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MODELLING CHLORIDE AND CO_2 CHEMISTRY AT THE WAIRAKEI GEOTHERMAL FIELD, NEW ZEALAND

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ABSTRACT

The chloride and CO_2 chemistry at the Wairakei geothermal field, New Zealand has been modelled using an extended version of the geothermal simulator TOUGH2 which solves the equations for the transport of reacting chemical species in multi-phase fluids. Reactions involving the speciation of aqueous CO_2 to H_2CO_3 and HCO_3^- are included in the model. Because CO_2 speciation in water is pH dependent, a reaction involving the most important weak acid buffer at Wairakei (H_4SiO_4) has also been included. A 'Henry's Law' reaction expresses the equilibrium between the aqueous and vapour components of CO_2. The chloride is treated as a conservative, non-reacting species which is present only in the liquid phase. Results from the model are compared with measured chloride and CO_2 data from Wairakei covering the period 1959 to 1987.

INTRODUCTION

In this paper we describe the first application of a chemical transport model to a detailed, large scale simulation model of a geothermal field. Our aim is to verify that some of the most important chemical processes which take place in a geothermal environment (for example boiling, dilution or deposition) do occur in the model. We do this by comparing the modelled chemistry with observed chemical data. Having verified the chemical model in this manner, we are able to predict future chemical changes that will take place in the field under exploitation. As an example, it is possible to include calcite deposition about two-phase wells in a reservoir model. This would allow determination of production scenarios that minimise the effect of reduced permeability resulting from such deposition.

For this study we have chosen the Wairakei field in New Zealand. This is a well studied geothermal field which has been extensively modelled in the past. Production of fluid started at Wairakei in the 1950's, and chemical and other data has been collected continuously from that time. A good summary of this data and early modelling studies of Wairakei is given by O'Sullivan and McKibbin (1989). In this study we use the latest in a series of 3-D Wairakei models (O'Sullivan and Bullivant (ECNZ, 1992)) with a new chemical transport simulator to further extend this model, and to check its validity against new chemical data.

We have chosen to model the transport of the chloride ion (Cl^-) and carbon dioxide (CO_2) in this study. These species complement each other because they each behave in a fundamentally different way when subjected to the various processes, such as boiling and dilution, which occur in a geothermal reservoir (see for example, Henley *et al.*, 1984). Consequently, modelling Cl^- and CO_2 provides us with independent information on these processes, and can give new insights into behaviour of the model.

Previous chemical modelling studies have been carried out with both chloride and CO_2, although not, to the authors' knowledge, simultaneously. The MULKOM (Pruess, 1982) simulator has been extended by a number of workers (Mendrinos and O'Sullivan, 1990, White and Kissling, 1992) to include the flow of chloride as a single non-reacting chemical species. In these codes the chloride is assumed to be a conservative species which flows only in the liquid phase. This idea is simple to implement and is very effective if the chloride concentration is low enough to have no significant effect on the physical and thermodynamic properties of water.

The situation with CO_2 is more difficult. Several geothermal simulators incorporating CO_2 (for example, O'Sullivan *et al.* (1985)) have used Henry's Law to express the equilibrium between aqueous CO_2 and CO_2 in the vapour phase. This approach takes no account of the pH dependence of this equilibrium. Simple considerations (see for example, Henley *et al.* 1984) show that this is necessary for modelling at Wairakei, where the pH of most 'active' reservoir fluids is in the range from about 6.0 to 7.5. The approach in this paper - including in the model formulation the chemical reactions which effect the pH - solves this 'pH problem' in a very natural way.

We begin this paper with a short description of the Wairakei reservoir model we have used. In the following section a summary of the chemical data used in this paper is described. We then outline the chemical transport model, and the chemical reactions we have used in this study. Next, we present some results from the model and discuss these in terms of real field data. Finally we conclude with some comments about the usefulness of this type of chemical modelling, and where we see potential for further work.

THE WAIRAKEI MODEL

The work described in this paper is based on a 3-D MULKOM (Pruess 1982) model of the Wairakei field developed for the Electricity Corporation of New Zealand (ECNZ) by O'Sullivan and Bullivant (ECNZ 1992). More complete details of the model are discussed in this reference, and we shall give only a brief overview here.

