MATERIAL DAMAGE IN A VOLCANIC ENVIRONMENT

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Key words - geothermal, metallic materials, corrosion, volcanic environment, White Island

ABSTRACT

Field testing of materials at White Island was undertaken to asses the corrosion performance of metals and alloys under the severe corrosive conditions encountered in geothermal volcanic environments. Metallic materials were tested in six different types of sites in the volcanic environments, of which the maximum temperature was 230°C. This paper reports preliminary results for these exposure tests.

In a high-temperature fumarole, nickel-base alloys containing more than 8% molybdenum and titanium alloys showed excellent resistance with corrosion rates less than 0.05 mm/y, but lower-alloy materials were severely corroded. In the nickel-base alloys molybdenum played a key role in enhancing resistance to corrosion. The corrosion rate increased linearly with decreasing molybdenum content in the range from 3% to 8%. Nickel-base alloys containing less than 3% molybdenum were corroded at rates of 1 to 2 mm/y greater than carbon and low-alloy steels.

In a low-temperature (108°C) fumarole, duplex stainless steels showed good resistance, with rates less than 0.04 mm/y, which was comparable with the nickel-base alloys containing more than 8% molybdenum.

1. INTRODUCTION

Research is being carried out on volcanic environments in fumaroles to understand volcanic processes. New methods are being developed to drill into regions close to magma, where aggressive environments prevent the use of conventional materials. Surveys have been carried out on construction materials for power production from conventional geothermal resources (DeBerry *et al.*, 1978, Ellis and Conver, 1981, Ellis *et al.*, 1983, Kurata *et al.*, 1992). Few studies have been done covering performance of materials in magmatic or volcanic fluids where aggressive environments are anticipated (Westrich *et al.*, 1986, Kurata *et al.*, 1994, Saito *et al.*, 1994).

White Island is the emergent summit of a volcano located at the north-east end of the Taupo Volcanic Zone in the Bay of Plenty, New Zealand. The Island provides an opportunity to investigate the energy potential and chemical transfer conditions from a magma system and to model the temperature distribution from the magma to the ground surface. Temperatures close to the active vents of White Island have varied between 100 and 800°C. A geochemical and geophysical database of the Island was constructed (Giggenbach and Sheppard, 1989), so the Island is considered an appropriate place for field testing of materials in a volcanic environment.

The present field testing on White Island started in January 1994. The objectives of the testing are: (1) to study the performance of materials exposed to volcanic environments to understand the rate and behavior of corrosion attack, and (2) to help in identifying materials suitable for construction of plant and equipment which may be used in aggressive volcanic environments.

2. METHODS

The field testing was a joint program of the high-performance materials group of Tohoku National Industrial Research Institute of Japan (Tohoku-NIRI) and the materials performance group of The New Zealand Institute for Industrial Research and Development (Industrial Research Ltd).

The two groups collaborated on the research program, and began exposure of metals and alloys in volcanic environments on White Island in the middle of January 1994. A one year period of testing was planned and initial samples of exposed materials were removed for examination after periods of 40 days and 111 days. Final material removals will be after 1 year exposure in the spring of 1995.

2.1 Materials

Table 1 lists the 27 materials selected for testing based on their known performance in Conventional geothermal environments.

- Carbon steels and low alloys are low cost and have good performances in conventional geothermal environments for applications such as bore casings, wellhead equipment, and transmission pipelines.
- Martensitic and ferritic stainless steels containing 12% to 17% Cr have improved performance over carbon steels in aerated or wet environments. Ferritic stainless steels with high Cr content (23 to 30%) possess good resistance to stress corrosion cracking (SCC).
- Austenitic stainless steels form an oxide layer which shows good corrosion resistance to geothermal condensates. Chloride or sulphide ions easily break down the oxide layer and can result in pitting corrosion and SCC.
- Some duplex stainless steels and high-alloy stainless steels possess better resistance to pitting corrosion or SCC than SUS 304 and 316.
- Nickel-base alloys such as Alloy 625 and C276 show excellent resistances to surface corrosion, SCC, and pitting corrosion.

Some alloys, when in contact with another corroding material, can be charged with hydrogen, which can subsequently induce hydrogen embrittlement.

Tests were designed to elucidate degradation due to general corrosion, pitting corrosion, stress corrosion cracking, and galvanic corrosion / hydrogen embrittlement. Dimensions of the coupon-type specimens are illustrated in Figure 1.

2.2 Exposure Sites

Six sites on White Island were selected for material exposures (Figure 2): two fumaroles, for exposure to gases at high and low temperatures, an acid pool, wet soils at high and low temperatures, and the atmosphere.

Site 1: High-temperature Fumarole Figure 3 shows a schematic drawing of "Noisy Nellie", a high-temperature fumarole which is 10

Table 1. Materials tested for resistance to corrosion at White Island.

Material Type	UNS Number	Normal Composition
Carbon and Low-Alloy Steels		
SS400	---	Carbon steel, tensile strength 400MPa
Corten	---	Atmospheric corrosion resisting steel
N80	---	API standard
LBO	---	API standard
Martensitic Stainless Steel		
13Cr	S41000	Yield strength 560MPa
Ferritic Stainless Steel		
23Cr-6Al	---	23Cr-6Al
Austenitic Stainless Steels		
SUS304	S30400	Standard alloy, 18Cr-8Ni
SUS316	531600	Standard alloy, 18Cr-10Ni-2.5Mo
Duplex Stainless Steels		
22Cr-5Ni	S31803	22Cr-5Ni-3.0Mo-0.15N
25Cr-7Ni	532750	25Cr-7Ni-3.5Mo-0.10N
25Cr-7Ni-N	S32750	25Cr-7Ni-3.5Mo-0.20N
High-Alloy Stainless Steels and Nickel-Base Alloys		
SS 2562	NO8904	19.5Cr-25Ni-4.5Mo-1.5Cu
1925hMo	NO8926	21.5Cr-25Ni-6Mo-1Cu
Alloy 625	NO6625	21.5Cr-61Ni-9Mo-2.5Fe-3.7(Nb + Ta)
Alloy 690	NO6690	30Cr-60Ni-9.5Fe-1(Nb + Ta)
Alloy 800	NO8800	21Cr-32.5Ni-46Fe-0.04C
Alloy 825	NO8825	21.5Cr-42Ni-3Mo-30Fe-2.2Cu-0.9Ti
Alloy 59	NO6059	23Cr-59Ni-16Mo-1Fe
Alloy 45TM	---	27Cr-47Ni-2.7Si-0.08N-Balance Fe
C276	N10276	16Cr-55Ni-16Mo-6Fe-4W
G3	NO6985	22.5Cr-43Ni-7Mo-20Fe-2Cu-Co
Alloy 903	N19903	38Ni-15Co-3Nb-1.4Ti-0.7Al-0.01C
Cobalt Alloy		
S816	---	20Cr-20Ni-47Co-4Mo-4W-4(Nb + Ta)
Aluminum Alloys		
Aluminum	A91025	A-1050, 99.5Al
Ai alloy	A95052	A-5052. 2.5Mg-0.2Cr
Titanium Alloys		
Ti grade 1	R50250	Ti(α)
Ti grade 5	R56400	Ti-6Al-4V

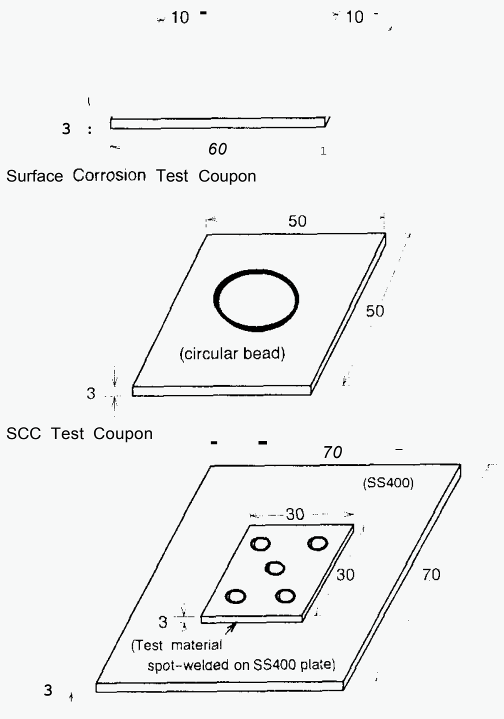

Figure 1. Dimensions of the test specimens.

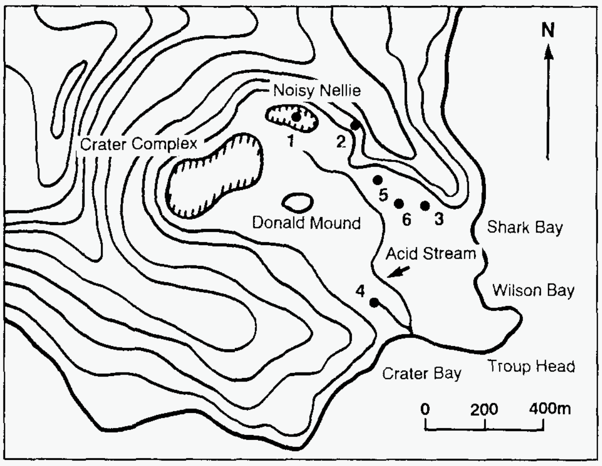

Figure 2. Sketch map of the SW corner of White Island showing positions of material exposures.
1: high-temperature fumarole, **2**: low-temperature fumarole
3: atmosphere, **4**: acid pool, **5**: high-temperature soil
6: low-temperature soil.

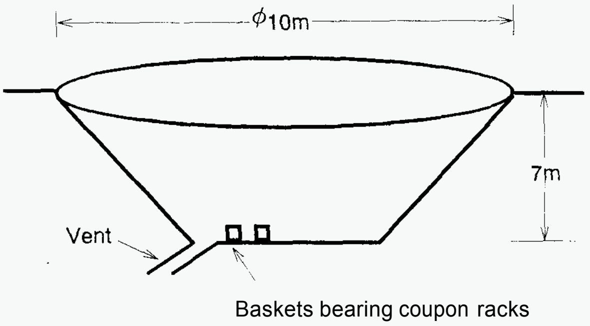

Figure 3. Schematic drawing of Noisy Nellie, a high-temperature fumarole at Site 1.

m in diameter, and 7 m in depth, and has a rough but narrow-flattish bottom. The measured temperature was 230°C on the first day of the exposure. The high-temperature bottom area was expected to stay dry, except for periods of heavy rainfall. The temperature was measured for 60 hours with a thermocouple, at which time the thermocouple failed due to corrosion.

Four baskets were placed on the bottom of the fumarole. Each basket carried an individual rack of coupons and was open to allow free flow of all gases, but was stable enough to prevent tipping in the turbulent environment. Twenty-five different metals and alloys from Table 1 (excluding two aluminum alloys) were placed at this site for surface corrosion, and sixteen were placed for stress corrosion cracking. Aluminum alloys were excluded from the test at Site 1 because they were expected to have a high corrosion rate in such an aggressive environment.

Site 2: Low-temperature Fumarole Fourteen different alloys were tested for surface corrosion in a low-temperature fumarole about 1 m x 1 m x 0.6 m deep having a temperature of approximately 100°C with some steam formation. When the corrosion test started the discharge from the low-temperature fumarole had been considered to be only moderately aggressive. Exposures in this fumarole were planned for 3 months and 1 year.

Site 3: Atmospheric Exposure Nine materials consisting of a carbon steel, low-alloy steels, aluminum alloys, and some stainless

Table 2. Chemical composition of discharges from the high-temperature test fumarole at Site 1 [Giggenbach and Sheppard, 1989].

(ppm-vol)

°C	H_2O	CO_2	H_2S	SO_2	HCl	HF	NH_3	H_2	N_2
280	991,000	4,250	825	3,090	53	2.5	2.3	347	44

Table 3. Chemical composition of discharges from the low-temperature fumarole at Site 2 [Christenson, 19941.

(ppm-vol)

°C	H_2O	CO_2	H_2S	SO_2	HCl	NH_3	He	H_2	N_2
98	906,000	91,707	537	400	9.4	1.0	0.33	0.69	681

Table 4. Chemical composition of discharges from the acid water pool at Site 4 [Christenson, 19941.

