CORROSION IN DEEP AND ACIDIC GEOTHERMAL WELLS

Keith **A** Lichti [a] and Stephen P. White [b]
[a] Materials Performance Technologies, [b] Applied Mathematics,
Industrial Research Limited, Lower Hutt, New Zealand
and
Norio **Sanada**
Tohoku National Industrial Research Institute,
AIST, MITI, Sendai, Japan

Abstract

Materials suitable for utilisation of deep and acidic geothermal resources have not been critically defined. Experimental and theoretical assessment work involving volcanic and acidic well fluids has advanced the understanding of the fluid chemistries and corrosion mechanisms, and practical performance of a range of engineering alloys exposed to these fluids: For example, carbon and low alloy steels have limited resistance, suitable high alloy materials are costly and intermediate alloy materials have not been fully evaluated. In this paper thermodynamic models are used to calculate the chemistry of the well inflow from measured surface chemistry and enthalpy. This information, together with wellbore simulation, allows the calculation of chemical conditions throughout the wellbore. Estimates of corrosion chemistry are incorporated into available models of corrosion based on the current materials performance knowledge base. These models assist in development of materials selection guidelines for deep and acidic geothermal well fluids and identify deficiencies in the current knowledge base. A materials testing program aimed at resolving these knowledge deficiencies and exploring engineering solutions to the materials selection problems is described.

1.0 INTRODUCTION

Deep drilling of geothermal fields can provide (Lichti and Sanada, 1997):

- the ability to increase capacity of existing geothermal systems and to do this 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 geothennal 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 from meteoric water inflow, or a mixture of the two (Lichti and Sanada, 1997).

It has been argued that the main areas where corrosion control methods will be required in deep and acidic two-phase production fluids are the wellbore and wellhead equipment where the water phase is handled

(Lichti and **Sanada.** 1997). The steam separated from more acidic two phase well fluids has been described as being no more corrosive than steam separated from conventional neutral pH fluids (Sato. 1997). although separated steam samples taken from some acid wells in the Philippines have shown unusually high levels of chloride suggesting the presence of HCl gas (Maturgo. 1996).

Production from dry steam fields which produce HCl acid gas is successfully achieved in many fields: eg Geysers (Truesdell et al. 1993). Mesico (Arriaga and Puente. **1993)** and Italy (Bracaloni et al. 1995). De-superheating of steam containing acid gases gives rise to acidc condensate and above ground corrosion control methods have been developed (Viviani et al.. 1995. Hirtz et al.. 1990. Bell. 1989). Avoidance of downhole corrosion has been achieved by variations in production practices such as closing some production levels (Truesdell. 1991). It has been proposed that injection practices which achieve de-superheating and neutralising of acid condensate in the reservoir. or in the well bore. may also be successful in controlling acid gas production (Bracaloni et al.. 1995).

Volcanic fumarole and hot spring environments reflect the chemistry of shallow magma-ambient conditions. Materials exposures in these environments permit predictions of alloy types which might be suitable for the development of deep and acid wells (Kurata et al. 1994. 1993. Lichti et al. 1997a, 1997b, Cherng and Wang. 1983)

The successful utilisation of more acidic well fluids will depend on the selection of cost effective corrosion control methods. The IEA Deep Geothermal Materials Subtask has included a survey of both materials performance knowledge and acid well fluid chemistries (Sanada et al. 1997). Efforts are under way to add the materials experience of geothermal developers to the survey. Materials experience in acidic fluids has a long history. and successes with moderate pH fluids have been recorded (eg Moeller and Cron. 1997). However. this experience has not been extended to the more acidc fluids having pH less than 3 (due to HCl) or to acid well fluids where the acidity is due to either SO_4 or a mix of HCl and SO_4 (Lichti et al, 1997a).

In this paper we consider the corrosion chemistries that are developed downhole in an acid well at Mahanagdong in the Philippines and compare these chemistries with those of acidic fluids previously tested in Japan and New Zealand. The aim of the work is to determine if the materials selection and corrosion control guidelines developed for HCl derived acid fluids. and those currently being developed for volcanic environments. can be applied to the SO_4. or mixed HCl plus SO_4, acid fluids encountered in an actual well.

2.0 MATERIALS TESTING RESULTS AND AVAILABLE GUIDELINES

The materials testing results and model corrosion mechanisms on which materials selection guidelines can be based are available for a range of aggressive geothermal fluids (see Table 1).

The resultant database of materials knowledge has some significant deficiencies. One such deficiency is in fluids where the acidity is from mixed acids and the temperature of the environment is above 100°C. Tests conducted in natural volcanic environments at atmospheric pressures and temperatures at or below 100°C provide a guide to material types which might be suitable, but do not provide adequate data for cost effective materials selection at higher temperatures and pressures. Conducting experimental work in acid well fluids under pressure is limited by the ability of the chosen wellbore casing and wellhead equipment materials to safely withstand the production environments for a period of time sufficient to obtain reliable kinetic results. As most geothermal wells are cased with carbon steels this deficiency is difficult to address. An alternative to in-situ testing is to evaluate materials and corrosion control methods in laboratory pressure vessels which aim to simulate the corrosive conditions (Inman et al., **1993).**

Table 1 Corrosion Results Matrix for Non-Aerated Aggressive Aqueous Geothermal Environments.

