MODELLING OF ACID FLUID WELLBORE CHEMISTRY AND IMPLICATIONS FOR UTILISATION

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SUMMARY - Thermodynamic models have been developed to calculate the chemistry of an acid geothermal well inflow fiom measured surface chemistry and enthalpy. **This** information, together with wellbore simulation, allows the calculation of chemical conditions throughout the wellbore. The results obtained are **further** modelled **as** potential-pH Pourbaix type diagrams, describing corrosion product stability, to aid in the development of guidelines for materials suitable for utilisation of deep and acidic geothermal resources. These models, together with experimental and theoretical assessment of volcanic and acidic well fluids, advance the understanding of fluid chemistries and corrosion mechanisms for a range of engineering alloys that might be used for energy production fiom such **fluids.**

1.0 INTRODUCTION

Deep drilling of geothermal fields can provide (Lichti and Sanada, 1997):
- increased capacity of existing geothermal systems without the need for resolving new environmental and resource ownership issues (eg Italy and Japan)
- opportunities for extended utilisation of plant having significant residual life after depletion of shallow reserves through drawdown (eg Ohaaki, New Zealand and Larderello, Italy).

Both deep and shallow geothermal wells which approach intrusive magmatic bodies are being drilled in many countries (Sanada et al., 1997). The corrosivity of deep two-phase production fluids is expected to be greater than that of conventional, shallower reserves because of an increase in temperature and acidity (Lichti et al., 1997a, Lichti and **Sanada,** 1997).

Acid wells have been encountered in many shallow geothermal reserves, but production from acidic geothermal wells is not commonplace. The ability to safely and cost effectively produce such wells will depend **on** the well chemistry and the selected corrosion control method. However, the feasibility of fluid utilisation has been asserted and the factors affecting the cost and **risks** have been defined (Lichti and Sanada, 1997). The chemistries of some acid wells encountered in Japan and the Philippines have been summarised (Sanada et al., 1997). In some instances, the acidity encountered is believed to reflect the deep

reservoir fluid chemistry, while in other cases the acidity is developed fiom meteoric water inflow, or a mixture of the two (Lichti and **Sanada,** 1997).

This paper considers the corrosion chemistries that are developed downhole in an acid well at Mahanagdong in the Philippines. The aim of the work is to define materials and corrosion control options for acid fluids encountered in an actual well (Lichti et al, 1998a).

2.0 CORROSION CONTROL OPTIONS

Materials testing results and model corrosion mechanisms, on which materials selection guidelines can be based, are available for a range of aggressive geothermal fluids (Sanada et al., 1995, Lichti et al., 1997a, 1997b, 1998b Lichti and Sanada, 1997, Sanada et al., 1997, Sanada et al., 1998).

Application of the guidelines requires a thorough understanding of the relevant damage mechanisms and the factors controlling them. The procedure promoted for achieving the required definition of the corrosion chemistry and for selection of corrosion control methods for new plant involves (Lichti et al., 1998):
- measurement of produced fluid chemistries
- calculation of the in-plant chemical conditions
- comparison of in-plant conditions with materials test environments where corrosion performance data and models of corrosion are available
- laboratory simulation of the in-plant corrosion chemistries of produced fluids tests where the available materials performance data is inadequate

- revision of developed models, or development of new models, describing the corrosion processes
- *summary* of the model implications for materials selection and corrosion control guidelines
- testing of preferred materials and corrosion control methods in-plant

Ideally, the corrosion chemistries of the desired plant will be identified first, so that tests are conducted in environments which accurately simulate the expected environments. In practice this is difficult to achieve, particularly if fluid velocity is a significant parameter (Sanada et al., **1995**, Ikeuchi et al., **1997**).

This paper addresses the first three bullet points noted above for an acidic geothermal well at Mahanagdong in the Philippines.

3.0   ACID WELL GEOCHEMISTRY

Geochemistry of acid well fluids fkom geothermal wells in the Philippines has been the subject of a number of recent publications (Maturgo, **1996,** Salonga, **1996,** Dulce et al., **1996,** Rosell and **Ramos, 1997,** Parrialla et al, **1997,** Salonga and Auman, **1997**). Downhole pH and sulfur chemistry as a function of boiling point temperatures were determined for a number of wells fkom different fields (Maturgo, **1996,** Salonga, **1996)** and these could be linked to the sulfide minerology of rocks recovered from the acid Cl-SO, wells (Dulce et al., 1996). The produced fluids are characterised as being one of three types (Maturgo, **1996**):
- low Cl, high SO, with Na+K>Cl
- high Cl, high SO, with Cl>Na+K
- high Cl, high SO, with Na+K>Cl

Equilibrium boiling models of these fluids suggest downhole conditions can be of two types, as defined by Salonga **(1996)**:
- *acid SO$_4$-Cl fluids* dominated by *SO,* fkom shallow-formed acid SO_4-Cl fluids
- *acid NaCl(+SO$_4$) brine* having high dissolved SO, and HSO_4 (from dissociation of H_2SO_4) which, under reservoir conditions, give neutral pH and, upon boiling, complete dissociation to SO, gives more acid pH.

