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PREDICTION OF SCALING IN GEOTHERMAL SYSTEMS

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ABSTRACT:

One of the main objectives of the DOE Geothermal Program is to improve the efficiency and reliability of geothermal operations so that this renewable form of energy can be integrated into the nation's energy system. Scale formation and other chemical problems associated with energy extraction from high temperature brines frequently inhibit the economical utilization of geothermal resources. In some cases, these chemical problems can be so severe that development of a site must be abandoned after considerable capital investment. The goal of our research efforts is to construct an accurate computer model for describing the chemical behavior of geothermal brines under a wide range of operating conditions. This technology will provide industry a cost-effective means of identifying scaling problems in production and reinjection wells as well as in surface equipment, and also devising and testing methods for solving these problems. These applications of the model as well as other uses described in table (1) can contribute significantly to meeting the objectives of the Geothermal Program.

The chemical model we have developed to date can simulate calcium carbonate scale formation and gas solubilities in concentrated brines containing sodium, potassium, calcium, chloride and sulfate ions as a function of temperature to 250°C and for variable partial pressure of CO₂. It can predict the solubility of other scale-forming minerals, such as amorphous silica, gypsum-anhydrite, halite and glasserite, as a function of brine composition to 250°C. The only required input for the model is the temperature, pressure and composition of the brine. Our modeling approach is based on semi-empirical thermodynamic descriptions of aqueous solutions. The model equations are parameterized by careful comparison to a variety of laboratory data. The ability of the resulting models to accurately predict the chemical behavior of even very concentrated high temperature brines is well-demonstrated. This ability is an unusual feature of our models which is vital for applications to many important geothermal systems, such as those found in the Imperial Valley of California.

In this report, the use of the present version of our model will be illustrated by an application to the prediction of the onset of two phase flow (breakout) in a brine-confined by an external pressure. Calculations of this kind are important in assessing the production potential of a geothermal resource because the initiation of breakout in a well bore or power plant is usually simultaneous with the appearance of massive scale deposition. It is therefore necessary to predict breakout and also to assess the consequences of breakout in designing more efficient energy extraction processes. For the geothermal brine for which we have reliable composition and breakout data (East Mesa in California), the model gives results which are essentially identical to the measured values. Calculations also illustrate the importance of contributions of dissolved gases to the total pressure of the brines. Applications to other scale formation problems in Dixie Valley geothermal brines will also be discussed.

INTRODUCTION:

The development of a geothermal resource requires a considerable financial commitment. As in other energy extraction ventures, the security of this investment can be jeopardized by the uncertain behavior of the resource under operating conditions. In geothermal energy production, a great number of major operating problems are related to the chemical properties of the working brines. Characterizing or predicting the chemical behavior of the brines is difficult because these properties are multi-variable dependent, site specific and changeable with various stages of geothermal operation.

Figure (1) illustrates a typical geothermal operating problem associated with brine chemistry. In this example, large amounts of carbonate and amorphous silica scale formed on the inside of a production line forcing costly downtime for equipment replacement and scale removal. Even more expensive problems are often experienced when the scale forms in well bores. In order to predict the economic feasibility of a geothermal operation and to efficiently exploit the resource, it is important to be able to accurately assess such chemical effects.

Since the control of chemical problems is critical for economical geothermal resource utilization, it is surprising that the industry has not placed greater emphasis on developing technol-

Table 1

<table>
<thead>
<tr>
<th>CAPABILITIES OF PRESENT MODEL</th>
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<tbody>
<tr>
<td>-Predicts Solubility of Calcium Carbonate Scale Formation in NaCl-Type Brines for T = 0°C to 250°C</td>
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<td>-Predicts Solubility of CO₂ in NaCl-Type Brines for T = 0°C to 250°C</td>
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<tr>
<td>-Predicts Solubility of Amorphous Silica Scale in Seawater-Type Brines for T = 0°C to 250°C</td>
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<tr>
<td>-Predicts Solubility of Methane in NaCl-Type Brines (preliminary) for T = 0°C to 250°C</td>
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<td>-Predicts Onset of Two Phase Behavior in NaCl-Type Brines</td>
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<tr>
<td>-Calculates Dissolution-Solution Characteristics of Rock-Water Systems Containing Na, K, Ca, Cl, and SO₄ for T = 0°C to 250°C</td>
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<tr>
<td>-Analyzes Mineral Recovery from Concentrated Seawater-Type Brines</td>
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</table>
ology for reliable prediction of brine chemical behavior. Prediction methods based on tabulated experience or on simulations with a limited number of brine compositions and limited ranges of extensive variables are not likely to be effective. Geothermal resources commonly involve concentrated brines. Accurate descriptions of their chemical behavior require sensitive functions of the fluid compositions and of the values of the intensive variables encountered in the energy extraction cycles. Prediction is made more difficult by the fact that the brine composition usually varies strongly as a function of location in the geothermal field and even of time.