Environment	Conditions	Results	Mechanisms	Models	Reference
Hot Pool	T = 100°C, Non-Aerated, pH = 3	Intermediate Alloy Materials Required,	Passive Films. Pitting	Potential-pH Alloy Content. (PRE) Pitting Resistance Equivalent	Lichti et al.. 1997a
Hot pool	T=100°C, Non-Aerated, pH = 1	High Alloy Materials Required.	Acid Dissolution	Potential-pH	Lichti et al.. 1997a
Acid Well, Flowing Conditions	T = 100-200°C, Non-Aerated, pH = 2 to 3 (HCI present)	Intermediate Alloy Materials Required. Alloy Type Required Depends on pH.	Erosion Corrosion	Potential-pH	Sanada et al.. 1995
Autoclave, Acidified Tap Water	T = 100-300°C, Non-Aerated, pH = 1 to 5 (HCl added)	Alloy Type Required Depends on pH.	Acid Dissolution	Potential-pH	Sanada et al.. 1995
High Chloride. Neutral pH	T = 223-315°C Non-Aerated pH = 5.8 C1= 300,000 mg/kg	High Alloy Materials, Titanium Alloys and Cement Linings Used	Acid Chloride Attack, Erosion and Pitting Corrosion	Potential-pH. Alloy Content. Chloride-Sulfide SCC	Moeller and Cron. 1997. Fry et al.. 1989. Cramer et al.. 1983

Corrosion control methods and mechanistic models. developed for natural volcanic and simulated laboratory environments can only be applied to actual well fluids if the corrosion Chemistries of the tested and considered environments are comparable. This 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 conducting these comparisons involves:

- measurement of produced fluid chemistries
- calculation of the in-plant chemical conditions
- comparison of in-plant conditions with materials lest environments where corrosion performance data and models of corrosion are available
- simulation of the in-plant corrosion chemistries of these produced fluids in laboratory 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 in 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 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 address the first three bullet pints noted above for an acidic geothermal well at Mahanagdong in the Philippines.

3.0 PHILIPPINE GEOCHEMISTRY PROGRESS

Geochemistry of acid well fluids from 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 weredetermined for a number of wells from different fields (Maturgo, 1996, Salonga, 1996) and these could be linked to the sulfide minerology of rocks recovered from the acid $Cl-SO_4$ wells (Dulce et al., 1996). The produced fluids are characterised as being one of three types (Maturgo, 1996):

- low Cl, high SO_4 with Na+K>Cl
- high Cl, high SO_4 with Cl>Na+K
- high Cl, high SO_4 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_4 from shallow-formed acid SO_4-Cl fluids
- ***acid NaCl(+SO_4) brine*** having high dissolved SO_4 and HSO_4 (from dissociation of H_2SO_4) which under reservoir conditions, give neutral pH and, upon boiling, complete dissociation to SO_4 gives more acid pH.

It has been argued that ***neutral-pH NaCl brines*** result from 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) reaflirmed the models which demonstrate pH decrease on boiling of ***near neutral pH acid NaCl(+SO_4) brine*** reservoir fluids which are controlled by the S chemistry. These authors also asserted that the acidity of the wellhead fluids derived from ***acid NaCl(+SO_4) brine*** [high Cl, high SO_4] appears to be dependent on the presence or absence of magmatic HCl in the reservoir. If present, excess acidity from HCl would control the pH and this would 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.

These physical conditions are routinely calculated using a wellbore simulator. In this work we have calculated the physical conditions in the wellbore using the GWELL (Aunzo et al., 1991) to estimate pressure, temperature and saturation as functions of a 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

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

where

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

Ψ_j is a generalised concentration of primary species j , S_{ji} is the staciometric **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

$$J_j = \rho_\ell S_\ell V_\ell C_j$$

$$J_i = \rho_\ell S_\ell V_\ell C_i \quad -i \quad \textit{liquid} \ \textbf{phase}$$

$$= \rho_g S_g V_g C_i \quad -i \quad \textbf{gas phase}$$

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

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

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. For example, if the total flux of HCO_3^- out the top of the well is 1 mole/sec then it has this value throughout the well (assuming a single feed point and no deposition in the well)., Note that the total flux of HCO_3^- includes the flux of the HCO_3^- ion itself, plus the flux of any secondary or gaseous species containing that ion. If gas and liquid velocities are identical then the chemical composition of the fluid can be calculated by setting

$$C_j = N_j / \textbf{Flow} / (1 - \textbf{Dryness}) \qquad (4)$$

where N_j is the measured total flow of primary species j from the well, Flow is the flow rate of the well and Dryness is the mass fraction of steam in the two phase **mixture.** The equilibrium speciation of the two phase mixture is then calculated using the methods of White (1994).

