

CORROSION TESTS IN HAWAIIAN GEOTHERMAL FLUIDS

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ABSTRACT - Exposure tests were conducted in binary geothermal brine on the island of Hawaii. The steam which flashes from the high pressure, high temperature water as it is brought to ambient pressure contains substantial amounts of H₂S. In the absence of oxygen this steam is only moderately aggressive but in the aerated state it is highly aggressive to carbon steels and copper alloys. The liquid after flashing is intermediately aggressive. The Hawaiian fluid is unique in chemistry and corrosion behavior; its corrosiveness is relatively mild for a geothermal fluid falling close to the Iceland-type resources.

INTRODUCTION

The energy crisis of the early 1970's fostered development of alternate energy sources in many parts of the world. Geothermal energy received special attention in certain areas because its feasibility had been proven many years ago, because no major technological break-throughs were needed, and because location of the resources was fairly well known.

At first glance the island of Hawaii with its active volcanoes would seem to be a perfect site for geothermal energy development. Closer inspection reveals, however, that most of the rock is porous and does not allow the build up of steam pressure and there are no geysers or active hot springs on the island. This was long thought to rule out the presence of usable geothermal reservoirs and a small drilling program carried out in the mid- to late 1950's seemed to confirm this - it did not hit any steam or pressurized hot water. In hindsight that drilling operation, which was a commercial venture, appears to have been ill-conceived and poorly planned. With the reawakening of interest after 1972 a careful geological survey was made and a successful well was drilled.

The well was finished in 1976, to a depth of 1970 m (1780 m below sea level) and a bottom hole temperature of 360°C was measured, making this one of the hottest geothermal wells in the world. A pilot power plant was constructed in 1980-81. It has operated since then and generates 3 MW of electric power. Geological exploration has demonstrated that a very large resource exists in the area and additional drilling is in progress.

The resource is liquid-dominated and produces a mixture of steam and liquid. At present, energy is extracted only from the steam, which accounts for 55-65% of the mixture while the hot liquid is discarded. This liquid has a temperature of around 180°C. It represents a significant thermal resource and when larger plants are built on the site

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it will be very desirable to utilize this liquid for secondary power generation or for industrial or agricultural heating.

From other geothermal systems, such as Lardarello in Italy (1), Krafla in Iceland (2), Wairakei in New Zealand (3), Cerro Prieto in Mexico (4), Matsukawa in Japan (5) and Geysers in California (6), it is known that the geothermal fluids can be very corrosive; careful materials selection is necessary for any secondary use systems, based on corrosion tests in the actual medium.

The purpose of this study was to make an initial assessment of the corrosiveness of Hawaiian geothermal fluids, in particular the fluid at the Hawaii Geothermal Project's well A (HGP-A).

EXPERIMENTAL

Location of the well is shown in Fig. 1. The site is in a volcanic rift zone on fairly level land with good access from the main port of Hilo. A sketch of the pilot plant is shown in Fig. 2. The wellhead fluid enters a separator in which flashing takes place; the steam portion with non-condensable gases is here separated from the liquid and passes through an H₂S abatement chamber on to the turbine. In order to dispose of the liquid, it must first be brought to ambient pressure. This takes place in the brine flash chamber and is accompanied by a second flashing. The steam from this flashing passes through another hydrogen sulfide abatement chamber before it is released to the atmosphere. The liquid flows through a settling pond, in which most of the suspended silica particles settle out, before it flows into the porous ground rock.

The tests were conducted during the period August 1981 - November 1982. Racks of test specimens were exposed in the settling pond and in the steam at the second flashing for various periods of time. In the initial steam tests there was free access of air while in later tests the chamber had been enclosed for hydrogen sulfide control and the steam was air free.

