Corrosion Properties of a Volcanic Hot Spring

Citation for published version (APA):
Engelberg, D., Lichti, K. L., Braham, V. J., Sanada, N., Kurata, J., Nanjo, H., Ikeuchi, J., & Christenson, B. W. (1998). Corrosion Properties of a Volcanic Hot Spring. In *PROCEEDINGS OF THE NEW ZEALAND GEOTHERMAL WORKSHOP* (pp. 97-102). University of Auckland, Geothermal Institute.

Published in:
PROCEEDINGS OF THE NEW ZEALAND GEOTHERMAL WORKSHOP

CORROSION PROPERTIES OF A VOLCANIC HOT SPRING

K.A. LICHTI[1], **V.J.** BRAHAM[1], D. ENGELBERG[1], N. SANADA[2], Y.KURATA[2],
H.NANJO[2], J. IKEUCHI[2] **AND** B.W. CHRISTENSON[3]

[1]Materials Performance Technologies Ltd., Lower Hutt, NZ
[2]Tohoku National Industrial Research Institute, **AIST**, MITI, Sendai, Japan
[3]Institute of Geological & Nuclear Sciences Ltd., Taupo, NZ

SUMMARY - Volcanic hot pools on White Island, New Zealand provide ready access to acidic fluids at atmospheric pressure. These hot pools can be used to study the corrosion properties of construction materials that might be used for energy production from deep-seated and magma-ambient geothermal systems, or from shallow resources producing acidic fluids. Preliminary corrosion results for a pH 1, hot pool are presented. A select group of moderate and high alloy materials appear suitable for energy plant applications. Chemistry and corrosion mechanism models provide some reasons for the experimental observations. Corrosion control experiments in fluids removed from the hot pool demonstrated that a decrease in the instantaneous corrosion rate of carbon steel can be achieved by pH adjustment.

1. INTRODUCTION

Deep geothermal resources, located below conventional shallow reservoirs, offer developers the opportunity to increase production capacity or field lifetime by tapping higher temperature fluids from areas feeding the shallower reservoirs. These fluids are of relatively low pH and consequently have higher corrosivity (Sanada et al, 1997). Geothermal wells cased with materials suitable for long term production of aggressive acidic fluids are rare. The work reported here was initiated in 1993 and is part of an effort to use natural volcanic environments to aid in the selection of materials for aggressive geothermal fluids (Kurata et al, 1994, 1995, Lichti et al, 1996, 1997a). Materials tests conducted on White Island involved the direct exposure of metal samples in volcanic features, including hot pools which provide a similar chemistry to that of aggressive deep well fluids, except that the hot pools are at a maximum of 100°C and are at atmospheric pressure. Deep well fluids may have temperatures in excess of 300°C and pressures in excess of 40 bar.

Acidic geothermal wells are encountered in many shallow geothermal resources and the chemistry and corrosivity of these systems have been partially explored (Sanada et al, 1995, 1998, Lichti and Sanada, 1997, Lichti et al, 1998a, 1998b, Ikeuchi et al, 1982, 1997). Materials, process and plant options considered by developers in their efforts to utilise these more aggressive fluids have been surveyed (Lichti and Sanada, 1997). Materials experience with deep wells, acid wells encountered in shallow reserves and volcanic environments was used to assert the feasibility,

potential costs and risk of development of acidic and deep geothermal resources, with the proviso that downhole corrosion control would be required. The need for downhole corrosion control has been further explored from a modelling point of view (Ikeuchi et al, 1997, Lichti et al, 1998a, 1998b).

The work reported here uses one of these readily available volcanic hot pools to determine the corrosion behaviour of candidate alloys and to explore options for downhole corrosion control.

