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GEOTHERMAL MATERIALS STUDIES

Metallurgy Division Quarterly Report, April-June 1976

By
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METALLURGY DIVISION QUARTERLY REPORT -- April-June 1976

GEOHERMAL MATERIALS STUDIES

By Alfred Goldberg

with Contributions from

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1. Introduction

Since its inception in 1974, the LLL Geothermal Program has evolved into two basic activities:

- To provide advanced technologies for hydrothermal systems with emphasis on the Total Flow Process
- A recently initiated Industrial Support Program to provide technical assistance to joint ERDA/industry projects.

The Metallurgy Division is carrying out a materials effort in support of both activities.

In the Total Flow Process, the total flow of the wellhead is expanded through converging-diverging nozzles to convert the enthalpy contained in the fluid into kinetic energy in the form of low temperature, high velocity streams for two-phase fluids to drive impulse turbines. This process is expected to be as much as 60% more efficient than either the flashed-steam or binary-cycle process. In the latter two processes, a large fraction of the enthalpy is lost in the relatively high temperature brine that is rejected. The goal for the Total Flow Process Program is to solve the brine chemistry and materials problems in order to be able to test this process using the high temperature/high salinity brines located in the Salton Sea Geothermal Field. This particular resource was chosen because it represents the greatest technical challenge and economic potential.

The short-range goal of the geothermal materials group is to select structural materials and fabrication processes for a 100-kW, brine tolerant turbine scheduled to be field tested by the end of FY 1977. The materials selected must be corrosion resistant to the high salinity acid brines and exhibit resistance to erosion or erosion-assisted corrosion that may arise from impingement by the high velocity brine droplets and entrained

particulates. The turbine material must also be capable of supporting high sustained stresses due to centrifugal forces without being subjected to delayed failure by stress corrosion cracking or corrosion fatigue. Candidate materials will be evaluated through an integrated program of laboratory activity and field testing.

In the Industrial Support Program, we will monitor corrosion during operation of the San Diego Gas and Electric Company's (SDG&E) Geothermal Test Loop Facility. Other candidate plant materials will also be tested for their corrosion resistance to provide a basis for substitution should present materials prove to be inadequate. In addition, selected materials will be tested to provide corrosion information for long-range alloy development of economical corrosion resistant geothermal structural materials.

2. Total Flow Process

2.1. Nozzle-and-Turbine Materials Erosion Studies

a) Introduction

A number of metallic materials (e.g., Ti-, Ta-, Co-, Ni-, and Fe-base alloys) are available which will not exhibit significant corrosion rates -- even in acid brine environments under static situations. However, the severe environment present in the high velocity nozzle exhaust might be expected to destroy the protective films that are responsible for the corrosion resistance of such materials and, thereby, result in high wear rates from the erosion-assisted corrosion. It is highly unlikely that a material will be obtained that will show adequate resistance to both erosion-assisted corrosion and stress corrosion and, therefore, some type of composite approach will have to be used. Alternatives that we are considering to provide the required structural strength and resistance to erosion-assisted corrosion are surface hardening by chemical diffusion, the use of coatings, and the use of inserts both for the turbine blades and nozzles.

Currently, the chemical diffusion studies are limited to Ti-base alloys and, in particular, Ti and Ti-6Al-4V. Coatings are being applied by several techniques, primarily on Ti-, Fe-, Ni-, and Co-base alloys. Ceramic materials, because of their lack of toughness, are limited in their use to inserts in nozzles and, possibly, in blades. We are also

examining some of the noble metals and their alloys (Au, Pt, Rh) as either substrates or coatings. Because of the unusually wide range of passivity of its oxide (Pourbaix diagram) Ta and some of its alloys are also being considered. All these materials, in the form of wedge-shaped wear plates and/or nozzle inserts, will be exposed to high velocity fluids. The wear plates have an overall dimension of 12.70 by 44.45 by 66.68 mm (0.5 by 1.75 x 2.63 in.). The wedge edge is tapered to an included angle of 0.34 rad (20°) and a tip radius of 250 μm (0.010 in.). The outside dimensions of the nozzle inserts are 22.2 mm diameter by 43.6 mm long. The erosion test nozzle-and-wear plate assembly was described in detail in the previous quarterly. A large number of samples have been prepared, or are in the process of being prepared, for exposure. Pending the startup of the LLL geothermal field test unit, samples are being exposed in the LLL fresh water facility to provide some interim data. We are interacting with industry in developing techniques for producing erosion/corrosion resistant hard surfaces.

