

## REDUCING COST AND ENVIRONMENTAL IMPACT OF GEOTHERMAL POWER THROUGH MODELING OF CHEMICAL PROCESSES IN THE RESERVOIR

*by*

Minh Pham, Christopher Klein, and Subir Sanyal  
GeothermEx, Inc.  
Richmond, California  
e-mail: mw@geothermex.com

*and*

Tianfu Xu and Karsten Pruess  
Lawrence Berkeley National Laboratory  
Berkeley, California  
e-mail: tianfu\_xu@lbl.gov; k\_pruess@lbl.gov

**Key Words:** geothermal reservoir, chemical processes, numerical modeling, geochemical modeling.

### ABSTRACT

Geothermal power generation and mineral extraction from geothermal brines are affected by chemical processes within the reservoir. Until recently, numerical simulation technology for geothermal systems could not handle most chemical processes, except for tracking total salinity, one or two non-condensable gases, and non-reactive tracers. The Lawrence Berkeley National Laboratory (LBNL) has developed an enhanced version of their geothermal reservoir simulation software TOUGH2, developed with funding from the U.S. Department of Energy. This highly innovative software (TOUGHREACT) includes comprehensive chemical interactions between liquid, gaseous and solid phases that are coupled to the modeling of solute transport and subsurface multiphase fluid and heat flow.

GeothermEx, Inc., in collaboration with LBNL, is verifying the applicability of the TOUGHREACT software to a set of practical chemical problems encountered in typical geothermal fields in California. These example problems, drawn from published industry experience, include: (i) recovery of minerals from geothermal brines, (ii) effect of injecting silica-supersaturated brine in wells, (iii) effect of injecting acidic brine originating from various fluid handling processes; (iv) minimizing gas production through optimized water injection, and (v) modeling of chemically-reactive tracers. All five problems are important to the geothermal industry in California; their solution can help reduce the cost and environmental impact of geothermal power.

To date, our evaluation has confirmed the ability of TOUGHREACT to handle the first four of the above-mentioned problems; the last problem is now under consideration. This study has pointed out the need for improvements in some features of TOUGHREACT to make it more useful for practical application.

### 1. INTRODUCTION

Geothermal power generation and mineral extraction from geothermal brines are significantly impacted by the chemical processes within the reservoir. Until recently, numerical simulation technology for geothermal systems could not handle most chemical processes, except for tracking total salinity, one or two non-condensable gases, and non-reactive tracers. The Lawrence Berkeley National Laboratory (LBNL) has developed an enhanced version of their geothermal reservoir simulation software TOUGH2, developed with funding from the U.S. Department of Energy. This highly innovative software (TOUGHREACT) includes comprehensive chemical interactions between liquid, gaseous and solid phases that are coupled to the modeling of solute transport and subsurface multiphase fluid and heat flow. The new software is fully developed and undergoing evaluation to determine its utility and application to the chemical processes in actual geothermal systems. Such field trials are needed to verify the practical feasibility of this modeling approach for actual fields and to identify needed improvements in the software's capabilities and "user friendliness".

GeothermEx, Inc., is working in collaboration with LBNL to verify the applicability of the TOUGHREACT software in solving a set of practical chemical problems encountered in typical geothermal fields in California. Solutions to these problems can

help reduce the cost and environmental impact of geothermal power.

## 2. DESCRIPTION OF TOUGHREACT

This study involves numerical simulations of non-isothermal reactive geochemical transport using the TOUGHREACT software [Xu and Pruess, 1998]. This model was developed by introducing reactive geochemistry into the framework of the existing multi-phase fluid and heat flow code TOUGH2 [Pruess, 1991]. The flow and transport in geologic media are based on space discretization by means of integrated finite differences [Narasimhan and Witherspoon, 1976]. An implicit time-weighting scheme is used for the individual components of the model: fluid flow, heat transfer, chemical transport, and geochemical reactions.

TOUGHREACT uses a sequential iteration approach similar to Yeh and Tripathi [1991]. After solution of the flow equations, the fluid velocities and phase saturations are used for chemical transport simulation. The chemical transport is solved on a component basis. The resulting concentrations obtained from the transport are substituted into the chemical reaction model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration, similar to Parkhurst [1980], Reed [1982], and Wolery [1992]. The chemical transport and reactions are iteratively solved until convergence.