Geothermal resources commonly involve concentrated brines. Therefore, it overcomes the limiting restrictions of the lookup (table reference) and simulation methods now used to predict chemical behavior in geothermal operations.

In order to illustrate application of the model, we have predicted scale formation in the well when the Dixie Valley brine is produced for energy extraction. The cost of predicting the occurrence and amount of scale formation in this system using our model calculations is very small. On the other hand, the cost of scale removal from the well is very substantial. The expense of developing and implementing the remedial action needed to overcome this scaling problem should be included in the estimates of the economic viability of the resource. In the early development of the Dixie Valley resource, these chemical problems were not projected. Consequently, approximately one million dollars of well clean up was required.

The model in its present form may be used to predict the formation of amorphous silica scale and carbonate scale as a function of temperature from 0 - 250°C and for arbitrary brine composition. In addition to the amount of potential scale formation, the model can predict other brine properties which affect resource exploitation. For example, in this article we also apply the model to the estimation of the total pressure required to keep the brine in a single phase. This pressure is important in the design of a power plant since the onset of two phase behavior is usually coincidental with the formation of massive scale deposition in well bores.

In the final section of this article, we discuss future developments of the model. New correlations are being developed which will allow the prediction of a greater variety of processes. Gas solubilities for methane and hydrogen sulfide will be improved and included. The aqueous chemistry of the sulfide system will be added to the model so that we will be able, with further research, to predict sulfide scale formation.

PRESENT CAPABILITIES OF MODEL:

The chemical processes that result in scale formation and in other problems related to geothermal operations are often far from equilibrium. In order to describe these processes in all aspects requires detailed rate information. Such information is rarely available. Therefore it is very difficult to predict how fast a particular reaction will go. On the other hand, much less information is needed to calculate if a system is out of equilibrium or to predict that a particular reaction can occur (e.g., that scale can form). In other words, it is possible to predict if a reaction is likely to occur and how far it will go. These predictions can be made using thermodynamic information which for many systems is already available or can be obtained from routine laboratory measurements. For this reason, our program has concentrated on the development of equilibrium models of brine chemistry.

In this article, we present results of the application of a new thermodynamic model for geothermal fluids recently developed by our research group. This model is currently available, and can be used to predict the brine chemistry related to many phases of power plant operation. The model summarizes in an efficient manner the chemical behavior of complex brines as a function of their composition and the intensive variables, temperature and pressure. It is highly flexible, and is applicable to a wide class of natural hydrothermal waters, including concentrated brines. Therefore, it overcomes the limiting restrictions of the lookup (table reference) and simulation methods now used to predict chemical behavior in geothermal operations.

Our modeling approach is based on parameterizing the species' chemical potentials, $\mu_i$, in the free energy, $G$, expression,

$$ G = \sum_{i} \mu_i n_i, \quad (1) $$

where the summation over $i$ is over all solution and solid phases, and $n_i$ is the number of moles of species $i$. The free
energy if minimized subject to mass balance constraints gives the amount of each species (including solid phases) in the system at equilibrium (e.g., after flash and scale precipitation). For example, if scale is going to form under a particular set of conditions, the minimization of the free energy will indicate the presence of solid scale species.

To further simplify the description of the various functions in the free energy, the excess activity coefficient, \( \gamma^{\text{exc}} \), is defined via the equations,

\[
\mu_i = \mu_i^\circ + RT \ln \gamma_i^\circ m_i \quad (2)
\]

and

\[
\ln \gamma_i^\circ = \ln \gamma_i^{\text{exc}} + \ln \gamma_i^{\text{exc}}, \quad (3)
\]

where \( \gamma_i^{\text{exc}} \) is the usual Debye-Hückel expression, \( \mu_i^\circ \) is the standard chemical potential and \( m_i \) is the molality of species \( i \).

