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TESTING OF MATERIALS IN CORROSIVE WELLS AT THE GEYSERS GEOTHERMAL FIELD

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SUMMARY – Carbon steel tubulars and piping corrode at accelerated rates in the presence of superheated steam containing HCl gas at The Geysers field. The observed corrosion is very similar to acid dew point corrosion observed in flue stacks of fossil fuel plants. A series of tests were conducted to find cost effective materials for handling this corrosive steam. In general, Ni-Cr-Mo alloys and concrete-linings were immune to corrosion. Cracking developed in some stainless, duplex and Cr-Mo alloys. Corrosion is mitigated by caustic treatment and Ni alloy linings, or by operating wells and steamlines at superheated conditions above the acid dew point temperature.

1. INTRODUCTION

Corrosion of well casings and surface piping in superheated steam service at The Geysers, USA, and Lardarello, Italy, has been accelerated by the presence of hydrogen chloride (HCl) gas. "Chlorine etching" of carbon steel piping was initially reported at Lardarello by Allegrini and Benvenuti (1970). The corrodant was later identified as HCl gas produced in steam which forms the aqueous acid where condensation/heat sinks occur (D'Amore *et al.,* 1977). In late 1986, Unocal observed accelerated corrosion in piping at several Geysers wellheads. This corrosion was similar to that observed at Lardarello. A number of studies have since focused on the origin and transport of HCl in The Geysers and Lardarello steam; potential sources of HCl include deep, acidic boiling brines, salt hydrolysis, and chloride salt dissociation (*e.g.*, Foumier, 1983; Haizlip and Truesdell, 1988; Simonson and Palmer, 1995).

Mitigation of HCl corrosion at The Geysers and Lardarello fields is achieved by "washing" steam with alkaline solutions. Allegrini and Benvenuti (1970) reported that corrosion mitigation by water or soda solution washing has been carried out at Lardarello since 1956. Injection of potassium hydroxide (KOH) solution into steam was pilot tested by Unocal at The Geysers (Farison, 1987); K, essentially absent in Geyser condensate, functioned as a tracer to monitor carry-over through steam piping. Caustic soda (NaOH) washing of steam was later commercially installed. Descriptions of caustic mitigation processes utilized at The Geysers have been published (Bell, 1989; Hirtz *et al.*, 1990; Hirtz e?*al.,* 1991).

At Lardarello, 316 stainless steel was unsuccessfull in the processing of acidic condensates (Allegrini and Benvenuti, 1970). The corrosivity of weak HCl solutions at high temperature has been previously investigated. Carbon and stainless steels are not normally recommended in this high-temperature acid environment; it is generally recognized that only super alloys (*e.g.,* Hastelloys, Carpenter 20, Tantalum, Zirconium and other equivalents may be safely used in acid environments at temperatures approaching 260°C. In parallel with the pilot/demonstration of caustic mitigation testing at The Geysers, corrosion testing was conducted with various alloys and liner materials, This paper discusses the results of materials testing at The Geysers in the highly corrosive HCl environment at temperatures up to *–225°C.*

2. EXPERIMENTAL

Figure 1 shows a representative wellhead assembly at The Geysers. Condensates and corrosion products were collected fiom steam strainer boots and water knockout pots. These samples were analyzed by standard laboratory methods. Corrosion coupon racks and metal test spools were installed at or downstream of "rock catcher" screens. Upon completion of exposure tests, coupons and spools were retrieved and cleaned. Weight losses and dimensions were employed to measure general corrosion rates using standard methods. Pitting depths were measured with a pit gauge and annual rates of penetration were obtained by linear extrapolation. Examination of stress corrosion cracking at stressed weld beads on coupons was also conducted under microscope.

3. RESULTS

3.1 Corrosion Characteristics

Internal inspections of wellheads suffering severe corrosion revealed acidic erosion-corrosion at locations of condensation. In addition to localized attack, carbon steel exhibited hydrogen-grooving characteristic of acid attack. Figure 2 shows some of the corrosion damage caused by HCl produced in steam. Similar observations were made at Lardarello (Allegrini and Benvenuti, 1970).

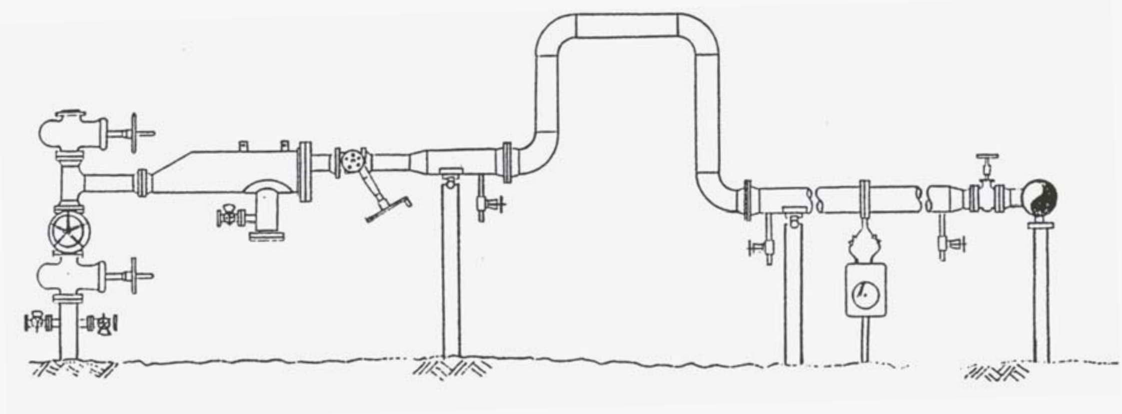

Figure 1 – Typical wellhead diagram

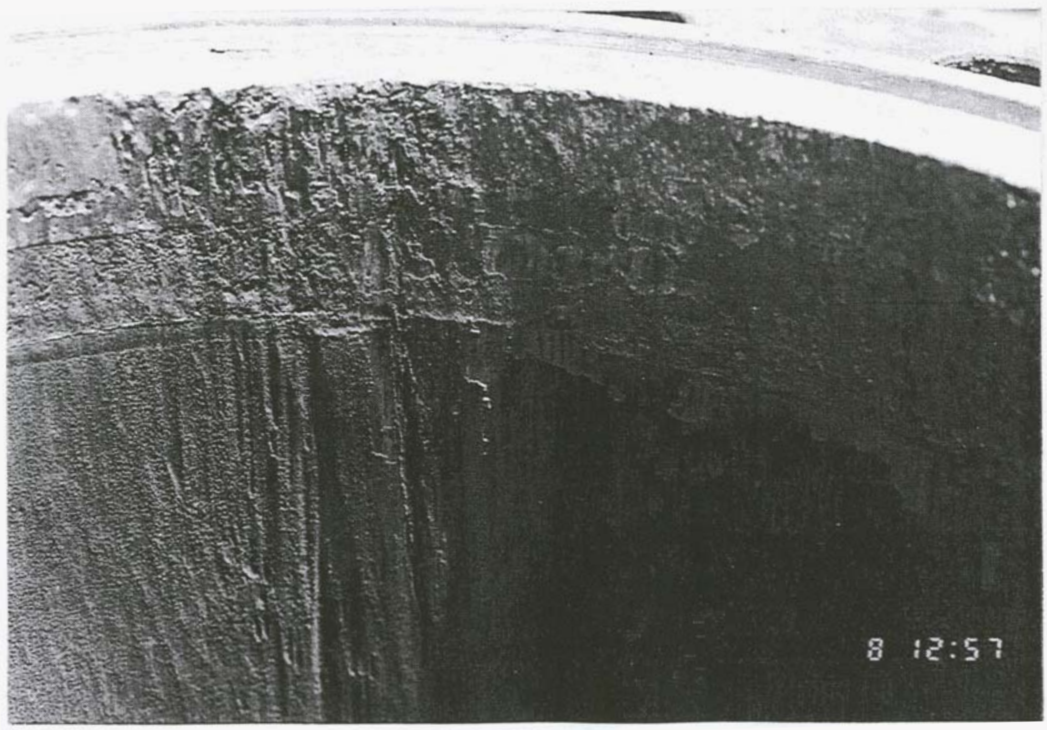

Figure 2 – Photograph of wellhead corrosion damage

3.2 Condensates and Corrosion Products

A representative composition of condensate collected fiom a corrosive well is provided in Table 1. Low pH, dissolved iron and excess chloride characterize the condensate. Corrosion product removed from etched piping consists primarily of akaganeite (FeOOH,Cl) and iron chlorides (see Table 1). Scanning electron micrographs of corrosion debris are provided in Figure 3.

