TRANSPORT OF REACTING CHEMICALS IN A TWO-PHASE RESERVOIR

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SUMMARY - A mathematical model of multi phase transport of heat, mass, and reacting chemical species in a porous media is developed. The model is appropriate for describing many of the reactions that take place in a geothermal reservoir. This model leads to the separation of transport terms from reaction terms in the equations for chemical species concentration. A numerical method for the solution of the transport equations is developed based on the integrated finite difference method. Four example problems representative of those of interest in geothermal reservoirs are solved. These examples consider up to 14 chemical species and 9 chemical reactions amongst these species.

1 Introduction

The interaction between chemical species and the transport and thermodynamic properties of the fluids within a geothermal system may be very important in determining the state of a system. For example, the presence of CO_2 may greatly alter the boiling point of fluid within a reservoir with obvious consequences for the thermodynamic state of the system. This behaviour is evident with many of the dissolved species, not just CO_2. Dissolved $NaCl$ may also be present in large enough amounts to give a significant change to the thermodynamic properties of fluid in the system from one containing pure water. Typically up to 10 chemical species concentrations are measured as part of the routine chemical monitoring of a productive geothermal field. One of the long term aims of this work is to improve predictions from numerical models of geothermal fields by specifically including many of these chemicals in the models. This will allow models to be tested against a much wider range of field measurements than at present with a consequent increase in reliability.

Precipitation of chemical species is an important consideration in geothermal reservoir management because of the effect it may have on reservoir permeability. It is also of interest in the exploitation of mineral deposits, for example porphyry copper deposits.

Chemical species measurements provide very valuable information about conditions within the earth that cannot be directly observed. This work aims to provide a tool that will enable surface chemical conditions to be predicted from assumed conditions (both chemical and physical) within the earth.

Recently much effort has been devoted to developing a quantitative approach to water rock interactions and also to reactions between chemicals being transported in the aqueous phase. These problems may be approached in a number of ways and depending on the physical characteristics of the problem a number of simplifying assumptions may be made. The most common assumptions are one or more of

1. the velocity field is uncoupled from chemical concentrations
2. thermal effects may be ignored
3. all chemical species are in equilibrium
4. no vapour phase.

Much of the work, particularly that concerned with transport of chemicals in the groundwater makes all these assumptions. Yeh and Tripathi (1989) provide a good review of this class of problem. Friedly (1991) and Friedly and Rubin (1992) consider a similar class of problems but without the assumption of chemical equilibrium. Lichtner (1992) has developed a quasi-stationary state approximation that works well for some problems but has a number of restrictions. Most recently Steefel and Lasaga (1994) have published a method that couples chemical transport with heat and mass transport and does not assume chemical equilibrium. They present several interesting examples and draw some conclusions about the assumption of chemical equilibrium in geothermal situations. Only the liquid phase is considered. White (1994) extended the approach of Friedly and Rubin (1992) to include the non-isothermal transport of chemical species in both the liquid and gas phases. And also to couple the equations for heat and mass transport to those for the transport of chemical species.

2 Model Formulation

In this section we outline the equations that describe the non-isothermal multi-phase flow of water, together with the transport of a system of reacting chemical species in a porous medium. The reacting chemicals may be in the gaseous, aqueous or solid phases. We assume: (a) that the Darcy equation describes fluid flow in the porous medium, (b) that the phases are in local thermal equilibrium and (c) that diffusion of chemical species may be ignored. No assumption is made regarding chemical equilibrium. There are N chemical species to be considered, although these may not all be present throughout the porous media. Of these, N_l are in the aqueous phase, N_g in the gaseous phase and N_s in the solid phase adsorbed on the rock matrix. Among these N chemical species, M chemical reactions can take place. The stoichiometry of these chemical reactions is written as (Friedly 1991)

$$0 = \sum_{i=1}^{N_l} \nu_{ij}^{(l)} A_i^{(l)} + \sum_{i=1}^{N_g} \nu_{ij}^{(g)} A_i^{(g)} + \sum_{i=1}^{N_s} \nu_{ij}^{(s)} A_i^{(s)} \qquad (1)$$

The matrices for the individual phases may be combined into the stoichiometric matrix for the system.

