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Computation of Gas-Liquid Equilibria in

High-Saline Geothermal Fluids

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ABSTRACT

The Lawrence Livermore Laboratory is actively engaged in the development of energy extraction processes for high-temperature, hypersaline brines, such as are found extensively in the Salton Sea Geothermal Field of California. A computer-assisted chemical modeling study of equilibria in flowing brine systems has been undertaken as part of the LLL program. Equilibria between liquid and volatile components of two-phase fluids have profound effects on such important phenomena as corrosion, scale formation, environmental quality, and the economics of energy extraction. The principal reactions considered are those involving volatiles naturally present in the fluid, including NH_3 , H_2S and CO_2 .

A computer code is described which performs stepwise equilibrium computations at 1°C intervals for a unit mass of fluid, between reservoir and reinjection temperatures. The data base used is the quality-temperature function for the brine, the chemical composition, and equilibrium constants for the solubility reactions of gases and dissociation of their aqueous species. Chemical changes that take place during cooling and expansion are illustrated by

References and illustrations at end of paper

distribution diagrams. Although the computations were developed for application to the high-saline resource, they are not fluid or system-specific, and should be of general usefulness where a chemical composition and temperature history can be specified.

INTRODUCTION

The objective of this study was to construct a predictive model for a flowing, high salinity geothermal fluid. It is intended to provide a theoretical basis for understanding experimental results, optimizing process control, and predicting the effects of changes in brine chemistry. The properties to be estimated include the amount and composition of gas released, pH changes, and concentrations of scale-forming species. Such a system is chemically very complex and cannot be treated adequately by hand calculations. It should, in principle, be modeled with the help of large, general purpose geochemical computer codes, which can simultaneously consider all the many coexisting equilibria. However, several considerations led to the writing of a relatively simple code for this specific modeling purpose. It is, in essence, a computer-assisted calculation of many of the more important individual equilibria.

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The chemical compositions of the brine phases change rapidly as they cool and expand, and it was necessary that the calculations cover the complete temperature range at close intervals. Compositions are also variable with time, geographical location of a well, and processing techniques. Large numbers of computations are therefore anticipated, requiring a fast code, with the input data in analytical form. It was thought possible to gain considerable understanding of brine chemistry by an approximate analysis without completely characterizing the system. A set of specific reactions are studied that control brine chemistry; that are most relevant to scale formation and gas distributions.

DESCRIPTION OF THE PHYSICAL SYSTEM

This study attempts to model some properties of a flowing, two-phase fluid from the Salton Sea Geothermal Field; specifically that from the Magmamax #1 well. Some characteristic properties of this fluid are shown in Table 1. It may be considered typical of the high temperature, hypersaline brines from this field, although many details of its origin are not known; it is not certain that it represents a single in-situ equilibrium chemical system. It flows into the well as a compressed liquid. As it is depressurized, part of its liquid water flashes to steam, causing further increases in the already very high concentrations of nonvolatile solutes, while some volatile materials enter the steam phase, notably CO_2 , H_2S , and NH_3 .

Several processes can be visualized for the extraction of energy from this fluid. Among these are the passage of either the vapor or liquid phase, or both, directly through turbines, or through heat exchangers, which use secondary working fluids. The choice of process for a specific site will depend on economics, but one of the important economic constraints is likely to be the cost resulting from the extraordinary chemical reactivity of the fluid. All development efforts with this resource have encountered problems in corrosion and scale formation, due to the high temperatures and concentrations of solutes.

The present model is capable of being used to analyze brine chemistry problems for a variety of conversion processes, including total flow¹ and flashed steam systems. In the total flow process, the liquid and vapor are passed together through specially designed nozzles and two-phase turbines. Most species in the two-phase fluid appear to remain in chemical equi-

brum. Known exceptions to this are in some precipitation reactions that lead to scale formation, where kinetic factors prevent the crystallization of the most thermodynamically stable minerals.

METHOD OF CALCULATION

The computation considers one kg of fluid initially at the downwell temperature and pressure, and follows the chemical and physical changes taking place during cooling and expansion to the point of reinjection. A complete set of equilibria is computed at intervals of 1°C . The computations for each gas distribution are made independently in individual subroutines in the sequence: steam, CO_2 , H_2S , NH_3 , and HCl .