The model can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity. The model can accommodate any number of chemical species present in liquid, gas and solid phases. A wide range of subsurface thermo-physical-chemical processes is considered. The major processes considered for fluid and heat flow are: (1) fluid flow in both liquid and gas phases under pressure and gravity forces, (2) capillary pressure effect, and (3) heat flow by conduction, convection and diffusion. Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid and gas phases. Aqueous chemical complexation and gas (CO<sub>2</sub> only, see below) dissolution/exsolution are considered under the local equilibrium assumption. Mineral dissolution and precipitation can be modeled either subject to local equilibrium or kinetic conditions.

The following processes are neglected in the current model: (1) compaction and thermal mechanics, such as micro-fracturing by thermal stress and hydro-fracturing by thermal expansion of pore fluid, (2) the effect of chemical concentration changes on fluid thermophysical properties such as density and viscosity which are otherwise primarily dependent on

pressure and temperature, and (3) the enthalpy of chemical reactions.

The model has previously been applied to a range of subsurface geochemical transport problems such as: (1) supergene copper enrichment in unsaturated-saturated media (Xu et al., 1999), (2) coupled thermal, hydrological, and chemical processes induced by emplacement of a strong heat source to represent a high-level nuclear waste repository (Sonnenthal and Spycher, 2000), and (3) mineral alteration in fractured caprock of magmatic hydrothermal systems (Xu and Pruess, 2001).

## 3. TEST CASES

To check the software capabilities in simulating chemical processes in actual geothermal reservoirs, five test cases were devised to examine the chemical features of TOUGHREACT. Each test case concerns a specific chemistry-related problem, the solution of which would help improve reservoir management or mineral recovery, and thereby, reduce the cost and environmental impact of geothermal power in California.

An idealized two-dimensional simulation model was used to simulate the behavior of the chemical species in the test cases. The model consists of 50 grid blocks, each 100m by 100m by 100m in dimension with 10 blocks in the x-direction, 5 blocks in the y-direction, and 1 block in the z-direction. The model contains a production well, an injection well, and an observation well (Figure 1). Temperature and pressure distributions in the model were maintained by one recharge source and one discharge sink as shown in figure 1. In each case, the model was run for 50,000 years to allow for thermodynamic conditions to reach steady state. Once thermodynamic steady state is achieved, chemical species were introduced into the model and the model was allowed to chemically stabilize for an additional 100 years before production or injection began.

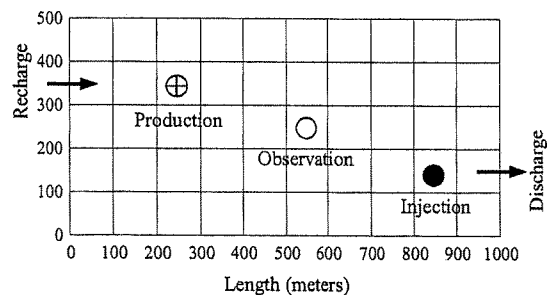


Figure 1: Two-dimensional model used in the study

### 3.1 Mineral Recovery

Commercial recovery of zinc from the geothermal brine is being practiced or considered at geothermal fields in Imperial Valley of California; recovery of silica and manganese will soon follow. Extraction of silver and lead from geothermal brine has also been considered. There are vast reserves of dissolved minerals in the brines of hyper-saline geothermal fields in the Imperial Valley. Therefore, this problem has major economic significance.

Publicly available chemical data on the hyper-saline brine from Imperial Valley geothermal fields were obtained and input to the model. The temperature and pressure of the recharge fluid were assigned values such that the initial-state thermodynamic condition of the model is representative of shallow subsurface conditions encountered in these hyper-saline fields. The reservoir rock in the model for this problem was assumed to contain only quartz (99% of rock volume), and sphalerite (ZnS) (1% of rock volume).

At steady state conditions, the zinc distribution in the aqueous phase is shown in Figure 2. The zinc distribution shown in Figure 2 was calculated by TOUGHREACT based on the thermodynamic and kinetic conditions in the model, the amount of zinc in the recharge fluid, and the amount of sphalerite in the reservoir rock. Chemical reactions from other chemical species in the reservoir fluid have an influence on the zinc distribution; however, this influence is small. With the initial zinc distribution calculated, we had a baseline for checking the effect of production and injection on the zinc distribution in the reservoir.