Table 1 – Representative condensate (ppm except as noted) and corrosion product analyses (wt%)

Condensate			
pH, unit	3.6	ORP, mV	-224
As	22	B	540
Fe	13	Na	1
SiO_2	3.5	Cl	54
Corrosion Product			
FeOOH	69.3	$FeCl_3$	23.2
Al_2O_3	0.8	CaO	0.2
MgO	0.3	MnO	0.2
SiO_2	4.7	TOTAL	98.7

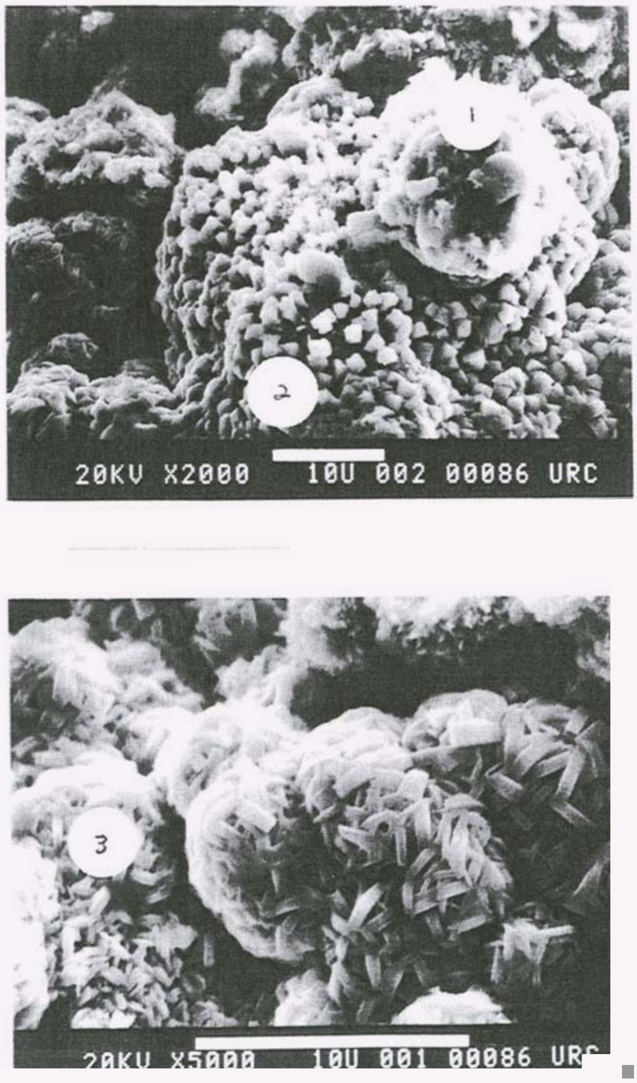

Figure 3 – Scanning electron micrographs of acidic corrosion products (#1 = elemental sulfur; #2 = ericaite; #3 = ferrous chloride)

3 3 Corrosion Coupon and Pipe Spool Tests

Several series of corrosion coupon and pipe spool tests were conducted at the field to find alternative materials for replacement of carbon steel (Amend, 1987). Table 2 presents the major alloying elements of materials examined in these tests. Maximum general and pitting corrosion rate data for three wells are depicted in Figures 4 – 6. Corrosion was generally greatest at the wellhead and progressively decreased at downstream locations. Metal loss did not appear to be caused by particle erosion, but rather low pH fluid corrosion. Steam velocity and turbulence did not significantly correlate with corrosion. Corrosion was most severe at locations of condensation, *i.e.,* heat sinks caused by external attachments on piping. These tests indicated that austenitic stainless steels yielded relatively low general and pitting corrosion rates, but they are were susceptible to chloride stress corrosion cracking. Corrosion was accelerated immediately adjacent to weld heat affected zones and did not appear to be related to the type of filler metals used. Figure 7 depicts photographs of some corroded mild steel coupons.