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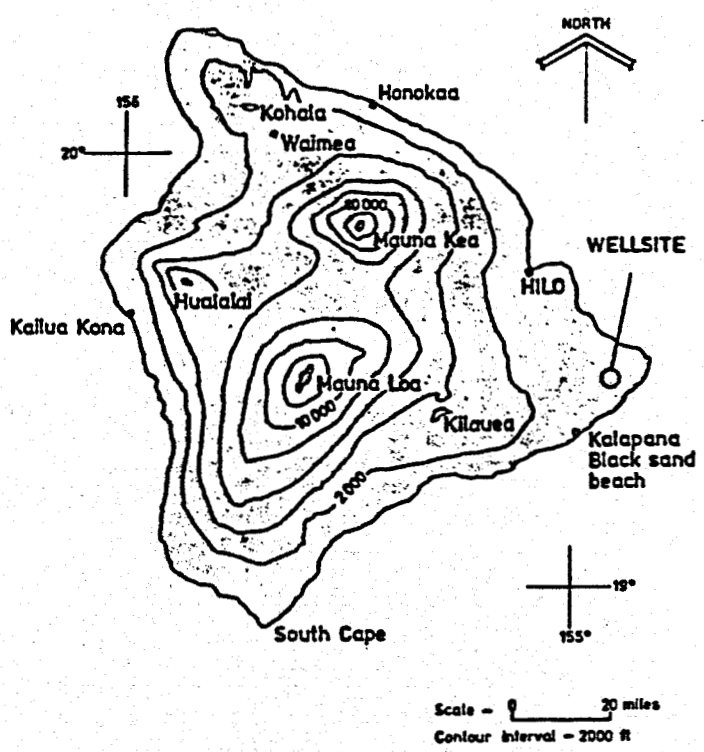


Fig. 1 Location of well site on the island of Hawaii

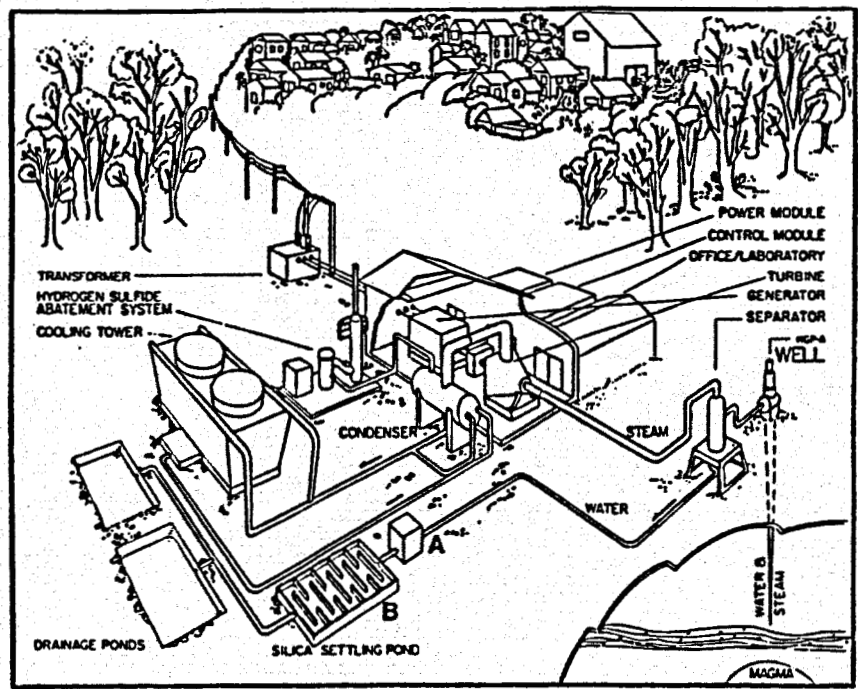


Fig. 2 Sketch of the HGPA pilot power plant. Sample strings were exposed in the flash chamber (A) and in the silica settling pond (B).

The liquid typically had a flow rate of 400 l/min, a temperature of 76°C, a pH of 7.45-8.8 and the following contents of dissolved salts and gases (ppm): H₂S - 20; Cl - 7230; Na - 3750; K - 620; Ca - 150; SiO₂ - 650; O₂ - 1.6 (7).

