Reaction and Transport of Chemicals in a Two Phase Geothermal Reservoir

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1 Introduction

Friedly (1991) and Friedly and Rubin (1992) developed a theory that described the transport of reacting chemicals in a porous media. This theory is limited to the isothermal transport of chemical species in the liquid phase but includes the possibility of precipitation of solids. Lichtner (1992) has considered simulation of fluid/rock interactions but also limits his consideration to the liquid phase. This work was extended by White (1994) by including the possibility of transport and reaction in the gas phase and by coupling the conservation equations for mass and energy transport to those for chemical species conservation. In this paper we outline this extension and then apply the method to several example problems.

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.

2 Model Formulation

In this section we develop 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. Where a single chemical species can exist in two phases (e.g. $CO_{2(aq)}$ and $CO_{2(gas)}$) these are regarded as different species.

The stoichiometry of these chemical reactions is written as (Friedly 1991)

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

This may be made clearer by considering an example.

Consider the reactions

$$\begin{aligned} A + 2\,8 &\rightleftharpoons AB_2 \downarrow \text{precipitate} \\ C + B &\rightleftharpoons D \\ D + E &\rightleftharpoons F \end{aligned}$$

where A, B, C, D, E and F are all in the liquid phase and AB_2 is precipitated as solid. We construct the stoichiometric matrix for this system as

$$\begin{array}{c|ccc|} A & -1 & 0 & 0 \\ B & -2 & -1 & 0 \\ C & 0 & -1 & 0 \\ D & 0 & 1 & -1 \\ E & 0 & 0 & 1 \\ F & 0 & 0 & 1 \\ \hline AB_2 & 1 & 0 & 0 \end{array} = \begin{bmatrix} \nu_{\text{mobile}} \\ \hline \nu_{\text{immobile}} \end{bmatrix} \qquad (2)$$

In the general case the matrices for the individual phases may be combined into the stoichiometric matrix for the system.

$$\mathbf{S} = \left| \begin{array}{ccc} \nu_{11}^{(l)} & \cdots & \nu_{1M}^{(l)} \\ \vdots & & \vdots \\ \nu_{N_l 1}^{(l)} & \cdots & \nu_{N_l M}^{(l)} \\ \nu_{11}^{(g)} & \cdots & \nu_{1M}^{(g)} \\ \vdots & & \vdots \\ \nu_{N_g 1}^{(g)} & \cdots & \nu_{N_g M}^{(g)} \\ \hline & \cdots & \nu_{1M}^{(s)} \\ \vdots & & \vdots \\ \nu_{N_s 1}^{(s)} & \cdots & \nu_{N_s M}^{(s)} \end{array} \right| = \left| \begin{array}{c} \nu_{\text{mobile}} \\ \\ \hline \\ \nu_{\text{immobile}} \end{array} \right| \qquad (3)$$

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

For water

$$\frac{a}{\partial t}\left[\phi\left(s_l\rho_l x_{wl} + s_g\rho_g x_{wg}\right)\right] = -\nabla.\mathrm{F_w} + q_w, \tag{4a}$$

where

$$-\mathbf{F_w} = x_{wl}\rho_l\frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathrm{g}) + x_{wg}\rho_g\frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g \mathrm{g}), \tag{4b}$$

for heat

$$\frac{\partial}{\partial t}\left[(1-\phi)\rho_r C_r T + \phi\left(s_l\rho_l U_l + s_g\rho_g U_g\right)\right] = -\nabla.\mathbf{F_H} + q_H \tag{5a}$$

where

$$-\mathbf{F_H} = H_l\rho_l\frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathrm{g}) + H_g\rho_g\frac{kk_{rg}}{Pa}(\nabla P_g - \rho_g \mathrm{g}) + \lambda\nabla T \tag{5b}$$

and for chemical species i

$$\frac{\partial}{\partial t}\left[(1-\phi)\frac{\rho_r x_{is}}{M_i} + \phi\left(s_l\rho_l x_{il} + s_g\rho_g x_{ig}\right)\right] = -\nabla.\mathbf{F}_\mathrm{i} + q_i \tag{6a}$$

where

$$\begin{aligned}-\mathbf{F}_\mathrm{i} &= x_{il}\rho_l\tfrac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l \mathrm{g}) + x_{ig}\rho_g\tfrac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g \mathrm{g}) && \text{for mobile species}\\ &= 0 && \text{otherwise.}\end{aligned} \tag{6b}$$

Here the subscripts l, 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; ϕ 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.