2. BACKGROUND

Materials tests in White Island hot pools had previously concentrated on a pool called Black Pot, a 99-100°C hot pool of pH 4. However, a more acidic hot spring area located next to fumarole #13, Hot Pool #13a, became available in 1997 (Lichti et al., 1997b). Realisation of the critical need for downhole corrosion control in the development of deep and shallow acidic wells (Lichti and Sanada, 1997) prompted additional studies of the corrosion properties of Pool #13a, at a temperature of 99-100°C and a pH of 1.4. Over the test period, Pool #13a had a central column of water/gas about 200 mm high. The water contained fine silty suspended material that was off-white in colour. The pool depth was approximately 200 mm and the pool diameter was approximately 1 m. Digging of the pool to give greater depth resulted in more vigorous discharge from numerous points in the bottom of the pool. Disturbing sulfur deposits by digging the edge of the pool resulted in a green film forming on top of the pool. Damming of the low side was a viable means of

increasing pool depth without causing excess damage to the natural tourist-type environment.

Previous experimental work concluded that (Kurata et al, 1995a, Lichti et al, 1997a):
- passive films or scales formed on metal coupons exposed in Black Pot and slowed corrosion to low levels although lower alloy materials were subject to pitting corrosion
- high unacceptable corrosion rates were observed in Pool #13a for all the materials tested; carbon steel, 12% Cr stainless steel, Types 304 and 316 stainless steels.

3. EXPERIMENT AND RESULTS

This work concentrated on measuring the corrosivity of Pool #13a, including (Figure 1):
- instantaneous corrosion rate measurements using the Linear Polarisation Resistance (LPR) technique on selected low and high alloy materials either directly exposed in the pool or in water removed from the pool (Lichti and Wilson (1980) provide a description of the LPR corrosion rate technique applied to g e o t h e d fluids)
- corrosion potential measurements of selected metals and alloys (including Pt for redox potential determination) and Cr-Plate vs $Ag/AgCl_2$ or Hg/Hg_2Cl_2 reference electrodes either in the pool or in water removed from the pool (reported as mV vs Standard Hydrogen Electrode, SHE)
- in-situ pH measurements with a single (pH 1) calibration solution of 0.1 N HCl at or near the pool temperature
- trials on the effect of pH adjustment, fiom 1.6 to 6 on the instantaneous LPR corrosion rate of carbon steel in water removed fiom the pool and in mixed acid (0.1 M HCl / 0.05 M H_2SO_4) solution in the laboratory
- coupon exposures of low alloy materials for 4 hours in the hot pool
- coupon exposures of high alloy materials for 43 days in the hot pool, the Teflon box containing the coupons was filled with the fine silt throughout the experiment.
- sampling of the water and suspended solids for chemical analysis.

The materials tested have been described elsewhere (Lichti et al., 1997a). The corrosion potential and LPR measurements at times gave spurious results, which were not understood at the time. Attempts to measure the LPR of the duplex alloy 2507, Alloy 33, Alloy 45TM and Alloy 28 occasionally failed due to exposed electrodes having differing corrosion reactions. For example, in one experiment, 2507 had one

electrode active ($\phi corr = -185$ mV) and the others passive ($\phi corr = 449$ mV).

The short term (4 hour) exposure of coupon materials, carbon steel, 12% Cr and Type 316L stainless steel, give a benchmark of the corrosivity of Pool #13a towards these materials

Cr-plate on carbon steel and Ni substrates was totally corroded within minutes of exposure.

The adjustment of pH was achieved by additions of 1 M NaOH solution to fluid removed from the pool and held in a preheated, heavy wall, glass container. Instantaneous corrosion rates for carbon steel were obtained as a function of pH. A series of experiments was required to complete the measurements as the temperature of the solutions rapidly dropped. The temperature range used was 80 to 60°C. Change of pH from 1.5 to 6.0 gave a roughly linear decrease in corrosion rate of carbon steel fiom 31.9 to 0.8 mm/y (Table 1).

Table 1- Corrosion rate of carbon steel in pH adjusted water fiom Pool #13a and laboratory solution (both solutions were naturally aerated).

