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RESERVOIR RELATED RESEARCH AT IDAHO NATIONAL ENGINEERING LABORATORY,
LAWRENCE LIVERMORE NATIONAL LABORATORY, AND OAK RIDGE NATIONAL LABORATORY

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A B S T R A C T

Idaho National Engineering Laboratory (INEL), Lawrence Livermore National Laboratory (LLNL), and Oak Ridge National Laboratory (ORNL) conduct research in reservoir engineering, geophysics, and geochemistry, respectively, in support of the DOE Reservoir Technology Research Program. INEL's research has centered on the development of a reservoir simulation code to predict heat and solute transfer in fractured, porous media. The results of that development were reported to the geothermal industry in a technical transfer workshop during 1989. In support of the initiatives for research at The Geysers, INEL will initiate in cooperation with Lawrence Berkeley Laboratory, studies of injection and related interference effects at The Geysers. Work at LLNL is centered on analysis of the seismicity associated with production and injection at geothermal systems and effects of geothermal systems on seismic signals. LLNL is continuing studies of seismic attenuation related to the presence of steam at The Geysers. ORNL conducts research to obtain the thermodynamic and kinetic data needed as input into geochemical models such as those being developed by John Weare of the University of California, San Diego that predict the phase behavior and corrosion characteristics of geothermal brines. The current program at ORNL addresses the ion interaction parameters of bisulfate ion (HSO_4^-) with H^+ and Na^+ , the dissociation constant of HSO_4^- , OH^- , and the solubility and specification of aluminum in the system H^+ - Na^+ - K^+ - Cl^- - OH^- . ORNL is initiating studies of the distribution of HCl in steam in support of the expanded research program at The Geysers.

INEL is also involved in several other activities in support of the development of geothermal resources. INEL acts as liaison between the Geothermal Technology Organization and DOE and provides contract support for initiation of joint research. INEL also participated with several other National Laboratories in preparation of an analytical study of renewable resources in support of DOE's ongoing National Energy Strategy. As a result of this study, INEL is initiating a review of geothermal reserves.

INEL
(J. L. Renner)

Simulation Code Development

The movement of injected fluid in a fractured reservoir is being modeled in response to a primary industry concern about the effect of

injection on pressure maintenance, thermal breakthrough, and water-rock interaction in a producing reservoir (Miller and Clemo, 1988). The Idaho National Engineering Laboratory (INEL) has developed the FRACSL code to simulate flow, solute transport, and heat transport in a saturated fractured-porous media. The code uses a dual permeability approach in which a common head distribution drives flow in matrix cells and in discrete fractures which lie on the edges and diagonals of the matrix cells. Solute and heat transport are modeled by moving marker particles in the matrix, in the fractures and between the two. Fractures and matrix are modeled explicitly to provide the most physically realistic models and potentially the most accurate tool for studying the movement of injected and produced fluids.

FRACSL (Miller et al., 1987, Miller and Clemo, 1988) provides a two-dimensional simulation of flow, solute transport and heat transport in a saturated, fractured-porous media. The following discussion of FRACSL is taken from Miller and Clemo (1988).

As shown in Figure 1, a distributed flow is computed through the porous matrix cells and a discrete flow is computed in the parallel plate fractures superimposed on the edges and diagonals of the matrix cells. This approach, termed dual permeability, is different from dual porosity in which flow is computed in the fractures and a one-dimensional interchange occurs with the storage in the adjacent matrix. In dual permeability a flow can be computed from fracture to fracture through intervening matrix and in dual porosity modeling it cannot.

The marker particle transport approach used in FRACSL is ideally suited to dual-permeability models since it permits explicitly addressing the fractures, the matrix, and the interchange between them in terms of the fundamental physical processes of advection, dispersion, and diffusion.

Movement within a fracture is computed based on random diffusion plus the longitudinal and transverse fluid velocities at the particle lateral position. The longitudinal velocity is selected from a Poiseuille distribution across the fracture aperture while the transverse velocity depends on the fluid movement from fracture to matrix due to advection across the matrix cell and storage within it. At a junction with another fracture the particle moves into the appropriate exit fracture by advection along a stream line plus a random diffusive movement.

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Particle transfers between fracture and matrix are computed due to advection and diffusion. For diffusively dominated conditions, the random walk approach used excessive amounts of computer time since a particle moving into the matrix has a 50% chance of moving back into the fracture in the next time step. A higher order model was, therefore, developed which determines the particle motion based on overall probability..

Particle movement within the matrix is computed as the sum of advective, dispersive and diffusive motions. Solute concentration or temperature within the model is computed from the distribution of particles at any particular time. Concentration or temperature is also monitored at a production well node.

