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MODELING TECHNOLOGY FOR INCREASING GEOTHERMAL ENERGY PRODUCTIVITY

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ABSTRACT:

The objective of our research program is to improve the productivity of geothermal operations and exploration by developing computer modeling technologies which accurately characterize the chemistry of many important geothermal systems and energy production processes. Our thermodynamic models are based on equations of state (EOS) which describe the free energy of gas-solid-water systems for wide ranges of temperature, pressure and composition. Different EOS approaches are used to treat aqueous systems under upper crustal conditions, where temperatures are below 300°C and pressures close to one atmosphere, and deep crustal/mantle systems which can reach supercritical conditions. The former incorporates the Pitzer electrolyte theory. New EOS, incorporating methodology such as the corresponding states and one fluid assumption or thermodynamic perturbation theory, are used to treat the increased compressibility of brines as T,P conditions near and surpass the critical region. To model XTPV space with few experimental data, molecular dynamics simulated “data” are used to constrain the behavior of the free energy. Models constructed using these different approaches can reliably reproduce downhole chemistry, chemical behaviors encountered during energy extraction, such as scaling, flashing and miscibility, and the high temperature and pressure chemistry associated with deep reservoirs that will be tapped in the future.

Our research program emphasizes effective transfer of our technologies. We have developed application software to facilitate the use of our modeling codes. A website now in development will expedite code distribution. Visualization postprocessing code, which takes advantage of internet capabilities, will process model calculations and display them in ways which help improve the fundamental understanding of the chemical phenomena occurring in present and future geothermal systems.

INTRODUCTION:

Heat in the earth’s crust represents the greatest potential contribution to the world’s energy base. Yet this important energy source is now markedly underutilized. The principal reasons for this situation are the high costs currently associated with geothermal energy production and exploration and the lack of technology to reduce these costs. Many of the significant problems encountered by the geothermal industry reflect complicated chemical interactions between solids, gases and liquids. Adverse chemical effects, such as scale formation, corrosion and noxious gas emission, which can arise from the manipulation of the high temperature natural fluids driving the energy production process, are expensive to control. Mineral precipitation, for example, can not only damage plant equipment and wells but also significantly decrease the permeability of the formations containing the geothermal fluids, thereby limiting the longevity of the resource itself. The ability to predict these chemical behaviors and heat content as well as to design optimal operating strategies would significantly increase the cost effectiveness of geothermal energy production. Predicting potential chemical problems will become even more important as deeper, higher temperature geothermal systems, with very high development costs, are utilized to meet future energy needs.

To predict the chemistry of geothermal energy production, it is necessary to understand the thermodynamics of the production processes. Unfortunately, the chemical behavior of high temperature brine systems is a very complex function of their composition, temperature and pressure. Since these variables can change significantly during the lifetime of the resource, past experience may not be a reliable guide for future performance. Laboratory simulations are costly and limited to the experimental conditions selected.

The UCSD Chemical Geology Group, with funding from the US Department of Energy’s Geothermal Program, is constructing computer models to accurately predict the chemical behavior of geothermal brines and their associated phases over wide ranges of composition, temperature and pressure. Our models are based on advanced theoretical developments in physical chemistry which allow description of the thermodynamics of solids, liquids and gases via their free energy. Parameterizing these expressions using experimental data provides a highly reliable representation of the equilibrium properties of complicated natural systems. The parameterization process can be extensive. However, the benefits of having the data represented by easily used modeling equations are considerable. In addition to interpreting and predicting the thermodynamics of a system under current T,P,X conditions, flexible computer models can easily and quickly simulate behavior under varying T,P,X conditions. Therefore, 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 approach. Furthermore, the modeling process increases the applicability of many experimental data by providing a means to extrapolate information from limited composition experiments (e.g., boiling data in binary systems) to the more complex situations typical of natural fluids (e.g., boiling in multi-component systems).

As we develop more theoretically based phenomenologies, the amount of required data will be reduced and the region of extrapolation increased.

As our models are developed, they are incorporated into interactive software packages (for PCs and UNIX based computers) that facilitate their application to problems encountered by the geothermal community. 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, by utilizing the interactive capabilities available over the Web, innovative visualization methods can help users understand the complicated thermodynamic relationships that are responsible for brine behavior.

In the following, our modeling approaches and various software packages are described. In addition, applications of the packages are illustrated via solutions to problems encountered in the production of geothermal energy.