Figure 1 shows the computational grid for the model. The area covered is about 22 × 16 kilometres. The smallest elements are about 800 metres across and represent the main production borefields. These are known as the Western and Eastern borefields, and are indicated by hatched regions on Figure 1. The large elements around the boundary provide pressure control for the model, and permit lateral flows into or out of the central region. The model extends well to the south of the main borefields, and includes the Tauhara geothermal field (as a single element), which is known to be hydrologically connected to Wairakei.

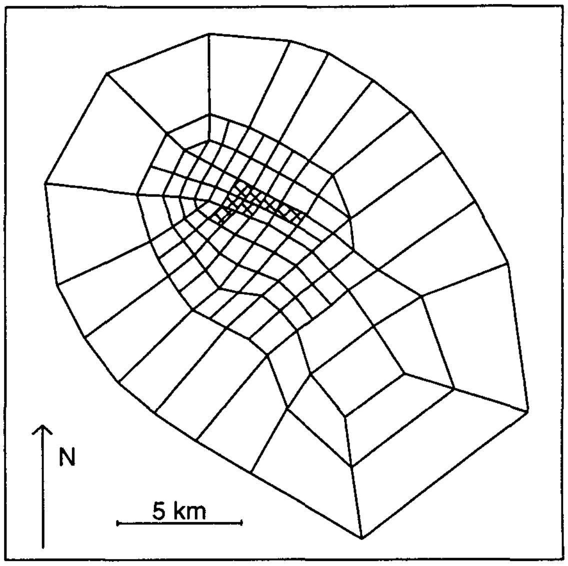

Figure 1: The computational grid for the Wairakei Model. The Western and Eastern borefields are indicated by the hatched elements.

Vertically, the model consists of 12 layers, each of 102 elements, and extends to a depth of 2500 m. Each of these layers corresponds to a particular rock type. A single extra element provides 'atmospheric' boundary conditions (1 bar, 10°C) at the top of the model. This element is fully saturated, and provides a realistic inflow of 'meteoric' water into the model. The shallow groundwater level is included by allowing the height of the top layer of elements to vary from block to block. This is important when considering the effects of geothermal production on the shallow groundwater system.

The natural state calculated by this model consists of a shallow two-phase zone overlying a fully saturated liquid zone, with the deep high temperature upflow balanced mainly by a shallow lateral outflow, and some discharges from natural surface manifestations. Using this as a stating point, most of the production occurs from the top 1200 m of the Western and Eastern borefields. The complete production history of the field is incorporated into the model for the period 1953 to the present.

WAIRAKEI CHEMICAL DATA

The chemical data for the deep reservoir that were used in this study were derived from a database of chemical analyses of steam and water samples (Henley *et al.* 1984, and others), from pre-production to 1986. The data used in this paper are chloride and CO_2 concentrations and pH. These are at aquifer conditions, and are presented in the form of yearly averages for the Western and Eastern borefields. For reasons explained in Kissling *et al.* (1995), these data pertain only to single phase aquifer fluids. More complete details of the derivation of this data, and the reservoir chemistry at Wairakei can be found in Kissling *et al.* (1995).

The chloride and the effects of exploitation

The two main processes that affect the chloride concentration at Wairakei are boiling and dilution by surface derived fluids. The former increases the aquifer chloride concentration, while dilution with surface derived fluids, which have low chloride concentrations, decreases the aquifer chloride concentration. Although both processes are taking place in the reservoir, it is dilution which has the larger effect on the chloride concentration at Wairakei.

The weighted average (according to the production flows from each well) chloride concentration for each year was calculated for both the Eastern and Western borefields and is shown in Figure 2. There were 504 measurements contributing to the Western borefield averages, and 177 contributing to the Eastern borefield averages. The greater number of data points for the Western borefield reflects the greater production from that area, and the occurrence of two-phase wells in the Eastern borefield. For the years 1976 to 1979 there is very little data, and so the averages for these years are not as reliable as those for the remainder of the period considered.

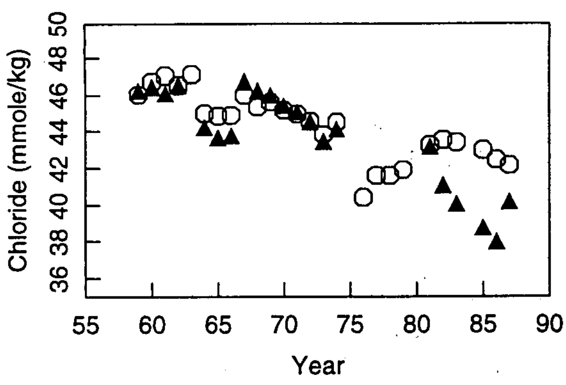

Figure 2: Weighted averages of measured aquifer chloride for the Eastern (triangles) and Western (circles) borefields.

