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CORROSION CHEMISTRY OF SOME VOLCANIC ENVIRONMENTS

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SUMMARY - Volcanic environments on White Island, New Zealand and Kuju-Iwoyama, Kyushu, Japan have been used to study corrosion properties of materials which might be used for engineering plant for energy production from deep-seated and magma-ambient geothermal systems. The corrosion chemistry of these natural volcanic features is described with reference to the performance of carbon steels. Models of corrosion are developed using thermodynamic principles and conventional corrosion theory to allow prediction of materials performance in similar environments.

1. INTRODUCTION

Exploration and development of energy from deep-seated (>3000 m) and magma-ambient (>4000 m) geothermal environments for energy production will only be viable if the corrosion chemistries of the encountered and produced fluids are sufficiently well understood to facilitate prediction of corrosion parameters and selection of reliable materials. Measurement of materials performance in fluids from all newly drilled wells is not economic and is also too late to select suitable materials for well completion equipment. Materials selection for reliable energy extraction processes and plant will require a knowledge of materials performance in well understood, well characterised corrosive environments so that models of corrosion can be developed to allow prediction of corrosion in a range of produced environments. High temperature, high pressure aggressive geothermal environments have not been readily available for testing of materials in Japan or in New Zealand. Definition of the geochemistry of aggressive deep-seated and magma-ambient geothermal environments is also in its infancy in these two countries (White, 1994; Kasai et al, 1996) although volcanic environments have been extensively characterised (see for example, Giggenbach et al, 1990). Corrosion testing of metals and alloys for anticipated deep-seated and magma-ambient energy applications has therefore concentrated on the evaluation of natural volcanic environments to develop models of corrosion suitable for identification of generic material types for handling aggressive geothermal fluids (Kurata et al, 1994, 1995; Saito et al, 1994; Lichti and McIlhone, 1994).

Volcanic environments such as those encountered in fumaroles have aggressive chemistries due to the presence of corrosive gases SO_2, H_2S, HCl and HF. Corrosion chemistries of such mixed gas environments have not previously been characterised. This paper describes experience in exposing alloys to a range of natural volcanic environments and develops some preliminary models for rationalising the behaviour of carbon steels.

White Island, New Zealand

Testing of materials in natural volcanic features on White Island in New Zealand was initiated under a joint Japan/New Zealand initiative in 1993 (Kurata et al, 1994). Surface corrosion tests and stress corrosion cracking tests were undertaken in a number of environments from 1993 to 1996 including (Kurata et al, 1995):

- a high temperature fumarole (Noisy Nellie, WI #9)
- a low temperature fumarole (WI #12)
- acidic hot pools (Black Pot and WI Pool #13a)
- volcanic soils
- atmospheric environments.

White Island was chosen for its relative ease of access and variety of environments available within a single site. The materials tests involved the direct exposure of the metal samples in the volcanic environments.

Kuju-Iwoyama, Kyushu, Japan

Corrosion studies at Kuju-Iwoyama in Kyushu, Japan were initiated in 1992 as part of a series of activities aimed at demonstrating the feasibility of producing energy from volcanic environments (Ehara, 1994). The geothermal environment was derived from a shallow borehole drilled into a fumarolic area and cased with a 2 inch carbon steel pipe. The discharge gases were directed into an insulated test chamber where the metal specimens were held on exposure racks. (Saito et al, 1994)

2. PHYSICAL CONDITIONS

The corrosion chemistry of readily available natural volcanic environments may be strongly influenced by the physical conditions of these environments. The effect of rainfall and other changes in the volcano throughout a period of in-situ testing can not necessarily be predicted. Changes in the geometry of volcanic features or exclusion of air for example may be difficult to control in natural environments where superheated steam is exhausted to atmosphere through fumarolic vents. Test environments for which corrosion results have been obtained are described in the following sections and where possible the thermodynamic description of the corrosion process is developed in order to rationalise observations made and summarise the possible range of behaviours expected as a function of corrosion chemistry.