METHODOLOGY:

Our present technology can be divided into two general free energy modeling approaches. (1) Aqueous solution models, based on the semiempirical electrolyte equations of Pitzer (Pitzer (1987)), which can be used to predict liquid-solid-gas equilibria in dilute to concentrated brines under upper crustal conditions, where temperatures are below 300°C and pressures are close to 1 atm. These models are incorporated into the application software package, TEQUIL. (2) Equation of state (EOS) models which can be used to calculate the XPVT properties and vapor-liquid equilibria of natural fluids experiencing supercritical temperatures and pressures. These models are incorporated into the GEOFLUIDS application package. First principle models, based on Molecular Dynamics (MD) and Monte Carlo (MC) simulations, have proven useful to generate the accurate thermodynamic data needed to parameterize these models in the high T, P ranges difficult or impossible to simulate experimentally. We are also developing heat content models, incorporating the aqueous solution and EOS technologies, which are incorporated into the GEOHEAT application package. Visualization code we are developing for internet use is being incorporated into a software package, GEOPHASES.

1-Aqueous solution models and the TEQUIL package:

In aqueous solutions, the density is not a strong function of pressure for temperatures below the critical point. Therefore the physical state of a system does not change for many important processes under near surface conditions. In modeling aqueous solutions and their solid-gas equilibria for these environments, the principal difficulty is to achieve an accurate representation of the liquid phase free energy. Contributions of the gas phases are easy to treat because these phases can be considered as nearly ideal. Pure solid phase activities are not composition dependent. The problems in accurately describing the liquid phase free energy arise from the large compositional variation and typically high concentration of natural brines. There are three main considerations in overcoming these problems. The first consideration is to initially specify the chemistry for the process of interest as well as possible. That is, identify what chemical reactions (e.g., hydrolysis and ion association) and what species are likely to be important in the solution. When reliable assessments are not available, speciation and the thermodynamics must be modeled simultaneously (see below). Secondly, a free energy function which will accurately describe the free energy of complex brines to high concentration must be developed. A number of models based on Debye-Huckel theory and its generalizations are available which provide useful information for low concentration ($I < 0.1m$) applications. However, the free energy varies considerably as a brine becomes more concentrated and contributions to the free energy from the species' interactions become increasingly important (see Table 1).

Corrections to the activities of the various species in these interactions are necessary to predict the thermodynamics of rock/water systems commonly found in geothermal applications. These corrections must be highly accurate because important processes, such as mineral formation (saturation solubility), are sensitive to very small changes in the solution free energy. For example, to predict the correct mineral assemblage forming in many settings, the uncertainty of the solution free energy must be less than 0.1 pK units (free energy/RT). To achieve this accuracy, a very flexible power series expansion of the free energy in the composition variables, introduced by Pitzer (see 1987), is used:

$$G^{ex}/n_w = f(I,T,P) + \sum m_i m_j \alpha_{ij}(I,T,P) + \sum m_i m_j m_k \beta_{ijk}(I,T,P).$$

In this expression $f(I,T,P)$ is the Debye-Huckel contribution to the free energy and can be determined from solvent properties only and the ionic strength, I. At constant T and P, the coefficients $\alpha_{ij}(I,T,P)$ and $\beta_{ijk}(I,T,P)$ are specified functions of ionic strength with parameters to be evaluated from experimental data. The third consideration is that the algorithm which solves the free energy minimization problem to find the distribution of species in the system must be efficient and reliable. The algorithm we have developed (Harvie et al., 1987) facilitates successful model construction, particularly of systems which display complicated aqueous chemistry. For example, in systems which include minerals with nonstoichiometric compositions, solid solutions (e.g., clays), the compositions of the solid phase is not well defined. In addition, the correct suite of minerals must often be chosen from a large list of possible candidates. Our solver is up to the task. Temperature variation is incorporated directly into the parameterization.

2-Variable density models and the GEOFLUIDS application package:

Modeling fluid behavior for ranges of T, P in which changes of state can occur is a very difficult problem, especially for mixtures. As T, P conditions approach and surpass the critical region, brines become more compressible. The free energy equations used to model liquid density systems (discussed above) cannot be applied to compressible fluids because of the substantial nonlinear coupling between the P,T,X variables which makes a power series expansion ineffective. The dielectric properties of water, which are strong functions of P and T, change rapidly near and above the critical region. As a result, polar salts, such as NaCl, which are highly dissociated at room temperature can be nearly completely associated above the critical temperature of water. In addition, the high solute mole fractions which can occur above the critical temperature of water cause problems with the molality representation in the liquid density model equations. Therefore new free energy modeling approaches had to be developed to successfully treat variable density systems. Since data are much less available for the supercritical region than for the subcritical, it is important that the modeling approach selected for this region be based as much as possible on fundamental theory.