The original version of FRACSL uses the Advanced Continuous Simulation Language (ACSL) (Mitchell and Gauthier Associates, 1986) for its user interface and numerics and is implemented on the INEL CDC Cyber 176 computer. This version has been phased out and the work load transferred to a UNIX based version with self-contained numerics. The new version (FRAC-UNIX) is operable on a SUN or equivalent workstation for field applications.

The FRAC-UNIX code is currently capable of modelling fluid flow and solute and heat transport in a two-dimensional, dual-permeability reservoir. Further development of FRAC-UNIX is not included in the fiscal year 1990 program.

INEL presented a two day workshop on the code to the geothermal industry in January 1989. A preliminary edition of the user's manual for the code was given to the attendees at the meeting. The final version of the manual is being edited and will be available soon. The code will be released through the National Energy Software Center.

Geysers Research

Current research at INEL is directed towards developing a better understanding of the effects of injection on reservoir performance. Two studies have been proposed. The first, which will be conducted in conjunction with Lawrence Berkeley Laboratory, proposes to study the relation between interference effects and injection. The second study will investigate modelling of injection at the Geysers and perform comparative studies of the MINC and Warren and Root approaches to simulation of fractured reservoirs.

LLNL
(P. W. Kasameyer)

Lawrence Livermore National Laboratory is developing and testing methods to image volcanic areas, gathering case-study information for

geophysical monitoring of geothermal fields, and evaluating practical geothermal applications of existing geochemical modelling codes. Only the development of seismic velocity and attenuation images at The Geysers to look for steam zones is discussed in this paper.

The method used at The Geysers is based on successful experiments at Medicine Lake Volcano, and at Newberry Crater. Rings of explosions provided seismic signals to produce 3-D images of these volcanic areas. At Medicine Lake, a low attenuation, normal velocity area was interpreted to be a dry or steam-saturated area beneath the water table.

Because of substantial industry interest in this method, LLNL decided to apply it at The Geysers, where the predictions of the existence of steam zones could be tested. In a cooperative project, Unocal Corporation and Lawrence Livermore National Laboratory are working together to utilize existing microearthquake data for a three-dimensional interpretation of both the seismic velocity structure and the attenuation properties of the geothermal field. In this study LLNL is using natural microearthquakes as seismic sources to test the hypothesis that high seismic velocity and low attenuation occur where steam is present. If this method is successful, it could be applied to other seismic data sets collected at The Geysers.

Unocal has recorded waveforms and picked P-wave arrival times for thousands of microearthquakes recorded over a five year period, and are providing LLNL with a comprehensive set of the "best" events. LLNL is using the data from selected events to determine the apparent attenuation for each signal and to run inversion programs to produce 3-D models of attenuation and velocity. Results of the study should provide an improved ability to locate earthquakes, additional information about geologic structures, and possibly, the location of steam zones.

The study area is 10 km square and 5 km deep. The number of stations and the distribution of earthquakes provides excellent coverage of the target volume. Presently, LLNL is resolving source volumes of 1 km cubed and is examining ways to improve resolution of the inversion to better than 0.5 km. This type of study is possible in most areas that have recorded microearthquakes or artificial explosions from a wide variety of locations with stations distributed over the area of interest.

Graphic presentation of the inversion results provides a means to compare the structural interpretations with geologic maps or hypocentral locations. When final images of velocity and attenuation are completed this summer, LLNL will relate them to geologic features and make predictions about the occurrence of steam.

The Unocal contribution to this work has been substantial. By supplying LLNL with high-quality seismic data collected over several years, they have saved DOE several hundred thousand dollars, and have allowed LLNL to complete this project in one year instead of three. LLNL looks forward to other fruitful cooperative efforts with industrial operators at The Geysers.

ORNL
(R. E. Mesmer)

Geochemical Research

The object of this research is to obtain needed thermodynamic and kinetic data for input into geochemical models which predict the phase behavior and corrosion characteristics of geothermal brines. Of particular interest are reactions involving highly saline solutions, for which no adequate theoretical predictive capabilities exist. Reactions important in controlling reservoir permeability, brine chemistry, plant scaling, and corrosion are the major concerns of this program. Needed data include activity coefficients, gas solubilities, and selected rate constants in the range of 0-350°C and 0-6 molal ionic strength for components of the system H-Na-K-Ca-Mg-Fe-Al-B-C-O-S-Si-Cl and the metals Pb-Mn-Zn-Cu, etc.

The current program addresses the ion interaction parameters of bisulfate ion-- HSO_4^- --with H^+ and Na^+ , the dissociation constant of HSO_4^- , the solubility and speciation of aluminum in the system H^+ - Na^+ - K^+ - Cl^- - OH^- , and the distribution of HCl to steam. Results are available as input to the computer codes being developed by J. Weare and others, which model the effects of chemical equilibria and salinity on the geochemistry and engineering chemistry of geothermal facilities.

Liquid-Vapor Distribution of HCl to 350°C:

This project addresses physical chemical measurements relative to understanding the origin and transport of chloride in superheated geothermal steam systems such as The Geysers and Larderello, Italy. In order to assess the physical and chemical conditions for production and handling of the HCl-containing steam, new information on the distribution of HCl between liquid and vapor are needed at high temperatures as a function of brine composition. The motivation for the work comes from the accelerated corrosion caused by the presence of HCl in steam in contact with well casings and parts of the steam collection and handling systems of geothermal power plants.

HCl is strongly dissociated in the liquid phase at temperatures well below the water critical temperature but is strongly associated in the steam phase. Mass action suggests an increase in

the volatility with decreasing pH and with increasing chloride activity in the liquid phase. We have constructed an apparatus for equilibrating HCl solutions in a noble metal lined pressure vessel fitted with a pressure transducer, inert tubing, and valves. The K_D values are being evaluated from volatility measurements to about 350°C on solutions for which activity coefficients for HCl are known.

Thermodynamic Parameters for NaHSO_4 and H_2SO_4 :

The electrolyte solutions encountered in real-world situations such as in geothermal brines typically contain several cations and anions, some at relatively high concentrations. The extents to which solids precipitate and various chemical reactions occur in these complex systems depend not only on the (generally known) concentrations of the individual components but also on their (generally unknown) activity coefficients. The sulfate-bisulfate ratio is an important pH buffer in many such systems and the thermodynamic information for bisulfate, as well as for the bisulfate ionization equilibrium, are lacking for a complete chemical model of these systems. We have obtained osmotic data from isopiestic measurements on NaHSO_4 and H_2SO_4 solutions to 250°C and to about 5 molal. These data are being analyzed in detail along with other relevant data in the literature to derive ion-interaction parameters useful in the Pitzer model. Results can be combined with other thermodynamics to develop a comprehensive model for multicomponent brines.

The osmotic coefficient is a useful thermodynamic function which is defined in terms of the activity of the solvent (water in the present case). Figure 2 compares the osmotic coefficients of $\text{NaCl}(\text{aq})$ and $\text{NaHSO}_4(\text{aq})$ at 100 and 200°C. Standard data for $\text{NaCl}(\text{aq})$ at these two temperatures are shown as the dashed lines. The points are results from ORNL isopiestic experiments on $\text{NaHSO}_4(\text{aq})$ with $\text{NaCl}(\text{aq})$ as the osmotic standard. Osmotic coefficients for $\text{NaHSO}_4(\text{aq})$ are stoichiometric, i.e., computed on the assumption that NaHSO_4 dissociates into three ions (the infinitely dilute standard-state condition), and are useful as is for calculations involving the solvent activity.

Dissociation Constant of Bisulfate in NaCl Brines to 5 Molal and 150°C:

The sulfate/bisulfate ratio is an important pH buffer in many geothermal systems and the activity coefficients of sulfate and bisulfate are needed for modeling the solubility of the sulfate minerals and calcium phases (such as calcite) in brines as a function of temperature and total salinity. The dissociation constant of bisulfate ion, $Q = \frac{m(\text{H}^+) m(\text{SO}_4^{2-})}{m(\text{HSO}_4^-)}$ was measured potentiometrically in a hydrogen-electrode concentration cell in 0.1 to 5.0 molal

NaCl solutions from 50 to 250°C. The results have been combined with literature data and fit to a function of temperature and ionic strength over the range 0-250°C and 0-5.0 molal ionic strength (Figure 3) using a modified form of the Pitzer ion interaction model (solid lines in Figure 3).

These results demonstrate the dominant effect of salinity, as well as temperature, on this important pH buffer. Because bisulfate dissociates appreciably to sulfate and hydrogen ions at elevated temperatures and ionic strengths, independent knowledge of the dissociation constant is needed in order to model the isopiestic data discussed above.