$$\mathbf{S} = \left[\begin{array}{ccc} \nu_{11}^{(l)} & \cdots & \nu_{1M}^{(l)} \\ \vdots & & \vdots \\ \nu_{N_l 1}^{(l)} & \cdots & \nu_{N_l M}^{(l)} \\ \nu_{11}^{(g)} & \cdots & \nu_{1M}^{(g)} \\ \vdots & & \vdots \\ \nu_{N_g 1}^{(g)} & \cdots & \nu_{N_g M}^{(g)} \\ \hline \nu_{11}^{(s)} & \cdots & \nu_{1M}^{(s)} \\ \vdots & & \vdots \\ \nu_{N_s 1}^{(s)} & \cdots & \nu_{N_s M}^{(s)} \end{array}\right] = \left|\begin{array}{c} \nu_{\textbf{mobile}} \\ \hline \nu_{\textbf{immobile}} \end{array}\right| \qquad (2)$$

This may be made clearer with an example. Consider the chemical reaction

$$FeCl_2 = Fe^{++} + 2Cl^-$$

This equation expresses the conservation of atoms in the chemical reaction. We take the coefficients of species on the left to be negative and the stoichiometric process can be represented as the chemical equation

$$0 = \sum_{i=1}^{3} \nu_i A_i$$

Where $A_i(i = 1 \cdots 3) = (FeCl_2, Fe^{++}, Cl^-)^T$ and $\nu_i(i = 1 \cdots 3) = (-1, 1, 2)^T$ If a chemical is present in the system but does not take part in a reaction the ν_i for that chemical is set to zero.

The conservation equations for this system can now be written down.

For water

$$\frac{\partial}{\partial t}\left[\phi\left(s_l \rho_l x_{wl} + s_g \rho_g x_{wg}\right)\right] = -\nabla.\mathbf{F_w} + q_u. \qquad (3a)$$

where

$$-\mathbf{F_w} = x_{wl}\rho_l \frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathbf{g}) + x_{wg}\rho_g \frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g \mathbf{g}). \qquad (3b)$$

for heat

$$\frac{\partial}{\partial t}\left[(1-\phi)\rho_r C_r T + \phi\left(s_l \rho_l U_l + s_g \rho_g U_g\right)\right] = -\nabla.\mathbf{F_H} + q_H \qquad (4a)$$

where

$$-\mathbf{F_H} = H_l \rho_l \frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathbf{g}) + H_g \rho_g \frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g \mathbf{g}) + \lambda \nabla T \qquad (4b)$$

and for chemical species i

$$\frac{\partial}{\partial t}\left[(1-\phi)\frac{\rho_r x_{is}}{M_i} + \phi\left(s_l \rho_l x_{il} + s_g \rho_g x_{ig}\right)\right] = -\nabla.\mathbf{F_i} + q_i \qquad (5a)$$

where

$$\begin{aligned} -\mathbf{F_i} &= x_{il}\rho_l \tfrac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathbf{g}) + x_{ig}\rho_g \tfrac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g \mathbf{g}) \quad \text{fo} \\ &= 0 \end{aligned} \qquad (5b)$$

Here the subscripts l, $\mathbf{g}$, s refer to the liquid, gaseous and solid phases respectively; the subscripts w, i and H refer to water, chemical species i and heat respectively; s_β is the phase saturation; + the porosity; ρ_β the phase density; $x_{w\beta}$ the mole fraction of water in phase β; $x_{i\beta}$ the mole fraction of species i in phase β; k is the permeability; $k_{r\beta}$ the relative permeability for phase β; μ_β the viscosity in phase β; H_β the specific enthalpy of phase β; U_β the internal energy of phase β; g is the acceleration due to gravity; P_β is the pressure in phase β; q_w,q_H and q_i are source terms for water, heat and chemical species i respectively.

Each reaction described by equation (1) will have a rate constant

$$r_j = f([A_1^{(l)}], \cdots [A_{N_l}^{(l)}], [A_1^{(g)}], \cdots [A_{N_g}^{(g)}], [A_1^{(g)}], \cdots [A_{N_s}^{(s)}], T) \qquad (6)$$

associated with it ([A] denotes some measure of the activity of species A, T is temperature). The source term q_i in equation (5a) is given by

$$q_i = \sum_{1}^{N} \nu_{ij} r_j \qquad (7)$$

where ν_{ij} is an element in the stoichiometric matrix defined in equation (2). Where the species involved in a particular reaction (j say) are in equilibrium this can be expressed mathematically as $r_j = 0$.

