Proceedings 25th NZ Geothermal Workshop 2003

UTILISATION OF ACIDIC GEOTHERMAL WELL FLUIDS: PROGRESS TO 2002

K. LICHTI[1], A. KLUMPERS[1] & N. SANADA[2]

[1]Materials Performance Technologies, IRL, Lower Hutt, New Zealand
[2]Institute for Structural and Engineering Materials Research, National Institute of Advanced Industrial Science and Technology (AIST), Japan

SUMMARY - Direct utilisation of acidic two-phase geothermal well fluids for power generation is feasible using present day technology *so* long as the initial downhole and production water pH is > 3. The corrosion can be controlled by pH adjustment, through for example, injection of NaOH or alternatively corrosion resistant alloy casing can be used in the upper part of the well. Superheated steam carrying HCl gas can be treated at or near the surface by pH adjustment to control corrosion. This paper gives a summary of recent progress and problems encountered in international demonstration plant and an update on work in laboratory pressure vessels in New Zealand.

1.0 INTRODUCTION

Geothermal wells that produce near neutral to alkaline waters (pH > 4.5) or steam having no acid gas concentrations can be developed for power generation using conventional production plant and process technologies and using conventional geothermal plant materials selection practices (Sanada et al, 2000). The reason for this is the formation of protective scales or passivating films that limit corrosion by blocking the corroding steel surface from the corrosive solution (Lichti et al, 1997, Lichti and Bacon, 1998).

Some fields and small areas of some fields have encountered acid waters or superheated steam containing acid gases. In these instances corrosion of conventional bore casing and wellhead equipment can limit the useful life of the wells. R&D and developer initiatives for application of corrosion control practices have been successful in finding solutions that allow continuing production from these marginal fluids (Sanada et al, 2000, Rivera et al, 2000).

Problematic acid fluids are also being encountered in surface energy plant and there is a trend to application of similar corrosion control practices giving synergistic progress in identifying solutions (Lichti et al, 2000, Villa et al, 2001 and 2002, Gallup, 2002).

This paper aims to review recent progress being made by a number of researchers and developers in the utilisation of acidic geothermal well fluids.

2.0 PROGRESS TO 2000

A previous International Energy Association (EA) Deep-Seated Geothermal Materials Subtask that was active from 1996 to 2000 (Sanada et al, 2000) documented that direct utilisation of the more acidic two-phase geothermal well fluids for power generation was economically feasible using present day technology provided the downhole and production water pH was > 3:

- Experimental results and demonstration plant provided evidence for economic utilisation of corrosion resistant alloy casing in the upper part of the wells.
- pH adjustment by injection of NaOH in two phase systems was demonstrated by a number of researchers to be a suitable means of corrosion control.
- Superheated steam carrying HCl gas has been successfully treated at or near the surface by NaOH injection to control corrosion
- Hyper-saline brines have been produced using sacrificial cement-lined production tubing, corrosion resistant Ni-Base alloy and titanium alloys.
- Velocity of produced moderate to low pH fluids was shown to be an important factor in the processes that facilitate passive film formation.

NaOH injection for control of corrosion in acidic well fluids was sufficiently well developed to allow predictive thermodynamic modelling of the chemistry and corrosion control mechanisms - namely adjustment of pH to achieve corrosion product stability (Sanada et al, 2000). It was also argued that once produced steam is separated from the two phase acid well fluids, or condensate is formed and separated from steam containing acid gas, the resultant separated steam was no more corrosive than that derived from conventional resources and available experience verifies this.