(ppm-mass)

Date	°C	pH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NH_3	B	SiO_2
13.02.91	na	4.25	246	43	208	na	807	na	127	0.78	332
22.10.93	93.5	3.20	338	32	266	196	895	1,602	104	0.85	328
15.01.94	93.0	5.24	268	48	208	192	785	1,141	108	0.82	318

na: not analvsed

Exposure	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Start	230	100	atmospheric	94	100	40
40 days	206'	108	atmospheric	93	100	37–40
111 days	190*	100	atmospheric	94	100	40

steels were placed on an atmospheric exposure rack and tested for surface corrosion. The ambient temperature was not expected to exceed 30°C.

Site 4: Acid Pool Samples of all materials listed in Table 1, except aluminum alloys, were placed in a turbid acid water pool about 3 m in diameter and 0.6 m deep and tested for surface corrosion. The acid water had a pH of 3.2 to 5.4 at 94°C. The liquid in the pool was in turbulent motion, which was cased by upsurging gases. Eleven different materials including stainless steels and nickel-base alloys were placed in this environment for SCC tests. Another six materials including nickel-base alloys and titanium alloys were tested for galvanic corrosionhydrogen embrittlement.

Sites 5 and 6: High- and Low-temperature Soil Eight materials, including a carbon steel, low-alloy steels and standard stainless steels were buried in the volcanic soils at 0.5 m below the ground surface. The soil was soft and wet, appeared to be predominantly ash, and contained a variety of sulphur species (Purchase, 1994). At 0.5 m below the ground surface, the high-temperature soil, Site 5, was at approximately 100°C and the low-temperature soil, Site 6, was at approximately 40°C.

2.3 Aggressive Environments

The geochemistry of magmatic gases at White Island has been reported to be approximately 75% H_2O, 18% CO_2, 5% SO_2 and 1.5% HCl. HF is also known to be present. These gases are modified by interaction with rock and water at high temperatures (~800°C). The chemistry varies with the intensity of magmatic activity (Giggenbach and Sheppard, 1989). These authors have measured the temperature, and sampled and determined the chemical composition of fumarole discharges over several years.

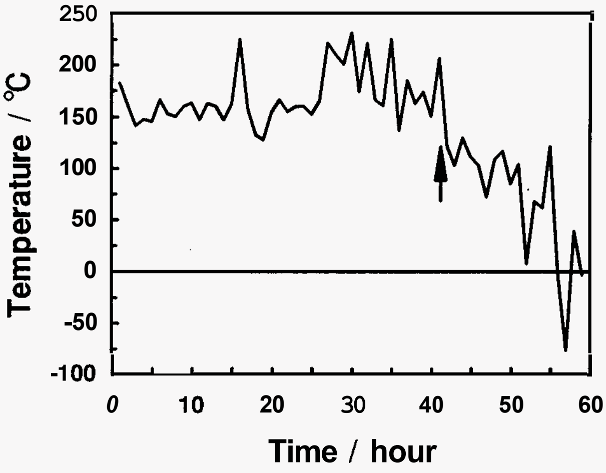

Figure 4. Thermocouple output showing the temperature at Site 1. The thermocouple failed after 40 hours.

Table 2 shows a typical chemical composition of discharges from the high-temperature fumarole, Noisy Nellie (Site 1). Noisy Nellie was the highest temperature fumarole which was accessible for placing of specimens. Table 3 shows the chemical composition of discharges from the low-temperature fumarole (Site 2). The chemical composition had not varied over several years (Christenson, 1994). Gases from the fumarole could mix with air, and wet steam was expected to form, in contrast to the gases from the high-temperature fumarole which were expected to be dry. The presence of aeration in moist geothermal steam environments can make the corrosion chemistry particularly severe. Table 4 gives the chemical analysis results obtained for the acid water test pool discharges (Site 3).

Table 5 lists the temperatures of all the exposure sites. The temperatures were primarily measured with a thermocouple and in some instances using an optical pyrometer. The temperature of Site 1 was measured with a K-type thermocouple, the tip of which was attached to one of the coupon racks in a cage placed on the bottom of the fumarole. The element wires of the thermocouple were 0.3 mm in diameter and 10 m long, and were inserted in a 316 stainless steel sheath, 1.6 mm dia., 10 m long, and 0.3 mm thick.