The aerated steam contained about 20% air. Its pH was 4-4.5 and it contained 100 ppm of CO₂ and 80 ppm of H₂S. The non-aerated steam had the same pH, only a trace of CO₂, and 100 ppm of H₂S. Trace gases in the steam (< 3 ppm) were He, A, CO, and possibly methane but, unlike most other geothermal systems, no ammonia was present (7). The temperature at the test site was 100°C and the steam was flowing at a rate corresponding to 75 l/min of water.

Test coupons were prepared from thin sheet or plate material or from tubes and rods, as available. Each coupon was finished with 120 µm silicon carbide abrasive paper, cleaned in acetone and weighed. Flat exposure coupons were 7.5x7.5 cm and the rod shaped samples were 9 cm long. A 1.3 cm diameter hole was drilled through the center of each for use in making up the sample string. A threaded, Tygon coated rod of stainless steel 316 was inserted through the holes and 2.5 cm long pieces of PTFE tubing were used as spacers between the coupons. Some U-bend specimen were added to each string to provide SCC data and also to put the string assembly under some compression. The U-bend samples were 22x4 cm strips of sheet with a hole near each end. They were bent to a 2.5 cm opening and strung on the rod of the assembly. A sample string typically contained 25-30 coupons.

Sample strings in the steam flash chamber were located horizontally on top of the rocks in the chamber. Sample strings in the silica settling pond were hung vertically in the water. Exposure times varied from 14 to 50 days in the steam and from 38 to 130 days in the liquid.

After exposure the samples were studied by optical and electron microscopy. Pit and crevice depths were measured by the depth of focus technique using an optical microscope. Corrosion products and silica scale could generally be removed by gentle brushing but for some materials the silica scale adhered quite strongly. In some of those cases the scale would flake off when the specimen was flexed. In other cases it was necessary to dip the specimen for a few seconds in 50% HF or to use the electrolyte cleaning method suggested by Braithwaite and Lichti (8). Corrosion products were removed by the usual ASTM methods (9) before the weight loss was determined.

RESULTS

The corrosion results are summarized in Table 1. The depths of pitting and crevice corrosion attacks varied from test run to test run and for these types of damage the largest values have been listed.

Some alloys were completely resistant: titanium, Hastelloys C-3 and C-276, and high-alloy stainless steels. The composition of these alloys is listed in Table 2.

The more common stainless steels are generally subject to substantial pitting in some of the environments but not in others. These steels include the austenitic 18/8 (304) type and the martensitic 431. The composition of this group of apparent borderline alloys is given in Table 3.

The pure nickel shows pitting and crevice corrosion only in the aerated steam, but as copper is added, to form monel 400, general attack is also experienced. The pure copper shows very severe uniform attack in the aerated steam, to 1.5 mm/yr, while the attack is only 2.5 µm/yr in the non-aerated steam and less than 50 µm/yr in the liquid. The 70:30 Cu:Zn brass shows similar relative values but at lower total rates while the pure zinc is attacked only by severe pitting. The zinc coating on galvanized steel performs in a similar manner, though the depths of attack are only 20-30% of those for the pure zinc.

The low carbon steel shows quite high general corrosion rates - 85 µm/yr in the aerated steam, 200 µm/yr in the non-aerated steam and up to 65 µm/yr in the liquid. In the latter environment the attack under the washer was even greater - up to 230 µm/yr. The high strength low alloy steels AISI 4140 and 4340 show generally good resistance except for crevice corrosion attacks in the liquid which are nearly as severe as for the low carbon steel.