It has been argued that *neutral-pH NaCl brines* result fiom long term equilibrium reactions of the *acid NaCl(+SO$_4$) brine* with reservoir rocks and from the associated mineral deposition (Salonga, **1996**). Acid alteration of rocks with remnants of acid fluids capable of causing severe corrosion **of** casings in acid wells was reported in the Cawayan sector of the Bacman field (Rosell and **Ramos, 1997**).

More recent geochemical modelling of wells at Mahanagdong and Alto Peak (Parrialla et al.,

1997) reaffirmed the models which demonstrate pH decrease on boiling of *near neutral pH acid NaCl(+SO$_4$) brine* reservoir fluids that are controlled by the S chemistry. These authors also asserted that the acidity of the wellhead fluids derived fkom *acid NaCl(+SO$_4$) brine* [high Cl, high SO,] appears to be dependent on the presence of magmatic HCl in the reservoir. If present, excess acidity fkom HCl would control the pH, which would then remain unaltered in the boiling fluid models.

4.0   MODELLING OF WELLBORE CORROSION CHEMISTRY

During production the chemical composition **of** fluids in the wellbore is governed by the temperature, pressure and saturation of the two-phase fluid.

In this work we have calculated these variables using the wellbore silmulator **GWELL (Aunzo** et al., **1991)** to estimate pressure, temperature and saturation as functions of depth at a representative flow rate. Also calculated are the liquid and vapour velocities within the wellbore.

If we assume that all chemical species within the wellbore fluid are in equilibrium, then the chemistry of the fluid is specified by the total concentration of a set of basis species (see Bethke, **1996** for a discussion of basis species).

Litchner, **1996, has** developed conservation equations in terms of total concentration of a basis species and refers to these as generalised concentrations. Using these ideas, the conservation of the **basis** species within the wellbore can be expressed by the equations

$$\frac{\partial \Psi_j}{\partial t} = \frac{\partial \Omega_j}{\partial x} \quad j = 1, 2, \cdots, \text{NoPrimary} \qquad (1)$$

where the generalised concentration Ψ_j is given by

$$\Psi_j = \left(C_j + \sum_{sec} S_{ji} C_i \right) S_L + \left(\sum_{gas} S_{ji} C_i \right) S_g \qquad (2)$$

S_{ji} is the stoichiometric **matrix,** $\sum_{sec}$ represents a sum over all secondary species, $\sum_{gas}$ represents a sum over all gaseous species, S_L and S_g are liquid and gas saturations respectively and NoPrimary is the number of **primary** species in the wellbore. Ω_j is a generalised flux defined **by**

$$\Omega_j = J_j + \sum_{sec} S_{ji} J_i + \sum_{gas} S_{ji} J_i \qquad (3)$$

where

$$J_j = \rho_\ell S_\ell V_\ell C_j$$
$$J_i = \rho_\ell S_\ell V_\ell C_i - i \text{ liquid phase}$$
$$= \rho_g S_g V_g C_i - i \text{ gas phase}$$

where ρ_l, ρ_g are liquid and gas densities, V_ℓ and V_g liquid and gas velocities, C_j is the molality of primary species j, C_i the molality of aqueous secondary species i or the concentration M/(kg of steam)) of a gas species.

If we assume chemical concentrations in the wellbore are at a steady state then equation (1) becomes

$$\frac{\partial \Omega_j}{\partial x} = 0 \text{ or } \Omega_j = \text{const.}$$

The value of the constant is determined from *the* chemistry of the produced fluid. Stated simply, the flux of any primary species is constant throughout the wellbore.

If the well contains only single phase liquid, the solution is obtained by setting the total concentration of each primary species to the amount measured in the produced fluid. Actual concentrations of primary and secondary species are then obtained by solving for equilibrium (eg. Spycher and Reed, 1990, White, 1994).

For a two-phase fluid the situation is generally more complex as the phases may be flowing with different velocities. In this case an iterative technique is used to adjust concentrations, where iterations are continued until the species fluxes are correct (Lichti et al. , 1998).

4.1 Example

As an example of this process we have taken the published chemistry of PNOC well MG-9D located in the Mahanagdong geothermal field in the Philippines (Parrilla et al., 1997). The data for well MG-9D is reproduced in Table 1.

Using the data from Table 1, the wellbore geometry shown in Table 2 and assuming a flow rate of 120 kg/s from the well, we have calculated the chemistry over the length of the wellbore. Some of the important results are shown in Figure 1.

Table 1 - Production chemistry for Well MG-9D, taken from Parrilla et al. (1997).

H	SP	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
kJ/kg	MPa(a)	mmoles/100 moles steam							
1287	0.480	400	24.3	0.24	n.a.	0.0878	0.051	12.667	0.954

pH	Na	K	Ca	Mg	Fe	Cl	F	$SO_4(t)$	$NH_3(t)$	SIO_2
25°C	mg/kg									
3.1	3117	950	82	25	282	6175	3.1	508	15.6	910

Table 2 - Wellbore Geometry for Mahanagdong Well MG-9D (Salonga, 1998). (The wellbore model assumed a straight well of 1683.4 mVD (Vertical Depth) with the casing diameter changes at the stated values of VD, rather than MD (Measured Depth)). Reservoir temperature was 289°C.

Well Depth	1940.4 mMD 1683.4 mVD
Casing Size and Depth	20" 109 mMD CHF
	13 3/8" 689.8 mMD 663.9 mVD
	9 5/8" 1433.5 mMD 1279.2 mVD
	7 5/8" 1934.4 mMD 1678.2 mVD

5.0 POTENTIAL-pH MODELS FOR STATIC CONDITIONS

The calculated wellbore chemistry was used to model the possibility of the formation of passivating films on carbon steel bore casing material using potential-pH Pourbaix diagrams. Figures 2 (a) to (d) were prepared for the conditions defined in Figure 1 for the Fe-S-H_2O system at 300, 250, 200 and 150°C and show corrosion product stability as functions of temperature of the produced fluid and water chemistry (Lichti et al., 1998a).