3. RESULTS AND DISCUSSION

3.1 High-temperature Fumarole, Site 1

Temperature Monitoring

The temperature of Site 1 had been expected to be measured at 1 hour intervals throughout the exposure, however, as shown in Figure 4, the thermocouple lasted for only 40 hours. The temperature varied considerably throughout the exposure time. Figure 4 indicates that the temperature varied between 230°C at maximum and 130°C at minimum through the first 40 hours of exposure. Pyrometer results given in Table 5 suggest a range of daytime temperatures of 190 to 230°C.

Coupon Recovery

The first coupon rack recoveries were done after a period of 40 days. The second recoveries were done after a period of 111 days when three baskets of coupons should have remained. At this time one of the baskets was missing probably because of severe corrosion of the

Figure 5. Test coupons after 40 days of exposure (Site 1). The rack is 200mm long, 130mm wide and 80mm deep.

Table 6. X-ray diffraction analysis of corrosion products and scales on the coupons (Site 1).

Material	Substance
SS400	Fe_2O_3, CaSO,
N80	Fe_2O_3, CaSO,
L80	Fe_2O_3, CaSO,
13Cr	Fe_2O_3, CaSO,
23Cr-6Al	Fe_2O_3, CaSO,
SUS304	
SUS316	
22Cr-5Ni	Fe_2O_3, FeOOH, CaSO,
25Cr-7Ni	Fe_2O_3
25Cr-7Ni-N	not analysed
SS 2562	Fe_2O_3, CrO_2
Alloy 690	$NiCl_2 \cdot 6H_2O$
Alloy 800	$NiCl_2 \cdot 6H_2O$, Fe_2O_3
Alloy 825	$NiCl_2 \cdot 6H_2O$, Fe_2O_3
Alloy 45	$NiCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 4H_2O$
G3	Fe_2O_3, $CrO_2(SO_4)_3$, CaSO,
S816	$CoCl_2 \cdot 6H_2O$

basket. The remaining two baskets, one of which was originally scheduled to be exposed for 1 year, were both recovered.

Corrosion Evaluation

Figure 5 shows the appearance of the test coupons on a rack recovered after 40 days. The rack holds 48 coupons consisting of 24 kinds of materials. The coupons are covered with corrosion products. Major corrosion products were identified by X-ray diffraction (Table 6). Hematite (Fe_2O_3) and calcium sulfate (CaSO,) formed on the carbon steel, low-alloy steels and stainless steels such as SS400, L80, 13Cr and 22Cr-5Ni. Hematite, chlorides and/or sulfates formed on the high-alloy stainless steels. nickel-base alloys, SS 2562, Alloy 690, Alloy 800, Alloy 825, Alloy 45, G3, and cobalt alloy S816. No data were obtained on 1925hMo, Alloy 625, C276, Alloy 59, Alloy 903 and Titanium alloys, because the amounts of their corrosion products sampled were too small to be analyzed by the diffractometer.

Table 7 lists corrosion rates calculated from weight loss after the 40-day and 111-day exposures for the more corrosion-resistant alloys.

Alloy	CR (mm/y)
Martensitic and Ferritic SS	2.0 - 3.0
Nickel Alloys (Mo ≤ 3%)	1.0 - 2.0
Duplex SS, Austenitic SS	0.5 - 1.4
Carbon and Low-Alloy Steels	0.5 - 0.8
Nickel Alloys (3% < Mo < 8%) and Cobalt Alloy	0.1 - 0.6
Nickel Alloys (Mo ≥ 8%), and Titanium Alloy	<0.05

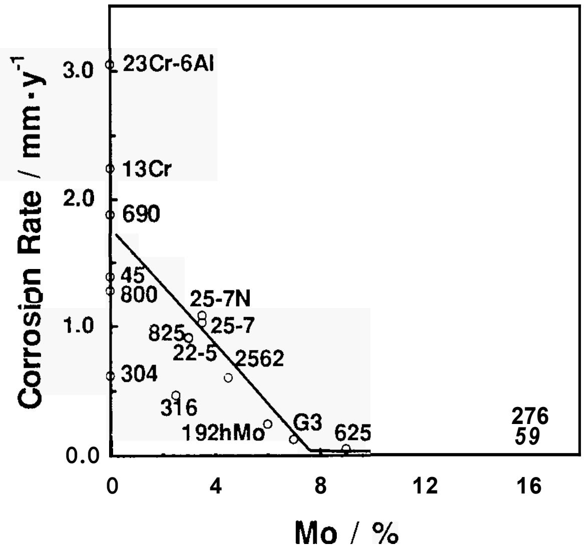

Figure 6. Effect of molybdenum content on the corrosion rate (Site 1).