Pool #13a Water			.1MHCl/.05MH$_2$SO$_4$		
pH	T °C	CR mm/y	pH	T °C	CR mm/y
1.52	77	31.9	1.10	95	47.4
2.26	71	23.3	2.00	95	37.1
3.28	80	11.5	3.25	95	31.7
4.19	68	6.1			
5.20	75	4.7	5.00	95	8.9
5.97	60	0.8			

4. CHEMISTRY

The corrosion chemistry of hot pools encountered in natural volcanic features varies, from near neutral or alkali pH-chloride type waters, to acidic-chloride/sulfate waters that are more aggressive to metals and alloys. Pool #13a was chosen for testing because of the temperature and acidity, as reported in Table 2. The vigorous discharge of gas through the pool results in the water having a high suspended load. XRD studies of this suspension shows that it consists of abundant alunite, elemental sulfur and amorphous silica (opal CT), with lesser quantities of pyrite.

REACT (Bethke, 1992) was used to model the speciation of dissolved constituents in the pool at the measured temperature of 100 "C. Since H_2S concentrations in the water (Table 2) were below the detection level, the presence of elemental sulfur in the pool was used to constrain the redox state of the fluid via S_e-SO_4

Corrosion Rates

Linear Polarisation Results
☐ Instantaneous/CR

ASTM Coupon Results
▨ Weight loss/CR
■ Local Penetration/CR

Corrosion Rate mm/year — axis: 1000.0, 100.0, 10.0, 1.0, 0.1, 0.01, 0.001, 0.0001

Alloy bars: 1007, 410, 316L, 2205 2507, 254SMO, 2RK65, 6XN, 28, 33, 825, 45TM, 690, C276, 625, S816, 59, Ni, Mo, Ti Gr.2, Ti Gr.5, Ti Gr.5, Ti Gr.29