b) Chemical Diffusion Coatings: (J. M. Johnson)

In the previous quarter, details were presented on case hardening of C.P. Ti and Ti-6Al-4V wear plates by carbonitriding. A case-hardened Ti-6Al-4V wear plate that had previously been exposed for 3-1/2 hours to the LLL geothermal fresh water facility (488 $\text{m}\cdot\text{s}^{-1}$ fluid velocity) was exposed for an additional 5-1/2 hours. No wear (weight loss) was detected. Eleven Ti-6Al-4V and six C.P. Ti case-hardened wear plates are now ready for testing. Several different hardening treatments were used for these plates; the erosion testing will determine what direction to take in optimizing the hardening treatment.

c) Hard Coatings: (R. E. Garrison)

In the previous quarterly, we described the various processes being used for applying hard coatings on nozzle inserts and wear plates. These included three types of spray techniques, chemical vapor deposition, and electroplating. Nozzle inserts and wear plates are also being made of ceramics and 3D carbon/carbon. This quarter we have primarily been involved with increasing our inventory of inserts and wear plates in preparation for field testing. Both coated and uncoated materials will be exposed. Wear plates and nozzle inserts ready for testing are listed

in Tables 2.1 and 2.2, respectively, while those still being fabricated are listed in Tables 2.3 and 2.4.

TABLE 2.1 WEAR PLATES READY FOR FIELD TESTING

Material	No.	Condition	Material	No.	Condition
Ti-C.P.-70	2	As received	TZM	2	As received
Ti-8Al-1Mo-1V	2	As received	TZM	2	carburized
Ti-6Al-6V-2Sn	2	As received	E-Brite 26-1	2	As received
Ti-6Al-2Nb-1Ta-1Mo	2	As received	"	2	Cr-electroplated
Ti-6Al-4V	2	As received	"	2	Ni-electroplated
Ti-1.5 Ni	2	As received	50Mo-50Re	2	Carburized
Ti-6Al-4V	11	Carbo-nitrided	Ni	2	As received
Ti-C.P.-40	6	Carbo-nitrided	Mo	2	As received
Illium-PD	2	As received	Ta	2	As received
Illium-B	2	As received	21-6-9	2	As received
Illium-98	2	As received	Mo	2	TiC coating*
Incoloy 833	2	As received	Mo	2	TaC coating*
Incoloy 862	2	As received	Mo	2	WC coating*
Fe-2.5Cr-1Mo	2	As received	3-D carbon/carbon	2	As received
200 Series Stainless Steel	2	As received			

* Coating applied by chemical vapor deposition (CVD)

TABLE 2.2 NOZZLE INSERTS READY FOR FIELD TESTING

Material	No.	Condition	Material	No.	Condition
Ti-6Al-4V	4	As received	Haynes 6B	2	As received
Au	4	As received	Ni(99.9%)	2	As received
Reactor Grade Graphite	12	As received	Ni(99.9%)	2	Pt-electroplated
Haynes 25	2	As received	Ni(99.9%)	2	Rh-electroplated

TABLE 2.3 WEAR PLATES IN FABRICATION

1. Metallic: 60Au-40Pt, Incoloy 800, Incoloy 600, Inconel 625, Incoloy 825, Carpenter 20, Fe-18Cr-2Mo, 316-L SS, Hastelloy C-276, Hastelloy G, Haynes 25, Beryllium Cu.
2. Coated: Ni, electroplated with Ni containing 5- μ m diamond particles (Diamonizing); Ni, electroplated with SiC particles in a Ni alloy matrix (Nye-Carb).
3. Ceramics: TiB_2 , Si_3N_4 , B_4C , AlN, and 502-1100 grade "Aremcoloy (machinable ceramic of $Al_2O_3 + TiC$).

