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INCLUDING CHLORIDE AND CO, CHEMISTRY IN LARGE SCALE RESERVOIR MODELS

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SUMMARY - This paper considers including several reacting chemical species in a large scale numerical model of a geothermal reservoir. A method is developed to determine when a single-phase liquid converts to a two-phase liquid-vapour mixture and vice versa in a fluid containing dissolved gases and solids. Finally these techniques are applied to a geothermal reservoir model and compare calculated chemical changes to those observed.

1 Introduction

Heat and mass transport and the interactions of fluid with the earth's crust are of interest for many reasons. The processes that may take place are diverse and include mineral dissolution and precipitation, redox reactions, gas-liquid interactions and biochemical reactions, to name but a few. Recently a number of researchers (e.g. Lichtner (1992), Steffel and Lasaga (1995) Bear and Nitao (1995) Friedly (1989), Friedly and Rubin (1992) White (1995)) have looked to combine hydrology and geochemistry to provide tools to study these processes.

White (1995) describes a method to treat the transport and reaction of chemicals in a geothermal setting. Chemical species concentrations often provide considerable insight into processes taking place within a geothermal reservoir. They may also be a much more sensitive indicator of processes such as boiling and dilution taking place within the reservoir than pressure and temperature measurements. Including chemical species concentrations in a numerical reservoir model and adjusting reservoir parameters to match measured physical (pressure, temperature etc.) and chemical data has the potential to both improve the predictive capabilities of the model and offer further insight into the processes taking place in the reservoir.

This was first done by Kissling *et al.* (1996) who included the chemistry associated with carbon dioxide in the Wairakei geothermal field. While this work was successful it did expose several shortcomings in the software used to implement the method of White (1995) when applied to a large three dimensional reservoir model.

In this paper we address those shortcomings and present results of calculating the initial chemical and thermodynamic state of the Wairakei reservoir and also look at chemical changes that take place in response to production from the reservoir. This example is similar to that presented by Kissling *et al.* (1996) but includes more chemical species.

2 Problems with the software

The primary difficulty with the software used in the work described by Kissling *et al.* (1996) was the time taken to complete a calculation. Several factors contributed to the long calculation time. Probably the most important was the method used to determine when a phase change took place. At times, because the effect of dissolved species other than gases was ignored, an incorrect determination of phase conditions would be made. While this did not lead to incorrect results it did led to "flip-flopping" between single and two-phase conditions which in turn lead to small time steps being taken while integrating the transport equations. A second problem was the way in which chemical concentrations were split into a transport part and a batch reaction part. Over long times the actual concentrations would be calculated as the difference of two large, almost equal numbers and eventually would become inaccurate. This meant several restarts were necessary when calculating steady state solutions by integrating in time until no further changes in the solution were observed. A third problem was that during the transport step negative concentrations of aqueous species sometimes resulted.

3 Phase Changes

The chemical simulation software we use is based on the widely used simulator TOUGH2 (Pruess 199 1). TOUGH2 uses different primary variables (see White **(1995)** for an explanation) in single phase regions (P(ressure), T(emperature) + chemical variables) from those used in two-phase regions (P, S(aturation) + chemical variables). It is not a trivial task to determine when an element undergoes a phase change from single-phase to two-phase when dissolved gases and solids are present.

For pure water at equilibrium the chemical potential of the gas and liquid phases are equal ($\mu_{gas} = \mu_{liquid}$) and this leads to the Clausius -Clapeyron equation (Denbigh **(1978)**)

$$\frac{dP_{sat}}{dT} = \frac{L}{T\Delta V}$$

where P_{sat} is the saturation pressure, L the latent heat of vapourization, ΔV the volume change associated with the phase change and T the temperature in degrees K. We can integrate this equation or use an empirical fit to experimental data to obtain an expression for the saturation pressure **as** a function of temperature. When the pressure and temperature of a single-phase element vary so **as** to cross this line, the element has become two-phase and needs to be treated **as** such.

When a dissolved gas, i, is present then the condition for equilibrium between the gas species in the aqueous phase and the gas phase is that the chemical potential in the vapour and aqueous phases are equal ($\mu_i^{gas} = \mu_i^{solution}$). This can be written **as**

$$\mu_i^{*gas}(T) + RT\ln(f_i) = \mu_i^{*solution}(T,P) + RT\ln(\gamma_i x_i)$$

where f_i the fugacity of gas i, and γ_i and x_i are the activity coefficientand mole fraction respectively for species i. This can be rearranged to give the well known Henry's law $f_i = K_H\gamma_i x_i$.

