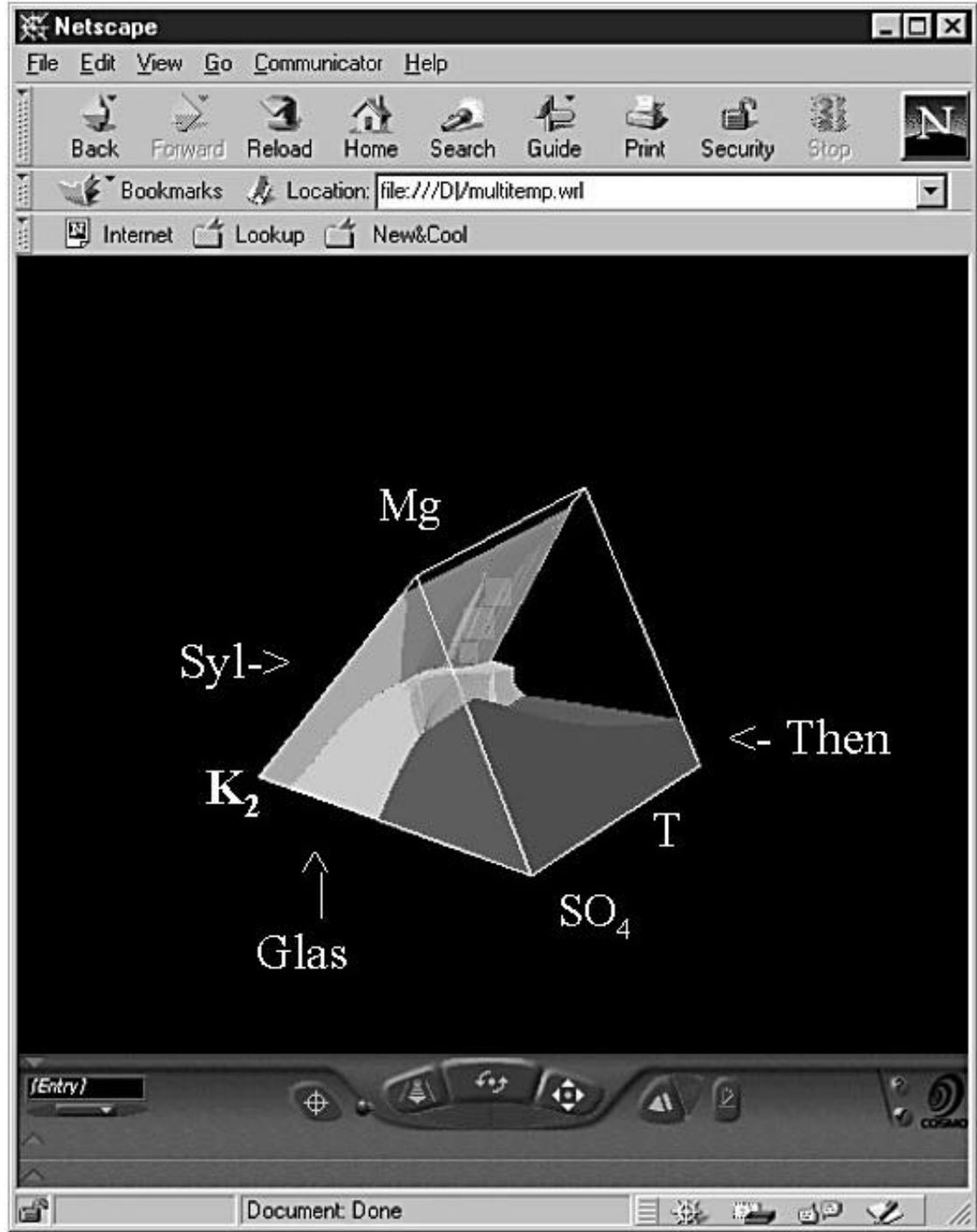


Figure 4: Phase diagram of the Na-K-Cl-SO₄-H₂O system (in equilibrium with halite) as a function of temperature.

TECHNOLOGY TRANSFER:

Selected Contacts (requests for models & information) During Grant Period:

ARMY CORPS. OF ENGINEERS
ASPENEC, Cambridge, MA
BEN HOLT COMPANY, Pasadena CA.
BHP MINERALS
CANADIAN POTASH OF SASKATCHEWAN:
CAL ENERGY INTERNATIONAL, LTD.
CARNEGIE INSTITUTION, Geophysical Laboratory, Washington, D.C
CFTA, Palermo, Italy
CREGU/CNRS, France
DEPARTMENT OF PETROLEUM ENGINEERING, HERIOT-WATT UNIVERSITY, Scotland
DOW CHEMICAL CO.
ENEL, Italy
ENERGETSKI INSTITUT, Croatia
EXXON
GEOFORSCHUNGS ZENTRUM, Potsdam, Germany
GEOSCIENCE, LTD., UK
GEOTHERMAL RESOURCE CENTER, Miravalles Geothermal Field
GEOTHERMEX
GOETTINGEN UNIVERSITY
HARVARD UNIVERSITY
HERIOT-WATT UNIVERSITY, Scotland
HYUNDAI ENGINEERING COMPANY, Seoul, Korea: geothermal applications
INDUSTRIAL RESEARCH, LTD., New Zealand
INEL
INSTITUTE FUR TIEFLAGERUNG, Germany.
INSTITUTO INVESTIGACIONES ELECTRICAS, Cuernavaca, Mexico
JMC GEOTHERMAL CO., JAPAN
KLUWER PUBLICATIONS: Requested review of chapter: "A Model for deep Geothermal Brines, I: T-P-X State-Space Description.
KOREA INST. OF SCIENCE AND TECHNOLOGY
LEYTE GEOTHERMAL POWER PROJECT, Philippines
LOS ALAMOS NATIONAL LABORATORY, reinjection data from Dixie Valley
MAGMA OPERATING COMPANY
MANCHESTER UN, Earth Science Dept.
MASSEY UNIVERSITY, New Zealand
McGILL UNIVERSITY, CANADA, Geosciences Dept.
MONTEREY AQUARIUM RESEARCH INSTITUTE
LAWRENCE LIVERMORE LABORATORY.
LOS ALAMOS NATIONAL LABORATORY.
NUCLEAR REGULATORY COMMISSION
OAK RIDGE NATIONAL LABORATORIES
OBSERVATORIA NACIONAL-CNPQ (Brazil)

