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VOLATILITY OF HCl AND THE THERMODYNAMICS OF BRINES DURING BRINE DRYOUT

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PROJECT BACKGROUND AND STATUS

Corrosive solutes in geothermal steam can limit or prevent economic production of steam from relatively high-temperature geothermal resources. Some wells in a high-temperature (> 300°C), vapor-dominated resource at the Northwest Geysers, California, have produced high levels of chloride at the wellhead, with observed levels greater than 100 ppm in some cases. This chloride-bearing steam is extremely corrosive to piping and well casings, leading in severe cases to loss of production within a few days. In addition to the current problem, the question of potential production of acidic steam in older wells at The Geysers as the reservoir dries out with continued production is of great long-term significance in the operation of the resource.

The high volatility of hydrochloric acid and the observed non-stoichiometry of chloride with cations in steam (e.g., Na⁺) lead to the hypothesis that the observed chloride is due to hydrochloric acid. A laboratory study of the partitioning of acid chlorides over both single electrolyte solutions and over brines likely to be encountered in the reservoir was undertaken to address the current problem of acidic steam production in deeper, hotter wells in the Northwest Geysers, and the projected behavior of the 'normal' reservoir with further production. Early results, including measurements of the partitioning of HCl from liquid to vapor in pure-acid solutions and NaCl(aq) brines, indicated that HCl was unlikely to be the sole source of chloride in steam due to the low brine pH required to give high HCl concentrations in steam.

Ammonium chloride volatility, a possible mechanism for transport of chloride from brine to steam in geothermal systems containing ammonia, was shown to give high chloride levels in steam over near-neutral high-temperature brines containing high concentrations of NaCl(aq). Furthermore, recent measurements have shown that, for temperatures ≤ 300°C, the volatility of NaCl over very concentrated (to halite saturation) NaCl(aq) brines is significantly lower than predicted from recently-developed equations of state for NaCl + H₂O. These new measurements are consistent with very low sodium ion concentrations found in wellhead condensate samples having high chloride as a result of HCl + NH₄Cl partitioning at high temperatures.

Measurements have also been made of the partitioning of solutes to steam over NaCl(aq) brines in the presence of finely-ground samples of reservoir rocks (well MLM-3) from The Geysers. Analyses of these condensed-steam samples showed that the chloride concentration in steam was not significantly enhanced by the presence of the rock sample. Although the rock sample was treated with hydrochloric acid prior to beginning the volatility measurements, relatively high concentrations of ammonia have been found in these condensate samples. Other ions found in significant quantity included thiosulfate ion. Efforts to identify and fully quantify these other volatile species were hindered by the high levels of ammonia and thiosulfate found in the condensed vapor samples. However, it was clear that there was no enhancement of chloride in steam above those levels expected on the basis of NaCl partitioning, and, consistently, that the high levels of ammonia observed indicated that the rock was imposing a pH in solution near or slightly above neutral. Noting that the rocks used in these initial studies were characteristic of cap rock.
from the 'normal' reservoir of the Central Geysers [J. Moore, EGI, personal communication], we have obtained core samples from the high-temperature reservoir of the Northwest Geysers (well L'Esperance #2) for further studies of the partitioning of chloride from brine to steam in the presence of reservoir rocks.

PROJECT OBJECTIVES

The goals of this project are to determine likely sources of highly corrosive steam from high-temperature geothermal wells and to suggest appropriate mitigation procedures based on the thermodynamics of liquid-vapor partitioning of corrosive solutes. This research is of particular importance to the control of chloride in the steam produced from the vapor-dominated reservoir at The Geysers geothermal field in California. However, the fundamental approach taken makes the results of this program generally applicable to a variety of geothermal-plant operating problems arising from partitioning of solutes between brine and steam.

Technical Objectives

- Carry out precise laboratory measurements of the partitioning of corrosive solutes to steam over ranges of temperature and brine composition appropriate to geothermal reservoirs, including equilibrations of brine in contact with rock samples from The Geysers.
- Represent the experimental data quantitatively, using sound thermodynamic models, in order to provide the means for reliable calculation of the composition of coexisting brine and steam under both reservoir and surface (e.g., piping and turbine) conditions.
- Propose and validate methods for mitigation of the production of corrosive steam from geothermal reservoirs based on the experimental and modeling results.