In order to proceed, it necessary both to specify the species in the summation and to assume a form for \( \gamma^{\text{exc}} \) in terms of the composition of the solid phases. Following Pitzer (1987), in our model a virial form is chosen.

\[
\ln \gamma_i^{\text{exc}} = \sum_j B_{ij}(I) m_j + \sum_{j<k} C_{ijk} m_j m_k + \ldots . \quad (4)
\]

The coefficient, \( B(I) \), in this expression is a function of ionic strength, as given by Pitzer (1987). The parameters in \( B(I) \) and the remaining parameters in Eq. (4) must be evaluated by comparison with measured data. In general, this requires fitting data in the binary and ternary subsystems which can be formed from the components in the system of interest. For example, to predict scaling in the NaCl-CaCO\(_3\)-H\(_2\)O system it is necessary to have data from the binary systems: NaCl-H\(_2\)O, CaCO\(_3\)-H\(_2\)O, CaCl\(_2\)-H\(_2\)O and Na\(_2\)CO\(_3\)-H\(_2\)O, as well as from the common ion, mixed ternary systems: NaCl-Na\(_2\)CO\(_3\)-H\(_2\)O and CaCl\(_2\)-CaCO\(_3\)-H\(_2\)O. However, once the model parameters for these subsystems have been evaluated, the model may be applied with confidence to predict carbonate scaling in systems of arbitrary composition within the full Na-Ca-Cl-CO\(_3\)-H\(_2\)O quaternary system with no additional adjustments.

The capabilities of our present model, which can predict the formation of the most important carbonate and silica scales from \( 0^\circ \) to \( 250^\circ \)C, are summarized in table (1). To illustrate how such a model can reduce the risk in geothermal ventures by predicting the outcome of various processes, we describe in the following sections two geothermal brine calculations. We hope that these calculations not only demonstrate the predictive capability of our present models but also stimulate use of such models in the geothermal community. Only through the wide application of accurate chemical models in geothermal operations will the knowledge be acquired to realize the full potential of the modeling approach in this industry. The feedback generated by application will lead to improved models and to more informed and productive use of the models.

**MODEL CALCULATIONS OF BREAKOUT PRESSURES:**

Figure (2) is a schematic diagram of the processes leading to scale formation in a geothermal process stream (well bore or production line). The important factors governing scale formation are the brine composition, temperature and pressure. The partial pressure of carbon dioxide is an especially important variable in the formation of carbonate scale. Unlike the silica system, the solubility of the scale forming mineral, calcite, increases as the temperature of the brine is lowered and is very sensitive to the concentration of dissolved CO\(_2\) in the brine. If the CO\(_2\) concentration in the brine decreases, calcite scale deposition occurs via the reaction,

\[
2\text{HCO}_3^- + \text{Ca}^{2+} = \text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O} . \quad (5)
\]

If the concentration of CO\(_2(aq)\) on the right in Eq. (5) is decreased, the equilibrium shifts to the right and CaCO\(_3\) scale forms.

![Fig. (2) Schematic diagram of scaling process in well bore.](image)

The interrelationship between dissolved CO\(_2\) and calcium carbonate precipitation shown in Eq. (5) results in a direct relation between the initiation of scale formation and the onset of two
phases in the working fluid. As long as the total pressure on the brine is maintained at a high enough value, the brine will remain in a single liquid phase and the dissolved CO₂ concentration will not change. However, if the total pressure is allowed to drop it may reach a point where the sum of the vapor pressures of the fluids plus the combined partial pressures of the dissolved gases exceed the total pressure on the system (for real gasses fugacity corrections may be important). At this point, the liquid phase may form a gas phase bubble (breakout) and exhibit a dramatic redistribution of dissolved gases from the liquid to the gas phase. This is an important mechanism for the precipitation of carbonate scales.

Measurements of the breakout point as a function of temperature have been reported by Robertus (private communication) for an East Mesa brine. Comparison of model predictions with these measurements may be used as a validation of our model for the carbonate and the methane systems. These results are similar to the preliminary values reported at the last Geothermal Program Review. At that time, however, we had results only for a few temperatures. Now we have completed, among other work, a continuous temperature measurement of the working fluid since breakout and scale precipitation may have removed species from the fluid.