When gas and liquid velocities are not equal this prescription leads to a chemical flux that is incorrect and C_j must be adjusted by

$$C_j = N_j \,/\, \text{Flow} \,/\, (1 - \text{Dryness}) - S_g \rho_g (V_g - V_\ell) \,/\, (1 - \text{Dryness}) \sum_{gas} S_{ji} C_i \,/\, (\rho_\ell V_\ell) \quad (5)$$

Here the C_i are gas phase concentrations calculated by the equilibrium code. This reduces the problem of determining the wellbore chemistry to solving equation (3) so that the generalised flux of each primary species is constant throughout the wellbore and all species are in equilibrium.

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 that uses equation (5) to adjust concentrations is used, where iterations are continued until the species fluxes are correct.

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 2.

H	SP	pH	Na	K	Ca	Mg	Fe	Cl	F	SO_4	SIO_2
kJ/kg	MPa(a)	25°C	mg/kg								
1287	0.480	3.1	3117	950	82	25	282	6175	3.1	508	910

H	SP	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
kJ/kg	Mpa(a)	mmoles/100moles steam							
1287	10.480	400	24.3	0.24	n.a.	0.088	0.051	12.667	0.954

Using the data from Table 2, the wellbore geometry shown in Table 3 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 3 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)).

Well Depth	Casing Size and Depth		Reservoir Temperature
1940.4 mMD	20"	109 mMD CHF	289°C
1683.4 mVD	13 3/8"	689.8 mMD 1663.9 mVD	
	9 5/8'	1433.5 mMD / 1279.2 mVD	
	7 5/8	1934.4 mMD / 1678.2 mVD	

5.6 POTENTIAL-pH MODEL§ FOR STATIC CONDITIONS

The calculated wellbore chemistry was used to model the potential for formation of passivating films on carbon steel bore casing material using potential-pH Pourbaix diagrams. Figures 2 to 5 were prepared for the conditions defined in Table 4 and for the Fe-S-H_2O system at 300, 250, 200 and 150°C and show corrosion product stability as a function of temperature of the produced fluid and water chemistry. The Pourbaix diagrams for these environments can be compared with those prepared previously for volcanic hot pools (Figure 6), HCl type acid wells (Figure 7) and for HCl laboratory test fluids (Figure 8) for which a database of materials results is available.

The diagrams were prepared using thermodynamic data from Cobble et al., 1982 and considering the stability of the following crystalline (c) and aqueous (aq) species; Fe(c), Fe^{++}(aq), Fe^{+++}(aq), Fe_2O_3(c), Fe_3O_4(c), $Fe(OH)^+$(aq) $Fe(OH)_2$(aq) $Fe(OH)_3^-$(aq), S(c). FeS(c), FeS_2(c), H_2S(aq), HS^-(c), HSO_4^-(c), SO_4^{--} (aq). The models presented in Figures 2 to 8 are for static conditions where long term equilibrium is acheved. Areas depicting expected corrosion potential range in Figures 2 to 5 were selected based on measured values in volcanic hot pools, Figure 6 (Lichti et al., 1997a). Verification of these in pressure vessel trials or on-site corrosion tests is required.