The aluminum alloys tested generally show remarkably high rates of pitting - to 11 mm/yr. The most severe attack is shown by the aluminum-zinc alloy 7075 but very substantial pit and crevice attacks are found also for the aluminum-magnesium alloys 5052 and 5086 and the aluminum-magnesium-silicon alloy 6061. The coating on aluminized steel behaves in the same general way as the straight aluminum alloys. The attacks on the aluminum alloys are severe in all three environments with non-aerated steam as possibly the worst environment, followed by the aerated steam and the liquid.

The nominal compositions of the alloys which show substantial attack are listed in Table 3.

No stress corrosion or hydrogen cracking was observed on any of the low carbon steel U-bend specimens.

DISCUSSION

It is difficult to make a direct comparison of the three different environments because test conditions were not always constant. For example; during some of the tests in aerated steam the flow conditions in the chamber changed somewhat, so that some splashing to liquid onto the samples may have occurred. It is also difficult to compare with results from other geothermal sites around the world because, again, test conditions vary considerably and complete information is not always available. For these reasons the following discussion is rather general and qualitative.

Data on uniform corrosion in various geothermal liquids are summarized in Table 4. It is seen that the secondary fluid from the Hawaiian site is

generally intermediate in its corrosiveness, as compared with other sites, falling between the New Zealand, Iceland and Central American sites on the milder side and the mainland U.S.A. sites on the severe side. The water chemistry data available do not, unfortunately, permit a more detailed analysis. It should be mentioned, however, that the very high corrosiveness towards steels of the Salton Sea fluids most probably is due to their very high salinity.

Data on uniform corrosion in steam are presented in Table 5. The values from the Hawaiian site should probably be compared only with literature data for flashed steam. However, insufficient information is available for a good study. In a general comparison with steam from other sites it is seen that the Hawaiian site is intermediate in aggressiveness towards carbon steels, mild towards low alloy steel, aggressive towards brass, and extremely aggressive towards copper and Monel 400. The sites which have steam aggressive to copper and Monel 400 all have 100 ppm or more of H₂S in combination with oxygen in the aerated steam, while the same steam free of oxygen is quite benign to copper and the 70 Ni 30 Cu Monel. An exception is the Matsukawa, Japan data which may represent both aerated and non-aerated steam environments. The Matsukawa site has an extremely high H₂S level (1500 ppm) and so do the other two sites which are somewhat aggressive to Monel in the nonaerated steam: Cerro Prieto (1500 ppm) and Ahuachapan (130 ppm).

Data for the carbon steel follow similar lines - heavy attack where H₂S and oxygen act together, moderate attack where the oxygen is excluded.

Little information is available in the literature on the behavior of aluminum alloys in geothermal fluids. The available data all show severe pitting. On the steam side this includes alloy 1100 in aerated and non-aerated steam at Wairakei, New Zealand (3) and in aerated steam at Cerro Prieto, Mexico (4,20); alloys 1100 and 5052 in non-aerated steam at Matsukawa, Japan (22); and alloy 5005 in flashed steam at East Mesa, U.S.A. (15). In the liquid, pitting has been found for alloys 1100, 5052 and 6063 at Raft River, U.S.A. (13) and for alloy 5005 at East Mesa, U.S.A. (15). There appears to be no reports of geothermal fluids which do not attack aluminum alloys by pitting corrosion.

The data for the severely pitted aluminum alloys do not clearly indicate that any one of the three environments tested in this study is more aggressive than any other. The other metals and alloys tested do, however, clearly show that the aerated steam is the most aggressive of the three environments, the non-aerated steam the least, and the liquid falls somewhere in between. This ranking is in agreement with findings from other sites around the world.

A study of the primary steam was not included in the present work. It was noticed during turbine overhaul, however, that no serious corrosion takes place in this environment, possibly because

virtually all of the H₂S has been removed upstream.