The dissolved gas composition in the original downhole brine may be reconstructed from the well head measurements by adding the amounts of gases released from the brine in going from downhole to well head conditions (measured at well head, see table (2)) to the well head liquid phase composition and equilibrating the model under closed system conditions (not allowing gases to escape from the liquid phase). To calculate the amounts of liquid phase components lost due to scale formation, it must first be determined which solids are supersaturated at the well head. Once this has been determined, the amount of solute removed by scale deposition may be estimated by reequilibrating the well head liquid phase composition with the solid scale phases at specified downhole temperatures and pressures. For the East Mesa brine, we assumed that there was no scale deposition during production. These downhole compositions may now be used in the model to calculate the total pressure required to prevent the formation of a gas phase (breakout). The calculated results are summarized in figure (3). These results are similar to the preliminary values reported at the last Geothermal Program Review. At that time, however, we had results only for a few temperatures. Now we have completed, among other work, a continuous temperature model for the carbonate and the methane systems. These models allow the prediction of the continuous pressure vs. breakout variation shown in figure (3).

Model calculations shown in figure (3) are in excellent agreement with experimental values. To illustrate the importance of dissolved gases in these breakout predictions, we show our estimates of the various gas contributions to the total breakout pressure in table (3). Since the East Mesa brine contains high amounts of noncondensible gases, the most important of which is methane, there is a considerable contribution to the breakout pressure from these species. We note that, while the concentration of methane in this fluid is only one tenth of that of CO₂, its contribution to breakout is of the same order of magnitude as that of CO₂. We also note from table (3), the dramatic changes in the relative contributions from the various species as a function of temperature. This result illustrates the importance of the model's capability to treat the specific composition of the working fluid of interest.
MODEL CALCULATIONS OF SCALING:

Carbonate Scale:

The following example illustrates how the model may be used to calculate the amounts of scale expected to form during well operation. The well head composition of a brine sample from Dixie Valley was supplied by Marshall Reed. Since this sample was taken at the well head, it does not include losses in the concentration from scale formation during production of the brine. Therefore to analyze the scaling potential of this brine by reconstructing the downhole brine composition, we first equilibrate the well head brine with the amount of released CO$_2$ added back (table 4, row 1). Then, we equilibrate the brine under assumed downhole temperature and pressure in the presence of calcium carbonate solid phase (table 4, row 2). By this analysis, approximately $1.58 \times 10^{-3}$ moles more of carbonate are calculated to be in the downhole brine than in the well head sample. Presumably this much carbonate is deposited in the well bore as the brine is produced. While this number seems small, it must be multiplied by the total amount of fluid produced to obtain the total scale deposited. Using the flow rate also supplied by Reed, we predict that approximately $3.792 \times 10^3$ kg of scale should form in the well bore in one year of operation.

Table 4

<table>
<thead>
<tr>
<th>Case</th>
<th>CO$_2$</th>
<th>HCO$_3$</th>
<th>CO$_3$</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>.0516</td>
<td>.00329</td>
<td>.000203</td>
<td>.000178</td>
</tr>
<tr>
<td>2$^b$</td>
<td>.0514</td>
<td>.00368</td>
<td>.000086</td>
<td>.000336</td>
</tr>
</tbody>
</table>

a. Well head composition equilibrated with released CO$_2$ added back.

b. Reconstructed downhole composition (row 1) composition equilibrated in the presence of solid phase calcium carbonate.

As we discussed above, the most likely cause of the calcite deposition is the transition of the working fluid from single phase to the two phase regime. Therefore, in table (5) we report breakout calculations (as in the prior section) for the Dixie Valley brine. The additional values for methane concentrations required for this calculation were supplied by Reed. The results of these calculations are also shown in figure (4). As can be seen by comparing figures (3) and (4), both the shapes of the curves and the values of the breakout pressure for the two brines, East Mesa and Dixie Valley, are significantly different. The prediction of the very different behaviors of these two brines without further experimental data illustrates a significant advantage of the flexible modeling approach.

In figure (4), we have also shown the temperature dependence of the saturation ratio, SR, of carbonate scale (calcite). SR is the ratio of the product of activities of the individual species over the equilibrium solubility product. If this ratio is 1, the system is in equilibrium with the solid phase. A ratio greater than 1 indicates that scale may form. For a ratio less than 1 scale cannot form. We note that the brine composition
assumed for Dixie Valley was found by equilibrating the brine with calcite. Therefore, since the downhole brine is in equilibrium with calcite in the formation, SR should equal one at the assumed downhole temperature of 250°C. From figure (4) we see that if the breakout pressure is maintained the saturation ratio of calcite decreases with decreasing temperature. This means that the scale is more soluble in the cooled brine than in the hot. As is well known, this phenomenon is responsible for the scale free behavior of binary power plants. In the power extraction process of a binary plant, the hydrothermal fluid is kept in the single phase region, thereby avoiding the formation of carbonate scale upon cooling. We also note in figure (4) the sharp decrease in the breakout pressure as the temperature is decreased.