The essential information that is required for the computations is the following:

- Chemical composition of the brine, in situ in the reservoir.
- Steam quality and pressure vs. temperature functions for the brine.
- Activity coefficients for dissolved species.
- Equilibrium constant functions for the gas and aqueous solution reactions of volatile species.

The composition of the in situ brine was estimated from chemical analyses of samples taken at the wellhead, where it first becomes accessible, and corrected for flashing. Steam quality and pressure are measured during field operations. For modeling purposes, they are commonly derived and expressed analytically in terms of equilibrium vapor pressure of NaCl solutions, since that is the major salt component, and considerable information exists on its properties. The chemical significance of flashing is that it determines the vapor volume, the remaining amounts of solvent, and the ionic strength.

Most activity coefficients and equilibrium constants were taken from the tabulations of Helgeson.² The simplifying assumption has been made that all chloride is present as NaCl . Since these data were tabulated only to 3 M NaCl , considerable extrapolation has been necessary. The actual chloride molality is as shown in Figure 1: the changes are solely due to flashing.

In order to make calculations at any required temperature and salt concentration, all available data for pressure, quality, activity coefficients and equilibrium constants have been fitted with equations whose coefficients were stored in data files. The code output is tables of species concentrations and partial pressures as a function of temperature from which plots are made as required.

DATA AND RESULTS

Several preliminary results of computations of the gas-liquid distributions of volatile species will be illustrated. Much of the computational coding for the various equilibria has been completed so that we have a qualitative picture of these relations. However, in many cases, estimates of activity coefficients have not yet been added so that the results are subject to revision.

Steam. Precision measurements of the physical properties of complex brines at high temperatures are difficult, and for the most part, unavailable. Several estimation procedures have been developed, differing slightly in predicted values for enthalpy, pressure, and steam quality.³⁻⁷ In the present study, the method of Grens³ has been used to derive the pressure and quality functions of Figures 2 and 3 for an isenthalpic expansion. Small uncertainties that may exist in these quantities are of little consequence in comparison with the probable errors in chemical data.

Carbon Dioxide. The principal reactions considered were (1) and (2):

Although many investigators have considered the problem of the solubility of CO_2 in water and salt solutions,⁸⁻¹³ no completely satisfactory treatment applicable to geothermal fluids has been made. The present computation of the CO_2 distribution as a function of chloride molality and temperature was made using the activity coefficients of Helgeson.² The resulting Henry's Law coefficients are shown in Figure 4. These are for a real fluid of continuously changing vapor/liquid ratio. The resulting distribution in terms of partial pressure and aqueous molalities is shown in Figure 5.

The pH of the brine temperatures is an important quantity which cannot be measured

directly. Because of the relatively large CO_2 content, it can be assumed that its distribution is an important factor in determining pH. If the reactions of other weak acids and bases in the system are neglected, it can be derived from reactions (1) and (2) that

$$a_{\text{H}^+} = (K_1 K_2 F_{\text{CO}_2} a_w)^{1/2} \quad (3)$$

where K_1 and K_2 are the equilibrium constants for reactions (1) and (2), respectively, F_{CO_2} is the CO_2 fugacity, and a_w is the activity of water.

The results of such calculations are shown in Figure 6 for several CO_2 contents. This dependence is of interest because the CO_2 content is variable. One consequence of the loss of CO_2 and increase in pH is a marked decrease in the solubilities of most scale-forming materials. Another consequence is buffering. It is observed in field studies that liquid samples collected at the wellhead and titrated with acid show typical carbonate buffering curves. It should be noted, however, that the concentration of ammonia in the fluid is not negligible. A more realistic computation of the system pH can be made by a simultaneous solution of the major reactions involving CO_2 , NH_3 , H_2S and H_2O .

Hydrogen Sulfide. The higher temperature, more concentrated brines from the Salton Sea area tend to be reducing, as evidenced by the presence of H_2S and even traces of H_2 and CH_4 . Sulfates are absent, and the deposition of heavy metal sulfides is observed from which an upper limit to the oxygen fugacity can be deduced. The code does not, at present, have the capability of actually computing the oxidation state of the brine. It is assumed to be reducing for most purposes, although calculations are also being made of the solubilities of some compounds of ions in higher oxidation states, such as sulfates and oxides.