Note that although we have written the flux term in equation (6b) in the most general terms. a particular chemical species is defined to be present only in a single phase (no more than one of (x_{il}, x_{ig}, x_{is}) will be non zero). When a chemical species can be present in two phases (for example CO_2) then the chemical in each phase is regarded as **a** separate species. Movement of chemical species between phases is treated as a chemical reaction and a column is included in the stoichiomemc matrix to describe this.

Each reaction described by equation (1) will have a rate constant $r_j([A_1^{(l)}], \cdots [A_{N_l}^{(l)}], [A_1^{(g)}], \cdots [A_{N_g}^{(g)}], [A_1^{(g)}], \cdots [A_{N_s}^{(s)}])$ associated with it ([A] denotes some measure of the activity of species A). The source term q_i in equation (6a) is given by

$$q_i = \sum_1^N s_{ij}r_j \tag{7}$$

where s_{ij} is an element in the stoichiometric matrix defined in equation (3). 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 this section we apply their methods to the more general problem of nonisothermal transport of reacting chemical species and include the possibility of chemical species in the **gas** phase. We define

$$\mathbf{X} = \left[\begin{array}{c} \phi s_l\rho_l x_{1l} \\ \vdots \\ \phi s_l\rho_l x_{N_l l} \\ \phi s_g\rho_g x_{1g} \\ \vdots \\ \phi s_g\rho_g x_{N_g g} \\ (1-\phi)\frac{\rho_r x_{1s}}{M_1} \\ \vdots \\ (1-\phi)\frac{\rho_r x_{N_s s}}{M_N^s} \end{array}\right] \tag{8}$$

and

$$-\mathbf{F} = \left|\begin{array}{c} x_{1l}\rho_l\frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l(g)) \\ \\ x_{N^l l}\rho_l\frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho_l(g)) \\ x_{1g}\rho_l\frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g(g)) \\ \vdots \\ x_{N^l g}\rho_l\frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho_g(g)) \\ 0 \quad \text{all solid species} \\ \\ 0 \end{array}\right| \tag{9}$$

Providing that all the chemical reactions in equation *(3)* are linearly independent the columns of **S** will form a basis for the vector space of concentration changes in the batch reaction problem. The batch reaction problem treats the chemicals as reacting in a well mixed tank with no transport into or out of the system. Expanding X in terms of the columns of S and an initial concentration vector X_0 we have

$$\mathbf{X} = \mathrm{X}_0 + \mathrm{S}\zeta \tag{10}$$

In batch reaction terminology ζ is the extent of reaction coordinate (Prigogine and Defray 1954). If $\mathrm{S}^\perp$ is the orthogonal complement of S then then $\mathbf{S} + \mathbf{S}^\perp$ span concentration space and we can write

$$\mathrm{X} = \mathrm{S}\zeta + \mathrm{S}^\perp\eta \tag{11}$$

Friedly (1991) extended these concepts to a two phase (liquid and solid) system with transport in the liquid phase. We follow this procedure and develop the equations for three phase (liquid, gas, solid) systems of reacting chemicals with transport in the liquid and gas phases. The concentration vector can be written as

$$\mathbf{X} = \mathrm{S}\zeta + \Psi \tag{12}$$

where ζ is defined to be the solution of

$$\frac{\partial\zeta}{\partial \mathrm{t}} = \mathbf{r} \tag{13}$$

r is **a** vector of reaction rates. **i.e.** ζ is the solution of the batch reaction problem. Substituting equation (12) into **(6a)** and using equation (7) gives

$$\frac{\partial \mathbf{X}}{\partial t} = -\nabla.F + \mathrm{S}r \tag{14}$$

and using the definition of ζ in **(13)** we have

$$\frac{\partial\Psi}{\partial t} = -\nabla.\mathrm{L}(\mathrm{S}\zeta + \Psi) \tag{15}$$