Friedly (1991) and Friedly and Rubin (1992) have developed a theory of isothermal transport of reacting chemicals in the liquid phase and this has been extended by White (1994) to the non-isothermal transport of reacting chemicals in the liquid and vapour phases. Precipitation and dissolution of a solid phase is included in the theory. The method is based of separating equation (5a) into a transport and a reaction part. The reaction part is described by an ordinary differential equation **(ODE)** and the transport part by a partial differential equation. The transport part together with equations (3a) and **(4a)** are solved using a modified version of the computer program TOUGH2 (Pruess [1987, 1991, 1993], White and Kissling [19921). The ODE can be solved using one of a number of well known methods such **as** Runge-Kutta or in some cases has an analytic solution. The equations are potentially all coupled and must be solved simultaneously.

3 Examples

3.1 1-D Reservoir Simulation

As a test of the code, one of the simulations published by O'Sullivan et.al. [1985] was repeated. The simulation is a one dimensional model of a geothermal reservoir similar to the Ohaaki reservoir in New Zealand. The model consists of a cap-rock with a permeability of 0.5 milli-Darcy (md) and a thickness of 300 meters, overlying a reservoir with a permeability of 20 md and a thickness of 700 meters. Both have a thermal conductivity of 2 W/m/° C and a porosity of 0.1. Fluid with an enthalpy of 1300 **kJ/kg** and 1% CO_2 by mass is injected into the bottom of the reservoir at a rate of 2.02 kg/s/km^2. Grant's curves (Grant (1977)) are assumed for the relative permeability with residual **gas** and liquid saturations of 0.05 and 0.3 respectively. The top surface of the reservoir is fixed at a temperature 20° C and a pressure of 1 bar.

The most important chemical reaction is the reaction between gaseous CO_2 and aqueous CO_2 but we have also included other aqueous species associated with CO_2. The reactions considered are

$$\begin{array}{rcl} H^+ + OH^- & = & H_2O \\ H^+ + HCO_3- & = & H_2CO_3^* \\ HCO_3^- & \rightleftharpoons & CO_3^{--} + H^+ \\ H_2CO_3^* & \rightleftharpoons & CO_2(gas) \end{array}$$

Although they do not take part directly in any of these reactions Na^+ and Cl^- are present in the aqueous phase for some of the alculations. The reactions are assumed to reach equilibrium instantaneously. The gas equilibrium equation [6] reduces to

$$r([CO_2(aq)], [CO_2(gas)]) = 0, \qquad (8)$$

which may be written, assuming Henry's law applies, **as**

$$[CO_2(gas)]/[CO_2(aq)] = K_{Henry}(T) \qquad (9)$$

Here $[X]$ represents the activity of species X ,typically the paral pressure in the gaseous phase and in this example the mole 'action in the aqueous phase. Equilibrium equations for aqueus species are considered in the next example. The solution f this equilibrium equation and those appearing in examples and 3 is accomplished using locally developed software, the gorithm is contained in Weir et. al. (1994). The results of e simulation are shown in Figure 1 together with those of O'Sullivan et al. The reservoir is two phase throughout its depth with a **gas** saturation of just above residual. There is good agreement with the work of O'Sullivan below 500 meters; above 500 meters there is some deviation between the two curves. It is believed this is due to the use of different approximations to the thermodynamic properties of water and CO_2 mixtures used in the current work (White et. al. [19941). The partial pressure of CO_2 at shallow depths is extremely sensitive to conditions at depth and the discrepancies in figure 1 are quite acceptable