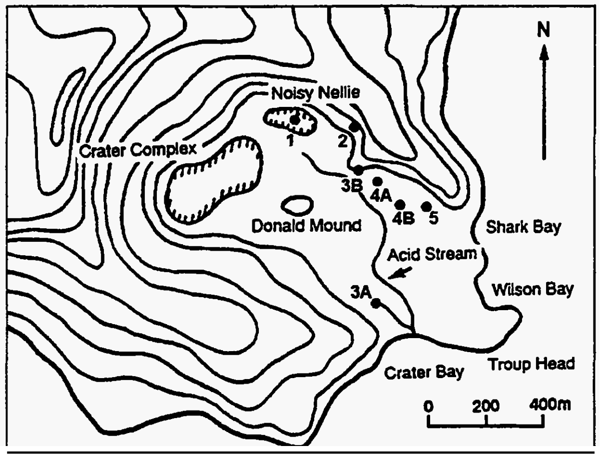

Figure 1- Location map for natural volcanic features selected for corrosion testing on White Island.
1: High-temperature fumarole "Noisy Nellie" #9
2: Low-temperature fumarole #12
3A: "Black Pot"; 3B: "WI Pool #13a" Hot pools
4A: High-; 4B: Low-temperature soils
5: Atmospheric

2.1 High-temperature fumaroles

The White Island high-temperature fumarole selected for testing was "Noisy Nellie", WI #9 (see Figure 1). This fumarole is of large diameter, >15 m and depth, >12 m and had for many years an apparently stable discharge. The corrosion tests performed were spread over three years and in this time period the fumarole experienced a slow decline in temperature (see Table 1). The fumarole also experienced apparent changes in discharge volume as evidenced by the vigour of the discharging steam. These effects coupled with changes in wind velocity and direction may also have resulted in a variation in the amount of air being drawn into the fumarole and around the exposed metal samples. The topography of the fumarole also changed considerably over this period, particularly under adverse conditions of heavy rainfall. Specimens were at times lost as a result of the walls of the fumarole collapsing. Temperatures were measured using thermocouples attached to coupon racks, to rods used to insert and remove coupon racks and to sampling tubes located close to the locations of the coupon racks.

Over the three year period of tests a number of differing environments were encountered, these included (Table 1):

- a period of stable high temperatures in the range 230°C to 190°C
- a period of lower temperatures apparently below the dew point for the gas mixture
- a period of very low temperatures in the base of the fumarole where the metal samples were exposed at 19°C to 114°C

In all of these environments the temperature was lower at night than during the day. Visits were not made to the Island during periods of rainfall and the physical effects of this rainfall can only be hypothesised.

Testing of metals in a fumarolic environment on Kuju-Iwoyama in Japan was done by drilling a small bore hole below an area where significant fumarolic activity was observed. The hole intersected what appeared to be a feed zone and gave single phase superheated steam at a temperature of 233°C. The tests were conducted in an insulated metal chamber at atmospheric pressure with steam feed taken directly from the discharge pipe and hence it is believed that air was excluded from this test environment.

2.2 Low-temperature fumarole

Testing on White Island was undertaken in only one low-temperature fumarole which was located on a side wall of the volcano above the floor of the main valley (see Figure 1). The fumarole discharge vent was about 100 mm across and was located in the bottom of the fumarole. There were relatively steep side walls with the fumarole being about 1 m deep and about 1.5 m in outer diameter. Temperatures were measured by insertion of a thermocouple, tied to a rod, into the mouth of the fumarole discharge vent. This fumarole was also subject to physical changes in the fumarole topography due to excessive rainfall and a number of exposures of metal samples were curtailed as a result of excessive corrosion being experience due to contact with soil. Formation of elemental sulfur on the metal samples and exposure racks was also observed.

This low-temperature fumarole was expected to experience steam condensation and aeration in the relatively shallow geometry. Metal coupon temperatures were lower than that observed in the fumarole vent area (Table 1).

2.3 Acidic hot pools

"Black pot" at 94°C, pH 4 to 5 which was about 3 m in diameter and 0.6 m deep was selected for testing (see Figure 1). This pool bubbled vigorously for the period of exposure as gases were continually being discharged. The gas discharge tended to keep sand in suspension in the pool and the turbulent mix caused the specimen chambers to settle into the sands in the bottom of the pool. The pool was "black", as suggested by the name, presumably due to the presence of iron-rich sands and metal sulfide precipitates in the relatively reducing environment.

Table 1- Temperatures recorded for natural volcanic environments used for corrosion tests.