The first approach we used was to select compressibility as an equation of state and to fit available XPVT data to this equation. The functional form of the compressibility equation is chosen to satisfy certain constraints such as representing the XPVT behavior of both the high density liquid and low density gas phases. In situations where there are many data and the system interactions are fairly simple (e.g., weakly polar components) this approach can accurately describe both PVTX properties and system free energies. Using simulated data generated by our molecular dynamics studies (see below), to constrain the model parameterization in regions of XTPV space with few experimental data and incorporating additional methodology, such as the corresponding states and one-fluid assumptions, we have developed highly accurate EOS for high T,P mixtures (e.g., CO_2-CH_4-N_2-H_2O).

For more complicated brine systems, theoretical guidance is particularly important to develop EOS, which accurately represent chemical behavior. Unfortunately, models soundly based on theory for systems experiencing large ranges of intensive variables are not available. We are presently developing models based on an expansion of the free energy using thermodynamic perturbation theory. In this approach, a reference system is chosen as the unperturbed system and deviations from the reference behavior are treated as perturbations. The reference system is supposed to provide an accurate zeroth order approximation to the free energy of the system. Fortunately, for many problems (XPVT properties, brine flash pressures, etc.) the compositions of geothermal fluids can be well approximated by brines in the system NaCl-$CaCl_2$-H_2O-CO_2-CH_4. In this approximation, the chemistry of 1-1 electrolytes is lumped into the NaCl variable and $CaCl_2$ is the surrogate for 2-1 electrolytes. The CH_4 and CO_2 species represent the presence of the two major insoluble gases in geothermal fluids. However, even at the simplest conceptual level this is a system with dipole molecules NaCl (associated at high temperature), quadrapole molecules $CaCl_2$ and nonpolar molecules. All of these interactions must be included at some level. For polar fluids, the choice of the reference system is difficult and the treatment of the reference system, once chosen, may have to be approximate.

In addition to the problems associated with developing efficient modeling equations, it is difficult to study the extreme T, P environments encountered in some important earth processes experimentally. Therefore, the only data available for these environments may be for conditions far away from those of interest. Because of this lack of data, the chemistry of these systems is poorly understood. We are developing simulation tools based at the molecular interaction level to treat these situations and have used simulated "data" to constrain the behavior of free energy expressions in regions where few experimental data are available.

3-Heat models and the GEOHEAT application package:

Since the models in TEQUIL and GEOFLUIDS are based on the free energy of a system, all other thermodynamic properties, including heat properties, can be derived by the appropriate derivatives. However, in order for this procedure to be successful it is generally necessary to include some heat data in the data base 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).

RESULTS:

1-TEQUIL models:

Currently, the TEQUIL package includes our 0-250°C model (Moller et al., 1998) for calcite and amorphous silica scale and CO_2 exchange and the Harvie-Moller-Weare 25°C model (1984) of the complete seawater system, Na-K-H-Ca-Mg-Cl-OH-SO_4-HCO_3-CO_3-H_2O-CO_2. Phase transitions (solid/liquid equilibria) within the carbonate-free seawater system have also been modeled from -55° to 25°C (Spencer, Moller and Weare (1990)) and to 250°C (Moller, in prep) as a function of brine composition. The former model is included in TEQUIL. These models provide variable temperature solubilities of scales in brines as a function of brine composition and of the partial pressure of gases coexisting with the solution phase. Such models can be used to predict scaling, gas breakout and brine properties, such as equilibrium concentrations, pH and saturation ratios, as a function of temperature and composition. Consequently, they can simulate a variety of process conditions, such as reservoir-brine interactions, brine mixing and heating/cooling effects. To illustrate the application of TEQUIL, we describe below the use of dissolved SiO_2 concentration 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.