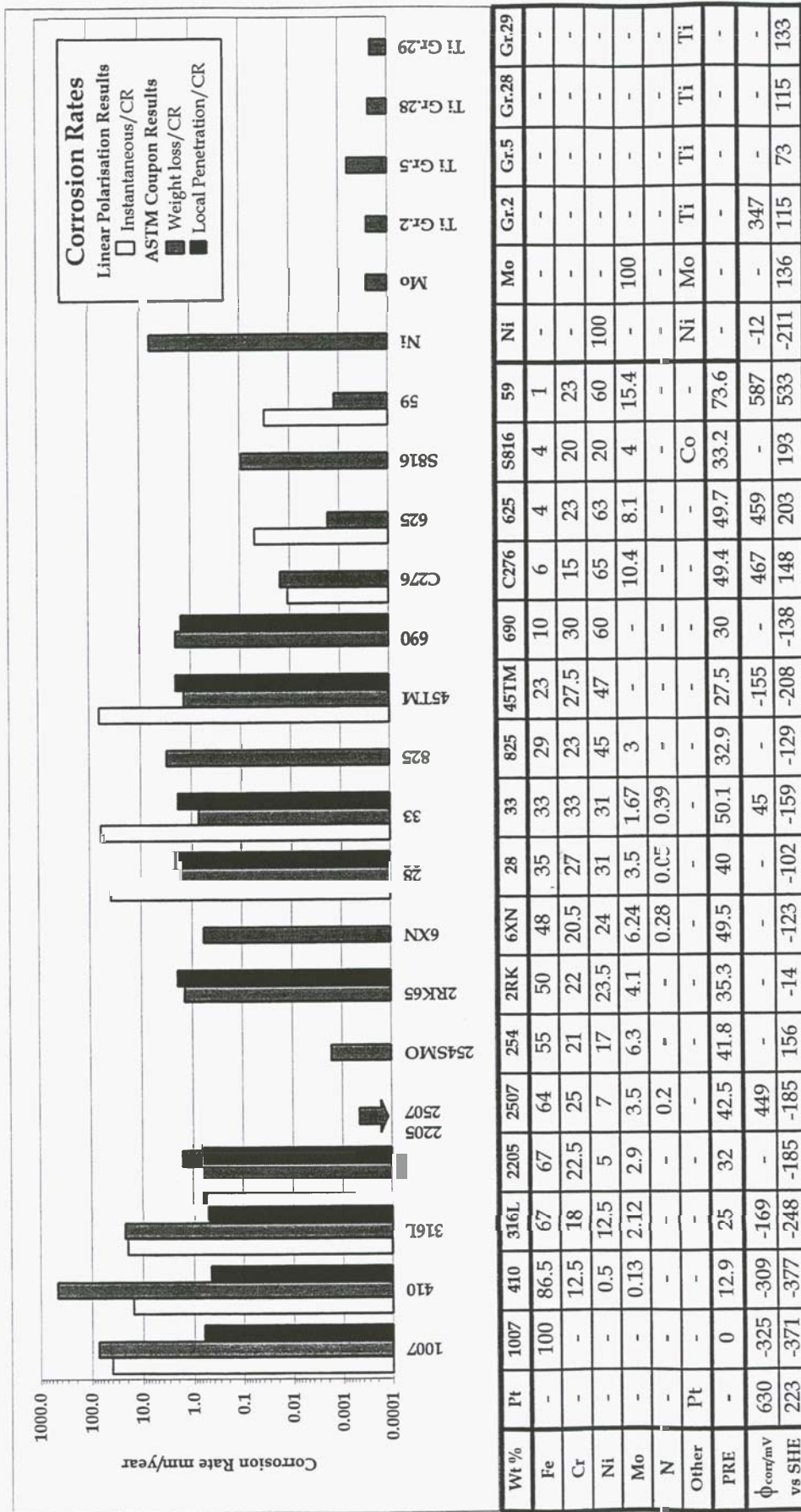| Wt %	Pt	1007	410	316L	2205	2507	254	2RK	6XN	28	33	825	45TM	690	C276	625	S816	59	Ni	Mo	Gr.2	Gr.5	Gr.28	Gr.29
Fe	-	100	86.5	67	67	64	55	50	48	35	33	29	23	10	6	4	4	1	-	-	-	-	-	-
Cr	-	-	12.5	18	22.5	25	21	22	20.5	27	33	23	27.5	30	15	23	20	23	-	-	-	-	-	-
Ni	-	-	0.5	12.5	5	7	17	23.5	24	31	31	45	47	60	65	63	20	60	100	-	-	-	-	-
Mo	-	-	0.13	2.12	2.9	3.5	6.3	4.1	6.24	3.5	1.67	3	-	-	10.4	8.1	4	15.4	-	100	-	-	-	-
N	-	-	-	-	-	0.2	-	-	0.28	0.05	0.39	-	-	-	-	-	-	-	-	-	-	-	-	-
Other	Pt	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Co	-	Ni	Mo	Ti	Ti	Ti	Ti
PRE	-	0	12.9	25	32	42.5	41.8	35.3	49.5	40	50.1	32.9	27.5	30	49.4	49.7	33.2	73.6	-	-	-	-	-	-
ϕ_{corr}/mV	630	-325	-309	-169	-	449	-	-14	-	-	45	-	-155	-	467	459	-	587	-12	136	347	-	-	-
vs SHE	223	-371	-377	-248	-185	-185	156	-123	-123	-102	-159	-129	-208	-138	148	203	193	533	-211	-	115	73	115	133

Figure 1- Corrosion rate and corrosion potential results for metals and alloys exposed in Pool #13a on White Island. LPR Instantaneous CR results were obtained within 30 minutes of exposure. ASTM Coupons of alloys 1007, 410 and 316L were exposed for 43 days while other alloys were exposed for 4 hours. Corrosion potential of Pt provides a measure of Eh and was 223 mV in the pool rising to 630 mV in aerated solution removed from the pool. Cr-plate on carbon steel and Ni substrates readily corroded and gave "mixed" potential readings for these alloy combinations, –211 mV and –223 mV on carbon steel and –215 mV on Ni. Pitting Resistance Equivalent (PRE) = wt%Cr + 3.3*wt%Mo + 30*wt%N.