Exposure Site	Start Date	Temperature	Comments
High-temperature fumaroles		°C	TIC = Thermocouple (location)
Noisy Nellie			Atmospheric pressure
- 1st test - (Coupons + SCC)	14.01.94	230 to 190	TIC (at coupons)
- 2nd test - (Coupons + SCC)	21.02.95	95 to 145	TIC (at coupons)
- gas sampling	21.02.95	192	TIC (on sampling tube)
- 3rd test - (Coupons + SCC)	28.02.95	90 to 119	TIC (at coupons)
- 4th test - (Coupons + SCC)	14.02.96	19-114	TIC (at coupons)
- gas sampling	14&17.02.96	120	TIC (at sampling tube)
Kuju-Iwoyama - (Coupons + SCC)			Atmospheric Pressure
- Insulated Steam Chamber	27-12-92	230	Fumarole area borehole
Low-temperature fumarole			Atmospheric Pressure
- 1st test - (Coupons)	15.01.94	98	TIC (at vent)
- 2nd test- (gas sampling + SCC)	21.02.95	98	TIC (22-80 at coupons)
Hot pools			
Black Pot - (Coupons + SCC)			Black sandy pool with vigorous
- Start of 1st test - Water Sampling	15.01.94	93	gas bubbling
- Day of 2nd test - (Electrochemical)	14.02.96	97	TIC (immersed in pool)
- Day of 3rd test - (Electrochemical)	19.02.96	97	TIC (immersed in pool)
WI Pool # 13a			Oily, sulfur rich pool
- Day of 1st test - (Electrochemical)	14.02.96	99	with some gas bubbling
- Day of 2nd test - (Electrochemical)	19.02.96	100	TIC (immersed in pool)
High-temperature soil - (Coupons)			Samples buried at 1 m
- Start of test - soil collection	15.01.94	100	TIC (at samples)
Low-temperature soil - (Coupons)			Samples buried at 1 m
- Start of test - soil collection	14.01.94	37-40	TIC (at samples)
Atmospheric		Noon Temp on	Ambient temperature
- Start of test - (Coupons)	14.01.94	**visit days ≈ 23°C**	**Northerly facing, samples at 45°**

In the final year of testing on White Island a number of other hot pools were observed to have formed in an area near the low-temperature fumarole. These pools were targeted for corrosion measurements using instantaneous electrochemical corrosion monitors to permit a comparison of corrosion rates and corrosion mechanisms with that of the Black Pot. Temperatures approaching boiling point of water were measured using immersed thermocouples and the surfaces of these pools appeared "oily" and were "rich" in sulfur compounds. One pool, named WI Pool #13a, see Table 1 was selected for corrosion measurements on two separate one day visits. Comparison tests were also done on these same days in Black Pot.

2.4 Volcanic soils

High-temperature soil

Metal coupon samples were exposed in high-temperature soil at a depth of 1 m from the surface and at a temperature of 100°C. The test site was located on the floor of the main valley of White Island and was though to have been well away from other active pool or fumarole sites (see Figure 1). The site was selected by probing for 1 m deep temperatures. The soil was removed by digging of a hole, the metal coupon racks were placed in the hole and the hot soil was replaced for the duration of the test. The soil in the bottom of the hole was a dark, dull grey colour, tended to "steam" when first opened and was "wet". Only the coupons to be removed were exposed to the air when the interim exposure period samples were removed. Temperatures were again measured by probing of the soil while removing the coupon racks. Burial depth decreased with time to 0.75 m due to surface erosion of the soil.

Low-temperature soil

Metal coupon samples were exposed to low-temperature soil at a depth of 1 m from the surface and at a temperature of 37 to 40°C. The test site was located about 100 m from the high-temperature soil site and at a slightly higher elevation (see Figure 1). The soil in the open hole at this site was a lighter grey/brown colour and was wet. Similar procedures, to those noted for high-temperature soil, were used when preparing the site and extracting the exposed coupon racks and when measuring the temperatures.

2.5 Atmospheric test site

This test site was chosen to be primarily volcanic in nature although it must be recognised that the sea was in close proximity, see Figure 1.

Temperature, relative humidity and time of wetness measurements were not made over the course of the one year exposures. Extremes of temperature and humidity might have been on the order of 4 to 35°C

Table 2- Geochemistry of Fumarole Environments Used for Corrosion Testing

Location	Date	T	CO_2	H_2S	SO_2	NH_3	HF	HCl	CO	H_2	O_2*	N_2	CH_4	Ar	H_2O	Gas**
		°C	mmol gas/100 mol steam													wt%
Noisy Nellie WI #9[1]	15.6.88	280	425	82.6	309	0.23	0.25	5.33	0.002	34.8	-	4.36	4.55	0.03	99134	2.3
Noisy Nellie WI #9[2]	21.2.95	193	1381	94.3	133	15.5	3.87	35.1	-	43.1	(62.8)	119	5.48	0.90	98169	4.3
Low-T WI #12[2]	15.1.94	98	9171	53.7	40.0	0.07	0.07	0.94	-	0.07	(0.13)	69.1	16.2	0.11	90649	22.8
Kuju-Iwoyama[3]	27.12.92	230	1400	750	240	-	10.0	30.0	-					-	97580	5.8

* O_2 in original samples, results shown are corrected for air contamination; **Total Gas in Steam
[13 Giggenbach and Sheppard, 1989; [2] This Work (abbreviated results); [3] Saito et al, 1994

and 0 to 100% respectively. Ash fallout was present on the coupons after only 2 days of exposure, with which localised corrosion sites were associated.