Attempts have been made to classify the corrosiveness of low temperature geothermal fluids on a global scale. Ellis (23) has proposed that geothermal sites can be divided into two different categories: Iceland-like resources and Madison-like resources. The classification is based on fluid chemistry parameters: pH, total alkalinity, bicarbonate, H₂S, chloride and sulfate and on the corrosion rate of carbon steel. The HGP-A fluid chemistry does not fit into the classification system while the corrosion rate for low carbon steel (7.5-65 $\mu\text{m}/\text{yr}$) places it closer to an Iceland-like resource (< 41 $\mu\text{m}/\text{yr}$) than to a Madison-like resource (120-450 $\mu\text{m}/\text{yr}$). A comparison on fluid chemistry alone also shows that the Hawaiian site appear to be somewhat unique, though not very different from some Icelandic wells (24).

CONCLUSIONS

The tests have shown that compared to geothermal sites world wide the Hawaiian geothermal fluid is a moderately aggressive geothermal resource. Of the three environments tested the aerated flashed steam was the most aggressive followed by the liquid after flashing. The non-aerated flashed steam was least aggressive. Aluminum alloys suffered severe pitting attack in all three environments while the high alloy stainless steels were fully resistant. Carbon steel and copper alloys suffered severe general corrosion in the aerated steam, moderate damage in non-aerated steam and considerable general or crevice corrosion damage in the liquid. Nickel, zinc and Monel 400 were attacked by severe pitting, especially in the aerated steam and in the liquid.

The results are preliminary in nature. Longer term tests must be conducted before materials selection guidelines can be firmly established for this geothermal fluid.

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Table 1

Corrosion Data, $\mu\text{m}/\text{yr}$.

Alloy	Aerated Steam	Non-aerated Steam	Liquid
Titanium, Gr. 2	R	R	R
Hastelloys C-3, C-276	R	R	R
High-alloy Stainless	R	R	R
SS 316 L	-	R	R
SS 304	P-6860/CC-1700	R	R
SS 303	-	R	P-145/CC-168
SS 431	-	R	P-56/CC-330
Ni 270	P-2286/CC-762	R	R
Monel 400	G381-762/P-2185	R	P-381/CC-330
Cu	G762-1524	G2.5	G46-48
70:30 Brass	G152-254	R	G20-41
Zn	P-3886/CC-889	P-406/CC-432	P-356/CC > 1525
Galv. Steel	P-1016/CC-432	P-152	P-229/CC-117
Low Carbon St.	G 84	G 0-203	G 716-64/CC-229
AISI 4140 St.	(R)	(R)	CC-196
AISI 4340 St.	(R)	CC-8	CC-183
Aluminized St.	P/CC-1829	P-76/CC-330	P-178/CC-229
Al 2024	P	P-2970	R
Al 7075	P-2160/CC-4520	P-7214/CC-152	P-11230/CC-2670
Al 5052	P-2440/CC-6705	P-7365/CC-6705	CC-890
Al 5086	P	-	CC-1015
Al 6061	P-3405/CC-8130	P-4725/CC-3275	CC-1145

P - pitting; CC - crevice corrosion; G - general attack; R - resistant

Table 2

Composition of Fully Resistant Stainless Steels

	C	Cr	Ni	Mo	Mn	Si	N	Cb	Cu
AL-6X	0.08m	20	24	6.0	8.25				
Jessop 700	0.025	21	25.6	4.5	1.8	0.5	0.02	0.3	
Jessop 777	0.025	21	25.6	4.5	1.4	0.5	0.03	0.3	2.2
Avesta 254SMO	0.014	20	18	6.1	0.5	0.3	0.22		0.7
Nitronic 50	0.035	21	12.5	2.1	4.8	0.4	0.23	0.13	
Ferrallium 255	0.02	25.6	5.5	3.0	0.8	0.4	0.25		1.75
Avesta 223 FAL	0.03m	22	5.5	3.0			0.12		
Avesta 3 RE 60	0.03m	18.5	5	2.8	1.2	1.5			
316 L	0.01	17.2	13	2.7	1.75	0.6			0.12