Dissolved species change the boiling point of a solution (Denbigh **(1978)**) by an amount given by

$$\Delta T = \frac{RT_B^2 \sum_j \gamma_j x_j}{L_B}$$

where ΔT is the change in boiling point, R the gas constant, T_B the boiling point of pure water γ_j, and x_j the activity coefficient and mole fraction of species j respectively. The summation extends over all dissolved species. For computational purposes this is most conveniently expressed **as** $P_s^{solution}(T - \Delta T) = P_s^{pure\ water}(T)$ where $P_s(T)$ is the saturation pressure at temperature T.

The gas phase should be described by an equation of state that includes cross terms between the different species present and the fugacity for each component derived from this. (See, for example Reid et *al.* **(1988)**). For the present work we have ignored cross terms and assumed the partial pressure of each gas present is independent and a function of temperature and pressure only. In fact we further assume that all gases other than CO_2 and H_2O are ideal gases.

To determine if a phase change should take place we assume two-phase conditions exist, and solve the equations for chemical equilibrium including the gas phase. Also we require that the partial pressure of water vapour be given by (2). If the system pressure is less than the calculated saturation pressure ($P_{sat} = \sum_i P_i$ where P_i is the partial pressure of gas species i) then there should be a phase change from liquid conditions to two-phase conditions. The algorithm used to solve these equations is given in the next section.

In this work these 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, without manual intervention. We have developed a method based on the concentration space concepts developed in White **(1995)** which meets these criteria.

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

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

and this must be solved together with the saturation line equation

$$p_{water\ vapour} - P_s(T - \Delta T) \tag{2}$$

where $[Xi]$ is the activity of species i; ν_{ij} is the coefficient of species i in reaction j and K_j is the equilibrium coefficient for reaction j. Generally the activity of aqueous species is given by the product of an activity coefficient γ and a concentration x and of gaseous species by the product of a fugacity coefficient f and a partial pressure. 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.

$$\{X_i\} = \{X_i^0\} + \sum_{k=1}^{M}\zeta_k\nu_{ik} \tag{3}$$

where $\{X_i\}$ is the concentration of species i;$\{X_i^0\}$ is the initial concentration of species **i** and $\zeta_k (k = 1\cdots \mathrm{M})$ are expansion coefficients. For aqueous species the activity of species **i** is given by $[Xi] = \gamma_i\{X_i\}$, where 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 $[X_i] = f(\{Xi\})$. Substituting equation *(3)* into equation **(1)** and taking logarithms gives the system of equations

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

$$(j = 1\cdots M) \tag{4}$$

$$F_{M+1} = P - \sum_{j=1}^{N_g} P_j \quad (5)$$

This is a system of M+1 equations with the expansion coefficients $c_k (k = 1 \cdots M)$ and ζ_{M+1} = pressure P as unknowns. These equations can be solved using a modified Newton iteration

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

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 or pressures). To avoid the problem of negative concentrations we choose a value of α that ensures all concentrations are positive. This is done by setting $\alpha = 1$ and calculating updated concentrations; if they are all positive then the solution is accepted. Otherwise α is divided by 2 and the process repeated. Eventually an acceptable solution is found.

4 Measured Chemical Data

Publicly available chemical data for the Wairakei reservoir are analysed in some detail in Kissling *et al.* (1996). Here we outline some of the key features of the data. There is some uncertainty in the composition of the fluids in the undisturbed reservoir, however the best available data suggest a deep upflow at a temperature of 265° C and with a chloride content of 48 mmol/kg (see Figure 2 of Kissling *et al.* (1996).

Boiling of this upflow with consequent steam loss and dilution by shallow low chloride waters gives rise to a lateral inflow to the productive reservoir at a temperature of 260° C and chloride content of 48.6 mmol/kg. Glover (1970) estimates the initial total inorganic carbon content of the reservoir to be 9.7 mmol/kg.

Reservoir processes that affect the chloride concentration during production are boiling (leading to an increased chloride concentration) and dilution (reducing the chloride concentration). Dilution is the dominant process at Wairakei and produced fluids show a steady decline in chloride concentration with time.