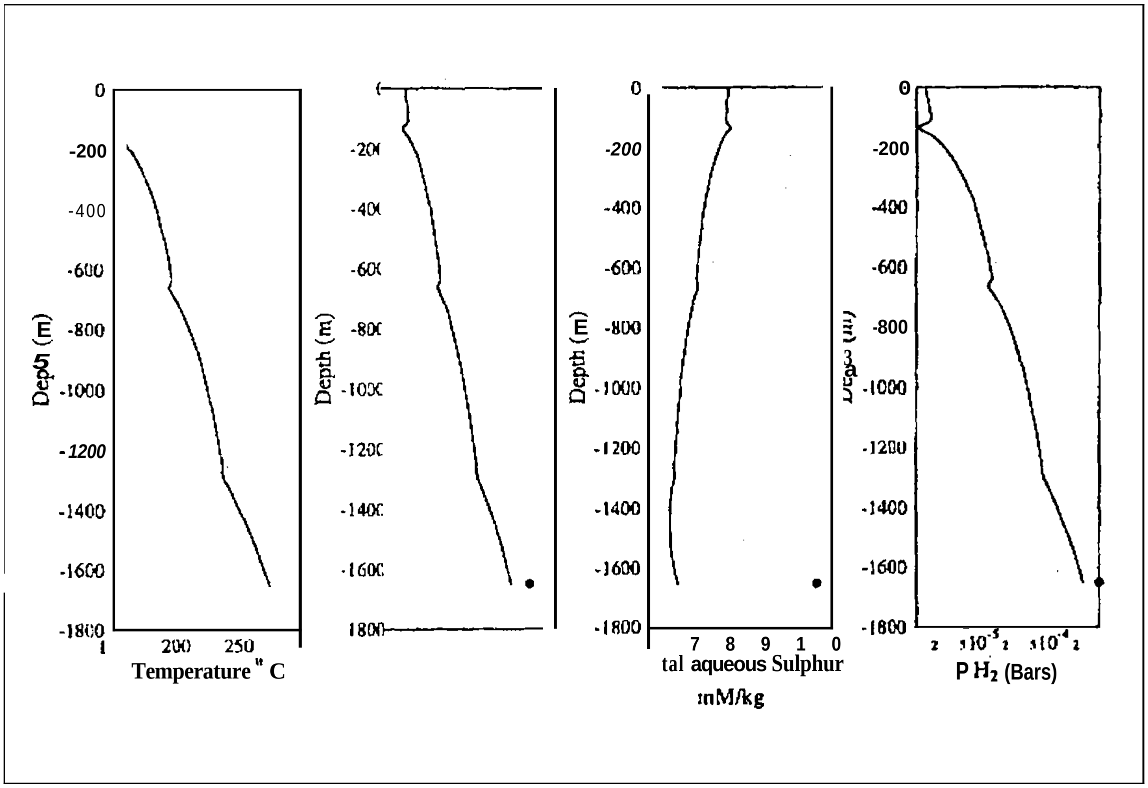

Figure 1 Results of Wellbore Chemistry Modelling. The Solid Circles Represent Values Obtained for Liquid at 300" C.

Table 4 Physical and Chemical Conditions of Wellbore Simulation Used for the Preparation of Potential-pH Pourbaix Diagrams for Mahanagdong MG-9D

Well Depth	Casing Dia	Temp	Total S in water	Total Fe in water	$p(H_2)$	pH	Figure Number
mVD		°C	mol/kg	mol/kg	bar(a)		
0	20" 0.5080m	150	$5.6x10^{-3}$	$5.0x10^{-3}$	$1.4x10^{-6}$	2.87	5
712	9 5/8" 0.2445m	200	$5.5x10^{-3}$	$4.0x10^{-3}$	$1.5x10^{-5}$	3.29	4
1404	7 5/8" 0.1937m	250	$5.5x10^{-3}$	$4.0x10^{-3}$	$1.1x10^{-5}$	3.79	3
--	Reservoir	300	$8.0x10^{-3}$	$3.5x10^{-3}$	$4.4x10^{-4}$	4.23	2

6.0 DISCUSSION

6.1 Comparison of Theoretical models and Prediction of Corrosion Kinetics

The potential-pH Pourbaix diagrams developed for Mahanagdong well MG-9D (Figures 2 to 5) show the following:

- Reservoir conditions at 300°C may promote formation of iron sulfides (Figure 2) which have been shown under lower temperature conditions to provide protection to the underlying steel and low, acceptable corrosion rates of carbon and low alloy steels. 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 3) is not dramatic in comparison with the diagram for 300°C (Figure 2). However, the pH of the water is decreased which moves the apparent equilibrium position for exposed iron towards and into 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 (Figures 4 and 5) however the continuing decrease in pH moves the estimated corrosion potential area below the lower pH limit for FeS (Figure 5) and into the region of Fe^{++} where free corrosion is predicted.
- Sulfur stability is predicted at low pH values at the lower temperatures (Figures 4 and 5). The kinetics of S formation have not been investigated. If S is formed the corrosion rates would be expected to increase further (Schaschl, 1980).

Comparison of the diagrams prepared for Mahanagdong with those reported previously by Lichti et al., 1997a, for White Island hot pools at 100°C (Figure 6), flowing acid wells in Japan (Figure 7) and simulated acidic test environments in Japan (Figure 8) suggests that:

- Under static or low flow fluid conditions, carbon steel in MG-9D carbon steel may experience similar corrosion processes as in the pH 3.8 Black Pot hot pool (compare Figure 5 with Figure 6). In this hot pool, carbon steels formed passive films but pitting corrosion was observed and corrosion rates were as high as 1.5 mm/year (see Figure 9).
- Under flowing well conditions at pH 3 (Figure 6) in Japan, (Sanada et al., 1995) corrosion rates of carbon steels were up to 7 times greater than in static laboratory pressure vessel trials characterised by the diagram of Figure 7. This suggests that under flowing conditions the iron-based wellbore materials (Figures 2 to 5) may be susceptible to corrosion if turbulence is significant.
- Figure 9 illustrates results of a previous comparison of kinetic results obtained from laboratory trials with kinetic results from White Island hot pools at 100°C. The simulated fluids used in the laboratory trials (Pourbaix diagram of Figure 8) gave comparable or lower corrosion rates to those obtained in the hot pools (**Pourbaix** diagram of Figure 6). The laboratory trials give good alloy performance ranking at 100°C but comparable high temperature data is not available for actual wells.

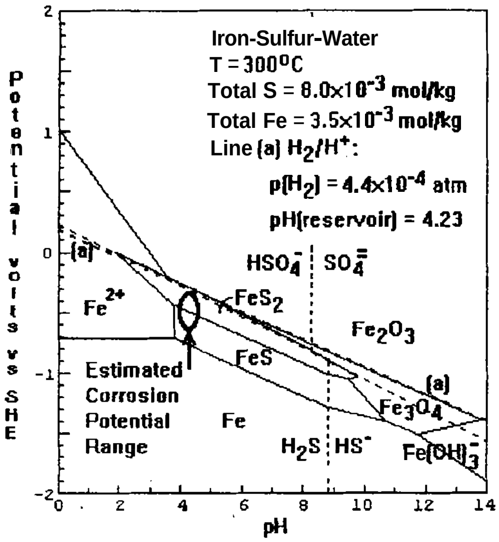

Figure 2 Potential-pH Pourbaix Diagram for Single Phase Reservoir Entry Fluid Conditions at 300°C for Mahanagdong Well MG-9D.

