CORROSION IN SIMULATED ACIDIC GEOTHERMAL WELL FLUIDS

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SUMMARY - Experiments were performed to develop a technique for laboratory testing of corrosion rates of carbon steels in simulated high pressure acidic geothermal fluids. A Hastelloy C pressure vessel was used with a once through refresh solution flow to maintain chemical conditions in the pressurised solution. Test solutions of mixed HCl and H_2SO_4 acids were used to simulate the corrosion properties of the geothermal waters. Addition of H_2S was achieved by bubbling 1% H_2S in nitrogen gas through a reservoir of mixed acid solution having the desired test pH prior to the test solution being pumped through the pressure vessel. Corrosion rates were measured throughout the exposure using the Linear Polarisation Resistance technique. Weight loss measurements on carbon steel electrodes were used to confirm or calibrate the LPR measurements. The developed methodology can now be used to trial corrosion control technologies for deep and acidic geothermal well production fluids under controlled laboratory conditions.

1.0 INTRODUCTION

The chemistry of deep geothermal fluids is expected to be more acidic than fluids encountered in conventional shallow reserves (Lichti and Sanada, 1997). Acidic fluids are sometimes encountered in shallow production wells, which are typically cased with carbon steels and are considered unexploitable because of the risk of corrosion. Corrosion measurements made in natural volcanic environments, such as hot springs, which reflect the anticipated deep fluid chemistry are constrained to tests at atmospheric pressure. Corrosion measurements made in pH adjusted fluids at the wellhead provide accurate kinetic results including the effect of temperature and flow rates (Sanada et al, 1998, Gallup and Farison, 1998). Thermodynamic models can be used to calculate the chemistry of the inflow into deep and acidic geothermal wells from the measured surface chemistry and enthalpy, This information together with wellbore simulation allows the calculation of chemical conditions throughout the wellbore (Lichti et al, 1998a).

The wellhead data obtained in pH adjusted geothermal fluids demonstrate that control of acidity of produced fluids gives control of corrosion rates. pH adjustment trials in natural, aerated volcanic hot spring fluids, from pH 1 to 5, similarly demonstrate that pH adjustment to lower acidity gives a decrease in corrosion rate. Laboratory tests in simple aerated acid mixtures at 95°C again indicate pH adjustment from 1 to 5 gives decrease in corrosion rate.

Materials alternatives for casing of acid wells have been identified as a function of pH (Sanada et al, 1998). However, most geothermal wells are cased with carbon and low alloy steels unless the reservoir fluid is predicted to be acidic before the well is drilled.

This work was initiated to establish parameters for simulation of acidic geothermal well production fluids in laboratory pressure vessels. The accurate simulation of such fluids is required to trial corrosion control methodologies (other than materials selection) for deep and acidic geothermal wells. Corrosion tests are required to develop technology that will allow the use of carbon and low alloy steels, or low cost stainless steels and these will include optimisation of (Lichti and Sanada, 1997):

- procedures for pH adjustment
- use of inhibitors for corrosion control
- combinations of pH control and inhibitors.

2.0 DEEP AND ACIDIC FLUID CORROSION CHEMISTRY

Sanada and Lichti (1997) and Sanada et al (1997) summarised the chemistry of acid wells in Japan and the Philippines and hypothesised that deep wells may encounter such acidity. Table 1 summarises the corrosion chemistry of acidic hot springs on White Island that were used for corrosion studies including pH adjustment trials in aerated fluids (Lichti et al, 1997, 1998b). Table 1 also lists the chemistry of an acidic production well, used for corrosion studies involving pH adjustment in Japan (Sanada et al., 1998). Table 2 summarises the corrosion chemistry of an acid well in the Philippines that was used to demonstrate methodologies for predicting downhole chemistry and thermodynamic predictions of corrosion mechanisms (Lichti et al, 1998a).