The stable form of silica in most high temperature formations is quartz. Dissolution of quartz in water, according to the reaction: SiO_2 (quartz)+H_2O= H_4SiO_4(aq), 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. Since the solubility of quartz is a farirly strong function of salt concentration, prediction of downhole temperatures will depend on the brine composition. 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 near the Salton Sea, in the Imperial Valley, CA geothermal area). From the equilibrium relation for the solubility, shown above, the effects of dissolved salt concentration can be expressed in terms of the activity coefficient for the H_4SiO_4 species in the solution. 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. 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°F would result if the pure water solubility curve was used instead of the Salton Sea curve to relate 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 evaporation, caused by the pressure decrease as the brine moves up the well bore to the surface, can increase the concentrations of the dissolved species. This problem can be treated by the GEOHEAT software program and will be discussed below.

Future directions include improving pressure prediction and adding more species to the TEQUIL models. Inclusion of aluminum species in the seawater models will greatly broaden their application to reservoir studies.

2-GEOFLUIDS models:

Our variable temperature models 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 reinjections as well as during the evolution of the resource when brines are cycled through high T, P regions in the formation. We have made some progress in constructing a model for the $NaCl\text{-}CaCl_2\text{-}H_2O\text{-}CO_2\text{-}CH_4$ system. At present, we have developed a model for the subsystem $NaCl\text{-}H_2O\text{-}CO_2\text{-}CH_4$ This model generalizes the earlier model for the NaCl-H2O system developed by Anderko and Pitzer (1993) and is related to earlier approach of Dimitrelis and Prausnitz (1986). The development of the EOS is based on the Helmholtz free energy. The system is first idealized as a system of interacting species. 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 PVTX data and phase equilibria data. The detailed equations describing the parameterization of these equation for the $NaCl\text{-}H_2O$ are very complicated and are given in Anderko and Pitzer (1993) and Duan, Moller and Weare (1995). Using the present model, which is in GEOFLUIDS, to predict the phase equilibria in subseafloor hydrothermal processes, we have shown good agreement of model calculations and experimental data. Our earlier model of the $CO_2\text{-}CH_4\text{-}H_2O$ system, which is included in the GEOFLUIDS package, is applicable to much wider ranges of temperature and pressure (50 to 1000°C and 0 to 1000 bar). GEOFLUIDS also includes our model for the more complex system, $H_2O\text{-}CO_2\text{-}CH_4\text{-}N_2\text{-}H_2S\text{-}O_2\text{-}H_2$, for application above the critical point of water.

In Fig. 2, the flashing pressures of a geothermal fluid of typical composition calculated by the GEOFLUIDS model as a function of temperature are presented. Because dissolved 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.

3-GEOHEAT models:

Models calculating the specific heat, heat of solution and enthalpy of complex brine/gas mixtures allow the rapid estimation of steam fractions, available heat and work, etc. The estimation of the internal energy content of brines is useful for the geothermal community. Such information is not only necessary to estimate the economic value of the resource but also, as we discuss below, can be an aid in developing models of the processes involved in energy extraction. The present GEOHEAT models are restricted to the system $NaCl\text{-}CO_2\text{-}H_2O$.

In Fig. 3, we have constructed an enthalpy/mol vs. pressure diagram using GEOHEAT for a brine similar in composition to that of the Salton Sea geothermal field. For a multicomponent system such a diagram is dependent on the total composition. In this calculation, we have lumped the entire Salton Sea 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 eventually 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) on 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 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 software.

As an application of the diagram shown in Fig. 3, reconsider Fig. 1. The measured wellhead brine 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). 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 evaporates 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 well head 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. To simplify here, rather than recalculate the solubility of SiO_2 (quartz) for the corrected downhole brine composition, we will use the concentrations at the wellhead to calculate the H_4SiO_4 activity in the brine. This allows us to use the calculated solubility curves of Fig. 1. Diluting the measured well head 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 (558°F) is 38°F less than the first estimate (Table 2, 596°F). Recalculated values for important well properties are summarized in Table 2. 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 well head temperature of the brine.

Using the TEQUIL and GEOFLUIDS models, the enthalpy models in GEOHEAT will be expanded to treat different regions of T,P space.