where L is the diagonal matrix defined **by**

$$\mathbf{L} = \left|\begin{array}{cccccc} \nwarrow & & & 0 & & \\ & \frac{1}{\phi}\frac{kk_{rl}}{\mu_l}(\nabla P_l - \rho\mathrm{g}) & & & & \\ & & \searrow & & & \\ & & & \nwarrow & & \\ & & & & \frac{1}{\phi}\frac{kk_{rg}}{\mu_g}(\nabla P_g - \rho\mathrm{g}) & \\ & 0 & & & & \searrow \\ & & & & & \nwarrow \end{array}\right.$$

Friedly (1991) argues that Ψ is only coupled to the extent of reaction vector ζ through the elements corresponding to the mobile phase species and that components of Ψ corresponding to the immobile phase are invariant (in time and space). He goes on to point out that by writing Ψ as

$$\Psi = S^{\perp}\eta + \begin{bmatrix} \Psi' \\ 0 \end{bmatrix} \tag{17}$$

then η satisfies the immobile phase part of equation (15) and Ψ' will satisfy the remainder. The terms corresponding to the immobile species in Ψ' have been set to zero.

The same arguments are applied to the three phase situation considered in this paper. Using equation (17) allows us to write (15) as

$$\frac{\partial \Psi'}{\partial t} = -\nabla \mathbf{F}'' \tag{18}$$

where

$$\mathbf{F}'' = \mathbf{L}'(\nu\zeta + \nu^{\perp}\eta + \Psi') \tag{19}$$

The matrix **L'** is formed by taking only the first $N_l + N_g$ rows and columns of **L.** The solution of equation (19) can be expressed in terms of basis vectors in much the same way as was the solution of equation (6a). An obvious choice for basis vectors is the mobile part of the stoichiometric matrix ν together with its orthogonal complement $\nu^{\perp}$. However, as there is no guarantee that the columns of ν are linearly independent we construct a new matrix s containing the linearly independent columns of ν s. s and its orthogonal complements' are used as a basis to expand the solution of equation (19).

Expanding Ψ in terms of this basis gives

$$\Psi = \mathrm{s}\zeta_m + \mathrm{s}^{\perp}\eta_m \tag{20}$$

which when substituted into equation (18) gives

$$\mathrm{s}\frac{\partial \zeta_m}{\partial t} + \mathrm{s}^{\perp}\frac{\partial \eta_m}{\partial t} = -\nabla.\mathbf{F}'' \tag{21}$$

and premultiplying by $(\mathrm{s}^T\mathrm{s})^{-1}\mathrm{s}^T$ gives

$$\frac{\partial \zeta_m}{\partial t} = -\nabla \mathbf{F}_{\zeta_m} \tag{22}$$

where

$$\mathbf{F}_{\zeta_m} = (\mathrm{s}^T\mathrm{s})^{-1}\mathrm{s}^T\mathbf{L}(\nu\zeta + \mathrm{s}\zeta_m + \mathrm{s}^{\perp}\eta_m) \tag{23}$$

Similarly premultiplying by $((\mathrm{s}^{\perp})^T\mathrm{s}^{\perp})^{-1}(\mathrm{s}^{\perp})^T$ gives

$$\frac{\partial \eta_m}{\partial t} = -\nabla \mathbf{F}_{\eta_m} \tag{24}$$

where

$$\mathbf{F}_{\eta_m} = ((\mathrm{s}^{\perp})^T\mathrm{s}^{\perp})^{-1}(\mathrm{s}^{\perp})^T\mathbf{L}(\nu\zeta + \mathrm{s}\zeta_m + \mathrm{s}^{\perp}\eta_m) \tag{25}$$

These equations are more complex than those for the two phase (liquid solid) case presented by Friedly (1991) as the inclusion of the gas phase means we cannot assume L will commute with the premultiplying matrices $(\mathbf{s}^T\mathbf{s})^{-1}\mathbf{s}^T$ and $((\mathbf{s}^{\perp})^T\mathbf{s}^{\perp})^{-1}(\mathbf{s}^{\perp})^T$. Friedly limits his derivation to cases where the transport operator is constant for all chemical species which in terms of our notation ensures the **L** matrix will commute with all matrices. Little is gained by solving (18) in terms of basis vectors if L does not commute with $(\mathbf{s}^\mathbf{T}\mathbf{s})^{-1}\mathbf{s}^\mathbf{T}$ and $((\mathbf{s}^{\perp})^\mathbf{T}\mathbf{S}^{\perp})^{-1}(s')'$. **An** alternative approach is to solve for Ψ' directly and this approach was adopted for the numerical work described later in this paper.