The data show a gradual reduction in the average chloride concentration following the commencement of production. The data for some years is very scattered due to the paucity of wells with suitable chemical data, however, a general reducing trend is clear, indicating continuing dilution of the production reservoir.

The CO_2 and the effects of exploitation

The total CO_2 concentration in the single phase wells is a very sensitive indicator of previous boiling, because gases dissolved in the reservoir fluids distribute preferentially into the vapour phase during boiling. Consequently, there is a considerable scatter in the CO_2 data with time, as individual wells react to local boiling conditions. However, in both the Eastern and Western borefields, the single phase wells show a general decrease in the total CO_2 concentrations with time, as shown in Figure 3. This is the expected trend as the initial production causes a pressure drop in the reservoir, leading to increased boiling of the upflow before the fluid reaches the production sectors.

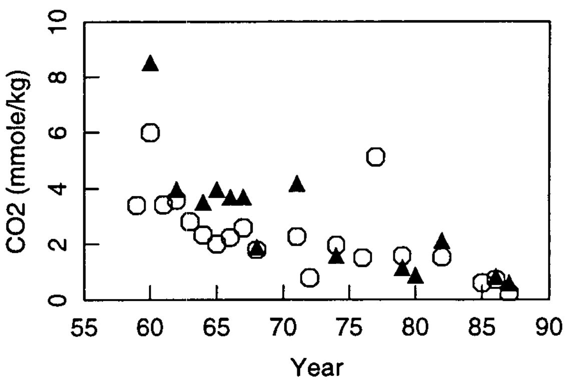

Figure 3: Weighted averages of measured aquifer CO_2 for the Eastern (triangles) and Western (circles) borefields.

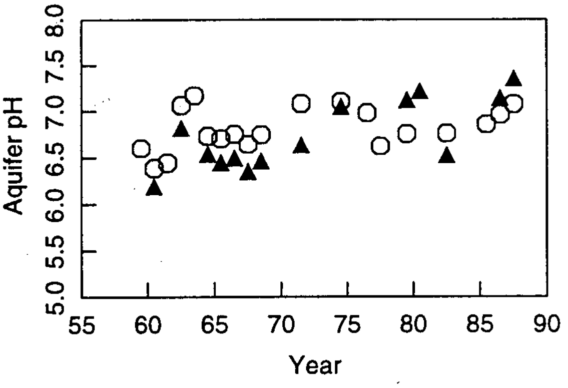

Figure 4: Mean values of measured aquifer pH for the Eastern (triangles) and Western (circles) borefields.

There is a large scatter due to the paucity of information contributing to the averages - in many years only one or two wells contribute to the Eastern borefield averages. There were 149 data points for the Western borefield and 25 for the Eastern borefield. In this paper we are also interested in the pH of the aquifer fluids, and mean values for these, the Eastern and Western borefields are shown in Figure 4.

THE CHEMICAL TRANSPORT MODEL

White (1995) has published an algorithm for the transport of reacting chemicals in multi-phase fluid systems such as those found in geothermal reservoirs. This algorithm has been incorporated into the geothermal simulator TOUGH2 (Pruess, 1987, 1991), and this code forms the basis of the work presented in this paper. More complete details of the extended TOUGH2 implementation can be found in White's paper.

The reactions included in the model are given below. The reaction for the dissociation of HCO_3^- to $CO_3^=$ has not been included as this becomes important only at higher pH's than those found at Wairakei. The chloride is assumed to be a non-reactive species, and so is not listed here, although its presence does effect the activities of the other species, and so changes the equilibria slightly.

$$\begin{aligned} H_2O &\rightleftharpoons H^+ + OH^- \\ H_2CO_3 &\rightleftharpoons H^+ + HCO_3^- \\ H_4SiO_4 &\rightleftharpoons H^+ + H_3SiO_4^- \end{aligned}$$

It is appropriate here to regard the species involved in these reactions as being in equilibrium, as the time scales for the geothermal processes considered in this paper are much longer than those relevant to the chemical reactions. The equilibria for these reactions are determined using temperature dependent equilibrium constants obtained from the SOLTHERM database compiled by Reed and Spycher (1992). The determination of chemical equilibria is discussed more fully in White (1994).