Table 2 – Approximate Compositions of Test Materials **(wt%)**

	Fe	Mn	Cr	Mo	Ni	Cu	N	C	Other
AISI 1018 mild steel	Bal	0.8						0.18	
9%Cr-1%Mo	Bal	0.48	8.27	0.96	0.06	0.11		0.13	
Type 410 stainless	Bal	0.35	11.86	0.2	0.23	0.05	0.02	0.14	
Type 316L stainless	Bal	1.70	16.22	2.12	10.12		0.04	0.02	
SAF2305 Duplex SS	Bal	1.44	22.65	0.28	4.90		0.10	0.021	
2205 Duplex SS	Bal	1.54	21.99	2.98	5.57		0.14	0.024	
Ferralium 255 Duplex	Bal	1.00	24.50	3.10	5.90	1.80	0.19	0.02	
SAF2507 Duplex SS	Bal	0.39	24.93	4.12	7.68		0.28	0.01	
AL 29-4-2 stainless	Bal	<0.1	28.45	3.8	2.45		0.01	0.002	
904L stainless	Bal	1.51	19.83	4.61	26.42	1.32		0.02	
254 SMO stainless	Bal	0.45	20.0	6.13	17.9	0.66	·0.20	0.012	
Carpenter 20-Cb3	Bal	<2.0	19-21	2-3	32-38	3-4		<0.07	Nb=8X%C
Inconel 825	29.08	0.37	22.68	2.72	42.17	1.75		0.02	
Monel 400	1.91	1.02			66.04	30.62		0.12	
Hastelloy G3	19.84	0.77	22.46	7.49	Bal	1.88		0.005	0.8W, 1.8Co, 0.36Nb
Hastelloy C22	4.10	0.28	21.10	13.8	Bal			0.002	2.9W, 0.9Co