TABLE 2.4 NOZZLE INSERTS IN FABRICATION

1. Metallic: 60 Au-40Pt.
2. Coated: AISI 1018 Ta-electroplated; Ti-6Al-4V Timadized; Haynes 6B, Haynes 25, AISI 1008, AISI 1055, and AISI 8645 - all Sheradized.
3. Non-Metallic: Reactor grade graphite chemical vapor deposited with TiC, TaC, WC, and SiC.

The terms "Timadized" and "Sheradized" in Table 2.4 refer to electrolytic anodizing treatments that are being carried out by Lovatt Technology Corporation. Timadizing is applicable for Ti-base alloys and may yield a penetration up to 125 μ m. Sheradizing is limited to steels and penetration can be controlled to $\pm 5 \mu$ m.

Jack Harrar measured the open-circuit corrosion potential of a Ti-6Al-4V timidized wear plate in simulated Niland brine. It gave a value of +0.33 volts vs Ag-AgCl attesting to its much more noble corrosion resistant character than the uncoated alloy; the latter gave a value of -0.43 volts. However, the anodized layer was easily removed with a wire brush wheel, with the corrosion potential reverting to that of the alloy. Therefore, unless deeper penetrations can be made, it would appear that Timidizing may have limited use where excessive erosion is present.

d) Erosion Specimen Orientation (R. E. Garrison and A. Goldberg)

An important parameter in erosion damage is the angle of incidence on impact. For brittle materials, maximum damage results for angles

close to 1.57 rad (90°); weight loss increases most rapidly at low angles with increasing angle. For non-brittle materials, maximum damage occurs at low impact angles from 0.17 to 0.43 rad (10 to 25°).

The wear plates that we are presently using for the erosion-assisted corrosion tests were designed to approximate conditions expected for the leading edge of the turbine blades. Therefore, the erosion of these plates from the impinging expanded brines will result from low-angle impact. This may cover the conditions for maximum erosion for non-brittle materials, but may lie in an orientation range of minimum damage for substrates or coatings that are brittle. To avoid over-estimating the potential of a material by failing to expose it to the most severe conditions, we have designed a new wear-plate fixture which will allow exposure over the complete range of impact angles from 0 to 1.57 rad (0 to 90°).

The variable angle wear plate fixture is shown in Fig. 2.1. A specimen measuring 51 by 51 mm and up to 3.2 mm-thick can be inserted into the holder. Availability of sheet materials, simpler design, easier coatability, lower cost, and variable impact angle favor the use of this type of specimen. However, simulating the leading edge of the turbine blade is an important factor in our tests. Therefore, for the immediate future the wedge-shaped wear blade will remain the principal test specimen.

e) Chemically Inert Hard Thin Surface Films (J. M. Johnson)

An alternative promising approach to the more conventional single layer coatings is the application of multiple layers of chemically inert, extremely hard thin films. Discussion with thin-film technologists indicate that best results are achieved when the films are applied on extremely tough substrate materials, and that ultra-adherence is essential if abrasion resistance is to be achieved. Also, it is imperative that the films remain fully compliant and adherant to the substrate region should plastic deformation of the substrate surface occur. Since we are dealing with brittle materials, for the most part, this deformation must be elastic, i.e., the films must be thin enough so that they do not establish mechanical rigidity in themselves.

It would appear that the best results in achieving resistance to erosion-assisted corrosion will come from the application of multiple thin layers of extremely hard and chemically inert thin films such as

carbides, nitrides, borides, and silicides of the refractory metals. The multiple layers should consist of alternate films of high and low Z materials. It is anticipated that the energy being imparted by the brine droplets and entrained particulates will be of high velocity point impact. The function of the multi-layered thin films, then, is to distribute this load over as large an area as possible to the tough substrate material. These elastic waves must then be scattered as effectively as possible. The phonons of the elastic wave transmissions are best scattered by interfaces; interface coupling is interfered with most effectively if the two mating surfaces are of grossly different atomic number. The interfaces will absorb some energy, but more importantly, they will diffract and scatter energy. The point impact will, therefore, be broadened to an area impact on the underlying tough surface.