In addition to the aqueous phase reactions, the model includes the equilibrium reaction between the vapour and aqueous phases of CO_2.

$$H_2CO_3(aq) \rightleftharpoons H_2O + CO_2(gas)$$

This equilibrium is expressed by Henry's Law. The Henry's constant for this reaction is taken from O'Sullivan *et al.* (1985).

Composition of the deep fluids

For modelling we must determine an equilibrium composition for the 'source' fluid which enters the model at depth. We take this fluid to be single phase liquid at a temperature of 260°C and a pressure of 250 bars. These are typical of the conditions found at the base of the model (2500 m) where the source fluid enters. The concentrations of the various species, calculated at these conditions, are given in Table 1. The total amounts of inorganic carbon, chloride and silicon are 9.7 mmole/kg, 48.6 mmole/kg and 10.0 mmole/kg respectively.

Species	Concentration (mmole/kg)
H^+	$.3496\times10^{-3}$
OH^-	$.2521\times10^{-1}$
H_2CO_3	$.9338\times10^{+1}$
HCO_3^-	$.3618\times10^{+0}$
H_4SiO_4	$.9961\times10^{+1}$
$H_3SiO_4^-$	$.3923\times10^{-1}$
Cl^-	$.4860\times10^{+2}$

Table 1. Equilibrium composition of source fluid at 260°C and 250 bars.

RESULTS

In this section we present aquifer CO_2 and Cl^- chemistry calculated with the model, and compare this with the field data presented in an earlier section. For this comparison, we plot the concentrations of CO_2 and Cl^- at aquifer conditions, and the pH, for each of the major production elements in the Western and Eastern borefields against time. There are twelve such elements in the Western borefield and four in the Eastern borefield. These elements all lie in the top 1200 m of the two borefields.

Figures 5, 6 and 7 show the calculated Cl^-, CO_2 and pH in the Western borefield, and the corresponding measurements. Figure 6 shows that the curves fall into three distinct groups, and different line styles have been used to accentuate this. This grouping reflects the depths of the elements involved. The solid lines show shallow (depth $<$ 500 m) elements, the dashed lines show deep (depth $>$ 700 m) elements, and the dotted lines show elements between these two extremes. The same groups of elements are indicated on all of the plots by the same line styles. Figure 8 shows the time variation of liquid saturation in these same elements. This will be of help in understanding the nature of the various chemical changes.

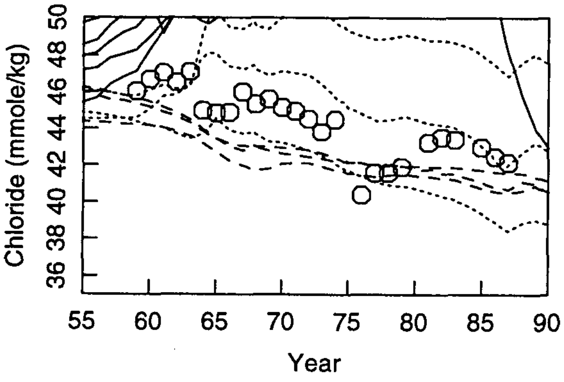

Figure 5: Calculated and measured (circles) Chloride concentrations for elements in the Western borefield.

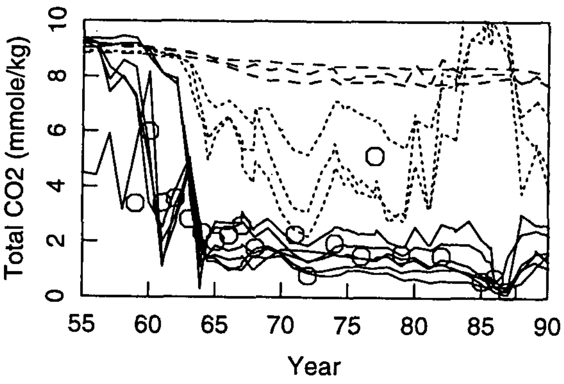

Figure 6: Calculated and measured (circles) CO_2 concentrations for elements in the Western borefield.