Silica Scale:

Also shown on figure (4) is the SR for the formation of amorphous silica scale. Unfortunately for geothermal operations, the solubility of silica minerals decreases rapidly with decreasing temperature. Therefore, if a system is initially in equilibrium with one of these minerals, scale can in principle form immediately when the thermal energy is removed from the brine. There is, however, an additional effect which greatly improves the situation.

In the SiO2 system there are several crystalline minerals more stable (less soluble) than amorphous silica. In principle, these minerals should form in place of the amorphous phase. However, these minerals are very slow to form. In fact, even in highly supersaturated brines, as in geothermal operations, this process is so slow that the precipitation of crystalline phases doesn't occur. The first precipitation occurs when the solubility product of the amorphous phase is exceeded and this relatively rapidly forming solid phase appears. Because the solubility of the amorphous phase is significantly higher than that of the crystalline phases, the concentration level of silica in the aqueous phase before precipitation is significantly higher than it would be if the less soluble phases could form.

Generally, geothermal water is in equilibrium with a crystalline silica phase at the formation temperature and therefore has a fairly low concentration of silica. At this temperature, the system is considerably undersaturated with respect to amorphous silica. When the brine is extracted from the formation that only pure silica phase that can form kinetically is amorphous silica but since this phase has a relatively high solubility it will not form until the temperature is lowered significantly. At this point silica scale may form.

This behavior is illustrated in figure (4). The Dixie Valley brine at the well head temperature of 250°C contains very little silica presumably because it is saturated with respect to crystalline silica. As expected, it is very undersaturated with respect to the formation of amorphous silica scale. However, as the temperature is lowered (as during the power extraction process) the SR increases from its low initial value to a value greater than 1 near 100°C. Therefore at temperatures below 100°C, silica scale precipitation from this brine is possible. We would like to point out, however, that our thermodynamic model only indicates if scale formation can occur. It does not include kinetic effects which may inhibit scale formation. For example, it is quite possible that the power plant may be operated somewhat below this temperature with no scale formation because the rate of precipitation is very slow when the SR value is not much higher than one. Nevertheless, it would be expected that the silica scale will form someplace in the system. For example, precipitation may occur in the injection system which may be even more difficult to handle than scale in the power plant.

FUTURE IMPROVEMENTS OF THE MODEL:

As we have demonstrated, the present model is capable of answering questions that are important to the successful exploitation of a geothermal resource. However, there are many problems of great importance which still cannot be treated. For example, we see from figure (1) that sulfide scale (FeS) may cause significant operating problems. The aqueous chemistry of the sulfide system is similar to the carbonate system. The precipitation of minerals in this system is strongly controlled by the concentration of dissolved H2S gas in the solution phase. Therefore the formation of scale is again strongly influenced by breakout. The presence of an additional acid-base system also greatly complicates the prediction of precipitation of other solids and other properties such as pH which is related to important effects such as corrosion. In addition, H2S gas release may pose significant environmental problems.

For these reasons, we have begun the research necessary to model the H2S system. Since H2S is a weak acid, there is very little dissociation of the dissolved H2S species. This implies that gas solubility models may be developed without including the H+ or HS- species. Unfortunately, even gas solubility data are rather scarce for this system. At present we have a preliminary model of H2S gas solubility below 100°C in NaCl dominated brines. Some data are available for other salt solutions. We are continuing our efforts to generate an accurate H2S solubility model.

The solubility of methane is important to many energy extraction processes. For example, in our calculations of gas breakout it was necessary to include estimations of the partial pressure of methane gas. This gas can be an important source of energy and therefore contribute significantly to the economic balance of the geothermal resource development. In geopressed systems the principle energy carrier is dissolved methane gas. A model of methane chemistry is necessary to accurately predict the available energy in such systems and to help in the design of efficient gas stripping technologies. Our present preliminary model of methane solubility is restricted to relative low pressures (< 30 atm) and to temperatures below 150°C. We are presently adding capabilities for application to higher pressures and temperatures.

REFERENCES:


