CORROSION OF IRON-NICKEL BASE AND TITANIUM ALLOYS IN AERATED GEOTHERMAL FLUIDS

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ABSTRACT: Worst case corrosion chemistries occur in geothermal steam and steam condensate when these fluids are exposed to air. The resultant corrosion chemistry can include dissolved sulphides and a range of oxidised sulphur species as well as chlorides carried over from steam/water separators or dissolved in direct contact cooling waters.

Pitting corrosion, crevice corrosion and stress corrosion cracking tests of austenitic. duplex and high-nickel stainless steels, iron-nickel base alloys and titanium alloys were conducted in aerated high temperature geothermal fluids using ASTM type U-Bends. Laboratory tests of AISI 304 and 316 austenitic stainless steels were conducted at lower temperatures in simulated geothermal fluids using the slow strain rate technique.

Resistance to pitting and SCC is dependent on alloy composition and can be predicted using the Pitting *Resistance* Equivalent formulation, PRE = wt% Cr + 3.3 wt% Mo + 16 wt% N together with an understanding of the influence of nickel on SCC. Environmental parameters which control corrosiveness, in addition to chloride are partial pressure of oxygen, pH, hydrogen sulphide concentration and temperature.

1. INTRODUCTION

Austenitic stainless steels and other more corrosion resistant alloys are commonly used in geothermal systems in applications where surface corrosion rates must be kept low to avoid corrosion fouling and where carbon steels and ferritic and martensitic stainless steels are known to corrode at uneconomical rates.

Austenitic stainless steels are however susceptible to pitting corrosion. crevice corrosion and stress corrosion cracking (SCC) in aggressive media containing chloride ions and/or corrosive sulphur species. Data are available which allow materials engineers to predict the severity of these corrosion phenomena as a function of material and environmental parameters eg NACE Standard MR-01-75 for sulphide containing environments. Susceptible materials are used in instances where the material-environment interaction can be identified and controlled to avoid conditions which are known to result in pitting corrosion, crevice corrosion and SCC. This predictive approach to corrosion control requires a knowledge of the materials' properties, an understanding of the corrosion chemistry, and an appreciation of the engineering limitations of the design.

The geothermal environment which causes SCC of austenitic stainless steels can be broadly described as:

- concentration of corrosive species, eg chlorides, sulphur, polysulphides and polythionates;
- moisture or wetness;
- tensile stress, eg residual stress;
- temperatures in the range 60 to 180°C;
- oxygen.

If one of these factors is absent, or present at very low levels, then SCC would not be expected to occur or would take a very long time to initiate, and hence design and process engineers together with materials engineers have some means of controlling SCC. The above conditions will also promote pitting corrosion and crevice corrosion although this can occur at lower temperatures if the concentration of corrosive species is high.

Aeration of geothermal fluids can not always be avoided, for example aeration can be:

- intermittent. during a shutdown/startup sequence;
- continuous, at a gland seal or valve stem packing;
- continuous, in steam gas exhausters;
- continuous, within a cooling water circuit

Resistance of stainless steels and nickel-base alloys to localised corrosion can be modelled as a function of alloy composition ie Pitting Resistance Equivalent, PRE = wt% Cr + 3.3 wt% Mo + 16 wt% N. (Nadezhdin and Wensley, 1992)

The resistance of stainless steels and nickel-base alloys to SCC in aggressive chloride media has long been recognised as being a function of the nickel content of these alloys. (Metals Handbook, 1987) Susceptibility to SCC is most pronounced at 8 to 12 wt% Ni and decreases at lower and higher levels. Above 42 wt% Ni the austenitic materials are immune to cracking in many industrial environments.

This paper provides a summary of field and laboratory corrosion tests designed to elucidate the corrosion properties of stainless steels and nickel-base alloys in aggressive fluids encountered in New Zealand geothermal fields. The selection of test environments and materials reflects the need for economic and reliable materials in power plants designed to utilise these fluids.

2. EXPERIMENTAL

Three environments were selected for testing:

- Evaporative Concentration, occurring when geothermal fluids contaminate hot surfaces exposed to air:
- Aerated Wet Steam, encountered when air is drawn into wet steam environments;
- Simulated Condensate, typical of recirculating cooling water in direct contact condensing systems.

2.1 Evaporative Concentration

In geothermal systems concentration of corrosive species can occur on internal surfaces and in crevices. Concentration on internal surfaces may occur at startup and shutdown, or during operation, in pipeline dead legs, while crevices may occur at design details such as in valve stem/packing nuts or between formed scales and internal metal surfaces.

U-Bends were exposed using a modification of the ASTM C692 wick test to conduct long term field exposure trials in an aggressive geothermal environment in *order* to rank material resistance to pitting corrosion and SCC.

Table 1: Chemical composition of geothermal condensate fluids dripped onto heated U-Bends. (Lichti et al, 1984)

Composition Ranges for Cold Condensate
Test Fluids P = 1 atmosphere

	Cond. Steam[a] mgkg^{-1}	30 ppm Cl$^-$ mgkg^{-1}	20 ppm Cl$^-$ 10 ppm SiO$_2$ mgkg^{-1}	No Cl$^-$ Added mgkg^{-1}
CO_2	1400	200 to 1400	20 to 1400	200 to 1400
HCO^-_3	130	50 to 200	50 to 200	50 to 200
H_2S	75	10 to 75	10 to 75	10 to 75
NH^+_4	44	30 to 40	30 to 40	30 to 40
HS^-	1	1 to 10	1 to 10	1 to 10
$SO^=_4$	<1	1 to 20	1 to 20	1 ti) 20
TotFe	0.2	0.2	0.2	0.2
SiO_2	<1	<1	10 to 15	<I
Cl^-	<<1	30 to 70	20 to 30	<<1
Na	<<1	20 to 45	10 to 15	<<1
K	<<1	<<1	2	<<1
pH	5.0	5.0 to 6.0	5.0 to 6.0	5.0 to 6.0
T (C)	15	10 to 20	10 to 20	10 to 20

a Condensate obtained by condensing 160°C, 630 kPa separated steam to 10 to 20°C, 300 kPa.

Test Environments

The basic test solution was steam condensate from Broadlands well BR22 (Lichti et al 1984) with the following chloride concentrations (see Table I):

- 30 ppm Cl^- ;
- 20 ppm Cl^- + 10 ppm SiO_2 (1 vol % separated water);
- chloride free.

When dripped onto heated U-Bends these solutions were intended to simulate fluids derived from geothermal steam at plant startup and shutdown and in areas where concentration of corrosive species and exposure to air are known to occur.

Materials

The test was designed to cause SCC of the AISI 300 series stainless steels. and AISI 304 for example cracked within 3 weeks. This alloy was used repeatedly throughout the long term exposures to ensure that the aggressive nature of the corrosion chemistry was maintained. The alloys tested in each environment together with the test exposure times are listed below and chemical compositions as well as the calculated PRE for these are given in Table 2.

Cold Condensate with 30 ppm Chloride Ions : 9 and 63 weeks
- AISI 316L (AISI 304 to 15 weeks maximum);
- Sandvik 2RK65, UHB 904L, Avesta 254 SMO;
- Incoloy 825, Inconel 600(9w) 601(9w) 625, Hastelloy C276;
- IMI 155 and 318.

Cold Condensate with 1 vol% Separated Water : 63 weeks
- AISI 304 and 316L;
- Incoloy 825.

Cold Condensate Free of Chloride Ions : 24 weeks
- AISI 304.

Experiment

The U-Bends were located over a PTFE-sleeved, thin walled titanium tube which was internally heated with separated steam at 160°C. Heat transfer losses resulted in temperatures of between 80 and 120°C king measured between the PTFE sleeve and the U-Bends with a full load of 29 specimens. The U-Bends were made following ASTM G30-70, for material thicknesses of 1.5 to 1.7 mm. The sheared edges of the test strips were retained to increase the severity of the test. Tests were conducted using duplicate specimens for exposure periods of up to 63 weeks. All long term exposure specimens were scratched periodically to break any protective surface films which may have formed. The corroded samples were cleaned using techniques similar to those described elsewhere (Braithwaite and Lichti, 1980). Cleaned U-Bends were examined for pitting corrosion and SCC.

2.2 Aerated Wet Steam

Aeration of steam environments is generally avoided in most geothermal energy systems because carbon and low alloy steels, and ferritic and martensitic stainless steels readily corrode in aerated wet stem.

Exposures of stressed metal U-Bends in continuously aerated steam were done in conjunction with coupon exposure trials at Broadlands well BR22, (Braithwaite and Lichti, 1980) a two phase, steam/water producing bore having 2.5 wt% non-condensible gas in the steam phase and 1400 mgkg^{-1} of chloride in the separated water. (Lichti and Wilson, 1983). In these tests the U-Bends were heated by the test environment and were subject to continuous steam condensate formation and washing in pressurised test vessels.

Test Environments

Tests were conducted in aerated wet low pressure steam containing 2.5 wt% non-condensible gas to which 3 wt% of air was added at 105°C and 126 kPa(a). Comparable exposures were done in non-aerated environments; a wet low pressure steam, a high pressure steam and a high pressure two phase fluid. In the latter test environment the exposed samples were exposed primarily to the steam phase in a horizontal test vessel where the water phase travelled along the floor of the vessel. Table 3 describes the gas phase chemistry and chemical composition of condensate in equilibrium with the steam phase in the four environments tested. (Lichti and Wilson, 1983) Many of the U-Bend and coupon specimens exposed in the aerated wet steam environment had deposits of elemental sulphur suggesting a complex sulphur chemistry had developed within this test environment. (Braithwaite and Lichti, 2980, Johnson, 1986)

Materials

The materials exposed in the four test environments are described in Table 2. (Johnson, 1986) Although the experimental matrix was comprehensive, detailed evaluation of exposed samples was restricted to the following environment-material combinations.

Aerated wet low pressure steam
- AISI 410, E-Brite 26/1;
- AISI 304 and 316;
- Sandvik 3RE60, Sandvik 2RK65;
- Incoloy 825, Carpenter 20Cb3.

Wet low pressure steam, Separated steam, Two phase fluid
- AISI 304 and 316.

Experiment

The prepared duplicate U-Bends were exposed in the 10 inch (250 mm) diameter horizontal test vessels. Fluid entry and discharge was at the vessel ends, entry king in the centre of one end and exit at the bottom of the other end. Test conditions are described in detail elsewhere. (Braithwaite and Lichti, 1980)

Corrosion products and deposits included elemental sulphur and iron, chromium and nickel containing corrosion products. Cleaned U-Bends were examined for surface corrosion and SCC. Occurrence of SCC was limited to the aerated environments.

2.3 Simulated Condensate

Slow strain rate testing techniques (Urgainsky and Payer, 1979) require significant control and monitoring procedures as well as variation of environment and material parameters to develop suitable predictive models of SCC. The difficulty in conducting such tests in a field environment prompted the development of environment simulation techniques to permit the study of corrosion mechanisms and the comparison of materials properties in sulphur containing environments at temperatures below 90°C. (Wilson and Mcllhone, 1993) This low temperature work with simulated condensate was aimed at identifying environmental parameters which determine acceptable operating limits for the safe use of AISI 304 and 316 in recirculating aerated cooling water in a geothermal power plant.

Corrosion Chemistry of Sulphur

The potential-pH Pourbaix diagram for the equilibrium sulphur-water system indicates that the thermodynamically stable dissolved specks are HSO_4^-, SO_4^{2-}, H_2S, and HS^- (Wilson and Mcllhone, 1993). However by mixing air with hydrogen sulphide, oxidation of hydrogen sulphide to sulphate may not occur spontaneously and a number of metastable species may form which influence the corrosiveness of the fluid. The thiosulphate ion in particular has been shown to cause intergranular SCC of sensitised type 304 stainless steel. (Newman et al, 1982)

Two variables, pH and electrode potential (E_H) have a controlling influence on rates of a corrosion reaction and in particular susceptibility to SCC. The pH is both measurable and controllable. The electrode potential (E_H) is also mensurable. but unless oxygen is excluded or scavenged, it is not controllable in the in-plant situation. However the potential may be controlled in a laboratory situation, using a potentiostat, which provides an experimentally accessible means of simulating the influence of oxygen on SCC.

In this work, Pourbaix diagrams for the metastable situation arising if sulphate is excluded have been used to assist in rationalising the results of tests aimed at identifying the threshold for resistance of AISI 304 and 316 stainless steels to SCC.

Test Environments

The test solution consisted of 9 mmolkg^{-1} sulphate and 1 mmolkg^{-1} chloride through which CP grade hydrogen sulphide was bubbled at atmospheric pressure or at lower pressures obtained by mixing it with oxygen-free nitrogen. Two concentrations of calculated dissolved sulphur concentration (U.75 and 24 mmolkg^{-1}) were tested at three pH values, 3.5 and 7. The test solutions were adjusted to pH 3, 5, or 7 at room temperature, by adding either sulphuric acid or sodium hydroxide. The pH was not measured at the working temperature. Tests were carried out at controlled potential simulating different levels of dissolved oxygen. (Wilson and Mcllhone, 1993)

Most of the tests were carried out at 80°C. Some tests were carried out with the test temperature being stepped from 25°C to 40°C and then at 10°C intervals with a 24 hour period between steps. The onset of cracking was signalled by a marked increase in anodic current.

Materials

Compositions of the AISI 304 and 316 stainless steels are summarised in Table 2. Environment-material combinations evaluated were as follows:

Total sulphur = 0.75 and 24 mmolkg^{-1}
pH = 5 for AISI 304 and 316 at S = 0.75 mmolkg^{-1}
pH = 5 for AISI 304 at S = 24 mmolkg^{-1}
pH = 3,5and 7 for AISI 316 at S = 24 mmolkg^{-1}
Temperature = 80°C

- AISI 304 and AISI 316 at E_H values ranging from -0.4 V to +0.5 V vs SHE (Standard Hydrogen Electrode) as required

Total sulphur = 24 mmolkg^{-1}
pH = 3,5 and 6
Temperature stepped from 25°C to 40°C and +10°C intervals

- AISI 304 and 316 at E_H = 0 or -0.1 V vs SHE

Table 2: Chemical composition of metals and alloys tested for resistance to pitting corrosion, crevice corrosion and SCC

Material Type	UNS Number	Approximate Chemical Composition. Element Weight Percent C	Cr	Ni	Mo	Cu	Co	Ti	Si	Mn	Fe	Other	PRE	0.33 Ni + PAE
EVAPORATIVE CONCENTRATION														
Austenitic Stainless Steels														
AISI 304	S30400	0.08	19	8 8	0.18	036	**0 2**	DO3	079	1.3	**Rem**		**20**	2
AISI 321	S32100	0 08	18	9.5	0.39	012	019	0.34	0 65	1.5	Rem		**19**	22
AISI 316L	S31603	<0.03	18	11	2.7	0.29	0.18	<0.01	059	1.9	Rem		26	30
Duplex (Ferritic-Austenitic) Stainless Steels														
Sandvik 3RE60	S31500	<0.03	20	5 1	**3 0**	o w	**3 1**	**DO2**	**1 1**	**1 5**	**Rem**	0 08 N	30	**32**
Sandvik SAF2205	531803	<0.03	**22**	5 9	**2 9**	0 05	0 04	0 01	**0 4**	1.5	Rem	0.2 N	34	36
High-Nickel Stainless Steels														
Sandvik 2RK65	N08904	<0.02	20	24	5 0	1 4	0 2	0.02	0 4	**1.5**	**Ram**		35	**43**
UHB 904L	N08904	<0.02	21	22	5 0	1 3	0 1	<0.01	0 5	1.6	Rem		36	**43**
Avesta 254 SMO	S31254	<0.02	21	17	6 3	0 6	**0 2**	001	0 5	D 6	**Rem**	*0 2 N*	**43**	**49**
Iron-Nickel Base Alloys														
Inconel 600	N06600	<0.08	16	Rem(73)	0.18	0.33	0 09	**022**	0 18	0 19	9 5		17	**41**
Inconel 601	N06601	0.05	**23**	Rem(63)	013	0.18	<0.05	0 5	025	0 26	13		23	44
Incoloy E25	N08825	<0.05	**23**	Rem(42)	3 0	**2 2**	0 08	*0 6*	D 33	0 34	29		32	**46**
Inconel 625	N06625	0 05	23	Rem(61)	8.1	0 5	007	0.3	0 5	0 2	**3 6**	3 6 Nb+Ta	47	**07**
Hastelloy C276	N10276	<0.02	15	Rem(61)	16	OG7	1.6	<0.05	0.05	0 5	6 1	**4 w**	63	B3
Titanium Base Alloys														
IMI 155	Ti-ASTM Gr 4	<0 ı					-	Rem	-	-	<0.5	<0.05 N, <0.015 H <0 40 *O*	-	-
IMI 318	Ti6A14V	<0.1						Rem			<0 3	6 1 Al, 4.1 V		-
									0 57	¹ 6	Rem	0 02 Al, 0 04 V	18	
														29
														41
E Brite 26/1	S44627	<0.01	25.1	**018**	122	0.04	OU2	001	0.26	0 08	Rem	0 02 Zr, 0.11 V	29	29
Duplex (Ferritic-Austenitic) Stainless Steels														
Sandvik 3RE60	S31500	0.04	19.5	**5 1**	3 0	o w	0.10	0 02	1 1	1.5	Rem	0 02 Al 0.04 V	29	30
Iron-Nickel Base **Alloy**														
Incoloy 825	N08825	<0.05	235	Rem(41)	3.0	2.2	0.08	061	033	0 34	28 7	-	33	46
SIMULATED CONDENSATE														
Austenitic Stainless Steels														
AISI 304 (mean)	S30400	0.06	**19.0**	8.7	0.14	0.16	0.17	<0.01	0.60	0.66	70.3		19	22
AISI 316 (mean)	S31600	0.06	**15.8**	9.9	1 a5	0.25	0.18	<0.01	0.35	0 86	70 6		**21**	*25*

Table 3: Gas phase chemistry and calculated composition of condensate in equilibrium with steam (Lichti and Wilson, 1983)

	Separated Steam T=160°C P=650kPa	Wet Steam T=105°C P=126kPa	Bore Ruid T=160°C P=650kPa	Aerated Wet Steam T=105°C P=126kPa
Gas Fraction in Steam wt%	2.1	2.0	≈2.1	≈5.0 =3% air
Gas as a fraction of non-condensible gas, mmol/mol (water free)				
CO_2	952	956	957	338
	21	18.7	19.6	11.6
NH_3	4.6	4.1	3.7	0.8
H_2	0.9	0.8	0.9	0.02
O_2/N_2				146/502
Calculated Condensate Composition, mg/kg				**
CO_2	20.6	5.0	26.5	–4.6
HCO^-_3	11.1	22	137	–20.2
H_2S	1.3	0.27	1.6	≈0.25
HS^-	0.48	0.52	5.5	4.50
NH_3	4.2	2.6	4.7	≈2.3
NH^+_4	3.6	7.0	0.43	≈6.34
pH	6.5	6.9	7.4	≈6.9
Solids in steam derived from carry-over, mg/kg of steam				
SiO_2	<1	<1	706	<1
Cl^-	<1	<1	1410	<1

** Oxidized products of sulphur not determined

Experimental

The slow strain rate technique was used to evaluate susceptibility to failure by SCC. This technique involves pulling a tensile test specimen to failure at a slow strain rate, typically 10^{-6} sec^{-1}, whilst immersed in the test environment. The results obtained are compared against those obtained in an inert solution to detect any influence the environment has on the failure of the specimen: comparison is made of mechanical and metallographic parameters. The current required to maintain the set potential was also monitored.

3. RESULTS

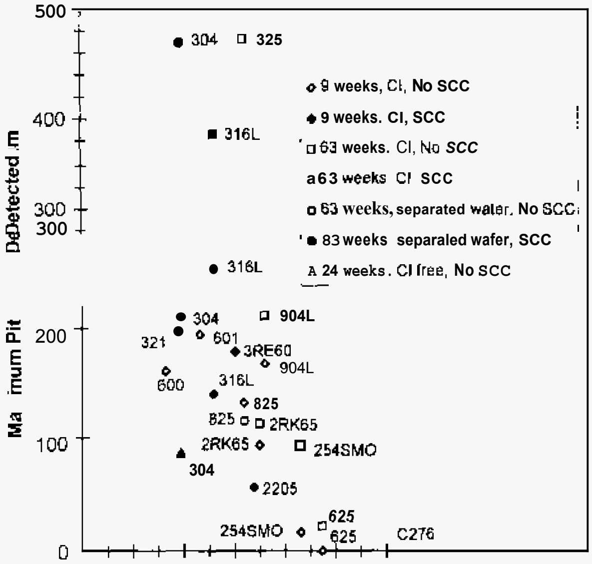
3.1 Evaporative Concentration

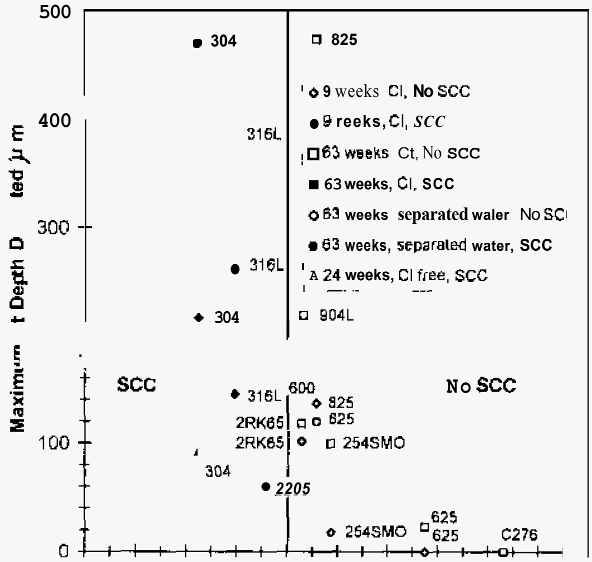
Pitting corrosion and SCC results are summarised for the evaporative concentration experiments for stainless steels and nickel-based alloys in *Figure 1*. Titanium alloys tested did not suffer pitting or SCC. These alloys do not have an equivalent PRE and are therefore not shown in the figure. Onset of pitting corrosion for all other alloys tested in environments containing both sulphur compounds and chlorides except Hastelloy C276 occurred within the 63 week test periods. AISI 304 stainless steel tested for 24 weeks without addition of chloride ions to the drip test solution experienced pitting and SCC.

Nickel-based alloys having >42 wt% Ni did not crack but those having lower PRE values were susceptible to pitting corrosion. High alloy stainless steels pitted but did not show extensive cracking. A revised presentation format for the combined SCC and pitting results *based* on substituting the sum of 0.33 wt% Ni *and* PRE for the x-axis in Figure 1 is shown in Figure 2.

3.2 Aerated Wet Steam

Table 4 gives a summary of SCC, pitting corrosion and crevice corrosion results obtained for the alloys examined in aerated wet steam. Only AKSI *304* and 316 alloys exposed to aerated wet steam experienced SCC, while the incidence of pitting corrosion and crevice corrosion was more extensive. No SCC or crevice corrosion occurred in materials exposed to *the* non-aerated environments. However, minor pitting was experienced, AISI 316 in all non-aerated environments after 52 weeks; AISI 316 in 2 phase fluid at 13 weeks; ALSI 304 in 2 phase fluid and *wet* low pressure steam at 52 weeks.





3.3 Simulated Condensate

Slow strain rate results showing the dependence of the susceptibility to SCC on environmental factors are summarised for AISI 304 and AISI 316 stainless steels on the Pourbaix diagrams of Figures 3 and 4 respectively. At the lower total sulphur content shown in Figure 3, AISI 316 did not suffer SCC when tested under these same conditions. At the higher total sulphur concentration shown in Figure 4 AISI 304 stainless steel tested at pH 5 *gave* similar results to those shown for AISI 316.

The influence of temperature on SCC threshold as determined at total dissolved sulphide of 24 mmol/kg and a control potential of E = -100 mV vs SHE is illustrated for AISI 316 in Figure 5.

Table 4: Localised corrosion and SCC results in aerated wet steam at T=160°C, P=650kPa (Johnson, 1986)

Exposed Material	Time weeks	Cracking Yes	Cracking No	Cracking Severe	Crevice Avg	Crevice Max	Pitting Avg	Pitting Max
S30400	4	X			-	-	64	154
	13	X		X	40	50	87	3IW
	52	X		X	79	115	131	578+
S31600^c	13		X			-	13	18
	52	X		X	136	257	212	534+
S41000	4		X		44	56	23	65
	13		X		63	88	60	300
	52		X		752	1720	433	1748
Sandvik 3RE60 S31500	4		X		<10	16	-	-
	13		X		<10	18	-	-
	52		X		39	41	-	-
E Brite 26/1 S44627	4		X		21	29	17	125
	13		X		30	49	25	300
	52		X		58	120	30	300
Carpenter 20Cb3^c N08020	13		X		<10	<10	-	-
	52		X		96	120	-	-
Incoloy 825 N08825	4		X		<10	<10	-	-
	13		X		<10	<10	-	-
	52		X		173	458	-	-
Sandvik 2RK65 N08904	4		X		12	25	-	-
	13		X		12	20	-	-
	52		X		25	29^b	-	-

Notes:
(a) Full penetration at a cut edge on S30400 at 13 weeks measured at 2410 µm.
(b) *Very* uniform attack varying only by 4 µm.
(c) Alloys not tested at 4 weeks.
(+) Pitting greater than measured due to cracking in pits.
(-) Not detected.

Threshold data was derived from similar plots for AISI 304 and 316 for pH 3, 5 and 6 as summarised in Table 5.

4. DISCUSSION

4.1 Alloy Composition Effects

The results of Figure 1 demonstrate the dependence of pitting corrosion on composition of the stainless steels and nickel-base alloys. The data suggests a minimum alloy PRE of 40 for geothermal applications subject to evaporative concentration and requiring pitting rates of less than 0.1 mm per year. In many situations alloys having lower PRE do give good performance in such environments but this can usually be attributed to less aggressive chemistry.