The numerical model used for this work is not detailed enough to distinguish individual wells but we do distinguish between the eastern and western borefields (see Figure 1).

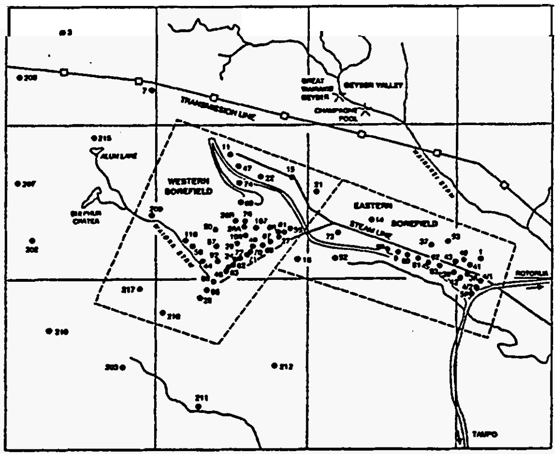

Figure 1: Borefield layout

Average reservoir values of chloride concentration for the eastern and western borefields are calculated from measured data weighted by well flow rate. These average Values are used in the comparison of calculated results with measured data.

Total CO_2 concentration in the single-phase wells is a sensitive indicator of previous boiling, because the gas distributes largely into the gas phase when boiling takes place. Consequently CO_2 data are more scattered than the chloride data as wells react to local boiling conditions. A trend of decreasing CO_2 concentration in the single phase wells with time is still apparent in the data. This is believed to be due to production induced boiling in the upflow zone.

5 Numerical Modeling

The numerical model used is that of O'Sullivan and Bullivant described in Kissling *et al.* (1996). Originally this model was used to calculate pressures and temperatures within the reservoir. We have used a modified version of the TOUGH2 (Pruess 1991) computer program that allows the inclusion of reacting chemicals as part of the model (White, 1995). This means that along with calculating pressure and temperature we may also calculate concentrations of a number of chemical species. In some cases these species may be more sensitive indicators of processes occuring in the reservoir than temperature and pressure. We have included most of the reactions associated with the dissolution and transport of CO_2 together with those associated with the two main pH buffers (H_4SiO_4, H_3BO_3) believed to operate at Wairakei. We have not included any water-rock interactions such as mica and K-feldspar as these are considered to be too slow to effect changes induced by boiling. We have included the buffer H_3BO_3 which was excluded in the earlier work by Kissling *et al.* (1996). The reactions associated with the $CO_3^=$ ion have been neglected as concentrations of this ion will be very small in fluids having a pH range of those found at Wairakei.

The reactions considered are

$$\begin{array}{ccc} H_2O & \rightleftharpoons & H^+ + OH^- \\ H_2CO_3 & \rightleftharpoons & H^+ + HCO_3- \\ H_4SiO_4 & \rightleftharpoons & H^+ + H_3SiO_4^- \\ H_3BO_3 & \rightleftharpoons & H^+ + H_2BO_3^- \\ H_2CO_3 & \rightleftharpoons & CO_2(gas) + H_2O \end{array}$$

We assume equilibrium between chemical species and have taken temperature dependent equilibrium coefficients of the form

$$\log_{10}(K(T)) = \sum_{i=0}^{4} b_i T^i$$

The b_is have been taken from the SOLTHERM database compiled by Reed and Spycher (1992).

Chemical concentrations in the upflow zone are given in Table 1 (units are mmolekg). Cl^- is regarded as a conserved species as is Na^+, neither of these species take part in any reactions but are simply transported. Therefore it is sufficient to include just one of these species in the transport equations. We assume the Na^+ concentration is always the same as Cl^-. When the source elements are equilibrated these concentrations result in a pH of about 7.2. This value is too high by 0.5 - 1 pH unit.