3. CHEMICAL COMPOSITIONS

3.1 High temperature fumarolic environments

Noisy Nellie, White Island

Gas and water samples suitable for the determination of the geochemistry of the "Noisy Nellie" fumarole were difficult to obtain because of the extreme depth and width of the fumarole. A gas sampling system was developed to establish discharge through small bore titanium tubing using a vacuum cleaner and with the top section heated using electrical heating tape. The gas samples obtained from Noisy Nellie on 21.02.95 were analysed to give results as shown in Table 2 which also lists a result from a previous sample for comparison.

Oxygen was present in all of the samples collected over the three year period. Gas content was 4.3 wt% and the predominant gases were CO_2, SO_2 and H_2S with significant concentrations of HCl, HF and NH_3.

The metal coupon samples exposed during 1994 were dry on removal from the fumarole whereas those exposed in subsequent years, when the temperature was lower, tended to have some condensed liquid on the surface.

Kuju-Iwoyama, Japan

Chemical sampling of gas and steam discharged from the test chamber used for the materials tests gave results as listed in Table 2 (Saito et al, 1994). The geochemistry indicated was air free suggesting minimal contamination of this environment was achieved by conducting the test in a steam fed insulated chamber. The potential for condensate formation in the discharge pipe was minimised by lagging of the pipework above the ground and by lagging of the box. It was reported that a temperature of 230°C was maintained throughout the test. Under these conditions the potential for acid formation at the dew point of the gas mixture was minimised.

3.2 Low-temperature fumarole

The low-temperature fumarole WI #12 used for materials tests on White Island had been regularly sampled as part of a monitoring programme for volcanic activity. Table 2 gives a typical result for the period of test from 15.01.94 to 13.04.95. The geochemistry of this fumarole was relatively stable throughout this period. The low temperature of the discharge and consequent condensation of H_2O in the vent is responsible for the relatively high C02 but lower H_2S, SO_2 and HCl gas contents of the discharge.

3.3 Acidic hot pools

The White Island Black Pot hot pool was again regularly sampled as part of a monitoring programme for volcanic activity. Table 3 gives typical results for this pool which was relatively stable throughout this period. The newer pool, WI Pool #13a, was sampled on 12.2.96 and the results are also given in Table 3 for comparison. The concentration of $SO_4^=$ and Cl^- were higher than that observed for Black Pot and the solution pH was also much lower at 1, compared to the pH of 4 to 5 observed for Black Pot.

3.4 Volcanic soils

High- and low-temperature soils collected on the first day when the coupons were exposed in these soils were analysed using conventional soil analysis methods. The results are summarised in Table 4. Dragger tube sampling, see Table 5 in the soil in the excavated holes on the final day of the exposures (26.02.95) indicated high concentrations of H_2S and SO_2 in the soil at the high-temperature soil site whereas the low-temperature site revealed only trace amounts.

3.5 Atmospheric environments

The atmosphere was expected to contain significant concentrations of SO_2, H_2S and HCl (ppm levels) but to also be influenced by the presence of ash fallout (Cl-rich and acidic particles) from eruptions emanating from the main crater. Atmospheric environments were measured using Dragger tubes Table 5 on the final day of the exposure tests (26.2.95). Plume aerosol sampling has been carried out in the vicinity of the main crater and very high concentrations of sulfuric and hydrochloric acids have been observed.

Table 3- Geochemistry of Hot Pool Environments used for Corrosion Testing on White Island.

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
		°C		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	97	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

Note: Results shown are abbreviated

Table 4- Soil Analysis, High- and Low-Temperature.