Engineering experience and research work with these fluids demonstrates a strong dependence of the corrosion chemistry and the kinetics of carbon steel corrosion on degree of aeration, acid type, pH, temperature and flow rate. Thermodynamic models of passive film formation, potential-pH Pourbaix diagrams, demonstrate additional dependence on sulfur species, dissolved iron concentration and the partial pressure of hydrogen (Lichti et al, 1998a).

3.0 EXPERIMENTAL

This work used a stepwise approach to develop an understanding of aspects of the corrosion chemistry which need to be controlled to give accurate simulation of acidic geothermal fluids. Figure 1 illustrates the final experimental arrangement for simulating acid well fluids in a 1 litre Hastelloy C pressure vessel using a flow-through system. Table 4 lists the sequence of experiments conducted. Monitoring of experimental parameters included selected measurements of dissolved oxygen (at ambient temperature), solution pH (at ambient temperature), temperature, pressure and solution refresh rate as well as pH and conductivity. In some instances water samples were collected for later iron analysis. Weight loss electrodes (measured to 0.01 mg) and Linear Polarisation Resistance (LPR) measurements were used to measure corrosion rates (Lichti and Wilson, 1980) and corrosion potential was monitored using standard (Ag/AgCl) and prepared (Ag/Ag_2S) reference electrodes at ambient temperature. Corrosion products formed on corroded carbon steel electrodes were selectively analysed by Scanning Electron Microscopy Energy Dispersive X-Ray (EDX) Analysis and X-Ray Diffraction (XRD).

The first series of experiments (E.1.1 and E.1.2) were done using pH 1 solution prepared by mixing equal volumes of pH 1 solutions of HCl (0.1 mol/kg) and H_2SO_4 (0.05 mol/kg). The pH 2 condition in E.1.2 was obtained by addition of NaOH. These experiments were similar to those undertaken previously on White Island and in laboratory glassware (Lichti et al 1998b). In this case, however, the dissolved oxygen was removed by bubbling with nitrogen gas and the experiments were much longer in duration, up to 68 hours. The test temperature was 95°C and the pressure was 1 atmosphere to allow the use of a glass salt bridge fitted with a porous frit and conventional Ag/AgCl reference electrode. LPR on-line corrosion rate measurements were made using a PAR 173/276 Potentiostat. The test electrode was used for the determination of corrosion rate from weight loss measurement. A platinum auxiliary electrode was used.

The second series of experiments (E.2.1 to E.2.5) was done using a solution refresh rate of approximately 5 ml/min. The cold mixed pH 1 acid was pH adjusted using additions of NaOH and again the solutions were de-aerated by bubbling with nitrogen. A second, electrically isolated electrode, was exposed in the bottom of the pressure vessel. Tests were done using pH 1 solution and pH 1 solution with pH adjusted by NaOH addition to pH 2, 3, 4 and 5.

The third test (E.3.1) was a repeat of the series 2 pH 3 test with a smaller test electrode. This arrangement gives a lower concentration of iron in solution.

A fourth series (E.4.1-E.4.2) was done at a temperature of 150°C and at a pressure just above saturation pressure (>7 bg). The smaller, single carbon steel electrode arrangement was used in these tests. As the system was under pressure, a solid Ag/Ag_2S electrode prepared using the method of Crow and Tromans (1986) was used as a reference. The electrode temperature was controlled by a cooling coil located on the pressure vessel outflow, just before the back-pressure regulator. A carbon steel working electrode and platinum auxiliary were used with a second working electrode available in the vessel and a third insulated electrode placed in the bottom of the vessel for weight loss only. The removable working electrodes were also available for weight loss corrosion rate determination and analysis of corrosion product.

The final series of experiments (S1 to S5) were done using pH3 solution prepared by mixing equal volumes of pH 3 solutions of HCl (0.001 mol/kg) and H_2SO_4 (0.0005 mol/kg). The solutions were bubbled with 1% H_2S in N_2 carrier gas. Runs were done at pH 3 and pH 5 (obtained by adding NaOH). These last solutions were of lower conductivity and solution resistance of the cell was measured to correct the LPR corrosion rate measurements for IR drop in the cell (Lichti and Wilson, 1980). This last series of experiments was plagued by initial pump operation problems and several differing flow rates resulted.