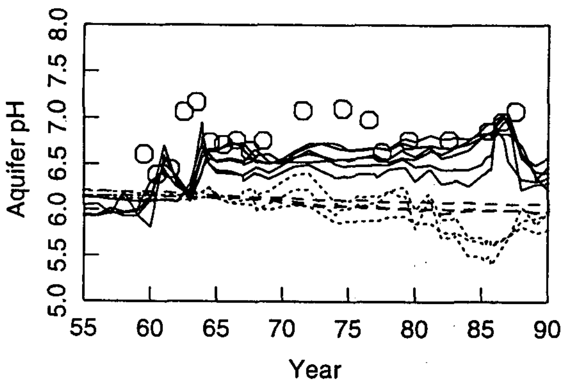

Figure 7: Calculated and measured (circles) pH for elements in the Western borefield.

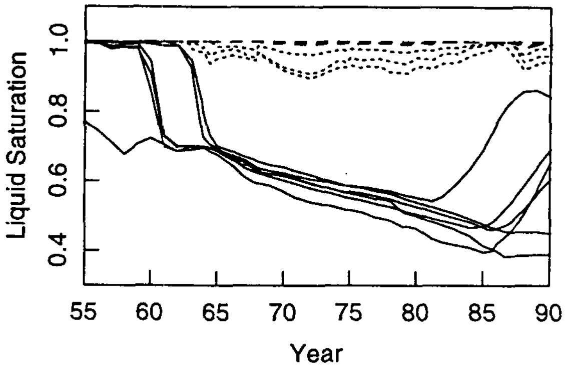

Figure 8: Calculated liquid saturation for elements in the Western borefield.

In Figure 6, the largest group of elements are the shallow ones, as indicated by solid lines, and these match the data well. Figure 8 shows that most of these elements were initially single phase, and have progressively boiled in response to production from the borefield. The drop in aquifer CO_2 is due to exsolution of aqueous CO_2 as this boiling proceeds. A simultaneous increase in aquifer pH would be expected, and this is shown in Figure 7. Note that, although the trend with time is reasonable, the calculated pH is about 0.5 unit too low over much of the production period. Finally, Figure 5, shows that the Cl^- concentration in this group of 'two-phase' elements has increased, as would be expected.

An interesting aspect of Figure 6 is the initial rapid drop in CO_2 concentration, followed by a much slower decrease from about 1964 onward. The initial drop corresponds to the formation of the two-phase zone, when aqueous CO_2 is partitioned into the vapour phase. This process is arrested when the liquid saturation decreases to the point where the liquid is immobile, as prescribed by the relative permeability functions. Although the liquid is immobile, the CO_2 laden vapour phase can still flow, and in response to this flow CO_2 will continue to be exsolved from the liquid. This behaviour gives some support to the choice of relative permeability functions used in the model.

The deepest group of elements in Figure 6 are shown by short dashed lines. Figure 8, shows that these are single phase elements which remain single phase throughout production. The calculated CO_2 and Cl^- both exhibit a gradual decline with time, indicating dilution by waters which contain no CO_2 or Cl^-. The slope of the dilution curves in Figure 5 matches the observed decline in Cl^- concentration. The calculated pH of these fluids declines by about 0.2 units over the production period. This is due to the change in temperature of these fluids, which drops by about 10°C due to the inflow of cooler surface waters.

The intermediate depth elements on Figure 6 are shown by dotted lines. These have similar behaviour to the 'deep' group, as Figure 8 shows them to be subject to only slight boiling. It can be seen from Figure 6 that even this slight boiling causes a significant change in the dissolved CO_2 concentration. These elements also undergo some dilution. Although the effect of this is masked by the great sensitivity of the CO_2 concentration to local boiling, it does show up in the Cl^- concentrations (Figure 5) of these elements, which exhibit the effects of both boiling and dilution. In this case the relative permeability functions allow the liquid to be almost fully mobile, while the vapour phase is essentially immobile.

Results for the Eastern borefield are shown in Figures 9, 10 and 11. Here there are only shallow and intermediate depth elements present, and most results are similar to those for the Western borefield. We note however, that the pH of the Eastern borefield is generally about 0.5 units higher than that in the Western borefield. This is consistent with the idea that the fluids in the Eastern borefield form the 'outflow' of the Western borefield, and have undergone additional boiling. Note also that the initial Cl^- concentrations in these elements (40 and 43 mmole/kg) are lower than indicated by the data, suggesting some refinement of the initial state may be required.