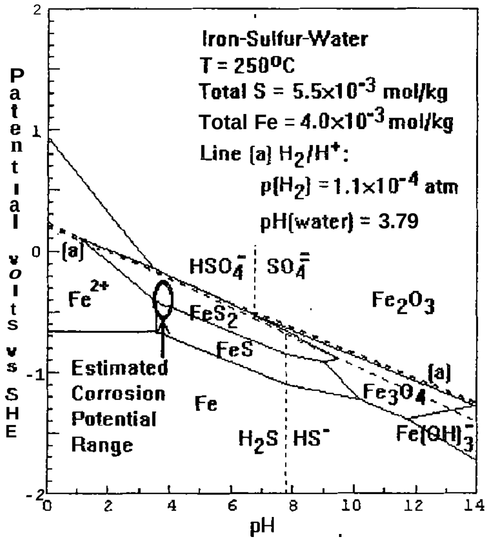

Figure 3 Potential-pH Pourbaix Diagram for Produced Wellbore Water Phase Conditions at 250°C for Mahanagdong Well MG-9D.

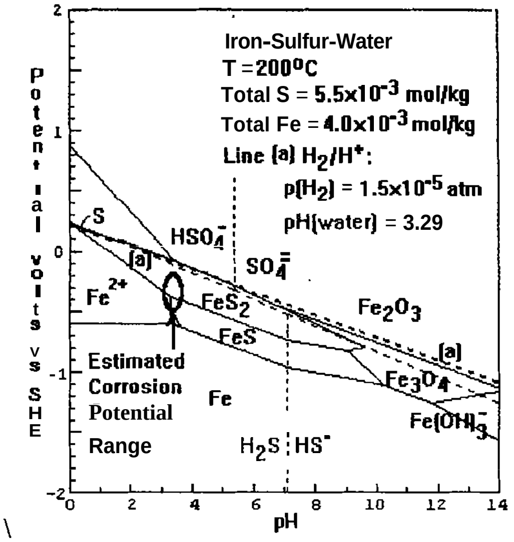

Figure **4** Potential-pH Pourbaix Diagram for Produced Wellbore Water **Phase** Conditions at 200°C for Mahanagdong Well MG-9D. Note S stability **area** extends to pH = 0.84.

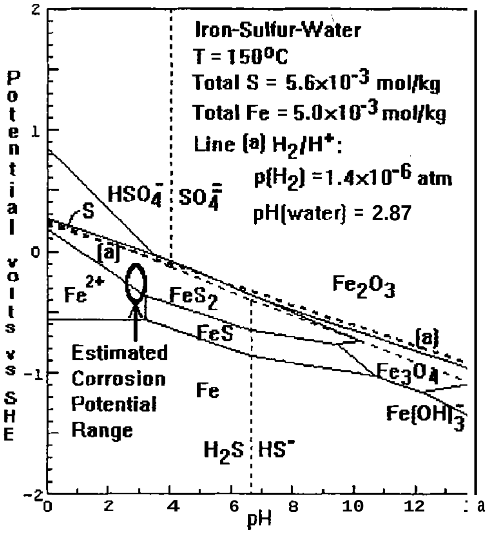

Figure 5 Potential-pH Pourbaix Diagram for Produced Wellbore Water Phase Conditions at 150°C for Mahanagdong Well MG-9D. Note S stability **area** extends to **pH** = 2.65.

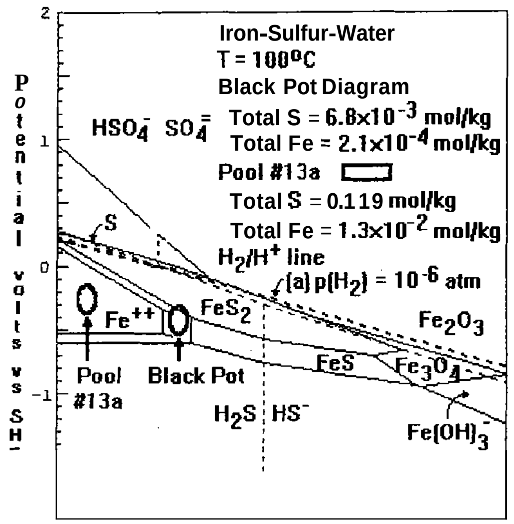

Figure 6 Potential-pH Pourbaix Diagram for White Island Hot Pools at 100°C (Lichti et al., 1997a). Potentials indicated based on measured values.