SOFTWARE, WEBSITE and the GEOPHASES APPLICATION PACKAGE:

The calculations that are reported in Fig's. (1-3) can all be done with the software available from our group via diskettes. We will continue to offer diskette based software. However, as models become more complex their computational load may outgrow the performance of reasonably available personal computers. To address this problem, 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 can be made immediately available to users

In addition to these capabilities, we are developing a postprocessing package called GEOPHASES which will compile and process data from the other application packages. The GEOPHASES package automatically calculates phase behavior in multicomponent systems and then constructs the requested phase diagrams for up to three dimensions. General phase relations for multicomponent solutions such as the $Na\text{-}K\text{-}Mg\text{-}Cl\text{-}SO_4\text{-}H_2O$ 5-component 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 Janecke projection shown in Fig. 4 all phases coexist with solid NaCl. To construct this figure, the solubility model for the 5 component system (Moller, in preparation) is used to calculate brine compositions in equilibrium with all the invariant mineral assemblages throughout the 0 to 250°C temperature range. The GEOPHASES software both directs computations and constructs the appropriate projections.

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Table 1: Saturation of Carbonate Scaling Minerals

In Seawater (I = .719m)		
	TEQUIL	B-dot (Bethke)
Calcite	6.86	0.81
Aragonite	4.88	0.64
In Dixie Valley Brine (I = .014m) (Reed)		
Calcite	0.667	0.611

Table 2: Combined Results Solution

Comparison between Pure Water and NaCl-H_2O System						
System	SR	Wellhead T		Wellhead P	Quartz T(F)	
Pure Water	0.29	174	345	10 bar	453	(510)
Brine (6.87m)	0.23	188	370	10 bar	558	(596)

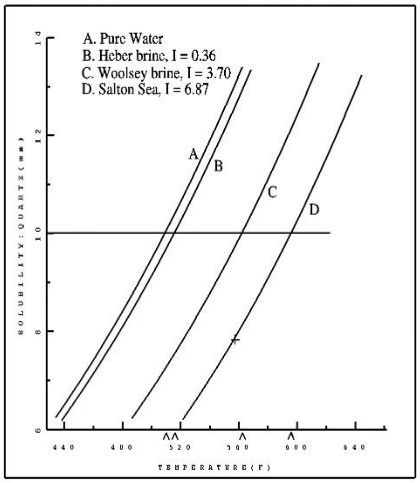

Figure 1: Solubility of amorphous silica in brine

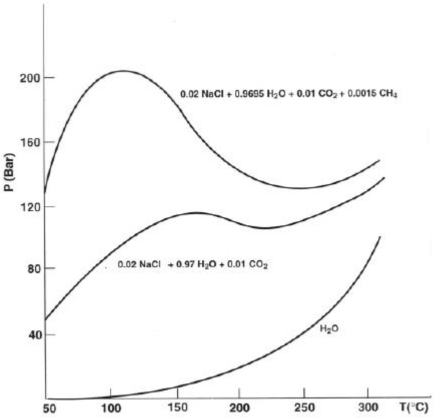

Figure 2: Breakout pressure for geothermal brines

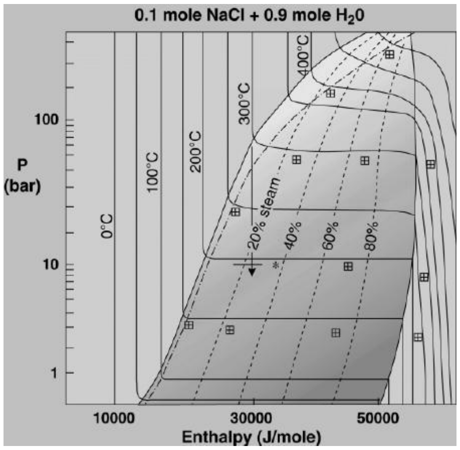

Figure 3: Enthalpy-Pressure diagram for a Salton Sea-like brine

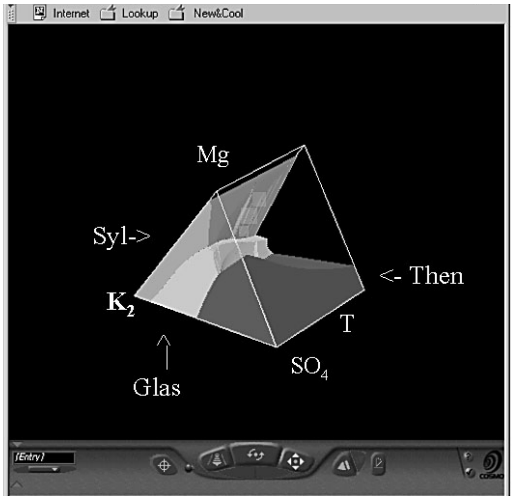

Figure 4: Janecke projected phase diagram (Halite saturation) for the Na-K-Mg-Cl-SO_4-H_2O (Moller, in preparation).