	High-T	Low-T	Units
Sampling T	100	37	C
Conductivity[1]	28.04	32.80	mS/cm
Resistivity (Calculated)[1]	11.9	10.2	ohms-cm
pH (H2O)[1]	3.3	3.9	
Total Carbon[1]	0.13	0.22	%
Soluble salts (Tot)[1]	9.81	11.48	%
Moisture[2]	2.5	2.3	%
Sulfur (Total)[2]	6.92	5.32	%

[1] Landcare Research NZ Ltd
[2] Coal Research Association NZ Ltd

Table 5- Atmospheric Dragger tube analysis (mg/kg)

	H_2S	SO_2	NO_2	HCl
Atmospheric	0.4	≤1	trace	trace
Low-T Soil	≤0.1	trace	trace	trace
High-T Soil	10.5	1,000	≤0.5	≤0.03
Black Pot	20.0	trace	trace	trace

4. THERMODYNAMIC MODELS

The analysis results can be interpreted using thermodynamic models of corrosion which have been developed previously to characterise similar environments. If the corrosion chemistry is similar to well understood environments, for which corrosion results are available then a comparison of the materials performance results can be justifiably undertaken and predictions made for materials and environments other than those tested.

4.1 High temperature fumarole discharge gases

The CSIRO Thermochemistry program (Turnbull and Wadsley, 1988) was used to estimate the high temperature equilibrium conditions for the results found for Noisy Nellie and Kuju-Iwoyama (Table 2). Under equilibrium conditions the program indicated O_2 partial pressures of 10^{-36} atm both with and without air as the oxygen was allowed to fully react. If the air is considered separately, and not allowed to reach equilibrium then an O_2 partial pressure of 10^{-3} atm is suggested.

Kellog diagrams provide a method for modelling of equilibrium high temperature dry gas corrosion reactions for metallic species as a function of log P(gas) vs log P(O_2) (Lai, 1990). Figure 2 illustrates such a diagram at 230°C for iron species. The diagram was constructed using thermodynamic data extracted from the CSIRO Thermochemistry database. Reactions of the Noisy Nellie and Kuju-Iwoyama fumarolic gas mixtures with iron are illustrated on the diagram. The air-free and air-in-equilibrium gas mixtures have partial pressures which give pyrite (FeS_2) and troilite (FeS) or pyrrhotite ($Fe_{(1-x)}S$) stability as the metal surface is approached, while the non-equilibrium air containing gas has a range of possible concentrations which coincide with ferrous and ferric sulfates and hematite (Fe_2O_3) and magnetite (Fe_3O_4) forming on the metal surface. The predicted sulfide stability on carbon steel metal samples is confirmed for the Kuju-Iwoyama tests (Saito et al, 1994) while oxide stability was observed on tests in Noisy Nellie at these temperatures (Kurata et al, 1995).

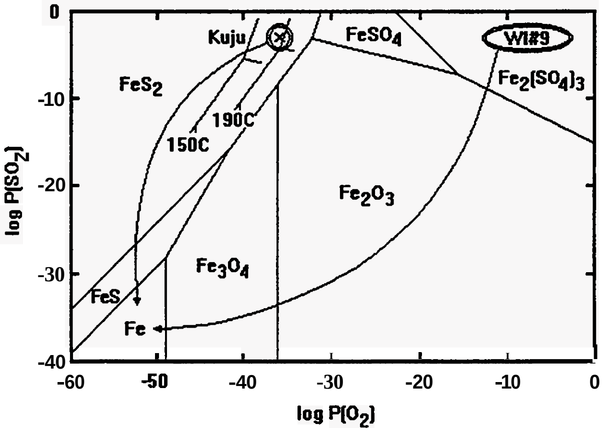

Figure 2- Stability diagram for Fe in volcanic gas derived from Noisy Nellie and Kuju-Iwoyama, 230°C. Arrows indicate possible reaction paths.

The model for corrosion product stability is confirmed by the above mentioned results and furthermore gives a reason for previously reported and discussed differences in corrosion rate for carbon steels exposed in these two environments (Lichti and McIlhone, 1994). The Kuju-Iwoyama test where sulfide stability dominates in the air free environment gave corrosion rates for these alloys of 0.03-0.04 mm/y while the tests in Noisy Nellie where oxide stability occurred, gave higher corrosion rates at 0.5-0.8 mm/y.

Similar diagrams can be prepared for other alloying elements such as for Cr, Ni and Mo to expand the model relevance for alloyed materials. These high-temperature thermodynamic calculations allow prediction of the reaction products but do not give quantitative predictions of corrosion kinetics. Corrosion exposure results are required to determine the capability of the stable corrosion products to control the corrosion at low levels by passivation or surface blocking mechanisms.