3 Numerical Methods

The solution of equations (4a) - (5a), (13) and (18) is accomplished using a modified version of the computer program **TOUGH2** developed at Lawrence Berkeley Laboratories by Pruess [1987, 1991, 19931. The algorithm described in Narasimhan and Witherspoon [1976] and Pruess [1993] needs modification to be applied to the solution of the equations developed in section 2 of this paper. These modifications are described in White (1994).

Equation (13) is an ODE and can be integrated using an appropriate technique. Note however that the solution may depend on many of the variables solved for in the transport equations and the ODE, PDE system should be solved simultaneously together with any equilibrium equations.

3.1 Solution of Equilibrium Equations

Often the time scale for chemical reactions is very much shorter than for heat and mass transport, in these cases it is convenient to assume that some (or all) of the reactions take place instantaneously and the chemicals are always in equilibrium. Nordstrom et.al. (1979) provides a review of methods for the solution of equilibrium chemical problems and more recently Reed (1982) has developed a method suitable for geochemical equilibrium problems.

In this work the equilibrium equations may be solved many thousands of times during the course of a computation and in order to keep computation times reasonable this must be done as efficiently as possible. Also the method must be able to converge from possibly very poor starting solutions and not rely on manual intervention. We have developed a method based on the concentration space concepts outlined in section 2 of this paper which meets these criteria. This method is firstly illustrated by means of an example then we consider solution to the general problem. Consider the chemical reactions

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3^* \tag{26a}$$

$$H^+ + CO_3^= \rightleftharpoons HCO_3^- \tag{26b}$$

$$H^+ + OH^- \rightleftharpoons H_2O \tag{26c}$$

At equilibrium the activities of the chemical species satisfy

$$\frac{[H^+][HCO3^-]}{[H_2CO_3^*]} = K_1 \tag{27a}$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{27b}$$

$$[H^+][H^-] = K_3 \tag{27c}$$

We write theequation (26a)-(26c) in terms of the general stoichiometry

$$0 \rightleftharpoons \sum_{i=1}^{6} s_{ij}\, A_i$$

where **A,** represents the species $(H^+, OH-, \ldots)$ and s_{ij} the stoichiometric coefficient. The coefficients of species on the left-hand side of equations (26a)-(26c) are taken to be negative. For the system of equations under consideration

$$s = \begin{bmatrix} 1 & -1 & -1 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \\ 1 & 1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$A = \left[H^+, OH^-, H_2CO_3^*, HCO_3^-, CO_3^{--}, H_2O\right]^T$$

The general equilibrium problem can be written as (Denbigh (1978))

$$\prod_{i=1}^{N}[X_i]^{\nu_{ij}} = K_j \tag{28}$$

where [X,]is the activity of species i; ν_{ij} is the coefficient of species i in reaction j and IC, is the equilibrium coefficient for reaction j. As we are concerned only with batch reactions here, we can expand the concentration of species i using the columns of the stoichiometric matrix as a basis.

$$\{X_i\} = \{X_i^0\} + \sum_{k=1}^{M}\zeta_k\nu_{ik} \tag{29}$$

where $\{X_i\}$ is the concentration of species i; $\{X_i^0\}$ is the initial concentration of species i and $\zeta_k (k = 1 \cdots M)$ are expansion coefficients. For aqueous species the activity of species i is given by $[X_i] = \gamma_i \{X_i\}$, γ_i is the Debye-Huckle activity coefficient. We assume the activity for water and solid species is 1. For gaseous species the activity is given by the product of the partial pressure of the species and an activity coefficient. Generally there will be an equation of state for the gaseous species that allows a partial pressure and activity coefficient to be calculated from the density and temperature. If no better approximation is available it can often be assumed the gaseous species act as perfect gases. Using the equation of state we may write $[X_i] = f(\{X_i\})$ Substituting equation (29) into equation (28) and taking logarithms gives

$$F_j = \sum_{i=1}^{N} \nu_{ij} \log(\{X_i^0\} + \sum_{k=1}^{M} \zeta_k \nu_{ik}) - \log(K_j) = 0 (j = 1 \cdots M) \quad (30)$$