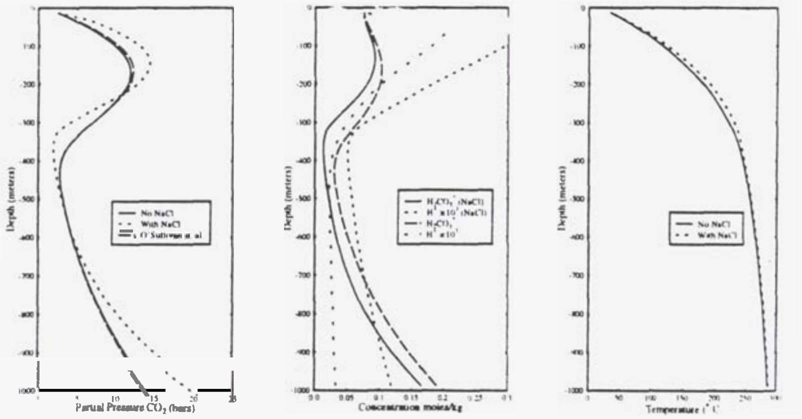


Figure 1: Vertical profiles of the partial pressure of CO_2 in a geothermal reservoir

3.2 Well-mixed Two-phase Reservoir

The second example considers the chemical changes occurring in an initially liquid dominated two phase reservoir **as** fluid is removed. In this example we assume the reservoir is well mixed and both thermodynamic and chemical properties are constant throughout the reservoir. The reactions considered are

$$\begin{array}{rcl} H^+ + OH^- & \rightleftharpoons & H_2O \\ CaCl^+ & \rightleftharpoons & Cl^- + Ca^{++} \\ CaCl_2 & \rightleftharpoons & 2Cl^- + Ca^{++} \\ CaHCO_3^+ & \rightleftharpoons & HCO_3^- + Ca^{++} \\ H^+ + CaOH^+ & \rightleftharpoons & Ca^{++} + H_2O \\ H_2CO_3^* & \rightleftharpoons & H^+ + HCO_3^- \\ NaHCO_3 & \rightleftharpoons & HCO3^- + Na^+ \\ NaOH & \rightleftharpoons & OH^- + Na^+ \\ H_2CO_3^* & \rightleftharpoons & CO_2(gas) \end{array}$$

$H_2CO_3^*$ represents total dissolved CO_2 which is made up of $CO_2(aq)$ and H_2CO_3 (Stumm and Morgan (1981)). The reservoir is represented by a single element of 1.2 x 10^8 m^3 and fluid is withdrawn at a rate of 10 kg/s. The composition of the withdrawn fluid is determined by the relative permeabilities of the two phases.

Again we assume all chemical species are in equilibrium and equation the batch reaction part of equation (5a) reduces to a system of non-linear algebraic equations. Equations involving only aqueous species or aqueous and solid species may be written in the form

$$\prod_{i=1}^{N}[X_i]^{\nu_{ij}} = K_j \qquad (10)$$

where $[X_i]$ is the activity of species i ν_{ij} the stoichiometric matrix from equation **(2)** and K_j the equilibrium coefficient for reaction j. Equations describing the precipitation of solids differ from those involving only aqueous species in that they apply only when the solubility product $[X_i][X_j]$ exceeds the equilibrium value. Gas - liquid equilibria are treated in the manner described earlier in this section by equation (9). The activity of aqueous species is calculated using Debye-Huckle theory (Helgeson et. al. (1981)). Activity of gaseous CO_2 is calculated using the method given in White et. al. (1994). Values for the equilibrium coefficients K_j were calculated using expressions in the SOLTHERM database (Reed and Spycher (1992))

Figure **2** plots the changes of several of the chemical species as a function of saturation.

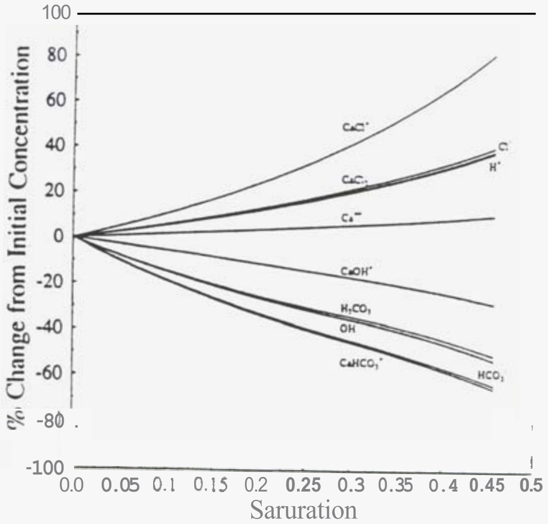


Figure 2: % Chemical changes in a two-phase geothermal reservoir. Initial concentrations are given in table 1.