The distribution of the major sulfide species is shown in Figure 7. The sulfides that precipitate from this brine provide a point of reference against which some thermochemical estimates can be checked. That is, the fluid *in situ* cannot be supersaturated with respect to any solids. Activity products can be computed from concentrations of ions and their activity coefficients. The activities of sulfide anions, however, are functions of pH. All these data must be consistent, and solubility products cannot be exceeded. We

will be examining these relationships closely.

Ammonia. The equilibrium constant for the vaporization of ammonia (Figure 8)

$$\text{NH}_3(\text{g}) = \text{NH}_3(\text{aq}, M = f(T)) \quad (4)$$

was interpolated between those for water¹⁴ (5), and saturated NaCl solution¹⁵ (6)

$$\text{NH}_3(\text{g}) = \text{NH}_3(\text{aq}, \text{water}) \quad (5)$$

$$\text{NH}_3(\text{g}) = \text{NH}_3(\text{aq}, \text{sat. NaCl}) \quad (6)$$

The required solubility of NaCl was taken from Liu.¹⁶ The resulting distribution of ammonia species is shown in Figure 9. It indicates that most of the ammonia is initially present as NH_4^+ , and the balance as solvated NH_3 . This changes very rapidly as the fluid cools, and a significant fraction goes into the steam phase. This is confirmed experimentally, as steam condensates are found to be quite alkaline, and contain a large fraction of the ammonia.

CONCLUSIONS AND DISCUSSION

It is concluded that a useful evaluation of vaporization processes in geothermal fluids of varying composition can be carried out by relatively simple equilibrium computations, even within the limitations of available chemical information. Such computations have the advantages of speed, flexibility, and guaranteed convergence. In addition, computer models have the very useful property that they can be continually revised as better data become available; this should be considered a preliminary report on a continuing study.

The general features of the distributions that have been derived thus far appear to be correct; they are consistent with experimental observations. Verification of such calculations is made more difficult by compositional variability and inhomogeneity of the fluid, and by equilibrium changes during cooling prior to analysis.

There are some evident limitations of the calculational method. This is a relatively unexplored area of chemistry; hot concentrated chloride solutions in which the solutes of most interest are relatively dilute. Few good data are available, and predictive methods are not well developed. Computations depend, in effect, on extra-

polations of estimated data for most reactions. Brines are treated as pure NaCl solutions which also introduces some error. The procedure is presently limited in scope in that it treats only individual reactions. Some judgment has been exercised in selecting the most significant reactions, which avoids a great deal of the more realistic complexity of an actual fluid. Close interaction with field experimentation is also useful in evaluating the importance of various possible reactions.

Although existing chemical data are only marginally adequate to treat high-temperature, high-saline fluids, it is anticipated that considerable improvements can be made in the data base. For example, a more precise vapor pressure function for the brine can probably be developed. Methods exist for the estimation of many additional activity and fugacity coefficients. The inclusion of other reactions is likely to improve the estimated pH functions.

It is planned to further develop this code as a process model by adding branching logic, to simulate such processes as separation, heat exchange, condensation, and the mixing of fluid streams.

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GEOHERMAL BRINE PROPERTIES, MAGMAMAX #1 FLUID

Downwell temperature	265° C
Depth, perforation	548-690 m
Total dissolved solids	19%
Wellhead quality	10%
Wellhead temperature	220° C

Table 1

CHLORIDE MOLALITY, MAGMAMAX 1 FLUID

Figure 1

STEAM PRESSURE, MAGMAMAX 1 FLUID

Figure 2

STEAM QUALITY, MAGMAMAX 1 FLUID

Figure 3

ESTIMATED HENRY'S LAW COEFFICIENTS FOR CO₂, MAGMAMAX 1 FLUID

Figure 4

CO₂ DISTRIBUTION IN MAGMAMAX 1 FLUID

Figure 5

ESTIMATED p_H VERSUS CO₂ CONTENT, MAGMAMAX 1 FLUID

Figure 6

SULFIDE DISTRIBUTION, MAGMAMAX 1 FLUID

Figure 7

LOG K FOR NH_3 (G) = NH_3 (AQ), MAGMAMAX 1 FLUID

Figure 8

AMMONIA DISTRIBUTION, MAGMAMAX 1 FLUID

Figure 9

WILLIAMSON'S
WINDMILL RECORD BOOK
1881-1882