Formation of sulfuric acid is possible in these environments if SO_3 is present and the temperature drops below the sulfuric acid dew point. SO_3 at for example 0.1 vol% SO_2 gives an H_2SO_4 dew point of 145°C, however with very low levels of SO_3 at for example 10^{-4} vol% the dew point will be determined by steam condensation, ie at 97°C (Ganapathy, 1993). The presence of *SO3* has not been confirmed.

At atmospheric pressure condensate formation at below 100°C will result in aqueous corrosion environments. In the absence of oxygen, a total sulfur concentration and pH at a temperature of 100°C for example can be calculated, assuming that a very small amount of water is formed to give a worst case pH prediction. Condensing 10^{-4} volume % of the steam results in Total **S** = 0.2689 mol/kg and pH = 0.4. (White, 1996) At this sulfur concentration and temperature a potential-pH Pourbaix diagram for the Fe-S-H_2O system such as is shown in Figure 3 can be constructed.

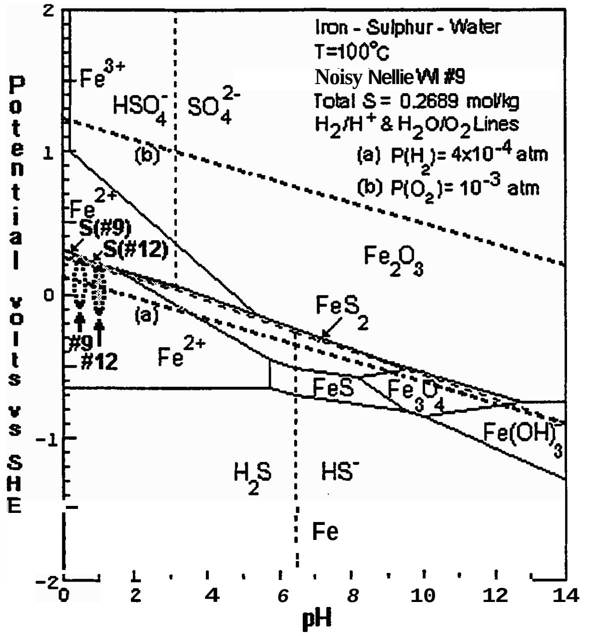

Figure 3- Potential-pH Fe-S-H_2O Diagram for Total **S** = 0.2689 mol/kg and T = 100°C.

In the absence of O_2 and SO_2 it is normal practice to assume that the corrosion reaction will be at or near the H_2/H^+ equilibrium line, however in the presence of SO_2 and/or O_2 the corrosion reaction will be influenced by the sulfur chemistry or the oxygen chemistry and will tend to move towards the H_2O/O_2 equilibrium line. At the calculated pH, possible regions of stability are predicted for Fe^{2+} in solution and HSO_4^- in solution, with no solid species being precipitated on iron.

4.2 Low-temperature fumarole

In the low-temperature fumarole, WI#12 it was assumed that aqueous reactions rather that dry gas reactions would dominate the corrosion chemistry. This assumption was based on the lower temperatures and lower discharge volume giving more cooling of discharged steam. Calculation of the corrosion chemistry at 80°C, again obtaining a worst case pH condition by assuming 10^{-4} volume % steam condensation gives a pH of 1.3 and Total **S** of 0.0464 mol/kg (White, 1996). Under these conditions a potential-pH diagram similar to that shown in Figure 3 is obtained although the increased stability area for elemental **S** is important and elemental **S** was seen to be precipitated on the exposed metal samples. Carbon steels were not tested in this environment because of the expected high corrosion, 12 % Cr alloys had corrosion rates of 3 to 4 mm/y (Kurata et al, 1995).

4.3 Acid pools

The acid pool corrosion chemistries can be assumed to be dominated by the pH and the sulfur chemistry (see Table 2). Black Pot corrosion rates of 1.5 mm/y were recorded for carbon steel, while the short term tests in the WI Pool #13a gave much higher corrosion rates estimated to be as high as 150 mm/y. The corrosion chemistry of these two aqueous environments can also be modelled using potential-pH diagrams, see Figure 4.