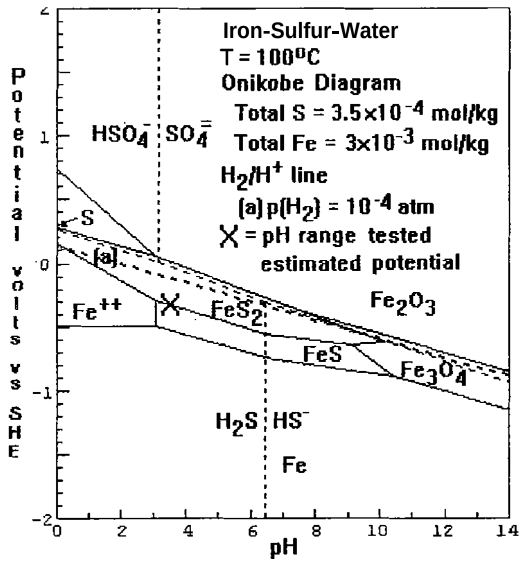

Figure 7 Potential-pH Pourbaix Diagram for Onikobe Acid Well no 105 separated water, T = 100 °C (Lichti et al., 1997a).

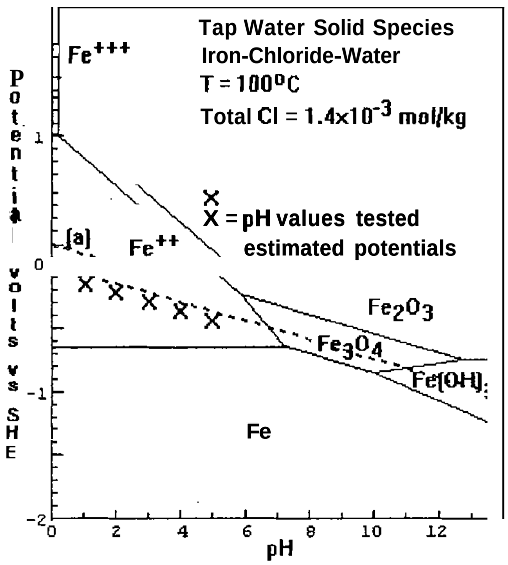

Figure 8 Potential-pH Pourbaix Diagram for Simulated Acid Well Fluid for Fe-Cl-H_2O having Cl = $1.4x10^{-3}$ mol/kg, T = 100°C (Lichti et al., 1997a)

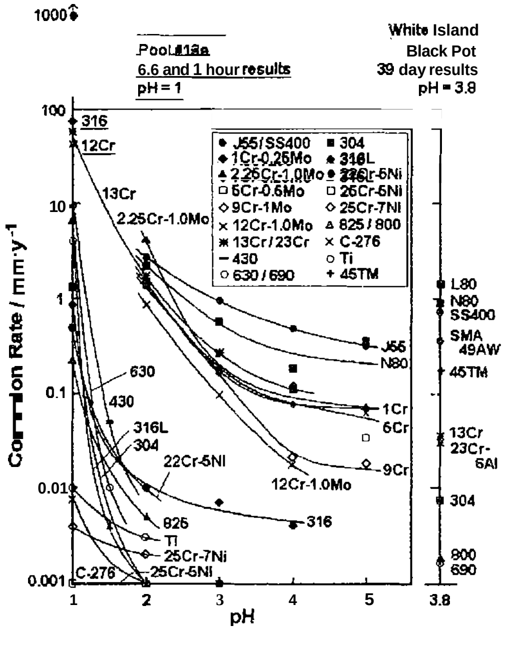

Figure 9 Corrosion Data for Simulated Acidic Fluids at 100°C with data for White Island Hot Pools added for comparison. (Lichti et al., 1997a).

6.2 Influence of Well Flow and Turbulence

The influence of flow rate on corrosion in HCl acidified solutions has been partially evaluated (Sanada et al.. 1995) in laboratory and field trials. Recent modelling of the fluid flow conditions in geothermal wells at Kakkonda. Japan. has suggested a tendency to high wall shear stress under conditions of slug flow (Ikeuchi et al., 1997). Well turbulence effects as demonstrated by these authors have not been considered in the wellbore simulations done in this work.

The relation between well turbulence and corrosion rate must be further evaluated. Data for fluids having HCl acidity is well defined (Sanada et al 1995) and indicates dramatic increases in corrosion under turbulent flow conditions. Additional trials are required to elucidate the corrosion properties of both static and flowing fluids having SO, acidity and HCl + SO_4 acidity, particularly at temperatures above 100°C (see Table 1).

6.3 HCl, SO_4 and HCI + SO_4 Acidity

Determining the presence or absence of HCI acidity is a significant problem in defining the type of acid fluids present in a well producing two phase fluid. Models of the type developed here and by others depend on the as analysed chemistry of separated steam and water samples. Waters having Cl > Na + K may indeed have some HCl acidity but this is difficult to verify. The presence of HCl gas in steam samples can be inferred from an analysis of chloride in the formed steam condensate. Significant levels of chloride are seldom seen in steam samples separated from two phase fluids unless the separation is less than desired. If chloride is seen. it is often attributed to steam phase solids transport or water droplet carryover. HCl acidity has. however. been asserted for some reservoir conditions and is readily identified in volcanic fumarole environments.

Chloride was not reported in the separated steam analysis results presented by Parrilla et al., 1997. for well MG-9D. but an earlier publication by Maturgo. 1996 indicated Chloride was present at 14 mmol/100 mol steam. This is at the low end of results provided by Maturgo, 1996, for a number of samples collected from acid wells in the Philippines (11 to 105 mmol/100 mol steam). HCI gas is, however, readily soluble in water and it is difficult to argue that gaseous HCl was present in the two phase fluid.