Table 1: Source concentrations (mmolekg)

Species	Inflow Concentration
H^+	1.10×10^{-4}
OH–	7.60×10^{-5}
CO_2	1.20×10^{-2}
HCO_3^-	1.00×10^{-3}
H_4SiO_4	9.50×10^{-3}
$H_3SiO_4^-$	1.23×10^{-4}
H_3BO_3	4.84×10^{-3}
$H_2BO_3^-$	3.20×10^{-3}
Cl^-	4.80×10^{-2}
Na^+	4.80×10^{-2}

6 Results

We have adopted a similar technique to that used to calculate a reservoir concentration from the measured data described in Kissling et al. (1996). The western and eastern borefields are treated separately. Each element of the model from which fluid is produced (called a production element) was examined, and data from any element with a gas saturation greater than 0.05 was discarded. The values in the remaining production elements were weighted according to production from the element and an average reservoir concentration calculated.

In Figures 2 and 3 we present calculated and measured chloride concentrations averaged in this manner. In Figs 2 through 7 calculated values are shown as a solid line and measured data is presented as points. We refer to a pH calculated from measured chemical concentration as a "measured pH" to distinguish it from the value calculated by our numerical model. There is good agreement between calculated and measured data both in the actual values and in the dilution trend.

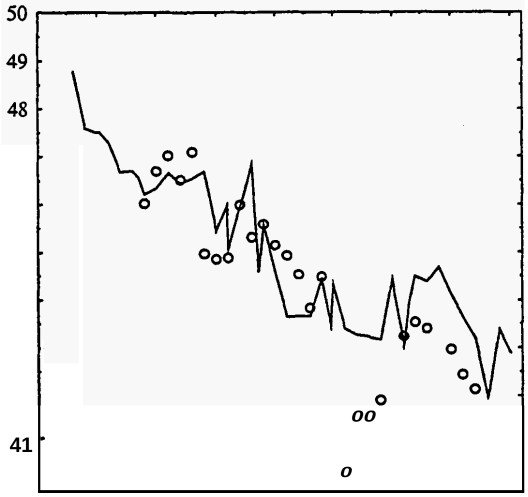

Figure 2: Western borefield chloride concentration

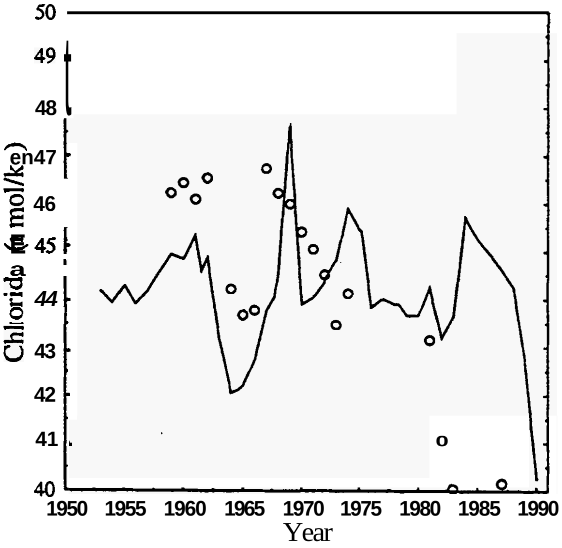

Figure 3: Eastern borefield chloride concentration

Figures 4 and 5 present calculated and measured CO_2 concentrations for the western and eastern borefields. The agreement for the western borefield is good both in the match between actual values and trends in the measured and calculated data. The situation in the eastern borefield is not quite so clearcut. Modelled CO_2 drops rapidly to almost zero about 1967. The same trend is apparent in measured data but is more gradual with an almost linear decrease in CO_2 concentration between 1965 and 1990.