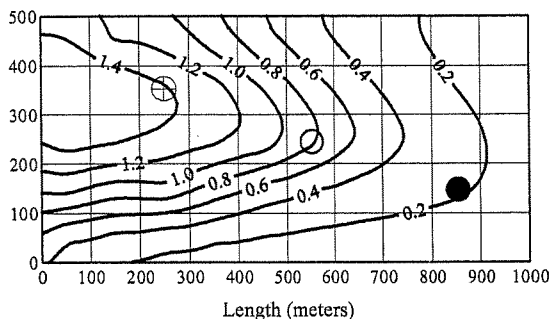


Figure 2: Initial zinc distribution in the geothermal brine (E-6 moles/liter of liquid)

A constant brine production rate of 8 kg/s was assigned for the production well. This rate was assumed to be much smaller than the production rate from an actual well in consideration of the small reservoir volume considered. This same amount of fluid brine was then injected back into the reservoir

assuming that the zinc in the produced fluid has been fully extracted at the surface. Temperature of the injected fluid was assumed to be 75°C.

Figure 3 shows the effect of injecting zinc-depleted brine on the reservoir zinc distribution after 20 years of production and injection. As injection of zinc-depleted brine continues, the plume of zinc-depleted, cool injection fluid begins to push outward in the direction of the production well. After 20 years, this plume reaches close to the observation well and the zinc concentration in this area approaches zero. The rate of change in the zinc concentration is, of course, highly dependent on the amount of production and injection assumed in the model.

The change in the zinc distribution shown in Figure 3 contains the effects of both mixing and chemical reaction between the zinc-depleted brine and the sphalerite (ZnS) mineral present in the rock. No attempt has been made to quantify these effects individually as this would require a much larger number of simulation runs, beyond the scope of the current study.

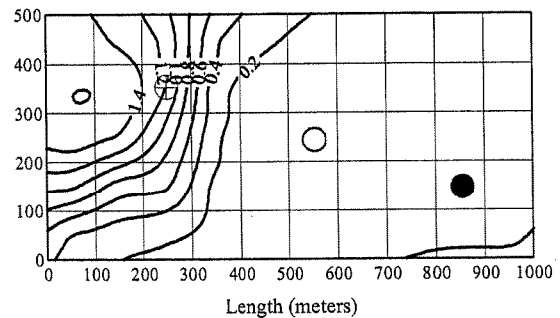


Figure 3: Final zinc distribution in the geothermal brine (moles/liter of liquid)

Figure 4 shows the change in the zinc concentration at the production well. As shown in this figure, zinc concentration remains relatively constant throughout the simulation period, as the zinc-depleted injection brine has not yet approached the assumed production area.

Appropriate data have been input to the model to reflect the actual brine conditions at Imperial Valley geothermal fields. As such, total dissolved solids (TDS) were assumed to be 28% by weight in the injection brine. Although TOUGHREACT is capable of performing the necessary calculations, the thermodynamic database used by the software considers TDS of up to only 20% by weight. Therefore the database was extrapolated for a 28% TDS level and calculations were done based on that extrapolation. It is necessary to modify the thermodynamic database in order to handle the

hyper-saline brine accurately; however, this is beyond the scope of the present study.

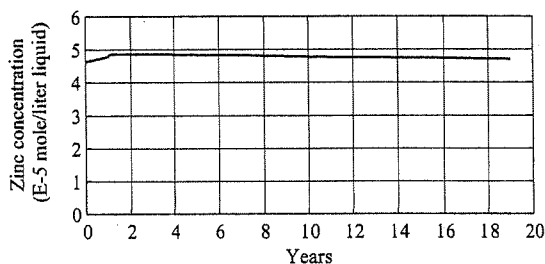


Figure 4: Changes in zinc concentration at the production well

The results from these simulation runs suggest that TOUGHREACT can model the zinc recovery process at the hyper-saline geothermal reservoirs in Imperial Valley, California. Zinc concentration distribution in the aqueous phase calculated by TOUGHREACT appears consistent with the zinc concentration distribution found in actual reservoir condition under similar temperature and pressure conditions. Exact comparison cannot be made at present, as the thermodynamic conditions in the test model do not correspond precisely with the actual thermodynamic conditions in the reservoir. However, they are sufficiently similar to conclude that the TOUGHREACT code can simulate zinc recovery from geothermal brine.