A number of initiatives that were being progressed up to 2000 to demonstrate feasibility of and plant development for NaOH injection for corrosion control of acidic fluids deserve special mention:

- Rivera et al (2000) completed a demonstration project for control of acid fluid corrosion by downhole injection of caustic at Miravalles, Cost Rica. They successfully adapted techniques used for downhole injection of scale control inhibitors.
- Giorgio et al (2000) calculated dew point composition of condensing superheated steam containing HCI (pH of **3.8**) and measured corrosion rates as a function of chloride content of the steam.
- Lichti et al (1999) simulated acid fluids in a laboratory pressure vessel and demonstrated that passive films containing iron sulfides and iron oxides could be formed in pH adjusted fluids at high temperatures. At pH **5** and 150°C corrosion rates of 0.3 mm/year were achieved after 12 hours but at 95°C the corrosion rate never dropped below 1.5 mm/year, even after *66* hours.
- Villa et al (2000) reported preliminary results of short term field trials for injection of NaOH to control corrosion in an acid well MG-9D in Leyte, Philippines. Pumping constraints prevented full pH control and pH values were lower than desired giving a maximum pH of 4 and limited corrosion control.
- White et al (2000) contrasted MG-9D corrosion properties with newly drilled Ohaaki, New Zealand deep wells of near neutral pH. Potential-pH Pourbaix diagrams were used to illustrated the relationship between pH and stability of corrosion products. The tendency to scale formation was calculated under production conditions but not for pH adjusted fluids, and calcite was predicted in one of the Ohaaki wells modelled.

3.0 PROGRESS TO 2002

The IEA initiative ended in 2000 but research and development efforts have continued.

3.1 Field Experience

Commercial experience at producing acid well fluids is now being reported:

- Results for a number of trials aimed at controlling acid well corrosion at Tiwi, Philippines were reported by Gardner et el (2001). Filming amines were successful at controlling corrosion in surface equipment at temperatures below 200°C. NaOH treatment to give pH **5** to *6* was also effective. Downhole injection trials were completed using Inconel **625** alloy tubing with 4% NaOH solution to give pH between 4.5 and 5, with these low pH values being chosen because previous work at pH *6* had exacerbated silicate scaling. Minor active corrosion at the wellhead was observed. At the end of the trial the injection tubing could not be removed because of downhole scaling (possibly anhydrite ($CaSO_4$)).
- Long term NaOH injection trials in 2 wells that produce pH **2.3** to 3.2 waters at Miravalles, Costa Rica were completed (Moya and Mainieri, 2002, Moya and Rivera, 2002). Increasing pH to the range 7.2 to 8.2 was effective at controlling corrosion, however oversaturation of anhydrite ($CaSO_4$) and complex amorphous silica was observed. Anhydrite deposition blocked the wellbore after *6* months of operation. Inhibitors for anhydrite scaling are being sought for testing.
- Sanchez et al (2001) calculated NaOH injection rates required to overcome a sulfate buffer in example wells in the Philippines. They reported increasing anhydrite oversaturation as temperature decreased (as a result of injectate dilution) and as pH was increased from 4 to 5.
- Acid wells that precipitated silica scales in wellhead equipment were successfully produced in Mindanao 11, the Philippines with no chemical additions (Nogara, 2001, private communication).
- NEDO (2000) evaluated galvanic corrosion of electrically coupled production pipes placed at 1100m deep in the Kakkonda Deep Well WD-1b. These were a set of joined pipes, 7 inches in

diameter and 100 m in total length, which consisted of 24 pieces of API L-80 pipes and stainless steel pipes. The set of pipes was exposed to the acidic production fluid for 40 days. The pipes were exposed primarily to wet steam and the **L-80** joined to stainless steel corroded at a rate of 0.2 mm/year compared to the uncoupled L80 which had negligible corrosion.

Above ground corrosion control testing in acid process fluids and theoretical studies are providing complimentary results:

- Corrosivity of aerated acid steam condensates (pH 4.5) from heat exchangers was decreased by means of a spray tower that forced CO_2 evolution from low temperature solutions (Villa et al, 2001). Adjusting pH to 7.5 and 8.0 was only partially successful at giving further decrease in corrosion as the reduction in corrosion is offset by oxygen pitting (Villa et **al, 2002).**
- Severe oxygen induced pitting corrosion was observed when aerated condensates were mixed with brine for reinjection (Gallup et al, 2002).
- Cordova and Ho (2001) tested a proprietary oxygen scavenger for use in combination with pH adjustment (5.5 to **6.5)** to control aerated condensate corrosion. Oxygen removal was reported to have been economically achieved - corrosion rates were not reported.
- Lichti et al (2000) measured corrosion rates in separated water (brine) solutions at *86* to 97°C when the pH was adjusted to control silica scaling. Localised pitting corrosion readily initiated at pH **5** but was less at pH *6*. Deposition of thin scales of silica retarded the corrosion.
- Kurata et al (2001) did computational simulation of galvanic corrosion of L-80 casing electrically coupled with stainless steel casing such as 15Cr, 22Cr, 25Cr and Type 304 stainless steel in an acidic well. The zone of galvanic corrosion of the L-80 pipe extended some hundreds of mm from the joined section. The predicted maximum enhanced corrosion rates for L-80 joined with 15Cr, 22Cr, 25Cr and 304 were **2.9,** 2.0, 2.1 and 5.3 mm/year respectively. **This** can be compared to a predicted corrosion rate of uncoupled L-80 of **0.4** mm/year.
- Hirtz et al (2002) tested amine type inhibitors for dry steam scrubbing with an amine regeneration step to recycle the inhibitor. Amines were shown to provide an economically viable alternative to NaOH pH adjustment. **They** also reported initial success in use of a calcite bed to absorb HCl gas from dry steam.

3.2 Laboratory Corrosion Results

Work by Lichti et al, **1999,** in simulated geothermal fluids in a laboratory pressure vessel has previously demonstrated passive scale formation and corrosion rate of **0.3** mm/year in acid solutions adjusted to pH 5. Attempts to repeat these early experiments were not always successful and more recent work has aimed to characterise the properties of the passive films or scales that form and to determine how their properties impact on the corrosion rate.

Figure **1** shows an SEM view of corrosion product scales formed on carbon steel, tested in a pressure vessel at 150°C at *6* bar(a). The test solution was prepared from sulphuric acid solution at pH **3** with 2000 ppm Cl^- added as NaCl, with the pH adjusted to pH 6 by caustic addition. Bubbling of **1**% H_2S through this solution gave pH **5** at room temperature and **this** solution was pumped through the pressure vessel at a rate of 15 ml/min for 52 hours. The end of test Linear Polarisation Resistance corrosion rate for carbon steel samples was measured as 0.26 mm/year. Experiments at higher pH appear to give lower corrosion rates in the short-term experiments conducted. Longer tests are planned.

Figure **1** shows an apparent underlying layer exposed by scratching the surface and flaking portions of the outer layer.

In-situ X-Ray Diffraction on the exposed sample indicated:

- **A** strong background of base iron
- Well-crystabed Troilite (FeS)
- Lesser amounts of Mackinawite **($Fe_{(1+x)}S$)** and Magnetite (Fe_3O_4)

Figure 2 shows the same sample in cross section with EDX line scans for oxygen, sulfur and iron across the scale. **This** figure shows a three-layer structure:

- Inner layer rich in Oxygen.
- Middle layer with both oxygen and sulphur present.

- Outer layer rich in sulphur.
- Iron at a seemingly uniform concentration in all three layers.

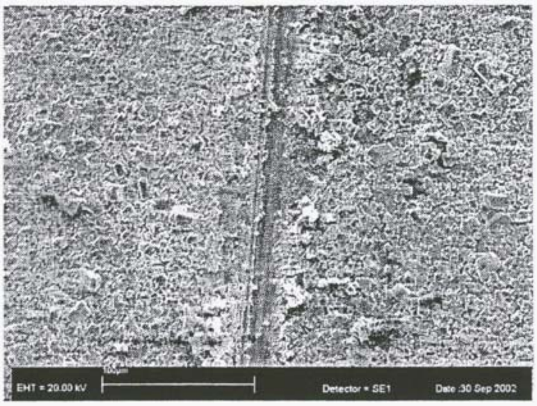

Figure 1: SEM View of Corrosion Product Scale on Carbon Steel, 150°C, 6 bar(a), pH 3 Adjusted to pH 5.