Table 2- Geochemistry of Hot Pool #13a used for corrosion testing on White Island, New Zealand.

Location White Island	Date!	T °C	K mS/cm	pH (99C)	pH (19C)	Li	Nn	K	Cn	Mg	Cl	SO, mg/kg	B	SiO₂	NH₃	H₂S(t)	Fe	Al
Pool #13a	12.2.96	99	-	-	1.03	0.34	105	51	394	228	3,474	12,040	0.97	456	0.81	-	782	103
Pool #13a	16.6.98	99	40	1.45	1.40	0.18	142	13.6	370	183	1,742	4,140	1.2	418	0.28	<0.05	430	122
Pool #13a	29.7.98	99	57	1.59	1.44	0.17	142	15.5	304	183	1,576	3,360	1.0	406	0.24	<0.05	430	122

Table 3- High temperature chemistry of Hot Pool #13a on White Island.

	Pool #13a	12/2/96	Pool #13a	16/6/98
T	99.0 C		100	
Pressure	1.013 bara		1.013 bara	
log fO2	-47.800		-48.376	
Eh	267.4 mV		208.8 mV	
pH(T)	.938		1.549	
	mol/kg	mg/k₁	mol/kg	Mg/kg
Cl-	.9532E-01	3320.	.5324E-01	1873
Na+	.4474E-02	101.0	.6121E42	139.6
SiO2(aq)	.7589E-02	448.0	.6957E-02	414.8
MgSO4(aq)	.3036E-02	359.0	.3205E-02	382.8
S04−	.3599E-02	339.6	.3495E-02	333.1
Ca++	.9191E-02	361.9	.8371E-02	332.9
Mg++	.6085E-02	145.3	.4204E-02	101.4
H2S(aq)	.8815E-04	2.952	.2133E-03	7.213
K+	.1273E-02	48.88	.3408E-03	13.22
CaSO4(aq)	.5426E-03	72.56	.7993E-03	108.0
NH4+	.4282E-04	.7589	.1599E-04	0.2862
HSO4-	.1155	11,010	.3566E-01	3,434
NaSO4-	.3067E-04	3.587		
Fe++	.1292E-01	708.9	.7502E-02	415.7
H+	.1476	146.2	.3535E-01	35.36
AlSO4+	.1822E-02	220.3		
FeSO4(aq)	.6003E-03	89.59		
NaCl(aq)	.6250E-04	3.589	.5570E-04	3.23
Li+	.4874E-04	.3323	.2588E-04	0.1783
KSO4-	.1320E-04	1.753	.4731E-07	0.6345
FeCl+	.4810E-03	43.14	.1975E-03	17.89
HCl(aq)	.1754E-02	62.82	.2613E-03	9.454

Components present at < E-04 not shown.

Mineral Saturation States (log Q/K)

Pyrite = 2.41, Quartz = 0.90, Tridymite = 0.76, Chalcedony = 0.49, Christobalite (alpha) = 0.49, Coesite = 0.24, Christobalite (beta) = 0.18, Si02 (amorphous) = 0.01, Sulfur =

equilibrium. This approach results in good agreement between observed mineralogy and the calculated saturation indices (Table 3). The calculated pH of the pool at 100 °C was 1.55 at a redox potential (Eh) of 210 mV, which correlates well with the measured parameters (compare Table 3 and Figure 1).