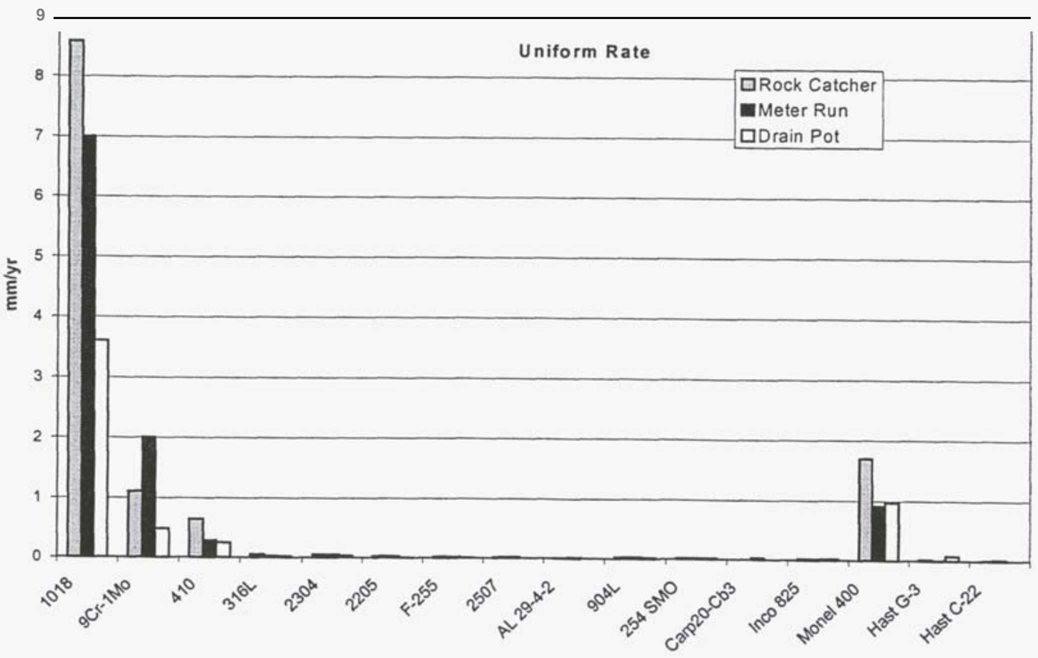

Figure 4 – Graphical comparison of uniform corrosion coupon results, Well A

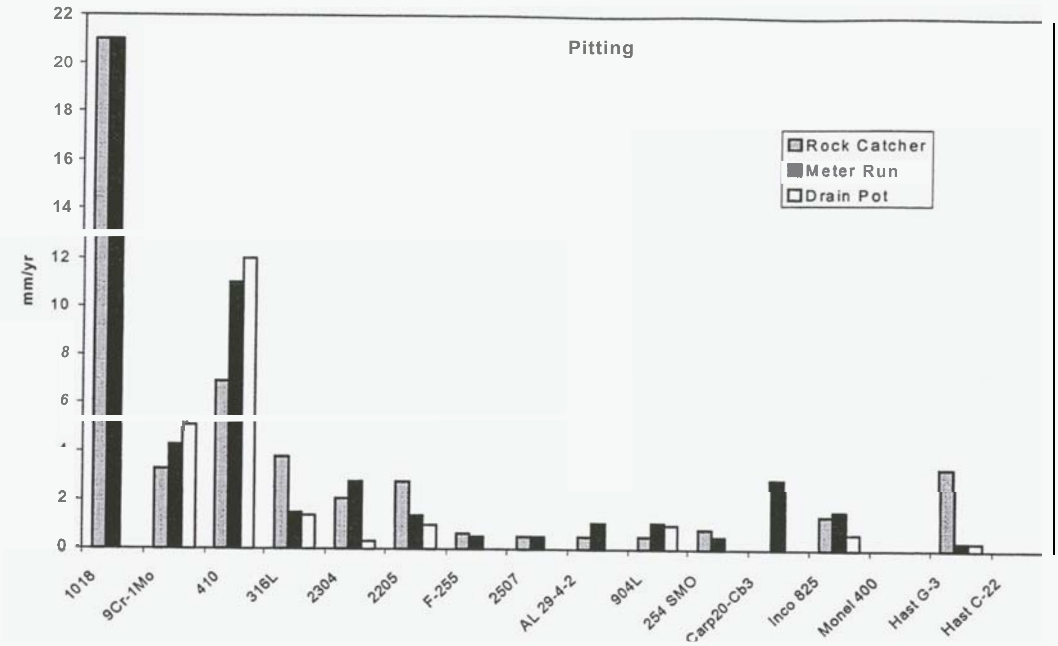

Figure 5 - Graphical comparison of pitting corrosion coupon results, Well A