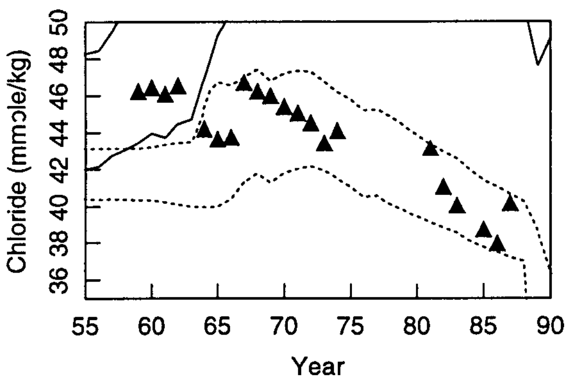

Figure 9: Calculated and measured (triangles) Chloride concentrations for elements in the Eastern borefield.

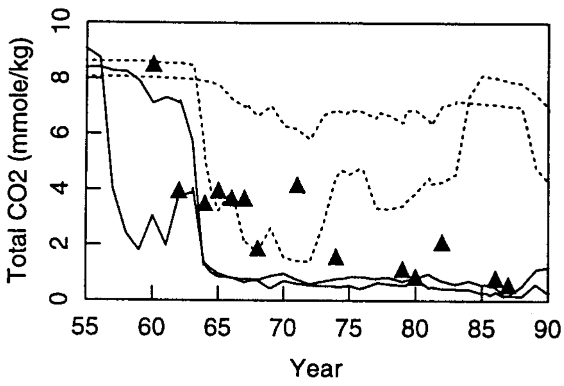

Figure 10: Calculated and measured (triangles) CO_2 concentrations for elements in the Eastern borefield.

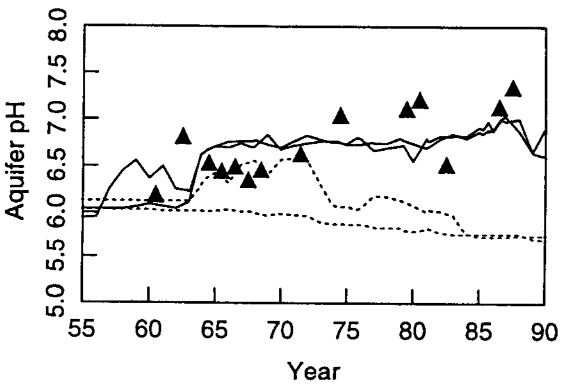

Figure 11: Calculated and measured (triangles) pH for elements in the Eastern borefield.

DISCUSSION and CONCLUSIONS

In this paper we have used an extended version of the geothermal simulator TOUGH2 to model the chloride and CO_2 chemistry of the Wairakei geothermal field. The results from this model are compared with chemical data collated for the period 1959 to 1987. Some specific conclusions concerning the Wairakei model are:

- Differences between observed and measured pre-production Cl^- concentrations suggest that some adjustment to the modelled natural state is necessary.
- The modelled Cl^- concentration in the single phase aquifer fluid shows the same dilution trend as the data. However the CO_2 concentration of these same fluids fails to match the observed values.

- The model shows a strong depth dependence in the predicted aquifer chemistry, with no single fluid in the model showing the correct behaviour of Cl^- and CO_2 simultaneously. The reason for this is still under investigation.
- A link between the observed aqueous CO_2 and the relative permeability functions is suggested. This provides some indirect evidence for the relative permeability functions that are appropriate to Wairakei.
- The predicted pH of the Eastern borefield fluids is about 0.5 units higher than the that from the Western borefield, consistent with the accepted conceptual picture that the Eastern borefield is partially fed by the outflow from the Western borefield, and is subject to further boiling.

In addition to these specific results, our work has shown that full scale chemical simulations are a practical and feasible way of providing further validation (or otherwise) for already successful geothermal models. As for the future, the work could be extended in several ways. Firstly, there is the temptation to add further chemical species to the model. For example, another aqueous-vapour species of different solubility to CO_2 would be very informative, *provided* that there is also suitable chemical data available. More generally, the capabilities of the extended TOUGH2 simulator are much wider than those used in this paper, and solid-aqueous, or non-equilibrium chemical reactions could be used to model many other new phenomena.

ACKNOWLEGDEMENTS

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