4.0 RESULTS OBTAINED

The weight loss and summarised on-line LPR corrosion rate results are shown in Table 3 together with the corrosion potential results.

Table 1 - Geochemistry of hot pool environments used for corrosion tests on White Island, NZ (Lichti et al, 1997, 1998b) and brine from Well No 105 used for corrosion tests at Onikobe, Japan geothermal field (Sanada et al, 1998)

Location	Date	T	pH	Li	Na	K	Ca	Mg	Cl	SO_4	B	SiO_2	NH_3	HCO_3(t)	H_2S(t)	Fe	Al	Cu	Pb
White Island		°C	(25C)	mg/kg										mg/kg					
Black Pot	15.1.94	93	5.24	0.28	268	48	208	192	785	1,141	0.82	318	108	15	<0.05	0.86	1.9	-	-
Black Pot	23.2.94	93	4.01	0.21	251	43	221	186	687	1,218	0.74	332	111	15	<0.05	2.2	3.2	-	-
Black Pot	5.5.94	98	4.98	0.2	233	44	188	174	641	1,056	0.67	305	107	47	0.06	0.97	2.6	-	-
Black Pot	14.2.96	93	5.07	0.26	270	49	188	157	619	1,044	0.68	327	102	-	0.07	14.5	6.5	-	-
Pool #13a	12.2.96	99	1.03	0.34	105	51	394	228	3474	12,040	0.97	456	0.81	-	-	782	103	-	-
Japan Acid Well																			
Onikobe	1981	158	3.2	-	1733	-	580	149	4630	33	-	92	-	-	trace	167	-	0.11	11.4

Table 2 - Production chemistry for Well MG-9D at Mahanagdong, The Philippines (Lichti et al, 1998)

H	SP	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
kJ/kg	MPa(a)	mmoles/100 moles steam							