Expected Outcomes

- The primary products of this research will be new data on the partitioning of potentially corrosive solutes between brine and steam over wide ranges of temperature and composition characteristic of various geothermal systems, and a quantitative method for calculating the composition of coexisting phases at various points in the geothermal steam cycle.
- In collaboration with personnel from companies operating geothermal power plants, these experimental results will be used to develop methods for the mitigation of problems (corrosion; solids deposition) encountered in energy production from geothermal resources. This research can also contribute to improved efficiency in existing geothermal power plants by providing guidelines for the operation of desuperheaters.

APPROACH

The problem is addressed through laboratory measurements of liquid-vapor partitioning equilibria. The partitioning of chlorides to the vapor phase has been measured at temperatures to 350°C over pure HCl(aq), from aqueous mixed brines at concentrations ranging to salt saturation, and from brines in contact with rock samples from The Geysers. These experiments provide the data needed to develop quantitative models for the partitioning of solutes to steam from the mixed electrolyte brines encountered in geothermal reservoirs.

This project is part of the program "Physical Chemistry of Geothermal Systems" at ORNL. Significant contributions to the general objectives of this program are provided by other closely-related programs in
progress at ORNL, including research in fundamental aqueous chemistry at high temperatures and measurements of solute volatilities important in fossil-fired and nuclear steam cycle chemistry.

RESEARCH RESULTS

A special apparatus has been constructed for these measurements of the partitioning of chloride between liquid and vapor phases, using a thin platinum liner within a stainless-steel pressure vessel to permit studies to high temperatures on these very corrosive solutions. Samples of both the liquid and vapor phases are obtained at temperature through chemically-inert tubing and valves, with condensed vapor-phase samples withdrawn at a precisely controlled rate in order to prevent disturbing equilibrium conditions and to minimize sample contamination by entrained liquid droplets. Sample compositions are determined quantitatively using methods appropriate for the solutes in a particular sample. Where practical, experiments are carried out over wide ranges of ionic strength and acidity/salinity ratios at each temperature, to insure that the correct thermodynamic equilibrium constant is obtained from the analysis of the results.

The thermodynamic equilibrium constant for the partitioning reaction may be written as 

$$K = \frac{m_v(MC1)}{m_l(M)m_l(Cl)} \gamma_2(MC1),$$

where $m_v$ and $m_l$ are molalities of the components in the vapor and liquid phases and $\gamma_2$ is the stoichiometric mean ionic activity coefficient for MC1 in the liquid phase. These activity coefficients, which are significantly different from unity at the conditions investigated, are known or can be estimated reliably from previous studies in this Laboratory; the activity coefficient for the neutral MC1 molecule in the vapor phase is assumed to be unity. The invariance of $K$ with observed liquid and vapor phase compositions and sampling rates serves as a check for the presence of mechanical carryover of solute, and of the accuracy of the activity coefficients.

The values of $K$ for HCl have been represented as a simple function of temperature and solvent (water) density for purposes of interpolation and extrapolation of the results to the solvent critical temperature ($374^\circ C$). The observed partitioning of NaCl is somewhat more complex: at constant temperature, values of $K$ decrease with the decreasing density of steam as the brine becomes more concentrated. We have shown that for $t \geq 300^\circ C$ and $pH \geq 3$, the volatility of HCl alone is not sufficient to give high ($\sim 100$ ppm) chloride concentrations in steam, even over highly saline brines. Additional measurements of the compositions of coexisting phases have been made to $350^\circ C$ for aqueous brines containing MgCl$_2$, MgCl$_3$ + NaCl, and CaCl$_2$. It is clear from these experiments that while HCl is produced by hydrolysis of cations in these solutions, the total amounts of HCl generated are again too small to account for the high levels of chloride observed in steam from the high-temperature reservoir at The Geysers.

The production of corrosive, high-chloride steam at The Geysers is often accompanied by relatively high levels of ammonia (to $\sim 1000$ ppm). We have combined these field observations with our laboratory measurements on volatilities of HCl and NaCl carried out in this program and our measurements of NH$_4$Cl partitioning supported by the Electric Power Research Institute to outline a mechanism for the formation of corrosive steam having high levels of both chloride and ammonia. In a mixed brine containing HCl, NH$_3$, NH$_4$Cl and NaCl, all four solutes partition from the brine to steam. The pH within the reservoir of a brine (predominantly NaCl) which is in equilibrium with steam having the observed wellhead concentrations of chloride and ammonia can be calculated from the partitioning results coupled with values of hydrolysis constants and activity coefficients of the solutes in the brine. The results of these calculations indicate that high concentrations of chloride can partition to steam (as HCl + NH$_4$Cl) from highly concentrated NaCl brines at a near-neutral pH, with minimal sodium concentrations in steam. These results are consistent with observed solute concentrations in condensate samples from some wells in the Northwest Geysers. Similar calculations can be made of the extent of desuperheating of steam (to partial condensation under equilibrium conditions) required to yield steam with the desired low chloride concentrations, including indications of chloride concentrations in steam for which plants could be operated reliably without desuperheating. With primary support from another program in this

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Laboratory, a computer model incorporating many of the features of these calculations has been written and tested.