### 3.2 Effects of Injecting Silica-Supersaturated Brine

The waste fluid from a geothermal power plant is often supersaturated with silica. Injection of this supersaturated fluid causes scaling around the wellbore. This increases the operating cost of a geothermal project. Therefore, control of silica scaling has significant economic impact.

The effects of injecting silica-supersaturated fluid on various parameters in the reservoir were investigated. To perform the comparison, a base case was considered in which the injected fluid contained the same TDS and silica concentration as the reservoir fluid. Once the base case was established, comparison could be made under different injection scenarios.

One of the runs considered a hyper-saline brine injection. This type of injection fluid is commonly found at geothermal fields in the Imperial Valley, California. The injected fluid was assumed to contain 28% TDS at a pH of 7. The chemical species contained in the injection fluid were assumed to be typical of the silica supersaturated injection brine at a temperature of 75°C.

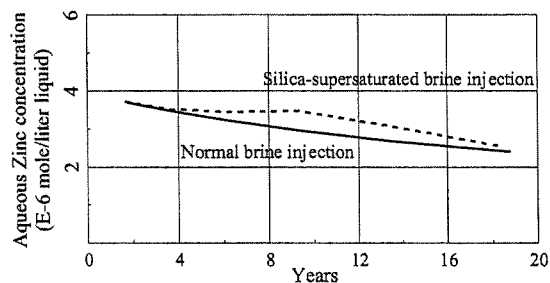


Figure 5: Effects of injecting the silica-supersaturated brine on aqueous zinc concentration at observation well

The results from the run (Figure 5) show that the injection of the silica-supersaturated brine has only a minor effect on the zinc concentration in the reservoir. Effects were similar on the extraction of other minerals in the model. This suggests that the injection of silica-supersaturated brine has only minimal impact on the chemical reactions occurring in the reservoir.

TOUGHREACT is capable of calculating the rate of silica scale deposition in the reservoir and the consequent change in the porosity of the reservoir rock. The amount of silica precipitation was calculated for each individual block in the model and this precipitation was assumed to occupy the available pore space, causing a reduction in the porosity of the rock. This change in porosity, in turn, results in a reduction in the permeability of the rock.

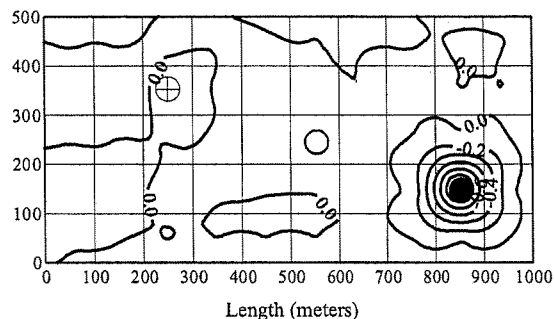


Figure 6: Porosity change (E-3) after 20 years due to injection of silica-supersaturated brine

In this run, the relative changes in the porosity and permeability were small as the fluid in the reservoir remains single-phase. Figure 6 shows the changes in porosity after 20 years of injecting the silica-supersaturated brine. The highest decrease is seen at the injection block with a value of about -0.001. This is extremely small, only 1% of the initial reservoir porosity of 0.1.

In another run, the pH of the injected brine was reduced from 7 to 2. This change in pH has a major impact on the rate of mineral dissolution, as shown in Figure 7. When pH of the injected brine was lowered to 2, the zinc from sphalerite in the rock began to dissolve resulting in an increase in the zinc concentration in the aqueous phase. As in the previous run, negligible changes in porosity and permeability were noted. This is expected as the reservoir was assumed to be single-phase and the rock types in the reservoir were not highly reactive.