If the argument against HCI gas being present in the steam is set aside and the chloride is assumed to arise from the presence of HCl gas then the model can be altered to add HCI to the well fluid. Addition of 10 and 100 mmol/100 mol steam to the wellbore chemistry model results in the water phase at 150°C having pH's of 2.6 and 1.8 respectively. Inclusion of HCl results in a low pH throughout the wellbore where the acidity is controlled primarily by the HCI and not the sulfur chemistry. This aspect is to be further modelled after resolution of the meaning of the reported chloride in the steam phase.

Corrosion kinetics observed for metallic specimens exposed in a hot pool at pH = 1 (see Figure 9) on White Island, New Zealand (Lichti et al., 1997a), suggest mixed acidity attributable to HCl + SO_4 gives higher rates of corrosion than solutions acidified only with HCl (Sanada et al., 1995). The White Island results are. however, limited to readily corroded materials and high alloy materials have yet to be tested in the mixed acid. pH 1 hot pool. Tests on White Island are also limited to naturally formed, atmospheric pressure hot pools at a maximum temperature of 100°C. Higher temperature work with HCl + SO, acidity has not been done.

6.4 Corrosion Control Options and Future Testing

Process and plant options for acid wells will depend on materials performance. The above models indicate that the primary areas where SO_4 acidity is encountered will be in the upper sections of the wells and at the wellhead where the pH is lowest and the influence of turbulence may be significant. 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 either dilution or inhibition of the acidic fluids to permit the use of carbon steels, or less expensive stainless steels, and ideally the beneficial effects of this corrosion control would continue to be effective as the heat energy is extracted from the produced fluid and reinjection is acheved.

Lichti and Sanada, 1997, proposed a series of tests aimed at finding methods for controlling casing corrosion problems in liquid dominated acidc systems. It was suggested that the preferred casing material would be carbon and low alloy steels unless acidity could be predicted whle dnlling. 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 the control of corrosion of carbon and low alloy stainless steels in the pH range 2 to 4 at temperatures up to 200°C
- downhole field testing of alternative casing materials, pH control options and candidate inhibitors.

7.0 CONCLUSIONS

Production of geothermal fluids having neutral to moderately acidic pH has historically been achieved using low carbon steels. Attempts at production of *acid* SO_4*-Cl fluids* and *acid* $NaCl(+SO_4)$ ***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 had previously demonstrated that at reservoir condtions the fluids can be near neutral pH, but on boiling there is a change in the S chemistry and a decrease in bore water pH which limits the useful life of carbon steels due to corrosion.

Application of a wellbore simulator has further optimised the chemistry models to give a measure of produced water chemical conditions throughout the wellbore. This chemistry was used to prepare potential-pH Pourbaix diagrams for the Fe-S-H_2O system at a range of temperatures throughout the producing well. The chemistry and developed diagrams suggest that corrosivity of the fluids will increase and the sensitivity to erosion corrosion will increase because of the decrease in pH.

The current progress with the wellbore simulation and corrosion process modelling provides guidelines for planning of corrosion experiments designed to determine the feasibility and optimal conditions for using pH adjustment and inhibitors for the control of corrosion in deep and acidic, two-phase geothermal wells.

8.0 ACKNOWLEDGEMENTS

This paper was prepared using financial support from New Zealand Foundation for Research Science and Technology and from AIST, MITI, Japan. The authors extend their thanks to Noel Salonga and PNOC-EDC for the provision of wellbore data and production results.

9.0 REFERENCES

Andreussi, P., Paglianti, A. and Pasqualetti. A. (1995) Design of an absorption column for steam washing. WGC, Florence, Italy, pp 2415-2420.

Arriaga. M-C.S. and Puente, HG. (1993) Case histories of two Mexican volcanic hydrothermal systems. GRC Trans, Vol 17, pp 185-201.

Aunzo. Z.P., Bjornsson, G.. Bodvarsson. G.S. (1991) Wellbore Models GWELL, GWNACL, and HOLA User's Guide. Lawrence Berkeley Laboratory Report LBL-31428

Bethke. C.M. (1996) Geochemical reaction modelling. Oxford University Press. New York

Bell D (1989) Description of an operational desuperheating and chloride scrub system, GRC Trans Vol 13, pp. 303-307.

Bracaloni, M., Culivicchi, G. and Fornari, B. (1995) Erosion and corrosion problems experienced during the operation of geothermal turbines, WGC, Florence, Italy, pp 2427-2432.

Cherng, F.P and Wang, J.R. (1983) Corrosion of metals by geothermal fluids in Tiawan's Tatun Volcanic Region and Novel Approaches for controlling the problem, in Proc Int Symp on Solving Corrosion and Scaling Problems in Geothermal Systems, San Francisco, NACE, pp 285-293.

Cobble, J.W., Murray, R.C. Jr., Turner, P.J. and Chen, K. (1982) High-temperature thermodynamic data for species in aqueous solution, NP-2400, Research Project 1167-1, Final Report to EPRI.