H^+	4.9×10^{-6}
Cl^-	.03
cog	3.3×10^{-6}
Ca^{++}	5.5×10^{-6}
Na^+	.03
$CaCl^+$	2.7×10^{-5}
$CaCl_2$	2.8×10^{-6}
$CaHCO_3^+$	4.1×10^{-8}
$CaOH^+$	9.1×10^{-10}
H_2CO_3	3.5×10^{-7}

Table 1: Initial chemical concentrations for example **2**

There are three effects apparent in figure **2.** Firstly there **is** an increase in concentration of the aqueous chemicals not associated with the bicarbonate equilibrium (e.g. $CaCl^+$) this is mainly caused by the reduction in the volume of water containing the chemicals. Secondly, aqueous chemicals associated with the bicarbonate ,equilibrium (e.g. H_2CO_3) decrease in concentration **as** CO_2 is removed from the system by boiling. Finally all the chemical concentrations are affected to some extent by reactions among the chemical species which cause the concentrations to vary from those expected from simple boiling.

3.3 Calcite Precipitation

This example example considers production from a geothermal reservoir initially containing liquid saturated in calcite and demonstrates the precipitation of calcite in the formation near the well. The reservoir is assumed to be cylindrically symmetric with a radius of 500 meters, a depth of 100 meters and with **a** single well at the centre. Initially the reservoir contains liquid at 280° C and a pressure of 79.0 bars. The outer boundary is maintained **at** this temperature and pressure during production, the top and bottom boundaries have no-flow boundary conditions imposed. Fluid is drawn from the centre of the reservoir at 20 kg/s. Initially reservoir permeability is 10 md and the porosity is $\cdot^{1}$**.** Reservoir permeability is assumed to vary **as** ϕ^3 (Phillips (1991)), **as** calcite is precipitated porosity (and thus permeability) is reduced.

Calcite solubility in CO_2 rich water has been considered by a number of authors, see for example Ellis (1959) Plummer and Busenberg (1982) and He and Morse (1993). Data on the solubility product for calcite **was** taken from Ellis (1959). The reactions included for this problem are

$$\begin{aligned} H^+ + OH^- &\rightleftharpoons H_2O \\ H^+ + HCO_3- &\rightleftharpoons H_2CO_3^* \\ HCO_3^- &\rightleftharpoons CO_3^{--} + H^+ \\ CO_3^{--} + Ca^{++} &\rightleftharpoons CaCO_3(solid) \\ H_2CO_3^* &\rightleftharpoons CO_2(gas) \end{aligned}$$

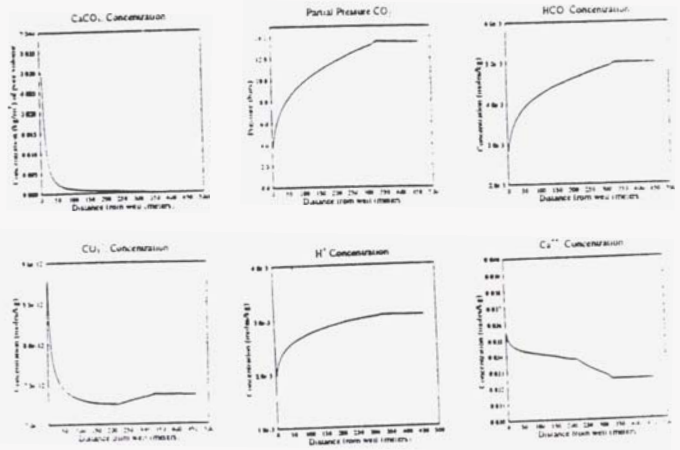


Figure 3: Calcite precipitation in a two-phase geothermal reservoir

Variation **of** chemical concentration with distance from the well is shown in figure 3. This figure shows the state of the reservoir after $2\frac{1}{2}$ years production. The reservoir is two-phase out to a distance of about 350 meters from the well with the gas phase mobile out to about 130 meters. The effects of the gas phase becoming mobile is to reduce the precipitation rate as can be seen in the discontinuous slope apparent in figures 3d and 3e. There is a dramatic increase in precipitation near the well with almost all the calcite precipitated within 10 meters of the well. The actual amount of calcite precipitated will fill less than 0.01% of the pore volume and this had no effect on formation permeability.