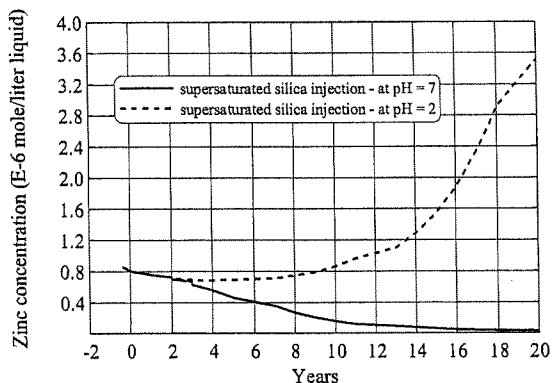


Figure 7: Effect of injecting low pH brine on aqueous zinc concentration at observation well

It appears that TOUGHREACT possesses the necessary features for the calculation of silica scale deposition in a hyper-saline brine reservoir undergoing zinc extraction. However, it is difficult to verify the accuracy of these calculations, as actual data on scale deposition in a geothermal reservoir are limited. Furthermore, the rate of scale deposition was calculated using reaction rates obtained from laboratory testing under ideal conditions. The validity of applying these laboratory reaction rates to actual field conditions requires further verification from field data.

### 3.3 Low pH Fluid Injection

The waste brine is sometimes acidified before injection to prevent silica scaling in the injection wellbore. There have been concerns regarding the long-term effects of this practice on the reservoir behavior. This problem was studied using TOUGHREACT. The basic two-dimensional model described above was used to examine the effect of this low pH fluid on different types of rock formations.

Three distinctly different reservoir rock formations were considered; sandstone (found in the reservoirs of the Imperial Valley), an intrusive rock (similar to the felsite unit encountered at The Geysers,

California or the granitic reservoir rock at Coso, California) and a volcanic rock (typical of many geothermal systems around the world). Table 1 shows the composition of the volcanic rock considered in the model.

| Mineral      | Volume Fraction |
|--------------|-----------------|
| Quartz       | 0.35            |
| Cristobalite | 0.25            |
| K-feldspar   | 0.30            |
| Albite       | 0.02            |
| Anorthite    | 0.02            |
| Kaolinite    | 0.01            |
| Muscovite    | 0.01            |
| Pyrophyllite | 0.01            |
| Calcite      | 0.02            |
| Paragonite   | 0.01            |

Table 1: Mineral composition of the volcanic rock

Figure 8 shows the changes in calcite and kaolinite concentrations in the volcanic rock (at the observation well block) with time due to a change in the pH of the injected fluid. Note that the concentration of calcite in the rock matrix of the observation well block declined as fluid pH was lowered, while the concentration of kaolinite, which precipitates in an acidic environment, increased.

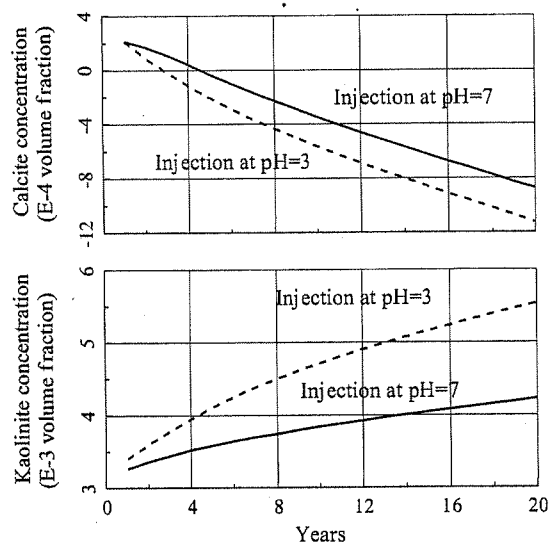


Figure 8: Effects of low pH injection on reservoir minerals

The trend in concentration change with time is highly dependent on the minerals present in the system, the relative amount of each mineral in the system, the value of the reaction rates associated with each rock type, and several other parameters.

The resulting changes in porosity and permeability caused by the dissolution of the rock cement or precipitation in the pore space were calculated by the simulator. In general, the rock with the highest reaction rate experiences the highest rate of dissolution/precipitation from the low pH injection fluid. However, the changes in rock porosity and permeability appear to be relatively small.

### 3.4 Long Term Trends in Gas Production

As the gas content in steam increases, the efficiency of generation at the power plant decreases, the abatement cost of H<sub>2</sub>S increases, and the discharge of greenhouse gases from the plant increases. Therefore, forecast of long-term trends in gas content of the produced steam affects the cost and environmental impact of geothermal power.