Hirtz, P., Miller, J. and Prabhu, E. (1990) Operational results of a dry-steam resource chloride corrosion mitigation system, GRC Trans Vol 14, Part II, pp 1667-1675.

Ikeuchi, J., Kimura, S., Kurata, Y., Pestov, I. and Sanada, N, (1997) Material damage in deep geothermal well-bores, in Proc 19th NZ Geo Workshop, pp 175-180.

Inman, M.E., Sharp, R.M., Wright, G.A. and Wilson, P.T. (1993) Predicting protective film behaviour on low carbon steel, Proc 15th NZ Geo Workshop, pp 75-80.

Kurata, Y., Sanada, N. Nanjo, H., Ikeuchi, J. and Lichti, K.A. (1994). Field testing of materials at White Island, Workshop on Deep-seated and Magma-Ambient Geothermal Systems, Tsukuba, Japan, Mar, pp 167-170.

Kurata, Y., Sanada, N. Nanjo, H., Ikeuchi, J. and Lichti, K.A. (1995). Material damage in a volcanic environment, WGC, Florence, Italy, May, pp 2409-2414.

Kurata, Y., Sanada, N. Nanjo, H. and Ikeuchi, J. (1995). Casing pipe materials for deep geothermal wells, GRC Trans, Vol 19, pp 105-109.

Lichti, K.A., Swann, S.S., Sanada, N., Kurata, Y., Nanjo, H., Ikeuchi, J. and Christenson, B.W. (1997a) Corrosion in volcanic hot springs, GRC Trans, Vol 21, pp 299-307.

Lichti, K.A., Swann, S.S., White, S.P., Sanada, N., Kurata, Y., Nanjo, H., Ikeuchi, J. and Christenson, B.W. (1997b). Corrosion in volcanic gases, in Proc NEDO Int Geo Symp, Mar 11&12, Sendai. Japan, pp 154-163.

Lichti. K A and Sanada. N, (1997) Materials Issues for Utilisation of Deep Geothermal Systems, in Proc 19th NZ Geo Workshop, pp 169-174.

Lichti. K.A.. Wilson. P.T. and Inman, M.E. (1997c) Corrosivity of Kawerau geothermal steam, GRC Trans, Vol 21, pp 25-32.

Lichtner, P.C. (1996) Continuum formulation of multicomponent-multiphase reactive transport, Rev in Mineralogy. Vol 34, pp 1-81.

Maturgo. O.O. (1996) Chemical characteristics of acid fluids in some PNOC geothermal wells. 17th PNOC-EDC Geo Conf, Manila, Phlippines, ppl 11-117.

Moeller. R H and Cron C J (1997) Corrosion performance of Ni-Cr-Fe alloys in the hyper-saline brines of the Salton Sea Geothermal Resource, Paper presented at Annual GRC Meeting, October.

Parrialla, E.V., Martinez, M.M. and Salonga, N.D. (1997) Assessment of fluid acidity in Alto Peak and Mahanagdong geothermal fields, Leyete, Philippines, 18th PNOC-EDC Geo Conf, Manila, Philippines. pp 182-188.

Pye, D.S. Holligan, D. Cron, C.J. and Love, W.W. (1989) The use of Beta-C Titanium for downhole production casing in geothermal wells, Geothermics, Vol 18, No 1/2, pp 259-267.

Rosell, J.B. and Ramos, S.G. (1997) Origin of acid fluids in the Cawayan sector Bacman geothermal production field. 18th PNOC-EDC Geo Conf, Manila, Phlippines, pp 36-43.

Sanada, N., Kurata, Y., Nanjo, H. and Ikeuchi, J. **(1995)** Material damage in **high** velocity **fluids,** GRC Trans, **Vol 19,** October, pp **359-363.**

Sanada, N., Kurata, Y. and Lichti, **K.A. (1997)** Evaluation and development of Deep Geothermal resources - Materials Subtask of IEA research Collaboration Program. GRC Trans, **Vol 21**, pp3**17-324..**

Sato, K. **(1997)** private communication.

Schaschl, E. **(1980)** Elemental sulfur as a corrodent in deaerated, neutral aqueous solutions. **NACE,** Materials Performance, July, pp **9-12.**

Spycher, **N.F.** and Reed **M.H.N.F.(1990)** SOLVEQ: **A** computer program for computing aqueous-mineral-gas equilibria. **U** of Oregon Report, **5** October, **36** pages.

Truesdell, A., Walters, **M.,** Kennedy, **M.** and Lippmann, **M. (1993)** *An* integrated model for the origin of the Geysers geothermal field, GRC Trans, Vol **17,** pp **273-280.**

Truesdell, A., **(1991)** Origins of acid **fluids** in geothermal resources, GRC Trans, Vol **15,** pp **289-296**

Viviani, E., Paglianti, A., Sabatelli, **F** and Tarquini, B. **(1995)** Abatement of hydrogen chloride in geothermal power plants, WGC, Florence, Italy, pp **242 1-2426**

White, S.P. **(1994)** Transport of reacting chemicals in a two-phase reservoir, in Proc 16th **NZ** Geothermal Workshop, **pp 175-180.**