Materials are listed in the descending order of corrosion rate as follows:

Martensitic and Ferritic SS > Nickel Alloys (Mo ≤ 3%)
> Duplex SS, Austenitic SS
> Carbon and Low Alloy Steels
> Nickel Alloys (3 < Mo < 8 %), and Cobalt Alloy
> Nickel Alloys (Mo ≥ 8%), and Titanium Alloy

Carbon and low-alloy steels were severely corroded at rates of 0.5 to 0.8 mm/y. The more alloyed materials like stainless steels, and nickel-base alloys having Mo ≤ 3%, which perform well in conventional geothermal environments, were corroded more severely than carbon and low-alloy steels.

Figure 6 shows the corrosion rate plotted versus the molybdenum content of the stainless steels and nickel-base alloys tested. The rates are very small or negligible for the alloys containing more than 8% Mo, and the rates for the duplex stainless steels, high-alloy stainless steels and nickel-base alloys increased linearly with decreasing Mo content in the range less than 8%. Molybdenum appears to play a key role in enhancing resistance to corrosion in this environment. Alloys containing about 6% Mo are known to give good performance in other aggressive environments (Davison and Redmond, 1988). In this instance, the corrosion rate for alloy 1925hMo, having 6% Mo, was about 0.26 mm/y, and for Alloy G3,

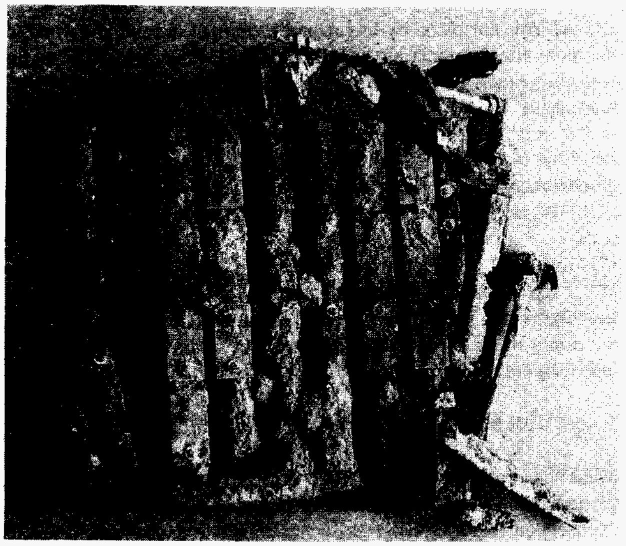

Figure 7. The disintegrated coupon rack recovered from Site 2 after 111 days of exposure.

with 7% Mo, was about 0.15 mm/y.

The effect of other alloying elements in determining corrosion performance is currently under review. The results obtained suggest Ni, W and Co are beneficial in this environment whereas Al, Si and Cr are deleterious.

3.2 Low-temperature Fumarole, Site 2

Examination of the fumarole and the exposed rack of coupons at 40 days revealed a change in the fumarole structure due to a tropical storm and heavy rains which occurred on the 20th day of the exposure. The environment had become more severe with the coupons being located directly over the fumarole vent and being subject to excess moisture from local steam formation, sulphur precipitation and contamination from soil transported by rain water run off. Suitable tools were not available to recover the rack at 40 days, and after 111 days the coupon rack was so severely corroded that a number of exposed coupons were lost (see Figure 7).

Alloy	CR (mm/y)
Martensitic SS	3.0 - 4.0
Austenitis SS	0.08 - 1.1
Nickel **Alloys** (3 < **Mo** < *8%)*	0.002 - 0.4
Duplex SS	0.002 - 0.04
Nickel **Alloys** (**Mo** ≥ *8%)*	0.008 - 0.014

Material	SCC	Pitting
SUS 304	N	X
SUS 316	N	X
22Cr-5Ni	N	X
25Cr-7Ni	N	trace
25Cr-7Ni-N	N	trace

X: detected
N: not detected

Table 8 shows the alloy types evaluated with corrosion rate ranges observed for this environment. Materials are listed in the descending order of corrosion rate.