At this stage, TOUGHREACT is not capable of calculating the chemical interactions between various chemical species in the gaseous phase. Only a single gaseous specie (such as CO<sub>2</sub> or H<sub>2</sub>S) and its dissolution/exsolution under local equilibrium can be included in the model at one time. Two additional gaseous components can also be specified as tracers. Their effect on the fluid thermodynamic conditions is ignored. However, since the most abundant non-condensable gas in a geothermal reservoir is usually CO<sub>2</sub>, this feature of TOUGHREACT still allows one to perform simulations to optimize the injection scheme in order to minimize the amount of gas production at the surface.

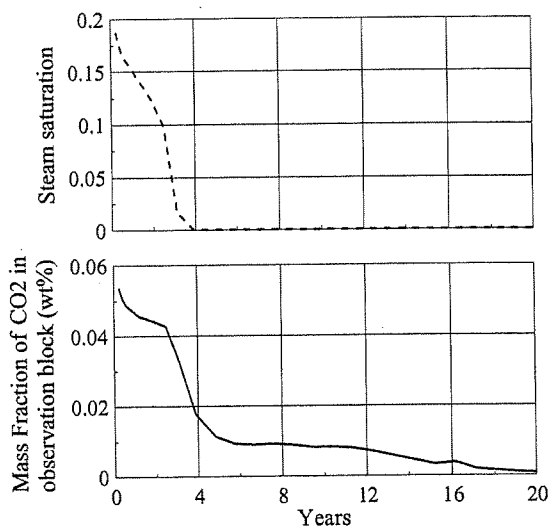


Figure 9: Effects of injection on long term gas production

To examine how the gas content can be affected by injection, the model was run assuming the reservoir fluid to be pure water/steam. CO<sub>2</sub> content in the reservoir was assigned at 0.05% weight in the reservoir two-phase mixture and the model was then run to steady-state. The distribution of CO<sub>2</sub> gas was automatically calculated by the model based on thermodynamic condition in the model and the content of CO<sub>2</sub> in the recharge fluid. After stabilization occurred, one injection and one production well were added to the model and the simulation was run for 20 years.

The effect of injection of gas-free waste fluid on the long-term gas production trend in the reservoir is seen from Figure 9. Plotted in this Figure are steam saturation and CO<sub>2</sub> mass fraction in the water/steam mixture in the observation well block. Steam saturation and CO<sub>2</sub> content decline as the cool, gas-free injection water migrates toward the production well. Therefore, injection of gas-free waste water would reduce the gas content of produced steam.

The results from the runs made to date suggest that TOUGHREACT is capable of simulating the main effects of injection on long-term production trends of the main gas component, CO<sub>2</sub>. Behavior of other gases such as H<sub>2</sub>S, ammonia, etc, cannot be properly modeled at this time. Chemical interactions between the various chemical species in the gaseous phase need to be incorporated into the software. However, this work is beyond the scope of the current study.

The chemically-reactive tracer feature of TOUGHREACT has not been tested yet; we have scheduled this test for the First Quarter of 2001.

### 4. CONCLUSIONS

- TOUGHREACT can be used for simulation of zinc recovery from geothermal brines. Dilution of *in-situ* fluids due to mixing between mineral-depleted injection fluid and reservoir brine, as well as chemical interactions between the injected brine and minerals in the rock matrix is accounted for in TOUGHREACT.
- The amount of TDS considered in the thermodynamic database used by the software is at present limited to 20% by weight. This is less than the TDS amount found in hyper-saline reservoirs, in the Imperial Valley, California, where vast reserves of minerals exist in the geothermal reservoirs. This limitation can be and should be removed.
- Effects of silica super-saturated liquid injection can be effectively modeled by TOUGHREACT. Silica precipitation is accounted for, and its

effect on reservoir porosity and permeability can be simulated.