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6/30/93 – 3/17/99

OXBOW GEOTHERMAL

PACIFIC NORTHWEST LAB.

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SC&A: geothermal studies

SCRIPPS INSTITUTE OF OCEANOGRAPHY

SHELL EXPO, Aberdeen, Scotland

SINICA CHINA GEOLOGICAL INST., Taiwan.

SOLID CHEMICALSOLUTIONS, Netherlands

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ST. FRANCIS UN., CANADA.

SOUTHWEST INSTITUTE

TECHNICAL UNIVERSITY, POLAND

TECHNISCHE UNIVERSITAT, Berlin, Germany.

TECHNISCHE UNIVERSITAT BERGAKADEMIE, Freiberg, Germany.

TRUESDELL, AL, geothermal consultant

UNION CARBIDE CORP.

UNIVERSITA DEGLI STUDI DI PALERMO

UNIVERSITAT BREMEN

UNIVERSITAT FREIBERG, Germany

UNIVERSITY OF AUCKLAND, New Zealand

UNIVERSITY OF CALIFORNIA, BERKELEY

UNIVERSITY OF CHICAGO, DEPARTMENT OF GEOPHYSICAL SCIENCE

UNIVERSITY OF GUANAJUATO, Mexico

UNIVERSITY OF ILLINOIS

UNIVERSITY OF MICHIGAN:

UNIVERSITY OF NANCY, France

UNIVERSITY OF NANJING

UNIVERSITY OF NEW MEXICO

UNOCAL, Texas

US ARMY COLD REGIONS RESEARCH AND ENGINEERING LABORATORY

USGS

UURI

VIRGINIA POLYTECHNICAL INSTITUTE

YANKEE/CAITHNESS

Selected Technical Meetings/Presentations During Grant Period:

Potash Corporation Workshop, Saskatchewan, Canada, Nov. 18, 1993.

DOE Geothermal Program review, San Francisco, CA, April 25, 1994.

Pan-American Fluid Inclusion Study Meeting, Mexico City, Mexico, May 18-22, 1994.

Annual Calorimetric Conference, New Mexico, August, 1994.

UURI Geothermal Energy Meeting, San Francisco, CA., Sept. 22-23, 1994.

Geothermal Research Council, Salt Lake City, Utah, Oct. 2-5, 1994.

GSA Meeting, Seattle, WA, Oct. 26, 1994.

DOE Geothermal Program Review XIII, San Francisco, CA, March 13-16, 1995.

Geothermal R&D Workshop, Geothermal Energy Assoc., San Francisco, CA, July 20-21, 1995.

User Interface Workshop on Parallel Programming Software (AAPSS), Santa Barbara, CA, July 22, 1995.

ACS National Meeting, New Orleans, La, March 24-28, 1996.

DOE Geothermal Program review XIV, San Francisco, CA, April 9-10, 1996.

30th. International Geological Congress, Beijing China (Z. Duan), August 4-14, 1996.

GRC Meeting, October, 1996.

DOE Geothermal Program Review, San Francisco, March 25, 1997.

DOE-BES review, Oak Ridge, April 27-30, 1997.

GRC meeting, San Francisco, April 30 - May 1, 1997.

DOE field trip and workshop, Dixie Valley, NV, May, 1997.

7th. Annual Goldschmidt Conference, Tucson, Arizona, June 2-6, 1997.

DOE Dixie Valley meeting, Reno NV, Aug. 26-27.

Asian Fluid Inclusion Conference (Z. Duan), Sept. 24-Oct. 15, 1997.

Calorimetry Conference, Midland, Michigan, August 9-15, 1998.

Environmental Chemistry Conference, UCSD, 1998.

Geothermal DOE Program Review XVI, Berkeley CA, April 1-2, 1998.

Goldschmidt Conference, Toulouse, France, Aug. 30-Sept. 3, 1998.

PACROFI VII, Pan American Current Research on Fluid Inclusions, Las Vegas, NV, June 1-4, 1998.

U.C. Berkeley, Earth Resources Center, Prof. Bremhall, December 9, 1998.

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Weare, Duan and Møller (1998). "Supercritical thermodynamics and fluid/fluid phase coexistence in thermodynamic systems." *Minerol. Mag* **62A**, (Part 3), 1637.

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