3.4 Convection Cell

The final example is somewhat artificial but it serves to illustrate a non-equilibrium situation. We consider a similar situation to that presented in Steefel and Lasaga (1994). A two dimensional reservoir is initially at hydrostatic pressure and the temperature increases with depth at 30°C per kilometre. Initial permeability is $\mathbb{K} = 10^{-14}$ and porosity $\phi = .05$. Fluid in the reservoir is saturated with SiO_2 and all boundaries are "no-flow". At time = 0 the temperature T on the bottom boundary is changed to be $T(x) = 100 + 200exp(-(10x/6000)^2)$. This is intended as a crude approximation to the temperature that might result from the intrusion of a pluton at depth.

If we ignore any chemical reactions then a convection cell is established and temperatures and pressures reach a steady state. When we include the reaction between fluid in the reservoir and quartz in the rock the situation is more complicated. In order to calculate reaction rates for precipitation and dissolution of quartz we must make some assumptions about the nature of permeability and porosity in the rock. We assume that all porosity and permeability is the result of fractures and that there are three sets of orthogonal fracture planes. With this assumption permeability is related to porosity by $k(t) = k_0(\phi(t)/\phi_0)^3$ where k_0 and ϕ_0 are the initial permeability and porosity and $k(t)$ and $\phi(t)$ are permeability and porosity at time t. $\phi(t)$ is obtained from the reaction rates (R) or the reaction quartz $\rightleftharpoons SiO_{2_{aq}}$ by

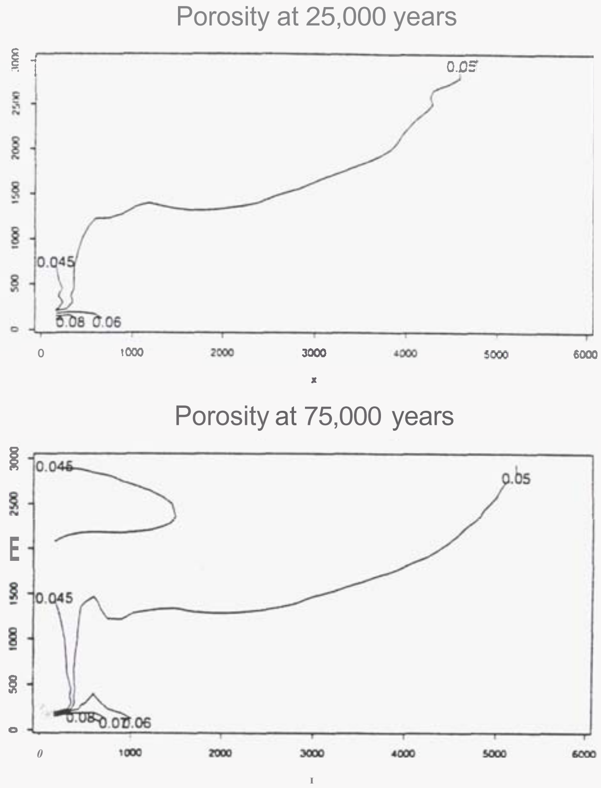
$$\phi(t) = 40 - \frac{1}{\rho_{quartz}} \int_0^t R(\tau) d\tau$$

ρ_{quartz} is the density of quartz in moles/meter^3 and R is assumed to have the form (Steefel and Lasaga (1994))

$$R = Ak_{25} \exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right)\left(\frac{[SiO_2]}{K_{SiO_2}} - 1\right)$$