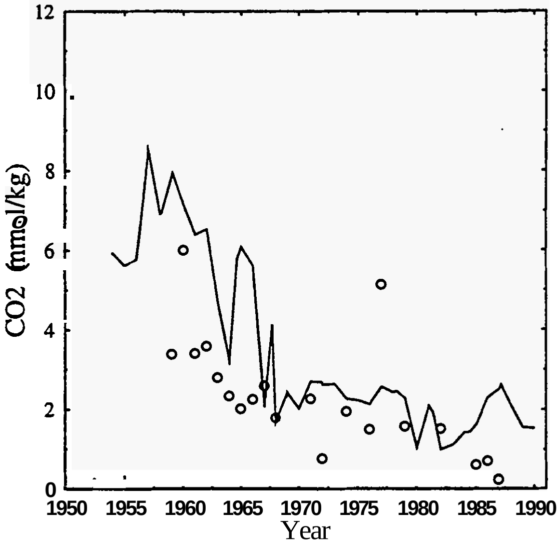

Figure 4: Western borefield C02 concentration

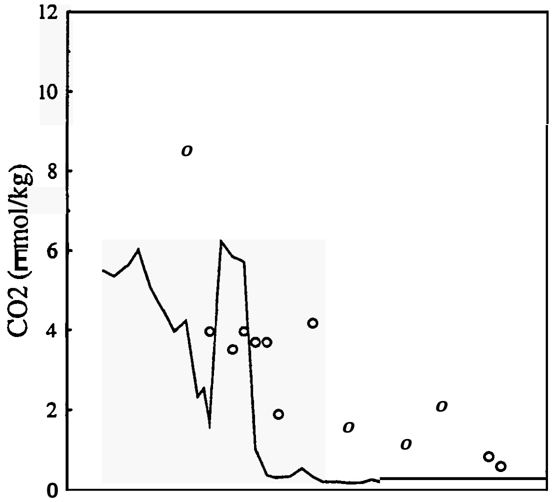

Figure 5: Eastern borefield CO_2 concentration

Figures 6 and 7 show the calculated and measured pH as a function of time. There has been no averaging of the measured pH values in this case. Calculated pH values have been weighted in the same manner as CO_2 and Cl^- data. Also shown on these figures are two straight line least squares *fits* to the data. From these lines we see that although the calculated pH is too high by about .5 units the trend of increasing pH is the same for both calculated and measured data.

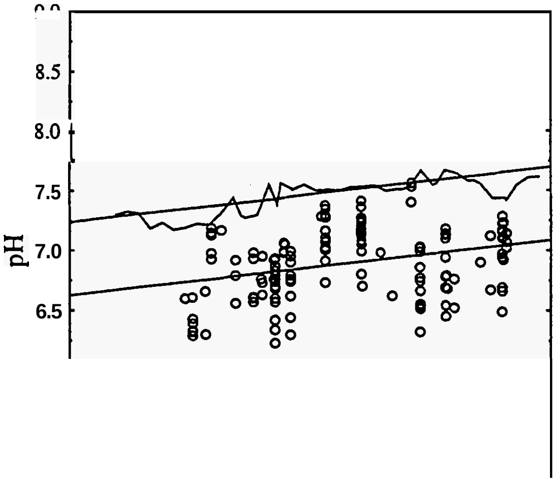

Figure *6:* Western borefield pH concentration

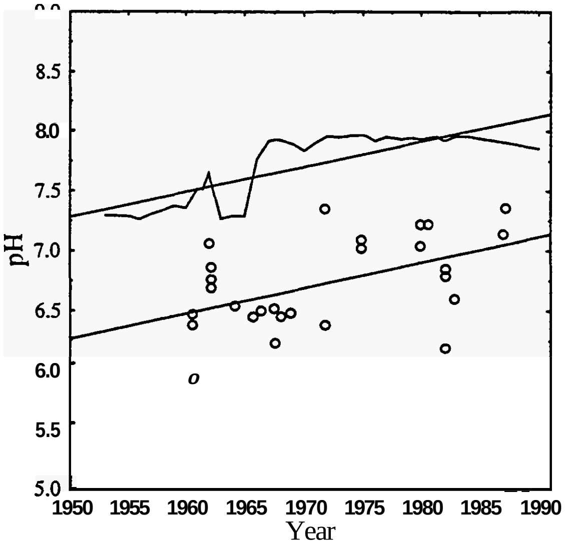

Figure 7: Eastern borefield pH concentration

The eastern borefield results could be interpreted as having a step increase of about 0.5 pH units rather than a steady increase in pH with time. The step appears in the modelled results in about 1967 and the measured data in 1971.

7 **Final** Comments

We have addressed several technical problems with our chemical simulation software. This has resulted in the reduction of execution times for steady state calculations by a factor of about 50. This greatly enhances the usefulness of including reservoir chemistry as part of the modelling process.

The calculations described here were carried out on an HP735 workstation with 80 Mbytes of memory, almost a modest machine by todays standards. Top of the line workstations would offer at least five times the speed of the 735 and large machines such as the SGI at Auckland University potentially offer up to **75** times the performance of the **735.** This would reduce the time for a calculation such as described here to **1-2** hours.

The generally good agreement between measured chemical data and model results indicate the important reservoir processes of boiling and dilution are well represented in the numerical model.

8 References

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