5. POTENTIAL–pH MODELS

Thermodynamic potential-pH diagrams (Figures 2 to 5) were prepared for the calculated corrosion chemistry (Table 3) and the primary alloy elements of the iron-containing materials tested, using data fiom Cobble et al. (1982). The estimated corrosion potential ranges in the diagrams were based on the measured results (Figure 1).

6. DISCUSSION

The instantaneous LPR measurements made after only a few minutes of exposure (Figure 1) gave corrosion rate results which were similar to those obtained from weight loss experiments for the low alloy materials (4 hours exposure), but were higher than the corrosion rates observed on the high alloy materials (43 days exposure). These differences suggest that, the low alloy materials did not passivate in 4 hours whereas the moderate to high alloy materials took some time to passivate and may exhibit variable performance. The coupons packed in silt could have benefited from the additional shielding of the surface fiom the turbulent fluids.

Both the coupon exposures and the instantaneous LPR results provide a comparative measure of long term performance, although intermediate alloy materials may be misrepresented by LPR results. Nevertheless, it is useful to compare corrosion rate results and potential measurements of the principal alloy types tested at pH 1.5 (see Figure 1):

o carbon steel (1007) corrosion rates are too high for common engineering applications
o 12% Cr (410) stainless steel corrosion rates were higher than carbon steel, suggesting that alloying with Cr alone will not give sufficient corrosion resistance
o austenitic stainless steels and low Mo content nickel-base alloys were readily corroded (316L, 825, 2RK65, Alloy 28, Alloy 33, Alloy 45TM)
o the two duplex stainless steels (2205 and 2507) showed different performance which is attributable to rapid passivation of the higher alloy material (2507), as indicated by the corrosion potential measurements
o corrosion rates for the high alloy, nickel-base alloys and the cobalt alloy appear to be directly dependent on Mo content and inversely dependent on Fe content
o Ni and Cr-plate readily corroded, but Mo gave a low corrosion rate
o titanium and titanium alloys gave low corrosion rates
o the corrosion potentials obtained for Pt (which give a measure of redox potential, Eh) in the pool, suggest that, in the undisturbed state, the water chemistry is indeed controlled by the S chemistry, while in removed waters and in turbulent waters, air is readily entrained and the Eh raises
o Pitting Resistance Equivalent did not correlate with the occurrence of localised corrosion initiation or penetration.
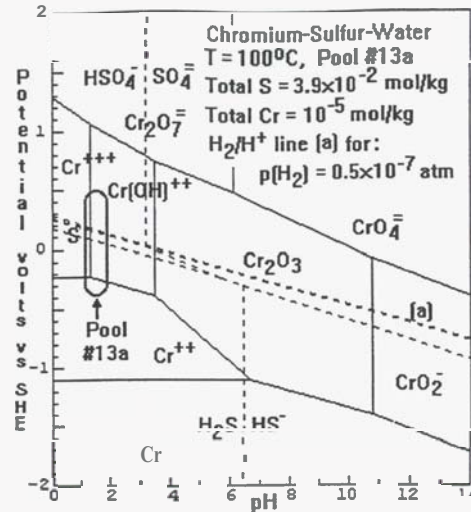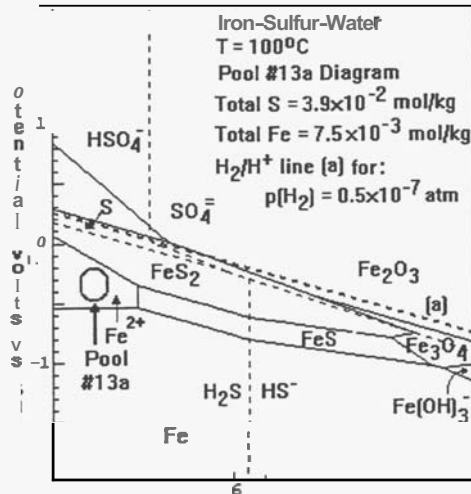
Iron-Sulfur-Water
T = 100°C
Pool #13a Diagram
Total S = 3.9×10^{-2} mol/kg
Total Fe = 7.5×10^{-3} mol/kg
H_2/H^+ line [a] for:
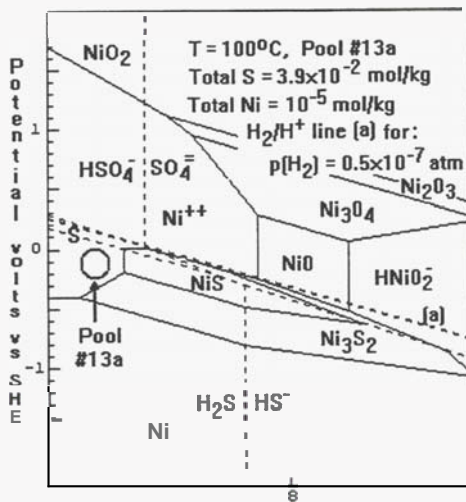$p[H_2] = 0.5\times10^{-7}$ atm