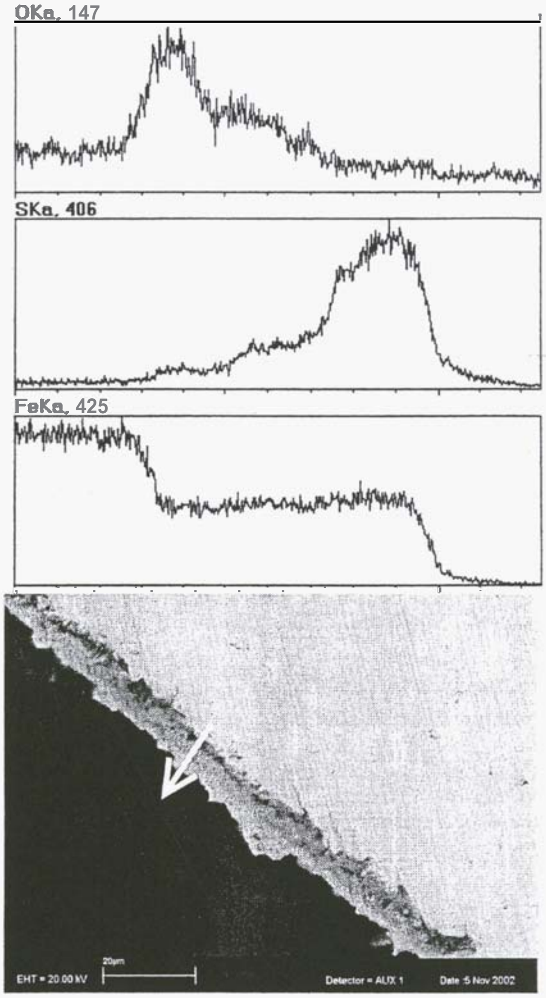

Figure 2: SEM View of Cross Section of Scale Shown in Figure 1 with EDX Line Scans For Oxygen, Sulfur and Iron Along the Path of the Arrow.

Table 1 gives estimates of the wt% of Fe_3O_4 and FeS in each of the three layers shown in in Figure 2 from spot EDX analysis results. The bottom layer is almost entirely magnetite, the middle layer is increasing in sulphide content, while the outer layer is almost entirely iron sulfide. The optical appearance of the scales suggests the middle and bottom layer sulphide is mackinawite while the outer layer sulfide is troilite.

Scales removed from carbon steel pipelines exposed to geothermal steam, where the corrosion rates are low due to passive film formation, generally have dual layers of magnetite overlaid with troilite or pyrrhotite ($Fe_{(1-x)}S$) (Lichti et al, 1997). Mackinawite is generally considered as being less protective (Tewari et al, 1979) and the apparent stability of mackinawite gives a reason for the poor reproducibility of pressure vessel experiments designed to form passive films by pH adjustment. It is not known if the quantity and impact of mackinawite will be less in longer exposure tests.

Table 1: SEM EDX Spot Analysis Results Presented as wt% Fe_3O_4 and FeS in Each of the Layers, Assuming Only These Phases Are Present.

	Bottom	Middle	Top
	wt%	wt%	wt%
Fe_3O_4	93	79	3
FeS	7	21	97

3.3 Prediction of Film Stability

A Pourbaix diagram was prepared for the conditions tested in the laboratory pressure vessel (Figure 3):

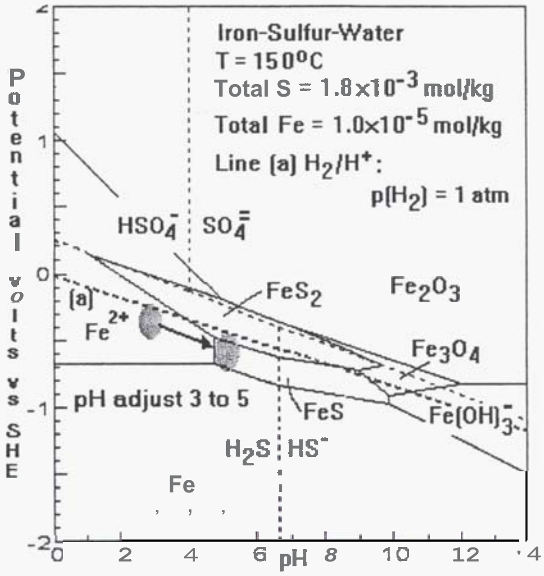

Figure 3: Potential-pH Pourbaix Diagram for Pressure Vessel Trials at 150°C.