The relationship between incidence of SCC and PRE is not clear from the data shown in Figure 1. Alloys having greater than 42 wt% Ni content but lower concentrations of Cr and Mo readily pit in the mixed chloride/sulphur containing environments but do not crack. It would be presumptuous to alter the PRE formula for these results, however a factor containing a fraction of nickel was added to the PRE to move these alloys to the right on the Figure. Replotting the pitting and SCC results vs 0.33 wt% Ni + PRE gives a revised model as shown in Figure 2 where three distinct areas are defined:

- 23 < 0.33 wt% Ni + PRE < 40
  - pitting and SCC predicted
- 40 < 0.33 wt% Ni + PRE < 50
  - pitting and no SCC predicted
- 50 < 0.33 wt% Ni + PRE
  - minimal pitting and no SCC predicted.

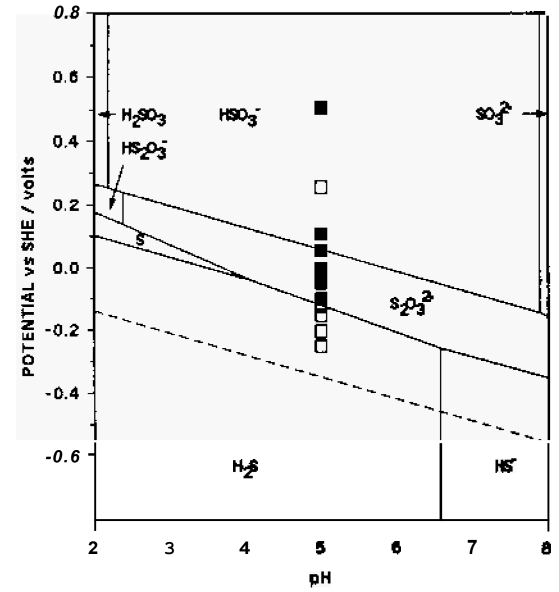


Figure 3: Pourbaix Diagram showing failure modes, AISI 304 tested at pH 5, [S] = 0.74 mmolkg^{-1} and T = 80°C; ■ SCC; ☐ no SCC; ☐ SCC on one of two samples (Wilson and McIlhone, 1993)

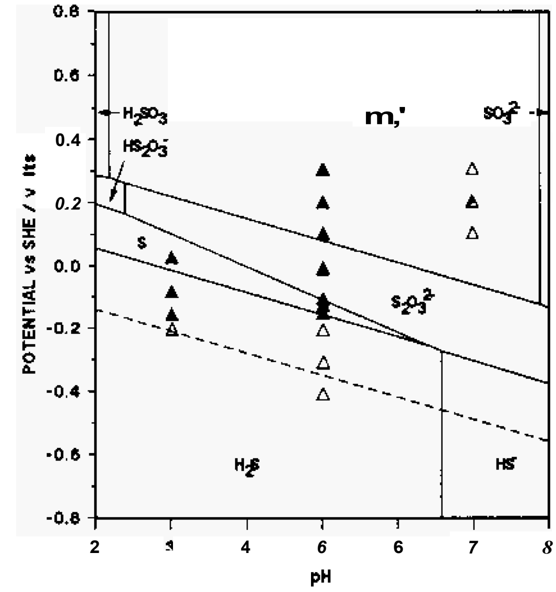


Figure 4: Pourbaix Diagram showing failure modes, AISI 316, [S] = 24 mmolkg^{-1} and T = 80°C; ▲ SCC; △ no SCC; ▲ SCC on one of two samples.

The vertical line at PRE = 40 in Figure 2 defines the transition from SCC to No SCC. Performance of other iron-nickel base alloys can be predicted from the data model of Figure 2 and a knowledge of the alloy composition.

In the pressurised steam environments only AISI 304 and 316 exhibited any indication of SCC and then only when air was deliberately added Table 4. The SCC performance of these alloys depends predominantly on environmental factors. Crevice corrosion was observed on all of the alloys tested in aerated steam, however, the results are erratic and do not follow a relation dependent on alloy content. Alloys having PRE greater than 30 (see Tables 2 and 4) appear to be resistant to pitting corrosion in the continuously aerated environment however for both crevice corrosion and pitting corrosion *the* performance appears to depend predominantly on environmental parameters (*see* Table 3).

The slow strain rate tests in simulated condensate Figures 3 to 5 and Table 5 clearly show improved performance of AISI 316 over *304*.