- TOUGHREACT is capable of simulating the effects of the pH of the injected fluid on chemical species in the reservoir fluid as well as on the reservoir rock. This feature is relevant to many fields in the world, where mitigation of silica scaling requires the injection of low pH fluid.
- Gas production trends for a producing geothermal field can be studied using TOUGHREACT. Although the software does not currently allow chemical interactions between the chemical species in the vapor phase, the CO<sub>2</sub> dissolution/exsolution feature in the software still permits forecasting of long-term gas production trend for most practical purposes. This feature can be useful in optimizing the injection scheme to reduce the content of non-condensable gases in the produced steam (assuming it is mainly CO<sub>2</sub>). Other gases such as H<sub>2</sub>S or ammonia are not included in the software at this time.
- The goal of this work is to evaluate the usefulness of the TOUGHREACT code in improving geothermal reservoir management and optimizing mineral recovery from geothermal brines, thus reducing the cost and environmental impact of geothermal power. Based on the work completed to date, we believe that this goal is achievable. The work done to date suggests that the software can vastly enhance the simulation capability currently available in the geothermal industry. Further testing to be undertaken during the next few months will shed additional light on the usefulness of TOUGHREACT in geothermal reservoir management, power generation and mineral recovery.
- TOUGHREACT currently possesses most of the necessary tools for the calculation of the chemical reactions occurring in a wide range of geothermal reservoir conditions and processes. The accuracy of the equations used in the software under actual reservoir conditions needs to be tested further. The equations used to calculate the chemical reactions are highly non-linear, and the coefficients used in these equations are mostly derived from limited laboratory data obtained under ideal conditions, which may not always represent actual reservoir conditions.

## 5. DISCLAIMER

The goal of this study is to evaluate the usefulness of the TOUGHREACT code in simulating the chemical interactions between chemical species in the geothermal fluid. Although publicly available data have been used, the model described in this paper is purely hypothetical and not intended to represent the performance of any actual wellfield.

## 6. ACKNOWLEDGEMENTS

The authors gratefully acknowledge two important funding sources. The first is California Energy Commission's Energy Innovations Small Grant Program to GeothermEx, Inc. (Grant Number 51391A/99-25). The work was also funded in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Geothermal and Wind Technologies, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## 6. REFERENCES

- Helgeson C. H., 1968. Geologic and thermodynamic characteristics of the Salton Sea geothermal system, *American Journal of Science*, Vol. 266, pp 129-166, March 1968.
- Narasimhan, T. N., and P. A. Witherspoon, 1976. An integrated finite difference method for analyzing fluid flow in porous media, *Water Resour. Res.*, 12, pp. 57-64.
- Parkhurst, D. L., D. C. Thorstenson, and L. N. Plummer, 1980. PHREEQE: A computer program for geochemical calculations, US Geol. Surv. Water Resour. Invest. 80-96, 174 pp.
- Pruess, K., 1991. TOUGH2: A general numerical simulator for multiphase fluid and heat flow, Lawrence Berkeley Laboratory Report LBL-29400, Berkeley, California, 37 pp.
- Reed, M. H., 1982. Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases and aqueous phase, *Geochim. Cosmochim. Acta*, 46, pp. 513-528.
- Sonnenthal, E., and N. Spycher, 2000. Drift-scale coupled processes model, analysis and model report (AMR) N0120/U0110, Yucca Mountain Nuclear Waste Disposal Project, Lawrence Berkeley National Laboratory, Berkeley, California.
- Wolery, T. J., 1992. EQ3/6: Software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7.0),

Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, California.

Xu, T., and K. Pruess, 1998. Coupled modeling of non-isothermal multiphase flow, solute transport and reactive chemistry in porous and fractured media: 1. Model development and validation, Lawrence Berkeley National Laboratory Report LBNL-42050, Berkeley, California, 38 pp.

Xu, T., K. Pruess, and G. Brimhall, 1999. An improved equilibrium-kinetics speciation algorithm for redox reactions in variably saturated flow systems, *Computers & Geosciences*, 25, pp. 655-666.

Xu, T., and Pruess, K., 2001. On fluid flow and mineral alteration in fractured caprock of magmatic hydrothermal systems, *Journal of Geophysical Research*, (also Lawrence Berkeley National Laboratory report LBNL 44804; both in press).

Yeh, G. T., and V. S. Tripathi, 1991. A model for simulating transport of reactive multispecies components: model development and demonstration, *Water Resour. Res.*, 27, pp. 3075-3094.