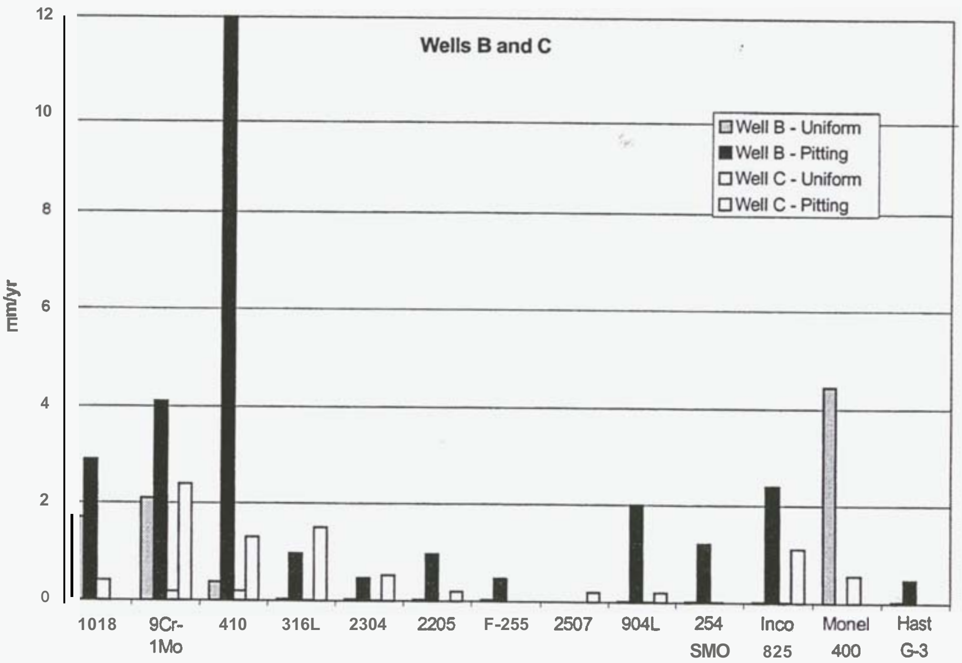

Figure 6 - Graphical comparison of corrosion coupon results, Wells B & C

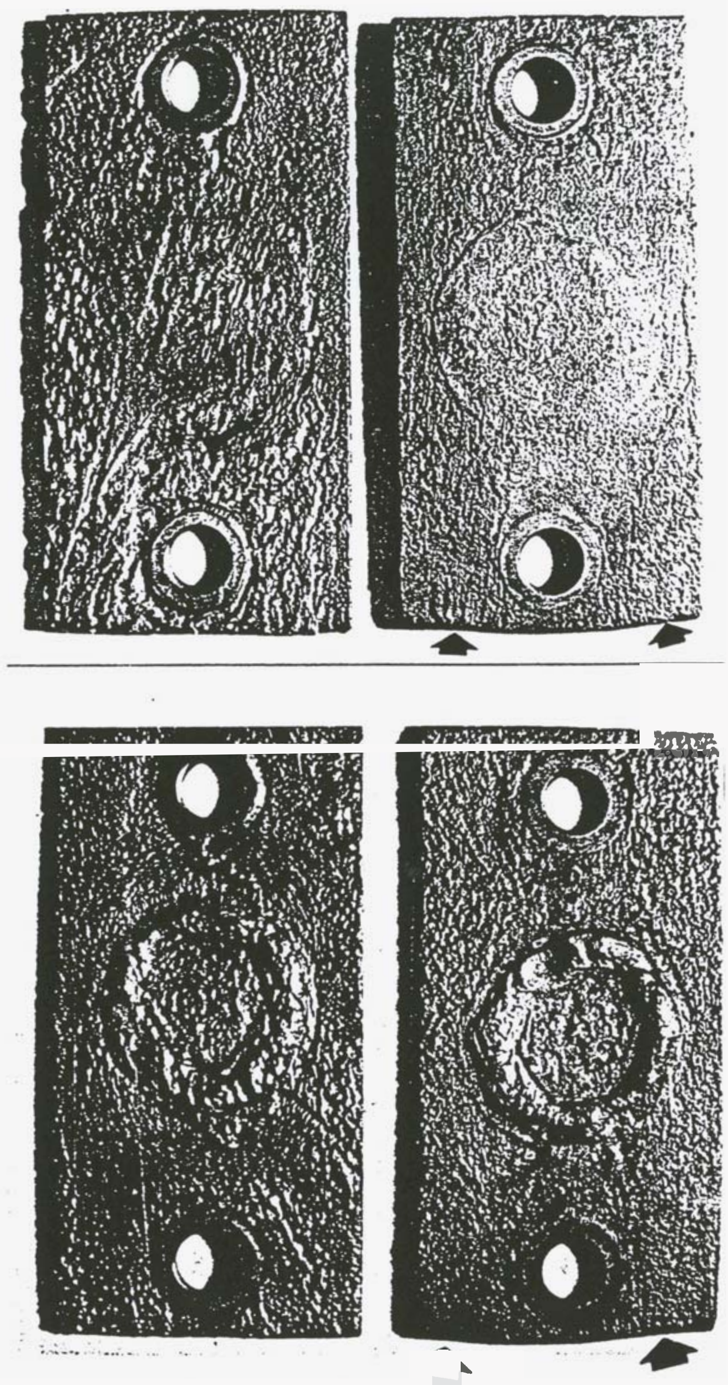

Figure 7 – Examples of corroded mild steel coupons (arrows indicate flow direction)