Table 3

Nominal Composition of Corroding Alloys

304 Stainless Steel	C:0.08 max, Cr:19, Ni:10
303 " "	C:0.15 max, Cr:18; Ni:9, S:0.15 min.
431 " "	C:0.2 max, Cr:17, Ni:2
Nickel 270	Commercially pure nickel
Monel 400	Ni:63-70; Fe:2.5 max, Cu:rem.
Copper	99.99% Cu. min.
70:30 Brass	Cartridge brass, Cu:68.5-71.5, Zn rem.
Zinc	99.9% Zn min.
Low Carbon Steel	ASTM A 366: C 0.06
AISI 4140 Steel	C:0.4, Mn 1.0, Cr: 0.8-1.1, Mo:0.15-0.25
AISI 4340 Steel	C:0.4, Mn 0.8, Cr:0.7-0.9, Ni:1.65-2, Mo:0.2-0.3
Al 2024	Cu:3.8-4.9, Mg:1.2-1.8
Al 7075	Zn:5.1-6.0, Mg:2.1-2.9, Cu:1.2-2.0
Al 5052	Mg 2.2-2.8; Cr:0.15-0.35
Al 5086	Mg 3.5-4.5; Cr:0.05-0.25
Al 6061	Mg 0.8-1.2; Si:0.4-0.8

Table 4

Literature Corrosion Data for Geothermal Liquids, $\mu\text{m}/\text{yr}$

Location	Reference	Carbon Steel	4130/ 4140	Monel 400	Cu	Brass
<u>Separated Water:</u>						
Wairakei, N.Z.	3	< 25		25-250	25-250	
Broadland, N.Z.	8	2.5-7.5 ^x	2.5 ^x			
Krafla, Iceland	10	10				
Ahuachapan, El Salvador	11	10		46	700	41
Brady Hot Springs, U.S.A.	11			76		
<u>Well Water:</u>						
Diamond Ring, U.S.A.	12	389		11	86	
Raft River, U.S.A.	13	46 ^x	20 ^x	2030		4165
<u>Flashed Fluid:</u>						
Bara, U.S.A.	14	813		76		76
East Mesa, U.S.A.	15	84 ⁺	30 [‡]			
Salton Sea, U.S.A., 1976-7	16/17	1220 ^x	56/262 ^x			
Same, 1978	18	1905 ^x	584			

Hawaii HGP-A	This Study	7.6-64 ⁺	0 [‡]	0 ^x	48	203-406

x - Pits

+ - Crevice Corrosion

Table 5

Literature Corrosion Data for Geothermal Steam, $\mu\text{m}/\text{yr}$.

Location	Reference	Carbon Steel	4130/ 4140	Monel 400	Cu	Brass
<u>Aerated Steam:</u>						
Wairakei, N.Z.	3,19	508	< 25	255	1015	1015
Broadland, N.Z.	8	965 ^x	865 ^x			
Ahuachapan, El Salvador	11	183	137	213	691	602
Cerro Prieto, Mexico	4,20,21	110			569	
<u>Non-aerated Steam:</u>						
Broadland, N.Z.	8	17 ^x	23 ^x		15	
Hachobaru, Japan	11	86	46			11
Otake, Japan	11	41	43		15	~ 0
Cerro Prieto, Mexico	4,20,21	38		99		
Matsukawa, Japan	22	635 ⁺		25-255 ⁺	255-1524	255-1270
Ahuachapan, El Salvador	11	34	7	83	16	7
<u>Flashed Steam:</u>						
Salton Sea, U.S.A. '76-77	16,17	635 ^x	208 ^x			
Salton Sea, U.S.A. '78	18	432 ^x	279 ^x			
Baca, U.S.A.	14			51		127
East Mesa, U.S.A.	15	81 ⁺	64 ⁺			

HGP-A, Hawaii, aerated	This Study	84	~ 0	381-762	762-1524	152-254
" " , non-aerated	"	0-203	~ 0 ⁺	0 ^x	2.5	~ 0

x - Pits + - Crevice Corrosion

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