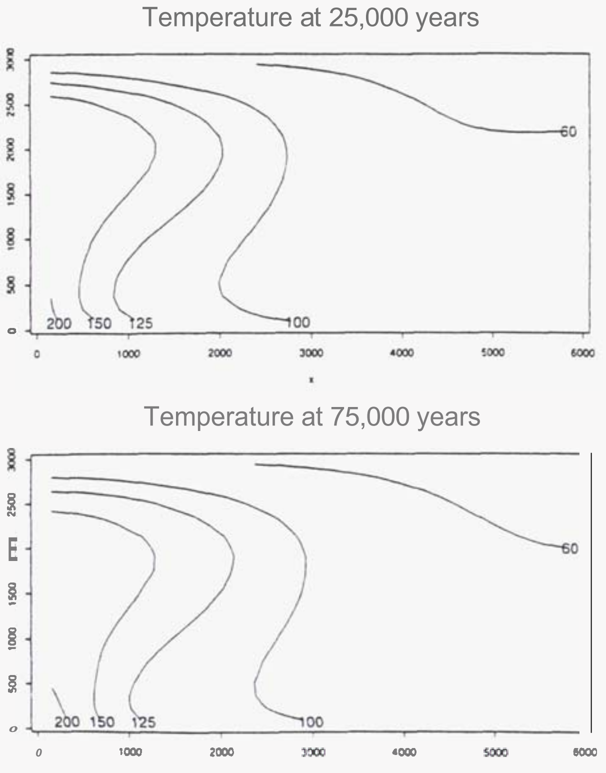
where k_{25} is the reaction rate constant at 25° C and we have ssumed an Arrhenius equation for temperature dependence. E_a is the activation energy; A the area over which the reaction ccurs ; T the temperature in ° K; R the gas constant; $[SiO_2]$ he activity of aqueous SiO_2 and K_{SiO_2} the equilibrium contant for the dissolution of quartz reaction. Dove (1994) gives more complex expression for the reaction rate but for the hemical conditions of this example the simpler expression is dequate.

igure 4 shows the porosity at 25,000 and 75,000 years. There s an enhancement of porosity where fluid flows from a cooler to a hotter region as K_{SiO_2} increases with temperature and water initially saturated with SiO_2 becomes under saturated as it is heated and dissolves some of the rock. This effect can be seen in the increased porosity near the bottom of the plume. The reverse occurs in the plume as the rising water cools. There is some precipitation a little above the base of the plume then more near the top of the plume where there is a high temperature gradient. The effect of these porosity changes over time on temperature can be seen in figure 5. The top of the plume becomes cooler as flow near the top reduces and the area over which upflow occurs is increased slightly.


Porosity at 25,000 years

Porosity at 75,000 years

Figure 4: Variation of porosity


Temperature at 25,000 years

Temperature at 75,000 years

Figure 5: Effect of porosity changes on temperature

Figure **6** shows the reaction rate after 25,000 years and figure **7** shows log $\left(\frac{[SiO_2]}{K_{SiO_2}}\right)$ at 23,000 and 75,000 years. log $\left(\frac{[SiO_2]}{K_{SiO_2}}\right)$ is a measure of how near to equilibrium the quartz **rock** is with dissolved SiO_2. The only significant deviation from equilibrium is at the top of the convection cell with the largest value at the top of the plume. The reaction rate, however, is largest at the base of the plume. This reflects the strong temperature dependence of the reaction rate. It is interesting that in this example there is a horizontal barrier beginning to form at the top of the cell but no evidence of any vertical boundaries being formed **other than** immediately above the heat source.

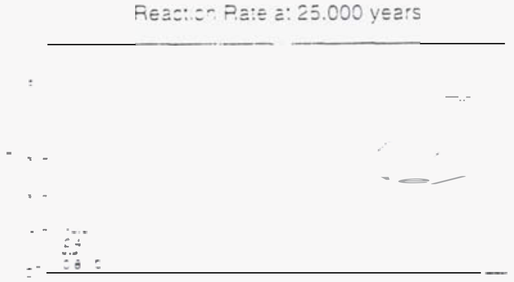
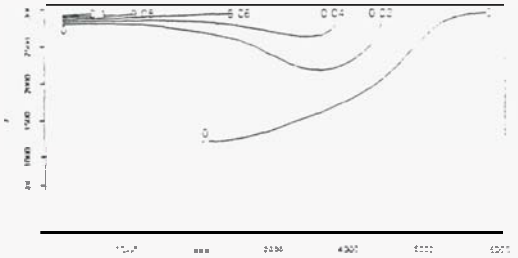