Table 3 – Hangdown liner corrosion test results (mm/yr)

	Top of Liner		Bottom of Liner	
	mm/yr	mils/yr	mm/yr	mils/yr
N-80/K-55	7.6	300	0.10	4
9Cr-1Mo	3.8	150	0.051	2
13Cr	Not Available		0.051	2
25Cr Duplex	Crack		0.025	1
Sanicro 28	0.15	6	0.025	1
Inconel 825	0.36 (pitting)	14	0.025	1
2035	0.25	10	0.025	1
2535	0.20	8	0.025	1
3040	0.18	7	0.025	1
2550	0.20	8	0.025	1

As part of the material testing program, a 1090-meter hangdown liner string (22-cm diameter) was run into Well A. The liner consisted primarily of mild steel (N-80 with a few joints of K-55) with a few alloy and polymer cement-lined pup joints. The alloy pup joints included 9Cr-1Mo, 13Cr, 25Cr Duplex, Sanicro 28, Inconel 825, 2035, 2535, 3040 and 2550. Pup joints of N80 lined with Unocal's patented polymer concrete were included in the string (Allen, 1997). The liner was retrieved after 540 days total and 210 days of flow prior to inspection. The string and pup joints were corroded to varying degrees. Table 3 summarizes the results of this test.

Similar to coupon studies, mild steel and 9Cr-1Mo were unacceptable in this service. The other alloy pup joints all showed corrosion rates that would make them suitable for long-term exposure to corrosive steam. The polymer concrete-lined sections exhibited little to no corrosion under the lining. However, thermal cycling caused some cracking and spalling of the concrete.

4.0 DISCUSSION

The acidic environment in producing wells at The Geysers, Lardarello and a few other fields world-wide is a serious obstacle to geothermal energy development. Steam condensate and corrosion product analyses confirm the presence hydrochloric acid corrosion in certain superheated steam wells at The Geysers field. It is postulated that HCl gas is transported in superheated steam, but at low concentrations. Especially where initial condensation of steam occurs, very corrosive environments may form. The HCl gas partitions into the condensate phase forming dilute, aqueous HCl solution. HCl gas alone may also corrode well casings and piping. The reaction of mild steel wellhead and surface piping with HCl produces dissolved iron and hydrogen gas. The dissolved iron may precipitate as iron oxide corrosion products or as chloride salts (for example):

$$Fe + 2\,HCl \rightarrow Fe^{2+} + 2\,Cl^- + H_{2(g)}\uparrow \quad (1)$$

$$Fe^{2+} + 2\,Cl^- + H_2O \rightarrow FeO(OH,Cl);\ FeCl_{(2,3)};\ Fe_xO_y;\ etc \quad (2)$$

Coupon and hangdown liner testing conducted at The Geysers field demonstrated that mild steel, 9Cr-1Mo, and Monel 400 consistently experienced high uniform corrosion rates (> 0.25 mm/yr) in the presence of HCl. These materials are unacceptable for this service (HCl corrosion in steam wells). Acceptable corrosion rates for different piping service classes utilized at The Geysers are less than about 0.2 mm/yr. Generally, stainless steels and nickel alloys exhibited uniform corrosion rates of less than about 0.2 mm/yr. The high corrosion rates obtained for some of the alloys may be biased due to relatively short exposure times, however. Corrosion rates have been observed to decrease over time with many materials exposed to geothermal fluids (Moeller and Cron, 1997). Short time exposure tests conducted by these authors at the Salton Sea geothermal field predicted corrosion rates up to seven times higher than actual results from long term tests. Polymer concrete linings appeared to afford generally good protection of piping.