Martensitic SS > Austenitic SS
> Nickel Alloys (3% < Mo < 8%)
> Duplex SS
> Nickel Alloys (Mo ≥ X%)

Carbon and low-alloy steels (SS400, Corten, N80, L80), aluminum alloys (A50, A52) and ferritic stainless steel (23Cr-6Al) were missing. Judging from the broken appearance of the rack frame of SUS 304, some might have been disconnected from the rack, and some were considered to have been totally corroded.

3.3 Atmosphere, Site 3

Figure 8 shows the material performance in the atmospheric exposure tests (as well as results for high- and low-temperature soils). In the

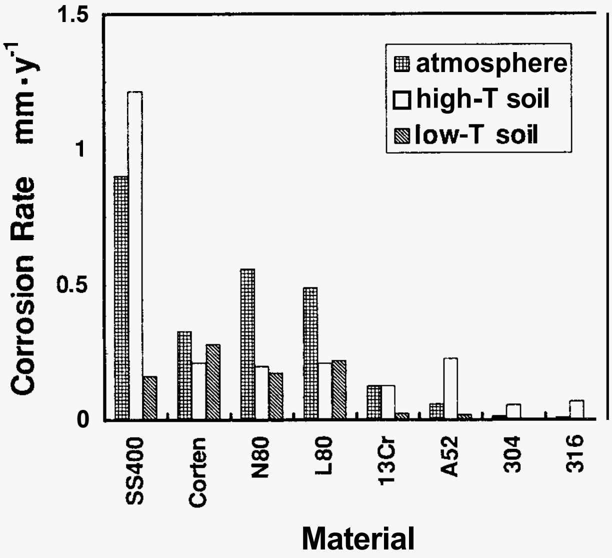

Figure 8. Corrosion rates of the materials exposed in the atmosphere (Site 3) and soils (Sites 5 and 6).

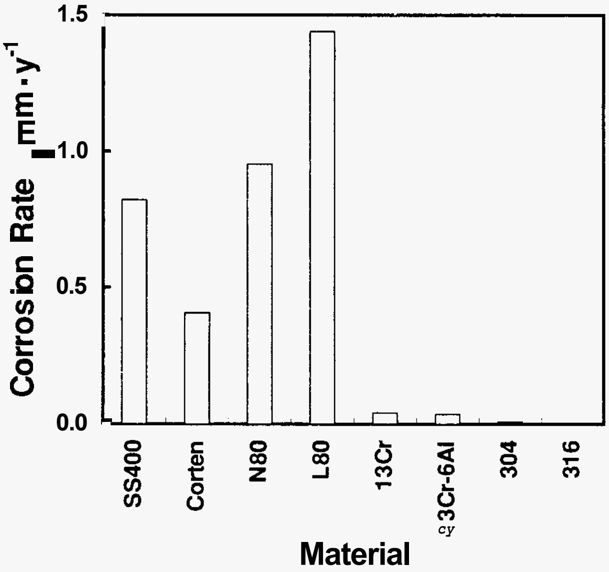

Figure 9. Corrosion rates of eight materials exposed in the acidic water pool (Site 4).

atmospheric test the carbon and low-alloy steel corrosion rates varied from 0.3 to 0.9 mmiy. The aluminum alloy (A52) gave a corrosion rate of 0.06 m d y.

3.4 Acid Hot Pool, Site 4

The first of 3 plastic cages bearing the coupon specimens for surface corrosion tests in the acid hot pool, Site 4, was recovered after 40 days. The cage was firmly imbedded in silt in the bottom of the pool, so pulling of a rope tied to the cage was required to remove the cage. The coupon cage was filled with this silt. Figure 9 shows corrosion rates of the more corroded alloys. The corrosion rates for the carbon and low-alloy steels (SS400, Corten, N80, L80) ranged from 0.4 to 1.4 mm/y. Corrosion rates of 0.3 to 0.4 mm/y were obtained for martensitic and ferritic stainless steels (13Cr, 23Cr-6Al), and approximately 0.01 mm/y for 304 SS, and less than 0.001 mm/y for 316 SS. Corrosion rates were less than 0.002 mm/y for the more alloyed materials exposed, except Alloy 45 which corroded at a rate of 0.02 mm/y.