Table 5: Influence of temperature on SCC Threshold at total S = 24 mmolkg' (Wilson and McIlhone, 1993)

pH	SCC Threshold Temperature/°C	
	AISI 304	AISI 316
3	T<25	25<t<40
5	25<t<40	40<T<50
6	25<t<40	50<T<60

This improvement is strongly dependent on environmental parameters.

4.2 Environment Effects

The test results from U-Bends exposed to concentrating environments are considered to represent some of the most aggressive which might be encountered in New Zealand geothermal energy plant. The environment consists of mixed chlorides/sulphides and reacted species which have not been critically defined in this work. Sulphide is sufficient to cause pitting corrosion and SCC of AISI 304 in such concentrating aerated environments (see Figures 1 and 2). There is some indication that silica can partially retard the rate of propagation of pits but has no benefit in inhibiting SCC in chloride containing environments.

The good resistance of AISI 304 and 316 to pitting corrosion in all ofthe non-aerated pressurised geothermal steam environments is due to the absence of oxygen together with an inability to concentrate corrosive species because of the free washing of specimens exposed in the steam environments. Periodic shutdowns when the environment contains steam condensate and oxygen at moderate temperatures eg when plant is cooling, however, are known to develop aggressive chemistries and to result in pitting corrosion and crevice corrosion of stainless steels and nickel-based alloys. (Braithwaite and Lichti, 1981) Crevice environments can and *did* develop in the aerated steam environment but the results are not as might be predicted suggesting a probabilistic initiation process.

The lower temperature tests with simulated aerated condensate showed a great dependence on temperature, pH, total dissolved sulphur and partial pressure of oxygen with the latter simulated potentiostatically. The theoretical Pourbaix diagram for the sulphur species considered gave a good correlation with onset of SCC which was determined by electrode potential and pH. As pH increases a more anodic potential (more oxygen) is required for SCC to occur. As total sulphur increases the resistance of AISI 304 and 316 are reduced.

The effect of temperature shown in Figure 5 and Table 5 provides realistic operating temperature limits for AISI 304 and 316 stainless steel exposed to aerated recirculating cooling waters at a total sulphur content of 24 mmolkg^{-1}.

5. CONCLUSIONS AND RECOMMENDATIONS

Performance of stainless steels and nickel-based alloys in aggressive geothermal environments derived from mixing of air with steam and/or evaporative concentration at temperatures above about 90°C can be described as a function of nickel alloy content and Pitting Resistance Equivalent (PRE):

- $23 < 0.33$ wt% Ni + PRE < 40
    - pitting and SCC predicted
- $40 < 0.33$ wt% Ni + PRE < 50
    - pitting and no SCC predicted
- $50 < 0.33$ wt% Ni + PRE
    - minimal pitting and no SCC predicted.

In lower temperature aerated waters containing dissolved sulphur species environmental parameters control the corrosiveness of the solution towards AISI 304 and 316:

- increasing hydrogen sulphide concentration is more corrosive
- decreasing pH is more corrosive
- increasing chloride concentration is more corrosive
- increasing partial pressure of oxygen is more corrosive
- increasing temperature is more corrosive.

At a total sulphur concentration of 24 mmolkg^{-1} in recirculating cooling water, temperature limits for SCC of 40 and 60°C at pH 6 are suggested for AISI 304 and 316 stainless steels respectively.

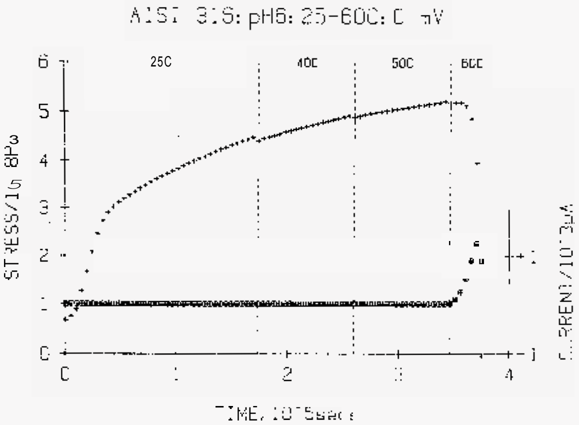


Figure 5: Slow strain rate result showing effect of temperature on SCC threshold, ALSI 316, tested at pH 6, [S] = 24 mmolkg'. (Wilson and McIlhone, 1993)

6. ACKNOWLEDGEMENTS

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