Pitting corrosion was observed for most materials tested. Pitting was usually most severe in weld heat affected zones, areas of heat tint near welds, or in crevice areas under coupon mounting fasteners. Hastelloy C-22 and G-3 were immune to pitting. The super-austenitic stainless steels, 904L and 254, and super-ferritic steel, AL 29-4-2, displayed good corrosion resistance. Intermediate alloys generally performed well with respect to uniform corrosion, although variations in pitting rates were observed. Carpenter 20Cb-3 suffered rather **significant** pitting. Type 316L and 410 stainless steels, 9Cr-1Mo, and *SAF* 2304 duplex stainless steel were prone to chloride and sulfide stress cracking. That a duplex alloy cracked in this service is attributed to low pH, chloride-rich solution (possibly coupled with a trace of oxygen ingress and the presence of CO_2. Duplex alloys (*i.e.,* 2205) have been observed to crack in low pH, high salinity environments at the Salton Sea (Moeller and Cron, 1997). Available test data and a literature search indicate that the concentration of H_2S in The Geysers steam is well below that required to crack annealed duplex alloys. The 904L and 254 SMO coupons were more resistant to stress corrosion cracking in the presence of hydrogen sulfide and chloride ion than the duplex stainless steels. AL 29-4-2 also yielded excellent resistance to cracking. The best-performing duplex stainless steel was SAF 2507. Corrosion resistance of duplex stainless steels is greatly influenced by welding procedures and the different microstructures that result from different heat inputs and filler metals, so they must be used with precaution.

5.0 ENGINEERING APPLICATION

Considering the results of these corrosion tests, mild steel, 9Cr-1Mo, 410, and 316L, 2304 Duplex, Carpenter 20-Cb3 and Monel 400 were not recommended as future construction materials due to observed severe corrosion or cracking. However, mild steel continues to be used in conjunction with caustic corrosion mitigation systems. Only expensive super- or high nickel-alloys could be expected to provide long-term service in this application. Life cycle cost analyses of these alloys has been performed. The use of these alloys must be balanced against their high costs; Hastelloys were eliminated from consideration as a result. Materials recommended for future consideration were 2205 Duplex, Ferralium 255 Duplex, SAF 2507 Duplex, AL 29-4-2, 904L 254 SMO, Inconel 825, and polymer concrete-lines mild steel. Table 4 lists selection considerations for materials recommended to resist the corrosive fluids produced at The Geysers.

Several additional measures may be taken to improve corrosion resistance of the materials examined in this test program. Increased corrosion resistance to pitting may potentially be obtained by pickling or sandblasting welds prior to placing the components in service. The resistance of weldments to stress corrosion cracking can be increased by post-weld stress relief heat treatments. However, duplex stainless steels cannot be stress relieved in the field, while austenitic stainless steel can. Furthermore, the austenitics require lower heat input during welding than is customarily used for the duplex stainless steels. Welding time for joining austenitic alloys may be shorter than duplex alloys. Highly alloyed filler metals (*i.e.,* Inconel 825) are usually required to obtain weld corrosion resistance that matches that of the base metal.

Ultimately, acidic corrosion has been mitigated at The Geysers by caustic injection at the wellhead or downhole through capillary tubing. Unocal Corporation has also utilized extensive non-destructive corrosion monitoring techniques, inspections and maintenance scheduling to prevent failures. Downhole cameras have allowed inspection of casings during steam production. Improved understanding and prediction of acidic corrosion has been achieved through fluid chemistry, corrosion chemistry and material

Table 4 – Materials Selection Considerations

	Cost Factor Relative to Mild Steel	Code	Allowable Stress @ 240C, MPa
Mild Steel	1	ANSI B31.1	379
2205 Duplex	18	ANSI B31.1	142
Ferralium 255	25	ASME Sec. VIII	170
2507 Duplex	25	ASME Sec. VIII	170
AL 29-4-2	21	ASME Sec. VIII	125
904L	18	ASME Sec. VIII	91
254 SMO	16	ASME Sec. VIII	131
Inconel 825	28	ANSIB31.1	129

behavior modeling. Cement-lined piping has been carefully researched and developed. An in-house life cycle cost analysis program has been successfully implemented for selection of the most cost effective materials for use in corrosive wells. Cladding and lining of mild steel have been employed in very aggressive environments. We have also developed alternative coupon testing and corrosion inhibitor testing protocols. Corroded wellheads have been successfully replaced.

New areas of research and development are underway. Alternatives to caustic treatment and steam water washing are under investigation. Studies of corrosion inhibitors are in progress. Improvements in linings are currently being tested.

6. ACKNOWLEDGMENT

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