Figure 3 - Potential-pH Cr-S-H_2O diagram for

T = 100°C, Pool #13a
Total S = 3.9×10^{-2} mol/kg
Total Ni = 10^{-5} mol/kg
H_2/H^+ line [a] for:
$p[H_2] = 0.5\times10^{-7}$ atm

Molybdenum-Sulfur-Water
T = 100°C, Pool #13a
Total S = 3.9×10^{-2} mol/kg
Total Mo = 10^{-5} mol/kg
$p[H_2] = 0.5\times10^{-7}$ atm
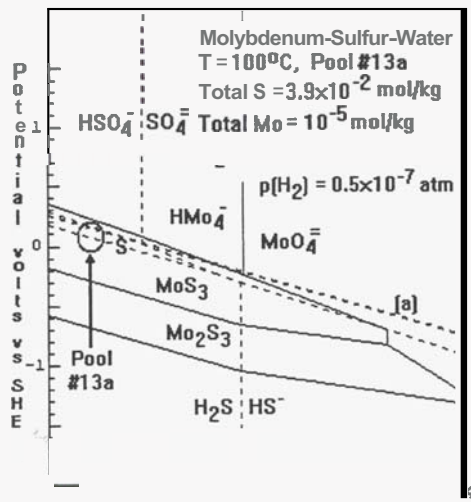
Figure 5 - Potential-pH Mo-S-H_2O diagram for Hot Pool #13a at T = 100°C (16/6/98).

Adjustment of pH to 6 by addition of NaOH decreased the instantaneous corrosion rate fiom 31.9 to 0.8 mm/year. Under long term non-aerated conditions, in static and turbulent environments, down to pH 3 or 4, passive films would be expected to form and the corrosion rate would decrease to lower levels (Sanada et al, 1998). The work in the laboratory has progressed to simulation of the field environments under aerated conditions, with a similar result In-plant field trials and non-aerated pressure vessel tests of pH adjustment as a means of corrosion control are planned.

The Potential-pH (Pourbaix) diagram models of corrosion product stability for Fe, Ni, Cr and Mo provide some additional explanation for the observed performance:

- Figure 2 shows the corrosion potential for Fe at pH 1.5 is in the Fe^{2+} region of the diagram — active corrosion would be predicted, as observed

o the redox potential of the solution (as measured on the Pt metal sample) was 220 mV and is in the middle of the S region of stability, which is consistent with the method of calculation of the chemistry and the observed presence of fiee S in the pool

o Figures 3 and 4 imply that pure Cr and Ni will freely corrode in these low pH solutions and this is consistent with the experimental results for Ni, Cr-plate and, Ni-Cr-Fe (low Mo) alloys

o Figure 5 shows a large stability area for MoS_3 which is nearly independent of pH, and the results of Figure 1 indicate alloying with Mo is a key parameter in controlling corrosion, but the presence of sulfides or oxides of molybdenum has not been experimentally or analytically confirmed.