Table 9 summarizes results of SCC testing of the austenitic and duplex stainless steels submerged in the acid water pool for 111 days. No cracks were found in the stressed areas around the weld beads. Table 9 also indicates that pitting corrosion was evident on the austenitic and duplex stainless steels, but this has not yet been quantified.

The galvanic corrosionhydrogen embrittlement tests conducted in the acid water pool gave no indication of cracking. Hydrogen embrittlement was considered not to have occurred with these galvanic couples, possibly because the residual stresses arising from the spot welds were too low.

3.5 High- and Low-temperate Soils, Sites 5 and 6

In the high-temperature soil the low-alloy steels except SS400 corroded at a rate of approximately 0.2 mm/y and a similar rate was obtained in the low-temperature soil (Figure 8). The aluminum alloy was corroded at approximately 0.2 mm/y in the high-temperature soil but at approximately 0.02 mmiy in the low-temperature soil. The 304 and 316 stainless steels showed no trace of corrosion in the soils (Figure 8).

4. CONCLUSIONS

Field testing of materials at White Island, New Zealand, was undertaken to asses the corrosion performance of metals and alloys under the severe corrosive conditions of geothermal volcanic environments. The testing was also done to help to identify materials which may be suitable for construction of plant and equipment for handling these aggressive environments, Candidate plant construction materials were placed in six different types of sites in the volcanic environments, of which the maximum temperature was 230°C.

(1) High-temperature fumarole: Nickel-base alloys containing more than 8% Mo and titanium alloys showed the highest resistance. These alloys gave corrosion rates less than 0.05 mmiy in the high-temperature fumarole at 230°C. Remaining nickel-base alloys containing **less** than 3 % Mo corroded at corrosion rates of 1.0 to 2.0 mm/y. These nickel-base alloys corroded more severely than the carbon and low-alloy steels which corroded at rates of 0.5 to 0.8 mm/y. Molybdenum played a key role in enhancing resistance to the corrosion so that the corrosion rate increased linearly with decreasing Mo content in the range less than 8%. The influence of other alloying elements is under review.

(2) Low-temperature fumarole: The duplex stainless steels showed good resistance having corrosion rates **less** than 0.04 mmiy and compared well with the nickel-base alloys with more than 8% Mo in the low-temperature fumarole at 108°C.

(3) Acid water pool: Stress corrosion cracking, pitting corrosion and galvanic corrosionhydrogen embrittlement were not observed on the more alloyed materials tested in the acid water pool. Carbon and low-alloy steels corrosion rates varied from 0.4 to 1.4 mmiy while martensitic and ferritic stainless steels had much lower rates at 0.3 to 0.4 mm/y and the austenitic stainless steel corrosion rates were very low being less than 0.01 mm/y.

(4) Atmospheric exposure: Aluminum alloys and stainless steels SUS 304 and 316 gave good performance in atmospheric corrosion tests.

(5) High- and low-temperature soil: The low-alloy steels corroded at 0.2 mmiy in the high-temperature soil at 100°C as well as in the low-temperature soil at 40°C. The aluminum alloy also corroded at 0.2 mm/y in the high-temperature soil but at only 0.02 mmiy in the low-temperature soil.

5. FUTURE WORK

Materials exposed for 40 and 111 days are still being evaluated. In particular the stability of corrosion products present on the coupons exposed in Noisy Nellie will be considered to determine the predominant corrosive species present in such fumaroles and their influence on alloy performance. Coupons having a one year exposure period in the acid water pool, high- and low-temperature soil and in the atmospheric tests will be recovered in January 1995. Additional work in Noisy Nellie to obtain thin layers of corrosion product suitable for scientific evaluation is also planned.

6. ACKNOWLEDGMENTS

The authors wish to thank J.R. Buttle for permission to conduct material testing work on White Island, and B. Christenson of The New Zealand Institute of Geologicel and Nuclear Sciences for his assistance in selecting exposure sites and conducting chemical analysis of the fumarole discharges and acid hot water.

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