pH	Na	K	Ca	Mg	Fe	Cl	F	SO_4(t)	NH_3(t)	SIO_2
25°C	mg/kg									

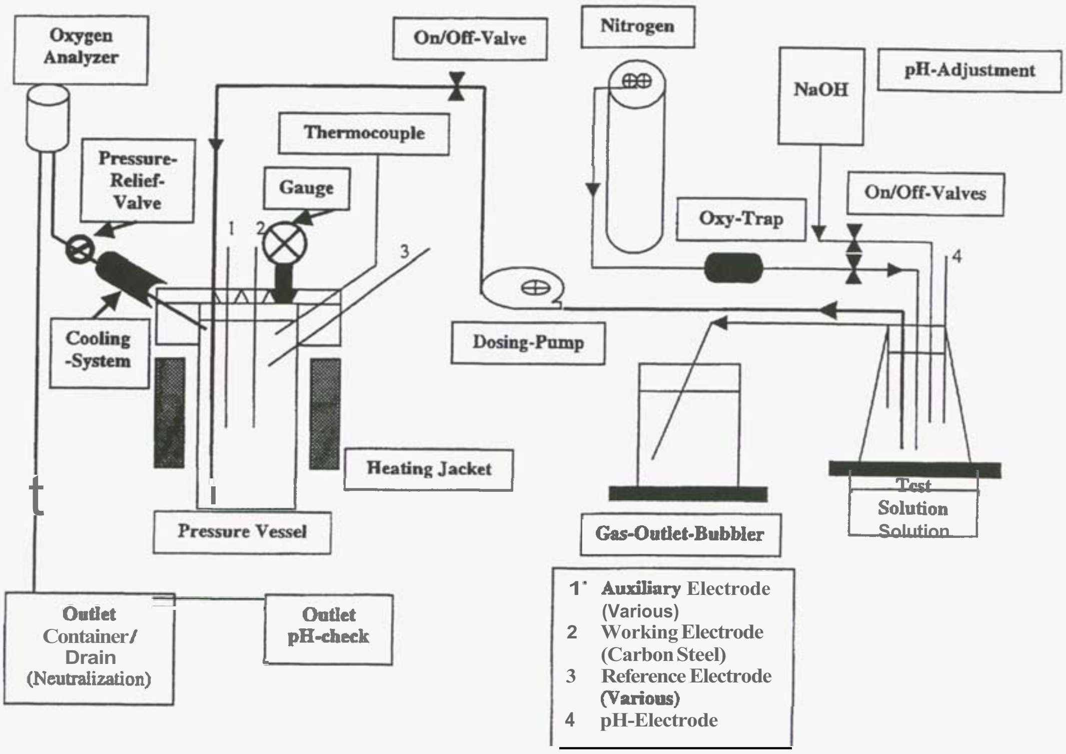
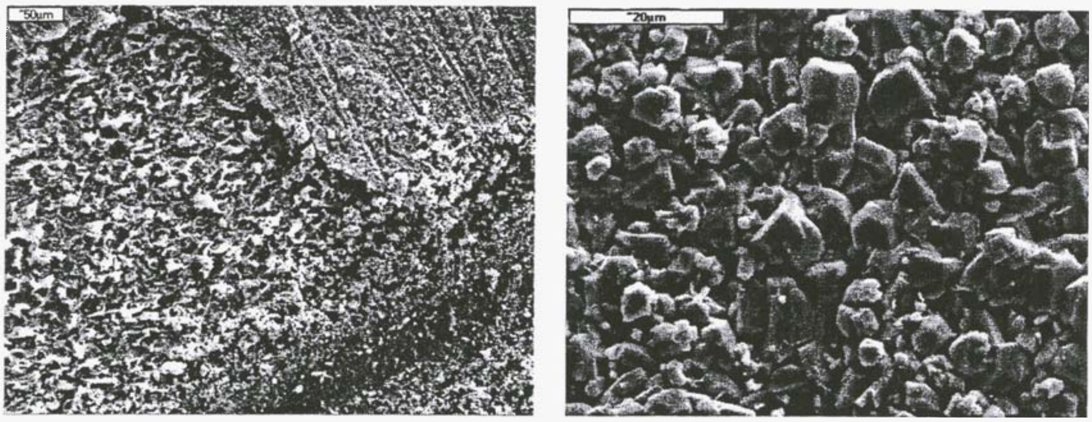


Figure 1: Test arrangement for simulation of acidic geothermal fluids in a pressure vessel.

Table 3 - Sequence of Experiments Completed and Results

Test	Conditions	Exposure Time	Weight Loss Corrosion Rate	LPR Corrosion rate	Corrosion Potential
					SHE
	pH \ T (°C) \ Flow Rate (ml/minute)	Hours	mm/year \ Film Adhesion	mm/year	MV
	N_2 De-aerated			Initial \ Final	Initial \ Final
E.1.1	1 \ 95 \ 5	48	70 \ Poor	180 \ 3	-300 \ -400
E.1.2	2 \ 95 \ 5	67	3.5 \ Poor	60 \ 1	-330 \ -460
E.2.1	1 \ 95 \ 5	36	340 \ Lost	160	-220
E.2.2	2 \ 95 \ 5	20	30 \ Poor	60 \ 35	-350
E.2.3	3 \ 95 \ 5	19	5 \ Poor	23 \ 15	-390
E.2.4	4 \ 95 \ 5	68	0.5 \ Fair	20 \ 3	-430
E.2.5	5 \ 95 \ 5	66	0.7 \ Thin Film	8 \ 1.5	-480
E.3.1	3 \ 95 \ 5	24	11 \ Fair	21 \ 2.6	-480
E.4.1	3 \ 150 \ 5	27	9 \ Poor	18 \ 3	-300 to –480*
E.4.2	3 \ 150 \ 5	21	11 \ Poor	21 \ 2	-180 to –580*
	1 % H_2S in N_2				
S1	3 \ 150 \ 7 unstable flow	22	7.5 \ Fair	0.5 **	-670*
S2	3 \ 150 \ 4 unstable flow	16	4.2 \ Fair	0.3 **	–530*
s4	3 \ 150 \ 17	24	8.8 \Fair	5 **	-350 to –500*
S5	5 \ 150 \ 20	12	1.6**\ Thin Layer	1 / 0.3 **	-600 \ –500*