Measurements of solute volatilities from brines in contact with Geysers reservoir rock samples (MLM-3) were carried out at 250, 300, and 350°C. Analyses of condensed-steam samples from equilibrations with NaCl(aq) and these reservoir rocks indicated the presence of significant concentrations of additional solutes (i.e., other than sodium, hydrogen ion, and chloride); these solutes included significant concentrations of ammonia and thiosulfate ion. The presence of these solutes also complicated the determination of sodium and chloride concentrations in the samples. While it was not possible to quantify fully the concentrations of all solutes in the condensed vapor samples, it was clear that no enhancement of the chloride concentration over that expected for NaCl partitioning was observed in these experiments.

Our results for NaCl volatility in the two-phase (brine + steam) region [Simonson et al., 1994] did not appear to extrapolate smoothly to the published values for NaCl content in steam along the three-phase line (brine + steam + halite). Given the importance of NaCl in the high-temperature reservoir as indicated by fluid inclusion studies and the implications of NaCl partitioning for development of a model for overall chloride partitioning from brines to steam, it was considered crucial to investigate in detail the partitioning of NaCl brine concentrations extending to halite saturation. An initial series of measurements on unbuffered solutions gave results which indicated that HCl partitioning due to the auto-ionization of water at high temperature resulted in chloride concentrations in steam condensate samples which were significantly higher (>1 order of magnitude) than the corresponding sodium levels. These experiments were consistent with the expected solution pH and the known partitioning of HCl, but were not sufficiently precise to quantify the actual partitioning of NaCl from these brines.

A second series of measurements on this system was carried out with a small amount of NaOH added to suppress the partitioning of HCl. These experiments gave good agreement of the concentrations of sodium and chloride in the condensed steam samples and appear to extend smoothly from our previous results at lower NaCl(aq) molalities to the three-phase condition. This study provides the first measured values for NaCl partitioning to steam along the three-phase line at temperatures below 300°C, and will be an important component of a complete description of chloride partitioning to steam in geothermal systems.

FUTURE PLANS

Further measurements of the partitioning of chloride to steam over NaCl(aq) brines equilibrated with core samples from the Northwest Geysers is currently in progress. Interactions between brines and reservoir rocks may control important variables (e.g., brine pH) in determining the partitioning of solutes to steam in geothermal reservoirs. We expect that new information on a number of volatile components arising from the rocks, in addition to chloride, will be available from these studies.

The experimental techniques and modeling approaches developed in this program and complementary programs in this Laboratory have applications to geothermal systems beyond the original problem of corrosive-steam production at The Geysers. It is anticipated that this work will be extended to similar problems encountered in other geothermal systems (e.g., corrosion in process units at Magma Power Company sites in California and increasing chloride in steam from two-phase wells at Los Azufres), including liquid-dominated as well as vapor-dominated resources.

It is apparent that the application of measured equilibrium constants to the wide range of conditions (temperature, pressure, brine composition) encountered in geothermal systems requires a broad and accurate knowledge of the thermodynamic properties of solutes in brines at high temperatures, including homogeneous reactions (e.g., ion association) and excess properties (i.e., activity coefficients). We expect that further quantitative modeling of the volatility results, and applications to field observations
from geothermal systems, will indicate that some closely-targeted experimental measurements of these properties under clearly defined conditions could contribute significantly to an overall understanding of liquid-vapor phase behavior of solutes in geothermal systems. We will propose to perform these experiments in an extension of this program in cases where it is clear that this information is essential to the development of quantitative descriptions of geothermal systems.

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

Technology transfer has been an integral component of this program from its inception. Results have been communicated frequently to the geothermal industry through both periodic, focused update meetings and participation in geothermal conferences of broader scope. Direct contact and consultation on the application of these results to problems arising from volatility of solutes are continuing with the organizations listed below.

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<th>Organization</th>
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REFERENCES


