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ANNUAL PROGRESS REPORT
UCSD GEOTHERMAL CHEMISTRY PROGRAM
FY1989

submitted by

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I. INTRODUCTION:

1. Background:

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. Many of the most significant problems limiting the development of geothermal power are related to the chemical properties of the high temperature and highly pressured formation fluids from which the energy is extracted. When the pressure and temperature conditions on these fluids are changed either during the production phase (pressure changes) or during the extraction phase (temperature changes) of the operation, the fluids which were originally in equilibrium with formation minerals return to chemical equilibrium under the new conditions by precipitation of solid materials (scales) or release of dissolved gases (some toxic) in the formation and well bores or in the plant equipment.

Problems of this sort occur for essentially every water dominated geothermal resource. For some, these problems are only minor and can be handled by routine maintenance. However, for many large and important resources (e.g. the Imperial Valley of California) the control of chemical problems may determine the viability of the resource. In some cases the problem is so severe that the resource must be abandoned even after considerable capital investment.

Unfortunately, predicting the behavior of the production fluids is difficult, because it is a function of many variables. Furthermore the brine compositions, temperature and pressure characteristics are site specific and may change during the various stages of the operation. In order to address these problems the Department of Energy is developing a computer model describing the chemistry of geothermal fluids. This model will provide the geothermal industry with a cost effective method of identifying chemical problems during site assessment as well as an inexpensive means for testing strategies for abatement of problems in systems already in operation.

The model under development at UCSD is based on recent progress in the physical chemistry of concentrated aqueous solutions.

Unfortunately, the behavior of concentrated brines cannot be predicted from first principle theories. However, because of the importance of these fluids to many industrial and natural processes, there has been a continuing effort to develop phenomenological approaches which can be parameterized from empirical data. The model we are developing incorporates the most successful of these proposed by Pitzer and co-workers. We have shown that using this approach we can create models of brine chemistry which are highly accurate. These models are parameterized by very careful fitting of experimental measurements and require extensive data sets. However, the required data is for systems of considerably less complication than those found in field applications and in many cases is readily available.

The original applications of the models we developed were to surface problems (near standard conditions). In this work we were able to show that the model predictions were sufficiently accurate that important information about various geological and low temperature industrial processes could be predicted. The model predictions were compared with remarkable success directly to field measurements and laboratory simulations.

More recently and with the support of the geothermal program, the model has been parameterized for the high temperatures which are characteristic of geothermal fluids. Again our results show excellent agreement between laboratory measurements and model predictions. *For example the present model predicts all the laboratory data for calcite, amorphous silica, and CO₂ solubility within the accuracy of the measurements for a temperature range from 0-250 °C.*

Similar results have been found for applications to field measurements. For example the model has been used to predict the breakout conditions for the East Mesa brine with remarkable accuracy. As in the case of the laboratory measurements, the predicted results are within the accuracy of the field measurements. We emphasize that these results are the only known example of the accurate prediction of brine behavior at near formation condition. We have used the model to predict the scaling behavior of Dixie Valley geothermal water. Again results agree with well performance.

The model we are developing has application to a large number of important problems in other energy technologies (e.g. oil production problems, solar pond thermodynamics etc.), in industrial process chemistry and nuclear waste isolation. In fact the isothermal models that our group has developed in prior years with DOE support have become the standard models (in for example the nuclear waste program) for use in studies of moderately concentrated aqueous solutions. Recently our program has been used by the Canadian Potash industry in studies of mining problems. Some research support is now being provided by both Central Canada Potash and the DOE Nuclear Waste program.

2. OBJECTIVES:

- i. Reduce geothermal production well maintenance cost related to scale production by 20% by 1992.
- ii. Reduce geothermal field surface equipment costs related to scale deposition by 20% by 1992.
- iii. Reduce geothermal power plant maintenance and equipment replacement costs related to scale deposition by 20% by 1992.
- iiii. Reduce cost of surface disposal of sludge from geothermal brines by 25% or more by 1995.

Various strategies (e.g. binary cycles, crystallizers, scale inhibitors) are available to control scaling problems in geothermal operations. These strategies generally require additional costs either in terms of disposable materials (e.g. scale inhibitors), additional equipment (e.g. crystallizers) or downtime (e.g. well cleanup). Because of these additional costs, it is important to fully assess the magnitude of the problems and the effectiveness of a strategy to relieve the problem. This assessment will be most effective if it can be done before the development of the resource. The computer program we are developing will contribute to this assessments. The model can also be used to cost effectively test various strategies of scale control and gas breakout in systems already in operation.

Brines precipitate scale or release dissolved gases when the intensive variables temperature and pressure are changed from the values in

the formation to the values experienced in various parts of the operating system during the extraction of energy. The behavior of these brines is a strong function of their composition, therefore, engineering approaches which are based on experience rather than a more detailed knowledge of the chemical processes involved with scale precipitation are not likely to be effective.

On the other hand the model we have developed can predict the chemical behavior of the brines as a function of the changes of temperature and pressure and as a function of composition. It therefore provides a highly accurate tool to predict the state of equilibrium of the brine at any point in the well bore, the power plant or the reinjection system. It can be used to predict the scaling problems likely to be encountered during operation of a potential resource. Or in the design of a new power plant, it can be used as a tool to tract the possible precipitation of scale through the operation of the plant to allow the design of the optimal cycle consistent with a strategy of scale control.