The diagrams were prepared using thermodynamic data from Cobble et al. (1982), and are for static conditions where long term equilibrium is achieved. Areas depicting the
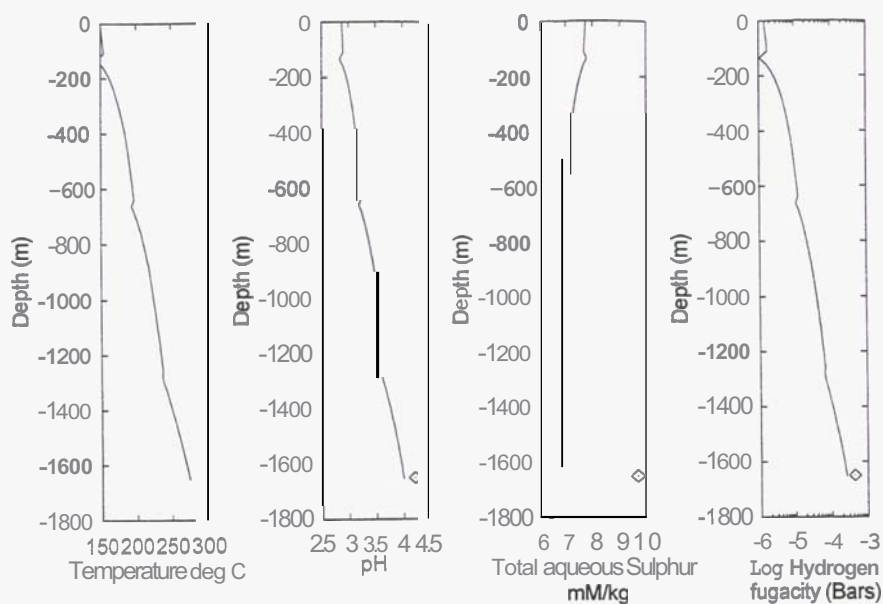
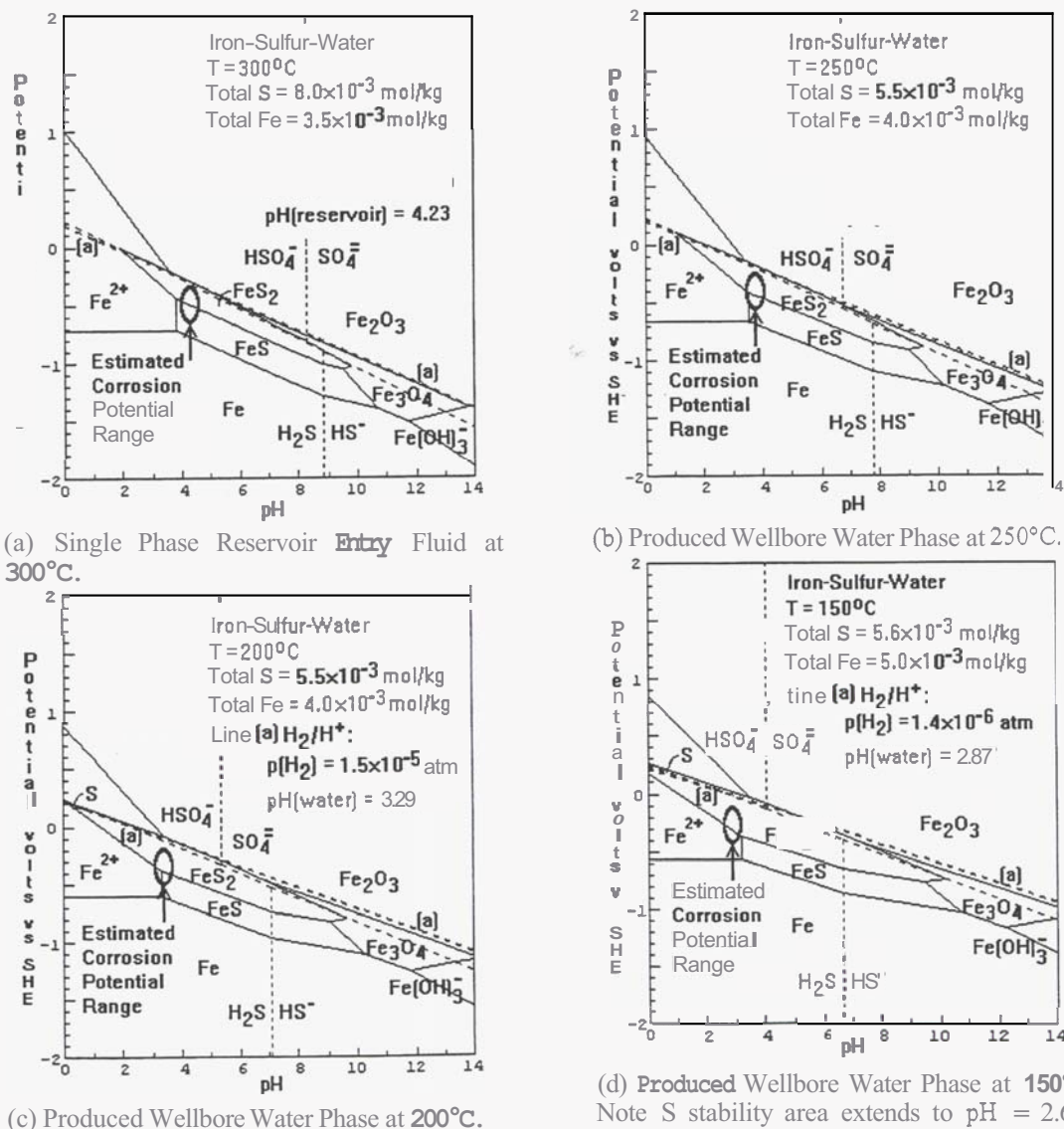Figure 1 - Results of wellbore chemistry modelling. The diamonds represent values for liquid water

(a) Single Phase Reservoir Entry Fluid at 300°C.

(b) Produced Wellbore Water Phase at 250°C.

(c) Produced Wellbore Water Phase at 200°C.

(d) Produced Wellbore Water Phase at 150°C. Note S stability area extends to pH = 2.65.

Figure 2 - Potential-pH Pourbaix diagram for Mahanagdong Well MG-9D wellbore chemistry.

expected corrosion potential range in Figure 2 were selected based on measured values in volcanic hot pools (Lichti et al., 1997a, 1998). Verification of these values in pressure vessel trials or on-site corrosion tests is required.