** Corrected for solution resistance *** Estimated from weight gain



(a) S4, pH 3 (b) S5, pH 5

Figure 2: SEM microphotograph of corrosion products on electrodes from test S4 (a) scratched region, original outer surface and inner layer and test S5 (b) crystalline deposits.

The first two experiments with non-refreshed solution gave corrosion rates that appeared to be dependent on dissolved iron as the LPR corrosion rate measurements rapidly decreased. However, the corrosion potentials also decreased over the duration of the experiments and subsequent to the second experiment it was established that the solution pH had increased to over 4. The corrosion reactions had depleted the available hydrogen ion concentration and corrosion rates dropped accordingly.

As expected refreshing the solution in the second series, resulted in a more normal high corrosion rate, 340 mm/year at pH 1. The corrosion rate was reduced to 29 mm/year at pH 2 and 4.5, 0.4 and 0.7 mm/year at pH 3, 4 and 5 respectively. The LPR measured corrosion rates consistently decreased with time and approached that of the weight loss results. Corrosion potential decreased as the pH was increased, but the potentials remained relatively constant at any given pH. The repeated pH 3 test suggests a 2 times variation in weight loss corrosion rate might be normal for his type of experiment. Iron oxide was seen to deposit on the exit tubing from the pressure vessel during the tests with the lower pH solutions. Only the low pH solutions collected from the exit tubing precipitated iron deposits after standing.

The pressurised, 150°C tests at pH 3 (E.4.1 and E.4.2) gave a similar weight loss corrosion rate to the second test of pH 3 solution (E.3.1) at 95°C and a similar LPR result.

The work with pH 3 starting solution and 1% H_2S (S1 to S5) was more rigorously monitored as the solution conductivity was decreased and IR correction was required for the LPR measurements. Problems with the pump gave variable flow rate in the first two trials at pH 3 and the data shows some dependence on flow rate. The work with the higher flow rates at pH 3 and pH 5 indicated lower absolute corrosion rate and decreasing corrosion rate with time at pH 5. Similar results were seen in the H_2S free tests at pH 4 and 5.

Results of selective analysis of corrosion products formed on electrodes exposed in some of the last series of tests, S1, S4 and S5 are given in Table 4. Figure 2 illustrates the form of corrosion products seen on electrodes exposed in tests S4 (pH 3) and S5 (pH 5).

5.0 DISCUSSION OF RESULTS

The results gave a good indication of the parameters which need to be controlled in order to simulate acidic geothermal fluids in a laboratory pressure vessel.

Firstly, the static experiments demonstrate that it is essential to use a solution flow through system to refresh the autoclave solution. Alternatively a solution circulating system can provide a large volume to corroding surface area ratio. These techniques help to preserve the hydrogen ion concentration and minimise the level of dissolved iron build-up.

Table 4 - SEM EDX and XRD Analysis Results.

Test	SEM EDX		XRD	
	Major	**Minor**	**Major**	**Minor**
S1	Fe, S	O,Cr*, Ni*	Fe_3O_4	$Fe_{(1+x)}S$,U
S4	Fe, S	O,Cr*, Ni*	$Fe_{(1+x)}S$	FeS
S5	S, Fe		FeS	$Fe_{(1+x)}S$,(Fe)

Fe_3O_4 = Magnetite, $Fe_{(1+x)}S$ = Mackinawite,
FeS = Troilite, U = Unidentified Peaks

* Cr and Ni are derived from corrosion of the stainless steel alloys used for the cold flow lines

The fluid flow rates used do not simulate erosion corrosion conditions and the effect of the change in flow rate in the final series of tests is considered due to changing iron levels and perhaps also to small changes in pH.