It can also be used to predict the success of failure of scale inhibitors and the regions in the operating system where the use of such brine treatment will have maximum effect. This will serve to increase the economic efficiency of the resource. The model will also be useful to predict the scaling behavior of the reinjection system and to investigate the effectiveness of well cleanup strategies such as acid treatment.

3. Work Breakdown Structure:

A. Conversion technology

- i. Heat cycle (INEL).
- ii. Materials (BNL).
- iii. Advanced Brine Chemistry. (UCSD and BNL)

All the objectives discussed in section 2. apply to item iii.(advanced brine chemistry, UCSD).

II. FISCAL YEAR ACCOMPLISHMENTS:

The principle achievement of this years support was the implementation of a model of the $\text{CaCO}_3\text{-SiO}_2\text{-CaSO}_4\text{-NaCl-CO}_2\text{-H-H}_2\text{O}$ system over a temperature range from 0-250 °C and to high ionic strength. This system contains most of the important carbonate sulfate and silica scale forming minerals. While the model is not fully parameterized, it does for the first time provide a model of sufficient accuracy that reliable estimates of the scaling potential of many geothermal systems may be obtained. The model can also calculate the conditions for boiling or onset of two phase flow of CO_2 dominated geothermal fluids (breakout).

This years progress has also included partial parameterizations of the remaining parts of the seawater system. In particular advances have been made to include the potassium in the system. With the further inclusion of magnesium the model will treat the entire seawater plus carbonate system. As well as providing an important design tool for geothermal engineering this model will represent a very significant advance in our ability to interpret general problems in geochemistry.

In a related program (only computing facility supplied by DOE) preliminary attempts have been made to parameterized the model at temperatures down to the eutectic point of the seawater system. This model is presently being used to noninvasively interpret the composition of fluid inclusions via mineral coexistence in a cooling cycle. This data may be of use in investigations of reservoir properties. The model supported by this program has also been used to investigate a number of other problems of general geochemical interest by the various visitors to our group.

III. MANAGEMENT:

1. Organization.

Program manager: Gladys Hooper(DOE)

Project manager: Ken Taylor (DOE)

Principle investigators: Nancy Moller and John Weare (UCSD)

2. Interface/Contacts:

The programs we are developing are widely used by many industrial and research organizations. We collaborate heavily with investigators in many countries. A number of these investigators visit our research group regularly and have taken research level versions of the code back to their home institutions.

The isothermal version (25 °C) of the code has been incorporated in the EQ3/6 model of the nuclear waste program, and the PHREEQE and SOLMINEQ models of the USGS. These programs have been very widely distributed in the minerals and oil industry. Recently the Canadian potash industry has used the code for mining engineering studies. This group (via. Central Canada Potash) and the nuclear waste program have provided a small amount of support for our program.

3. Meetings/Reviews:

March 21-23, 1989, San Francisco, Geothermal Program Review VII: DOE R&D for the Geothermal Market Place.

February 9, 1989, Washington, D.C., Geothermal Technical Program Review.

September 26-29, 1988, Los Angeles, ACS Conference, invited talk entitled "Solubility predictions in complex mineral systems."

4. Papers:

Jerry P. Greenberg and Nancy Moller. (1989) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO₄-H₂O system to high concentration from 0 to 250°C. *Geochim. Cosmochim. Acta* 53, 2503-2518.

Nancy Moller. (1988) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O system to high temperature and concentration. *Geochim. Cosmochim. Acta* 52, 821-837.

John H. Weare and Nancy E. Moller. Prediction of scaling in geothermal systems. To be published *Geothermal Program Review* No. VII.

Boaz Lazar, Heinrich D. Holland and John H. Weare. Fluid inclusions in Messinian halite from the Red Sea: Clues to the composition of Miocene seawater. Submitted for publication (GCA).

Andrew R. Felmy and John H. Weare. Calculation of multi-component diffusion in the system Na-K-Ca-Mg-Cl-SO₄-H₂O at 25°C from zero to high concentration. Submitted for publication (GCA).

Andrew R. Felmy and John H. Weare. Calculation of multi-component ionic diffusion from zero to high concentration: II. Inclusion of ion association species. Submitted for publication (GCA).

Ronald J. Spencer, Nancy Moller and John H. Weare. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system, at temperatures below 25°C. To be published (GCA).

IV. BUDGET:

Ken Taylor will take care of.

V. END of YEAR STATUS:

The program is now ready to be used by the industry at a research level. Versions are already in use in studies of scaling in geothermal and oil production systems.

VI. FUTURE PLANS:

We will continue the development of the equilibrium model and the documentation that will implement its distribution to the geothermal community. Most recently we have begun to bring the code up on a Macintosh computer. Preliminary results suggest that at least the isothermal versions will be implemented in this year of support.

The model is also being improved to include a wider range of species as the data base improves. Recently new data was taken for the SO₄-HSO₄-H₂O system with DOE support. The inclusion of this species will allow us to treat pH effects in brines with substantial SO₄.

Our research efforts to complete the high temperature seawater systems continues. We hope to have a model of the complete seawater (without carbonate) system by the end of this fiscal year.

We are starting a program to model the pressure dependance of scale deposition processes. This program will be initiated by modeling the gas phase $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ system which is of great importance in the analysis of geopressured systems.

We also initiated a program to model the $\text{H}_2\text{S-NaCl-H}_2\text{O}$ system. The initial stage of this program will provide a model of the solubility of sulfide gases in aqueous solutions.