This is a system of M equations with the expansion coefficients $\zeta_k (k = 1 \ldots M)$ as unknowns. These equations can be solved using a modified Newton iteration

$$\begin{aligned} \zeta^0 &= 0 \\ \zeta^{(i+1)} &= \zeta^i - \alpha \mathbf{J}^{-1} F \end{aligned}$$

J is the Jacobian matrix for the system $J_{ij} = \frac{\partial F_i}{\partial \zeta_j}$. For problems where the starting solution is not near to the converged solution the iteration may fail to converge or may give non physical solutions (negative concentrations). To avoid the problem of negative concentrations we choose a value of a that ensures all concentrations are positive. This is done by setting $a = 1$ and calculating updated concentrations, if they are all positive then we are done. Otherwise a is divided by 2 and the process repeated. Eventually an acceptable solution is found.

4 Examples

4.1 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.

Two cases are considered, the first (case a in figure 1) includes the chemicals $H_2CO3^*, OH-, H^+, CO_3^{--}, HCO_3-$ and the reactions between them while in the second case (case b in figure 1) only one chemical reaction is considered, the reaction between gaseous CO_2 and aqueous CO_2.

For case b the reaction is

$$CO_2(gas) \rightleftharpoons CO_2(aqueous) \quad (31)$$

The reaction is assumed to reach equilibrium instantaneously and equation [13] reduces to

$$r([CO_2(aq)], [CO_2(gas)]) = 0, \quad (32)$$

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

$$[CO_2(gas)]/[CO_2(aq)] = K_{Henry}(T) \quad (33)$$

Here $[X]$ represents the activity of species X, typically the partial pressure in the gaseous phase and in this example the mole fraction in the aqueous phase. The stoichiometric matrix for this example is simply

$$\mathbf{S} = \begin{bmatrix} -1 \\ 1 \end{bmatrix} \quad (34) \quad \text{and} \quad \mathbf{S}^{\perp} = \begin{bmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{bmatrix} \quad (35)$$

The results of the 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 between case a and 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. [1994]). 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. There is almost no difference between the partial pressures for case a and case b.

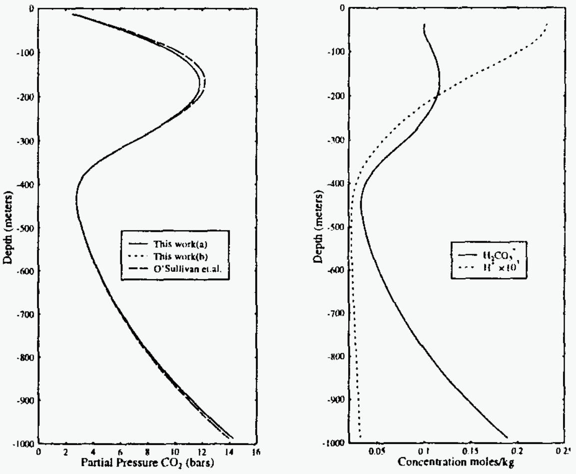

Figure 1 : Vertical profiles of the partial pressure of CO_2 and chemical concentrations in a geothermal reservoir

4.2 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

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

$H_2CO_3^*$ 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. Also in all this work we ignore any change in the amount of H_2O available for the reaction; this is equivalent to assuming the activity of water is always 1. The row associated with H_2O has been removed from these stoichiometric matrices. The stoichiometric matrix **S** for this problem is

The stoichiometric matrix **S** for this problem is

$$\begin{bmatrix} -1 & 0 & 0 & 0 & -1 & 1 & 0 & 1 & 0 \\ 0 & 1 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

and the $S^{\perp}$ matrix is

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \end{bmatrix}$$

Again we assume all chemical species are in equilibrium and equation (13) reduces to **a** system of non-linear algebraic equations. 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 (33). 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 *IC,* were calculated using expressions in the **SOLTHERM** database (Reed and Spycher (1992))