Use of higher conductivity fluids would simplify the application of LPR. Inert ionic solutions or excess chloride and sulfate could be added. However the effect of chloride and sulfate may be to induce film breakdown and localised corrosion.

The Ag/Ag_2S reference electrode requires HS^- in solution to maintain a stable Ag_2S layer and reproducible potential. Use of this electrode without H_2S bubbling in the stock solution gave variability in the measured potentials (E.4.1 and E.4.2).

In the H_2S-free solutions the passive film formation due to $SO_4^=$ reaction with the steel was most probably formation of ferrous sulfate and magnetite (this has not been confirmed analytically). The application of H_2S gave sulfide stability and good passive film formation at pH 5. The obvious formation of a thin adherent film, Figure 2(b) was not reflected in the corrosion rates obtained for the short term tests conducted here and longer run times would be required to better demonstrate the effect of passive film formation on corrosion rates.

The magnitude of the corrosion rates observed using the weight loss measurements were consistent with the results of Sanada et al (1998) for pH adjusted flowing wellhead solutions. A range of the order of two times in the measured corrosion rates is suggested for the measurement error in the short-term tests.

The corrosion potential measurements correlate well with thermodynamic phase stability diagrams as developed for White Island hot pool #13a for example (Lichti et al, 1998b) and for Mahangdong MG-9D an acid well in the Philippines (Lichti et al, 1998a). The diagrams predict that at pH less than about 4, free corrosion will occur while at pH 5 passive films of mackinawite, troilite, pyrrhotite can form. The kinetics of pyrite formation are slow in comparison with the lower order sulfide phases and it is not surprising that this phase is not formed in these short term laboratory tests.

6.0 CONCLUSIONS

This work was aimed at understanding the parameters that need to be considered and controlled in order to simulate acidic geothermal solutions in a laboratory pressure vessel.

The results suggest use of a test arrangement providing:

- a pressure vessel and high temperature piping of a construction material able to resist the most aggressive solutions tested
- high pressure pump capable of sustaining flow
- capability to measure and control fluid flow rates
- temperature and pressure monitoring with feedback control of the heating element
- either mixed or single acids contained in a reservoir of fluid ready to be pumped through the heated pressure vessel
- sufficiently high flow rate to minimise build up of species which unrealistically aid passive film formation
- sufficiently high flow rate of fresh or refreshed solution to avoid depletion of hydrogen ion concentration
- chloride and sulfate levels which match or exceed those of the actual solution to give conductivity for ease of application of LPR
- chloride and sulfate at realistic levels that stimulate corrosion processes
- bubbling with H_2S of the mixed cold test solutions
- on-line corrosion potential measurement capability
- on-line corrosion rate measurement capability.

The series of tests conducted in development of the experimental techniques again provide some indication that pH adjustment can be effective as a means of corrosion control in de-aerated sulfate and chloride acidity waters. Passive film formation was rapid under the combined conditions of pH 3 mixed sulfate and chloride acidity adjusted to pH 5 using NaOH with and without added H_2S. The techniques developed will allow experiment design to further elucidate the roles of chloride, sulfate, sulfide and solution pH in the corrosion of carbon steels. Stirring of the autoclave or fitting of a spinning electrode would be required to study the added effect of fluid velocity.

Laboratory pressure vessel trials provide opportunity to test corrosion control practices under controlled laboratory conditions without the cost of full-scale well production. This avoids the difficulty of conducting field experiments and the risk to site personnel of producing acid wells for extended test periods.

7.0 ACKNOWLEDGEMENTS

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