The diagram shows areas of stability for metal compounds FeS (mackinawite, pyrrhotite and troilite are not considered separately), FeS_2 (pyrite), Fe_3O_4 (magnetite), Fe_2O_3 (heamatite) and dissolved species.

Addition of NaOH to give pH adjustment from 3 to 5 gives a transition across the Fe^{2+} to FeS boundary. The corrosion potential is expected to be at or near the hydrogen - water stability line (a), drawn in this instances for $p(H_2)$ of 1 atm. Higher $p(H_2)$ will see the line (a) moved lower, while lower $p(H_2)$ will see the line moved higher. In either case the line will remain within the sulphide stability areas.

Phases expected to form first at pH 5 will be the iron rich sulfides, Mackinawaite and Troilite followed by Pyrrhotite. The diagram predicts that when the sulfides are stable and they present a partial barrier to the corrosive solution then the Total S available at the metal surface will decrease and Magnetite will form next to the metal surface (Lichti et al, 1999). Normally Mackinawite is not kinetically favoured in thin films of water that are in contact with well casing material in two-phase flow at high temperatures and hence this phase is not normally seen.

Addition of scale forming compounds provides more rapid sealing of corrosion product pores and grain boundaries and a more rapid decrease of initial corrosion rates. Presence of silica, complex silicates, calcite or anhydrite will help to provide film stability and slow corrosion.

4.0 CONCLUSIONS

The IEA initiative on Deep-Seated Geothermal Materials Subtask on materials provided significant opportunity to progress collaborative R&D in materials selection for deep and acidic geothermal wells from 1996 to 2000. Previously unpublished work and targeted R&D indicated suitable methodologies to develop more acidic geothermal fluids having pH 3 to 4.5.

Since the completion of the IEA initiative a number developers have demonstrated the viability of both pH adjustment and selection of corrosion resistant materials for control of corrosion in acidic geothermal well fluids. Demonstration plant using NaOH injection have shown a tendency to formation of anhydrite and complex silica scales that can have both negative and positive impact on the equipment used to achieve corrosion control. Additional modelling and inhibitor trials are required to explore solutions to these impediments to the technology.

Related work has improved understanding of the mechanisms controlling corrosion in pH adjusted solutions:

- Buffer capacity impacts on amount of NaOH required for pH adjustment
- Dissolved oxygen causes accelerated localised corrosion at pH values that give passive film formation in reducing environments.
- Presence of silica and sulphate, even with small tendencies to scale formation are likely contributing to the stability of the passivating films and acting as natural corrosion inhibitors.
- Tendency to problematic scale formation may be enhanced at higher pH values.
- Alternative corrosion inhibitors for controlling corrosion in dry steam containing acid gases are under development.

5.0 ACKNOWLEDGEMENTS

The authors acknowledge the financial assistance of the New Zealand Foundation for Research Science and Technology and Japan AIST in the preparation of this paper.

6.0 REFERENCES

Cordova, D B and Ho, P (2001) *An* Innovative Approach to Controlling Dissolved Oxygen and Corrosion in Corrosive Geothermal Reinjection Lines, 22nd Annual PNOC EDC Geothermal Conference, Manila, Philippines, pp 205-208.

Gardner, A B, Rivera, N N, Santos, R M, Villasenor, L B and Gallup, D L (2001) Mitigation of Corrosion in an Acid Producing Well at Tiwi Geothermal Field, 22nd Annual PNOC EDC Geothermal Conference, Manila, Philippines, pp 155-159.

Gallup, D L (2002) Differential Oxygen Cell Corrosion in Aerated Condensate or Brine Reinjection Wells, GRC Transactions, pp 651-655.