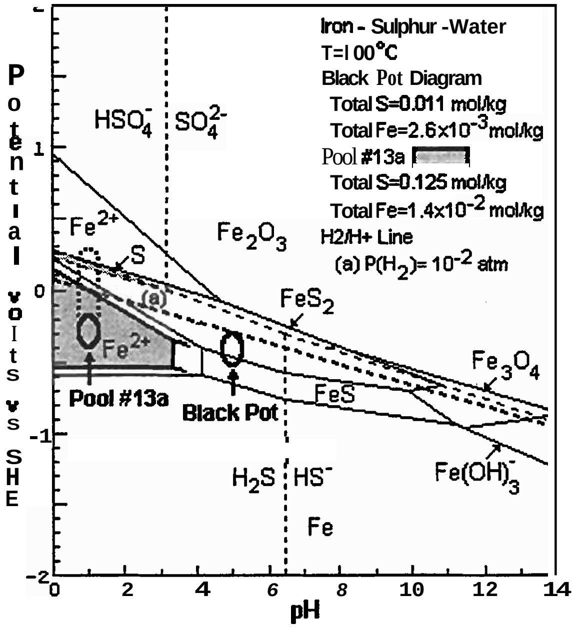

Figure 4- Potential-pH Fe-S-H_2O diagram for Black Pot with shaded areas representing variations in stability for Pool #13a.

The corrosion potential of carbon steel samples exposed in the two pools was measured using a Ag/AgCl reference electrode. SHE potentials of -411 mV and -260 mV were obtained in Black Pot and Pool #13a respectively. These potential areas are marked on Figure 3 together with an area of uncertainty for Pool #13a. The exact position of the H_2/H^+ equilibrium line in these pools is not known as the partial pressure of H_2 has not been determined, the value shown is for $p(H_2)$ of 10^{-2} atm. Formation of pyrite (FeS_2) is predicted for Black Pot at pH 5. During the corrosion tests in this pool pyrite (FeS_2) was formed in large sheets on the side of the exposure baskets. At the measured pH values, free corrosion with only Fe^{2+} in solution is predicted for Pool #13, which is in accord with the observed acid corrosion with minimal precipitation of corrosion products, although elemental sulfur was also observed.

4.4 soils

The corrosivity of soils is determined by soil and water chemistry (Wilson, 1995):

- concentration of soluble salts
- pH - total acidity
- wet/dry cycle
- degree of aeration
- soil temperature.

The most corrosive conventional soils are those which have high conductivity, or are strongly acidic with rapid drainage. The White Island soils tested had high temperatures, high conductivities, low pH (H_2O) values and were rich in soluble salts and sulfur (Table 4). Corrosion rates reported for carbon steel in the White Island soils at 1 mm/y (Kurata et al, 1995) were not significantly greater than the corrosion rates observed in other well aerated, wet/dry cycle, high conductivity soils. These soil corrosion results coupled with conventional soil corrosion models will be used to predict long term performance of metals exposed to volcanic soils.

4.5 Atmospheric

Corrosion in urban industrial environments where SO_2 is present has been linked to surface contaminant levels of sulfur of between 0.5 and 1.5 mg/dm^2/day (Feliu and Morcillo, 1984). SO_2 absorption and corrosion rates are strongly dependent on relative humidity with corrosion initiating and rapidly increasing at between 60 and 70 % Relative Humidity (RH) (Duncan and Spedding, 1973; Vernon, 1935). Addition of HCl gas contamination to SO_2 and H_2S containing environments gives a further 10 fold increase in the rate of corrosion (Rice et al, 1981). Deposition of even inert particles such as silica, results in accelerated corrosion in the presence of corrosive gases due to enhanced gas absorption and crevice formation as well as delays in surface drying when the RH again decreases below 60% (Vernon, 1935). Corrosion of carbon steel in the White Island atmospheric environment (Table 5) at 0.9 mm/y (Kurata et al, 1995) is higher than in tests with environments containing 0.1 % SO_2 with particulate deposits, 0.1 mm/y (Vernon, 1935).

5. PREDICTIVE CAPABILITIES/ LIMITATIONS OF MODELS

The corrosion chemistry of the dry high temperature fumarole environments has been described using a stability diagram for Fe as a function of log $P(SO_2)$ vs log $P(O_2)$ and is in accord with corrosion literature, Figure 2. Dry gas models of this type will be sufficient for initial predictions of corrosion in systems where steam superheat is maintained but will not apply when condensate formation is promoted by, for example extraction of energy.

The aqueous corrosion properties of initially formed condensate in equilibrium with the fumarole steam and gas has been estimated, pH = 0.4 at Total S of 0.2689 mol/kg, and modelled as a potential-pH, $Fe\text{-}S\text{-}H_2O$ stability diagram, Figure 3. The diagram can not be used to make predictions of corrosion without confirmation of corrosion rates from in-situ tests and these are still being analysed, however initial data for stainless steels suggests very high corrosion rates for carbon steels would be predicted because of the poor stability of corrosion products in the low pH condensate environments.