The low corrosion rate of the 2507 duplex alloy and 254SMO stainless steel are anomalous in regard to their alloy content and consequently, their performance calls for further comment. Stainless steels and nickel-base alloys obtain their corrosion resistance through formation of thin oxide films. In acid pH solutions these films can break-down or be dissolved resulting in general corrosion at potentials approaching that of freely corroding carbon steel. The surface is said to be "active". If the oxide film remains stable and is not dissolved then the surface is said to be in a "passive" state which occurs at a more positive potential. The range of potentials shown in Figure 1 for the stainless steels, and the observed variable performance of these alloys, indicates that mixed active/passive behaviour is occurring.

7. CONCLUSIONS

Volcanic hot pools can be used to test materials in acidic geothermal fluids at atmospheric pressure. Corrosion tests of candidate construction materials have been done in a pH 1 hot pool on White Island, as a necessary step in the development of deep and acidic g e o t h e d resources. A select group of alloys; duplex alloy 2507, austenitic stainless steel 254SMO and nickel-base alloys 625, C276 and 59, a cobalt alloy S816, pure Mo, Ti and Ti alloys exhibited low corrosion rates. The good performance of these alloys is attributed to the formation of passive films in the acidic environments. These films have yet to be fully characterised. Adjustment of pH by addition of NaOH solution gives a reduction in corrosion rate of carbon steel, but long term tests are required to demonstrate the feasibility of this method of corrosion control for deep and acidic geothermal wells.

8. ACKNOWLEDGEMENTS

9. REFERENCES

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.

Bethke, C. (1992) *The geochemist's workbench; a user's guide to Rxn, Act2, Tact and Gtplot.* Univ Illinios, 213 p.

Ikeuchi, J., Sanada, N., Asano, O., Kurata, Y., Odawara, O. and Okahara, Y. (1982). *Corrosion and erosion-corrosion of iron-base alloys in a geothermal resource area (Onikobe) in Japan.* Proc Int Conf on Geothermal Energy, Florence, Italy, pp 383-394.

Ikeuchi, J., Kimura, S., Kurata, Y., Pestov, 1. and Sanada, N. (1997). *Material damage in deep geothermal well-bores.* Proceedings 19th NZ Geo Workshop, pp 175-180.

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. (1995a). *Material damage in a volcanic environment.* WGC, Milan, Italy, May, 2409-2414.

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

Lichti, K.A. and Wilson, P.T. (1980). *The determination of metal corrosion rates in geothermal condensate using electrochemical techniques.* Proc 3rd NZ Geothermal Workshop, pp 37-42.

Lichti, K.A., Gilman, N.A., Sanada, N., Kurata, Y., Nanjo, H., Ikeuchi, J. and Christenson, B.W. (1996). *Corrosion chemistry of some volcanic environments.* Proc 18th NZ Geothermal Workshop, pp 21-28.

Lichti, K. A. and Sanada, N. (1997). *Materials issues for utilisation of deep geothermal systems,* Proc 19th NZ Geothermal Workshop, pp 169-174.

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

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

Lichti, K.A., White, S.P., Sanada, N. (1998a). *Corrosion in deep and acidic geothermal wells.* 19th PNOC-EDC Geo Conf, Manila, pp 199-212.

Lichti, K.A., White, S.P., Sanada, N. (1998b). *Modelling of acid fluid wellbore chemistry and implications for utilisation.* Proc 20th NZ Geothermal Workshop.

Sanada, N., Kurata, Y., Nanjo, H. and Ikeuchi, J. (1995) *Material damage in high velocity fluids.* GRC Trans, Vol 19, 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, pp 317-324.

Sanada, N., Kurata, Y., Nanjo, H., Ikeuchi, J. and Kimura, S. (1998). *Corrosion in acidic geothermal flows with high velocity.* Proc 20th NZ Geothermal Workshop.