Hirtz, P N, Broaddas, M and Gallup, D L (2002) Dry Steam Scrubbing for Impurity Removal from Superheated Geothermal Steam, GRC Transactions, pp 751-754.

Kurata, Y, Kim, H, Nanjo, H, Sanada, N, and Miyasaka, M (2001), Evaluation of Galvanic Corrosion at Casing Joint by Boundary Element Method, Journal of the Geothermal Energy Research & Development Co., Ltd., pp.80-88 (in Japanese).

Lichti K A, Wilson, P T and Inman M E (1997) Corrosivity of Kawerau Geothermal Steam, GRC Transactions, pp 25-32.

Lichti, K A and Bacon, L G (1998) Corrosion in Wairakei Steam Pipelines, 20* NZ Geothermal Workshop, U of Auckland, New Zealand, pp 51-58.

Lichti, K A, Brown, K L and Ilao, C M (2000) Scaling and Corrosion of pH Adjusted Separated Water, 22nd NZ Geothermal Workshop, U of Auckland, New Zealand, pp 169-176.

Lichti, K A, Engelberg, D and Young, M G (1999) Corrosion in Simulated Acidic Geothermal Well Fluids, 21st NZ Geothermal Workshop, U of Auckland, New Zealand, pp 187-192.

Moya, P and Mainieri, A (2002) Geothermal Energy Development in Costa Rica, GRC Transactions, Vol 26, pp 43-48.

Moya, P and Sanchez, E (2002) Neutralisation System for Production Wells at the Miravelles Geothermal Field, GRC Transactions, Vol 26, pp 667-672.

New Energy and Industrial Technology Development Organization (NEDO) (2000), FY1997 Report of the Deep Geothermal Resources Survey Program, p.785 (in Japanese).

Nogara, J B, (2001) PNOC Energy Development Corporation, private communication.

Rivera, E S, Sequeria, H G and Ruiz, O V (2000) Commercial Production of Acid Wells at the Miravalles Geothermal Field, Costa Rica, Proc World Geothermal Congress, Kyushu, Tohoku, Japan, pp 1629-1634.

Sanada, N, Kurata, Y, Nanjo, H, Kim, H, Ikeuchi, J and Lichti, K (2000) IEA Deep Geothermal Resources Subtask C: Materials, Progress with a Database for Materials Performance in Deep and Acidic Geothermal Wells, Proc World Geothermal Congress, Kyushu, Tohoku, Japan, pp 2411-2416.

Tewari, P H, Bailey, M G and Campbell, A B (1979) The Erosion-Corrosion of Carbon Steel in Aqueous H_2S Solutions up to 120°C and 1.6 MPa Pressure, Corrosion Science, Vol 19, pp 573-585.

Villa Jr, R R, Alcober, E H, Paraon, J R V and Talens, M A (2001) Corrosion Rates in Different Condensate Lines of Leyte Geothermal Production Field, Philippines, 22nd Annual PNOC EDC Geothermal Conference, Manila, Philippines, pp 239-245.

Villa, Jr, RR, Siega, F L, Olivar, M M M, Salonga, N D, Ogena, M S, Garcia, S E, Buning, B C, Lichti, K A and Sanada N (2000) A Demonstration Of The Feasibility Of Acid Well Utilization: The Philippines' Well MG-9D Experience, 22nd Annual PNOC EDC Geothermal Conference, Manila, Philippines.

Villa Jr, R R, Paraon, J R V and Lichti, K A (2002) Effect of pH Elevation by NaOH Dosing on the Corrosion Potential of Steam Condensate Fluds from the Upper Mahiao Power Station, Leyte, Philippines, GRC Transactions, Vol 26, pp 679-686.

White, S P, Lichti, K A and Bacon, L G (2000) Application of Chemical and Wellbore Modelling to the Corrosion and Scaling Properties of Ohaaki Deep Wells, Proc World Geothermal Congress, Kyushu, Tohoku, Japan, pp 3963-3967.