Aluminum Speciation and Gibbsite Solubility in Brines at Elevated Temperatures:

A knowledge of the aqueous chemistry of monomeric aluminum species is needed in order to model the evolution of porosity and solution chemistry (pH, cation ratios, etc.) in geothermal systems, because the stabilities of aluminosilicate minerals (clays, feldspars, zeolites, etc.) control these parameters. Therefore, we have undertaken a systematic study of the solubility of aluminum oxyhydroxides as a function of salinity and temperature, coupled with novel potentiometric measurements, in order to work out the speciation and activity coefficients of aqueous aluminum. Work completed thus far (funded jointly by DOE's Basic Energy Science and Geothermal Technology Division) includes the solubility of gibbsite, $\text{Al}(\text{OH})_3$, in: (a) NaCl-HCl brines from 30-70°C and 0-5 molal ionic strength (free energies and activity coefficients of Al^{3+}); (b) $\text{Na}^+\text{-K}^+\text{-OH}^-\text{-Cl}^-$ brines from 5 - 100°C (free energies and activity coefficients of $\text{Al}(\text{OH})_4^-$); and (c) NaCl brines buffered in the near neutral pH range at 50°C (species intermediate between Al^{3+} and $\text{Al}(\text{OH})_4^-$ as well as formation constants for complexes of these ions with acetate and other soluble organic compounds). We have also determined the formation constants of $\text{Al}(\text{OH})_2^+$ and aluminum acetate to 125°C in 0.1 molal NaCl from potentiometric titrations.

The logarithm of the total molality of dissolved aluminum in equilibrium with gibbsite at 50°C in 0.1 molal NaCl solutions is shown as a function of the negative log of the hydrogen ion molality on Figure 4. The plotted points were obtained by measuring gibbsite solubility in NaCl solutions in which the hydrogen ion molality was fixed by a variety of organic buffers. The straight lines indicate the results of other experiments in which the solubility of gibbsite was measured over a wide range of temperatures and ionic strengths in: sodium chloride plus HCl solutions in which Al^{3+} is the dominant aluminum species; and in sodium chloride plus sodium hydroxide solutions in which $\text{Al}(\text{OH})_4^-$ is the dominant species. The curve for $\text{Al}(\text{OH})_2^+$ was obtained from potentiometric titrations of Al^{3+} plus sodium chloride plus HCl

solutions using a hydrogen electrode concentration cell. As can be seen, the results of these earlier studies agree very well with the results from the buffer runs. The shape of the solubility curve near its minimum can now be used to extract the formation constants of species intermediate between $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_4^-$. Early in this study, it was discovered the Al^{3+} forms a strong complex with acetate, one of the buffers used in the study. This has very important implications for secondary porosity development in sedimentary basins and geothermal systems, because acetate is the most abundant soluble organic acid produced during the thermal decomposition of buried organic material in these settings.

Future work will involve boehmite, AlOOH , solubility studies at temperatures to 300°C and continued potentiometric studies of aluminum hydroxide species and complexes with chloride, other inorganic anions, and carboxylic acids. The interaction of aluminum with organic compounds is most interesting because it provides a mechanism for secondary porosity development in sedimentary basins and geothermal systems in which abundant organic material is thermally decomposing to produce carboxylic acids and other water-soluble organic compounds.

Geothermal Technology Organization

INEL also supports the geothermal industry's Geothermal Technology Organization, a geothermal industry group seeking to advance the state-of-the-art of geothermal technology through:

- o conducting cooperative research under the "National Cooperative Research Act of 1984,
- o sharing research costs with the DOE,
- o facilitating the industrial development of basic research results, and
- o advising the research community of the geothermal industry's needs.

The organization was formalized and entered into an agreement for cooperative research with DOE in the Spring of 1988. Membership is open to all who have an interest in geothermal development.

The Geothermal Technology Organization (GTO):

- o funds research in reservoir performance and energy conversion technology,
- o seeks research with high probability of short term benefits, and
- o shares costs -- industry 51%, DOE 49%.

GTO and DOE have completed a study of the applicability of advanced seismic techniques to monitor injection and productivity enhancement at the Geysers steam field and additional projects are under discussion. Much of the proposed cooperative research at The Geysers may be funded through the GTO.

National Energy Strategy

INEL, in conjunction with several other National Laboratories and the Solar Energy Research Institute, prepared an analytical study of the potential for development of renewable energy resources over the next 40 years. INEL was involved in the preparation of the portions of the document dealing with geothermal resources and hydropower. The geothermal section attempted to take a reasonable approach to the development of hydrothermal resources and the advanced geothermal resources such as geopressured, hot dry rock and magma. However, the anticipated growth in utilization of hydrothermal resources, in particular, may be too conservative.

One outcome of the preparation of this is the realization that there does not exist a suitable data base on which to estimate future geothermal production relative to increases in cost of electricity and little data is publically available with which to estimate undeveloped reserves or undeveloped, nearly economic resources. INEL is initiating a program to develop such data bases and is seeking the support of industry. In order to protect proprietary interests of the geothermal industry, reserve estimates will be made publically available only as a national aggregate.

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