In the liquid Black Pot pool at a Total S = 0.01 1 mol/kg and at pH 5, pyrite (FeS_2) is indeed formed as predicted by Figure 4 and in this region the model is clear and adequate. The model is incomplete for Pool #13a, at a Total S = 0.125 mol/kg and pH c 1. Free corrosion is predicted and observed but Figure 4 is not sufficiently accurate for making additional predictions without corrosion test results and model refinement with additional geochemical results.

The corrosion rate results in the volcanic soils, can be characterised using conventional models of soil corrosion, although the volcanic soils would be classified as extremely corrosive.

Corrosion in atmospheric environments contaminated by volcanic gases is dependent on contaminant gas absorption as determined by the local gas concentration as well as the local humidity and temperature. The deposition of volcanic ash rapidly promotes corrosion because of the high Cl and S content of the particles, enhanced absorbtion of contaminant gases around the particles and the formation of a crevice between the ash and the metal surface. Conventional models of corrosion in polluted industrial environments are inadequate for making long term predictions. In situ test results are required.

6. CONCLUSIONS

Thermodynamic models have been prepared to describe the dominant corrosion mechanisms for carbon steels exposed to natural and artificial volcanic environments. The preliminary models provide reasonable predictions of surface corrosion mechanisms and give reasons for some of the observed corrosion performance of exposed materials. Model deficiencies have been identified and more are expected to be found as the analysis of corrosion results proceeds. Refinement of the models will progress understanding of the corrosion mechanisms and enhance the predictive capabilities of the models.

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8. REFERENCES

Duncan, J.R. and Spedding, D.J. (1974). Corrosion Science, Vol 14, pp 241-249.

Ehara, S. (ed) (1994). Field study of power generation by using volcanic geothermal reservoir, Report of the Grant in Aid on General Research Supported by the Minsitry of Education Science and Culture, Japan, 19 Sept (in Japanese).

Feliu, S. and Morcillo, M. (1984) Br Corrosion J, Vol 19, No 3, pp 143-145.

Ganapathy, V. (1993) Compute dew point of acid gases, Hydrocarbon Processing, Feb, pp93 and 98.

Giggenbach, W.F., Gaecia, N., Londono C., A., Rodriguez V., L., Rojas G., N., and Calvache V., M.L. (1990). Jnl of Vol and Geothermal Res, 42, pp. 13-39.

Giggenbach, W.F. and Sheppard, D.S. (1989) Variations in the temperature and chemistry of White Island fumerolic discharges 1972-85, In NZ Geological Survey Bulletin 103, pp 119-126.

Kasai, K., Miyazaki, S., Sasaki, M., Yagi, M. and Uchida, T. (1996). Supersaline brine in the Kakkonda granite obtained from WD-1A in the Kakkonda Geothermal Field, Japan, in Proc VIIIth Int Symp on the Observation of the Continental Crust Through Drilling, Tsukuba, Japan, Feb 26 to Mar 2, pp359-364.

Kurata, Y., Sanada, N. Nanjo, H., Ikeuchi, J. and Lichti, K.A. (1994). Field testing of Materials at White Island, in Extended Abstracts of 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, World Geothermal Congress, Milan, Italy, May, pp 2409-2414.

Lai, G.Y. (1990). High Temperature Corrosion of Engineering Alloys, ASM International, Ohio, USA, 231 pgs.

Lichti, K.A. and McIlhone, P.G.H. (1994). Materials for volcanic environments, Where will the data come from, in Proc 16th NZ Geothermal Workshop, Geothermal Institute, U of Auckland, Nov, pp 35-40.

Rice, D.W. Peterson, E.B., Rigby, P.B.P., Cappell, R.J. and Tremourex, R. (1981). J Electrochem Soc, Feb, pp 275-284.

Saito, M., Takano, Y., Saito, S. and Kondo, T. (1994) Field testing of materials at Kuju-Iwoyama solfatara, in Extended Abstracts of Workshop on Deep-seated and Magma-Ambient Geothermal Systems, Tsukuba, Japan, Mar, pp 189-199.

Turnbull, A.G. and Wadsley, M.W. (1988). The CSIRO Thermochemistry System, Version V, CSIRO, Australia.

Vernon, W.H.J. (1935). Trans Faraday Society, Vol31, pp 1668-1700.

Wilson, P.T., Minchington, I.E. and Young, M.G. (1995) Electrochemical monitoring of soil corrosivity, in Proc ACA Conf, Paper No 30, 14 pgs.

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

White, S.P. (1996). Private Communication.