6.0 DISCUSSION

6.1 Corrosion Chemistry and Kinetics

The potential-pH Pourbaix diagrams (Figure 2) developed for Mahanagdong well MG-9D with the chemical conditions in Figure 1 indicate:

- Reservoir conditions at 300°C may promote foxmation of iron sulfides (Figure 2a), which have been shown under lower temperature conditions to provide protection to the underlying steel and acceptably low corrosion rates. The estimated pH and corrosion potential ranges are well within the stability areas for the formation of protective iron sulfide corrosion products (see for example Lichti et al., 1997c).

- The models predict that at 250°C the concentration of S species in the water phase is decreased by boiling and resultant phase separation. The effect on phase stability of the iron sulfide corrosion products (Figure 2b) is not dramatic in comparison with the diagram for 300°C (Figure 2a). However, the decrease in water pH shifts the apparent equilibrium position for exposed iron towards the Fe'' region of the diagram, where the risk of free corrosion is increased.

- Further decreases in temperature as the two-phase fluid moves up the well again give little change in the stability areas of the iron sulfides (Figure 2). However, the continuing decrease in pH moves the corrosion reaction area below the lower pH limit for FeS (Figure 2d) and into the region of Fe^{++}, where free corrosion is predicted.

- Sulfur stability is predicted at low pH values at the lower temperatures (Figures 2c and 2d). The kinetics of S formation have not been investigated. If S is formed, the corrosion rates would be expected to increase further (Schaschl, 1980).

6.2 Mixed Acids

The above models are for SO,, acidity. Corrosion kinetics observed for metallic specimens exposed in a hot pool at pH 1 on White Island, New Zealand (Lichti et al., 1997a, 1998), suggest mixed acidity attributable to C1+ SO, gives higher rates of corrosion than solutions acidified only with HCl (Sanada et al., 1995, 1998b). Tests on White Island are, however, limited to naturally formed, atmospheric pressure hot pools at a maximum temperature of 100°C.

6.3 Corrosion Control Options

Process and plant options for acid wells will depend on materials performance. The above models identify that the primary areas where SO, acidity is encountered are the upper well sections and the wellhead, where the pH is lowest and the turbulence may be significant (Ikeuchi et al., 1997). Two approaches to the selection of process and plant for these locations are available (Lichti and Sanada, 1997):

- To use more resistant alloys for bore casing and wellhead equipment, together with small sized separation or heat exchange plant close to the wellhead and immediate treatment and reinjection of the spent fluid.

- Downhole corrosion control by dilution, pH adjustment or inhibition of the acidic fluids to permit the use of carbon steels, or the least expensive stainless steels. Ideally, the beneficial effects of this corrosion control would continue as the heat energy is extracted and reinjection is achieved.

Lichti and Sanada (1997), proposed a series of tests aimed at finding methods for controlling casing corrosion problems in liquid dominated acidic systems. It was suggested that the preferred casing material would be carbon or low alloy steels, unless acidity could be predicted while drilling. This requires:

- Development of monitoring methods for candidate alloy materials tests downhole.

- Laboratory trials to determine if pH control and application of inhibitors are suitable techniques for controlling corrosion of -carbon and low cost stainless steels, for pH 2 to 4 fluids at temperatures up to 200°C.

- Downhole or wellhead plant field testing of alternative casing materials, pH control options and candidate inhibitors.

7.0 CONCLUSIONS

Wellbore production of geothermal fluids having neutral to moderately acidic pH has historically been achieved using low carbon steels. Attempts at production of *acid SO,-Cl fluids* and *acid NaCl(+SO,) brines* having pH less than 4 have not been successful in the Philippines due to corrosion of the bore casing steels and wellhead equipment. Models of the wellbore chemistry using a boiling fluid approach have previously demonstrated that at reservoir conditions the fluids can be near neutral pH, but on boiling, the S chemistry changes and the bore water pH decreases, thus limiting the useful life of carbon steels due to corrosion.

Application of a wellbore simulator further optimised the chemistry models for produced water chemical Conditions throughout the wellbore. This chemistry was used to prepare

potential-pH Pourbaix diagrams for the Fe-S-H_2O system for a range of temperatures throughout the producing well. The calculated chemistry and potential-pH diagrams suggest the corrosivity and sensitivity to erosion corrosion will increase because of the decrease in pH.

The wellbore simulation and corrosion process modelling will aid in the design of experiments for evaluation of pH adjustment and inhibitor options for the control of corrosion in deep and acidic, two-phase geothermal wells.

8.0 ACKNOWLEDGEMENTS

9.0 REFERENCES

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