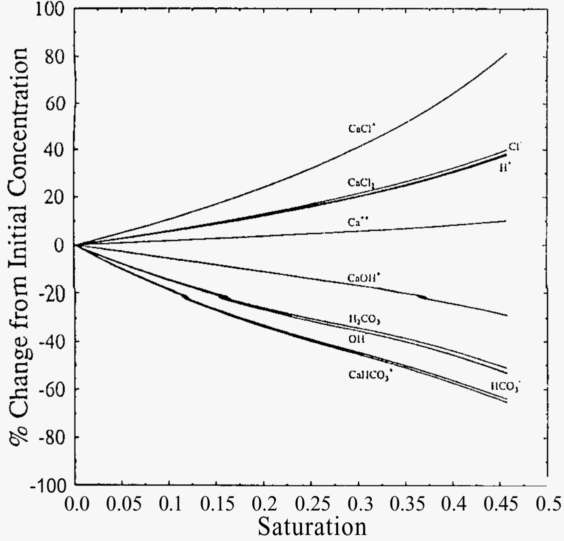

Figure 2: % Chemical changes in **a** two-phase geothermal reservoir. Initial concentrations are given in table 1.

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

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.

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

Table 1: Initial chemical concentrations for example 2

4.3 Calcite Precipitation

This 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-llow **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 .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

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

The matrices associated with these **reactions** are

$$\mathbf{S} = \begin{bmatrix} -1 & 1 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 \end{bmatrix} \qquad \mathbf{S}^{\perp} = \begin{bmatrix} 9 & 0 & 0 \\ -9 & 0 & 0 \\ 8 & 2 & 0 \\ 1 & 2 & 0 \\ -9 & 2 & 0 \\ 5 & -1 & 1 \\ 8 & 2 & 0 \\ -5 & 1 & 1 \end{bmatrix}$$

Variation of chemical concentration with distance from the well is shown in **figure 3.** This **figure** shows the state of the reservoir after ten 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 figure **2.** 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.

5 Conclusions

By representing the solution of the multi-phase 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.

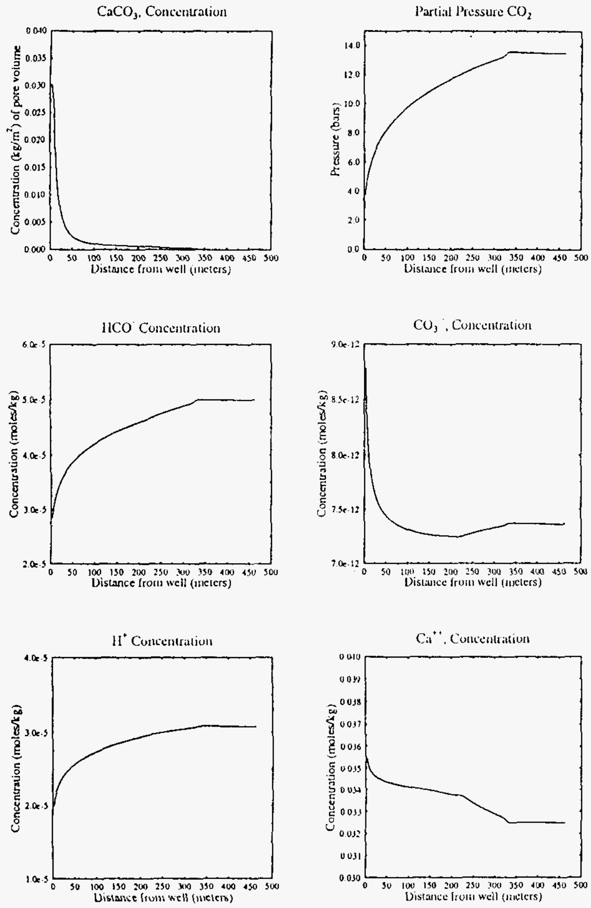

Figure 3: Calcite precipitation in a two-phase geothermal reservoir

6 References

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