Figure **6:** Reaction rate

Log10(Q/K) at 25.000 years



Log10(Q/K) at 75,000 years

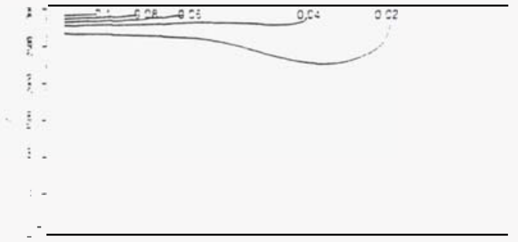


Figure **7:** Deviation from equilibrium

4 Conclusions

By representing the solution of the multiphase chemical **transport** problem using a basis constructed from the stoichiometric matrix **of** the chemical system the batch reaction and transport parts **of** the problem may be separated. The separated problems may be solved by coupling techniques for the solution **of** the batch reaction problem to some method of solving transport equations. In this work a widely **used** computer code **TOUGH2** has been coupled with locally written code for the solution **of** batch chemical reaction problems and used for several example problems.

5 References

Ellis, A.J., (1959), The Solubility of Calcite in Carbon Dioxide Solutions, *American Journal of Science, 257,* **354-365, 1959.**

Friedly, J.C., (1991) Extent of Reaction for Open Systems With Multiple Heterogeneous Reactions, *AIChE* J., 37, **687-693,1991.**

Friedly, J.C., Rubin, J., **(1992)** Solute Transport with Multiple Equilibrium-Controlled or Kinetically Controlled Chemical Reactions, ***Water Resour:*** *Res.,* ***28,*** 1935- **1953, 1992.**

Grant, M.A., Permeability Reduction Factors at Wairakei, paper **77-HT-52,** presented at ASME/AIChE Heat Transfer Conference, Salt Lake City **1977.**

He, S., Morse, **J.W. (1993)** The carbonic acid system and calcite solubility in aqueous $Na - K - Ca - Mg - Cl - SO_4$ solutions from 0 to 90° C. ***Geochim. Cosmochim. Acta 57*** **3533-3554 1993.**

Lichtner, P.C. (**1992)** Time-Space Continuum Description of Fluid/Rock Interaction in Permeable Media. ***Water Resour: Res., 28 3*** **135-3155 (1992).**

O'Sullivan, M.J. Bodvarsson, ***G.S.*** Pruess, K. Blakeley, **M.R. (1985)** Fluid and Heat Flow In Gas-Rich Geothermal Reservoirs, ***Soc. Pet. Enj. J. 25(2),*** **215-226 (1985).**

Plummer, L.N., Busenberg, E. **(1982)** The solubilities of calcite, argonite and vaterite in $CO_2 - H_2O$ solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3 - CO_2 - H_2O$. ***Geochim. Cosmochim. Acta 46*** **1011-1040 1982.**

Phillips, O.M., (1991), **Flow** and Reactions in Permeable **Rocks.** ***Cambridge University Press, Cambridge Pub.*** **1991.**

Pruess, K. **(1982)**, Development **of** the General Purpose Simulator **MULKOM,** ***Report LBL-15500, Lawrence Berkeley Laboratory.*** **1982.**

Steefel, C.I., Lasaga, A.C. **(1994) A** coupled model for transport of multiple species and kinetic precipitation/dissolution reactions with application to reactive **flow** in single phase hydrothermal systems. ***Amer J. Sci.*** **249,529-592** May **1994.**

Stumm, **W.,** Morgan J.J., **(1981)** Aquatic Chemistry An introduction Emphasizing Chemical Equilibria in Natural Waters. ***Wiley-Interscience New York Pub.*** **1981.**

Weir, G.J., White, **S.P., (1994) A** transport Model for Crevice Corrosion, ***Report IRL-141, Industrial Research Ltd.*** **1994.**

White, S.P., Kissling, **W.M. (1992)** Modelling Geothermal Reservoirs, Recent Developments ***Proc. 14th New Zealand Geotheml Workshop*** **99- 104 1992.**

White, S.P., Weir, G.J., Kissling, W.M., **(1994)** Reservoir Storage and Containment of Greenhouse Gases, ***In preparation*** *for* ***TIPM*** **1994.**

Yeh, G.T., Tripathi, V.S. **(1989) A** critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components, ***Water Resour: Res., 25,*** **93-108, 1989.**