The following materials are being investigated for thin film layered coatings using Ti-6Al-4V as the initial substrate material:

High Z Number		Low Z Number	
Tungsten Carbide	Tantalum Carbide	Boron Carbide	Aluminum Oxide
Hafnium Carbide	Niobium Carbide	Mixed Silicide Oxide	
Tungsten Boride	Mixed Silicide	Silicon Carbide	Silicon Oxide
		Titanium Nitride	Titanium Boride

As a starting point, an attempt will be made to achieve thin-film ultra-adherence of all of the above compositions to surfaces of the Ti-6Al-4V substrate. The initial adherence studies are being done on flat stock instead of standard wearplate specimens. The flat stock specimens allow testing for adherence by the following two methods:

1. Diamond indentation and draw followed by scanning electron microscopy to determine compliance, and
2. Diamond wear tests where 10- μ m diamond is rubbed against the test surface until failure occurs.

While neither of the above tests examine films for impact resistance, they do critically examine the presence or absence of ultra-adherence. The second test, while giving some estimate of surface hardness, has its greatest value as a test for ultra-adherence.

In addition to the two tests above, it is planned to test selected specimen flats at impact angles ranging from 0.79 to 1.57 rad (45° to 90°) in expanded brine or, at the very least, in the fresh water facility

Depending upon the preliminary results obtained with these flats, a subsequent series of films will be prepared on standard wearplates for field testing.

2.2. Stress Corrosion Cracking

a) Introduction

High static stresses due to the centrifugal forces, which are proportional to the material density, will be developed in the rotating turbine wheel. Based on the behavior of various materials in chloride containing environments and their strength-to-weight ratio, Ti-base alloys appear to be the favored materials for turbine applications in the geothermal field environment. Static stresses of the order of 350 MPa (51 ksi) are estimated for a Ti alloy turbine wheel. Superimposed will be cyclic stresses arising, in part, from the cyclic impact of the exhaust from the nozzles. Therefore, the effect of the environment on limiting the material to withstand either static or cyclic loading must be considered. In cyclic loading, the effect of a corrosive environment is to cause a continuous drop in fatigue strength relative to that obtained in an inert environment and without the appearance of a well defined fatigue limit. Under a static load, failure may occur at a stress level considerably below the yield strength of the material in an inert environment. Both of these phenomena should be similarly affected by similar environments and, since studies to static (noncyclic) loading are more widely documented, we will address the question of static loading as an illustration of the problem. Needless to say, in the final choice of materials, both static and cyclic testing must be done; however, for the initial screening process of many materials we have elected to use the much simpler static loading techniques.

The failure (cracking) which occurs under the combined action of a static stress and corrosion is referred to as stress corrosion cracking (SCC). It does not take place if either the stress or the corrosion action act independently. It occurs predominantly in alloys and seldom in pure metals. Stresses may be due to applied loads, residual stresses, or to the wedging action of corrosive products. One of the more insidious characteristics of SCC is that frequently the alloy is virtually, or almost, inert to the environment in which SCC occurred. For example, trace quantities of chloride in drinking water can cause failure within several hours for most

stainless steels loaded to below their yield strength. In general, the susceptibility of a given material to SCC refers to a specific environment. Frequently, it is the presence of only trace amounts of some constituent in that environment that causes the damage, i.e., different alloys or groups of alloys are susceptible to different environments and, furthermore, this susceptibility will vary with even minor changes of a given environment. The pH, temperature, and oxidizing potential are also important parameters. Thus, although it may be advisable for economical or logistic reasons that initial screening tests on various candidate materials be performed in simulated environments, it is extremely important that the final selection of materials is based on analyses made from their exposure in the actual service environment.

The literature is prolific with examples of industrial failures, laboratory test results, and mechanistic interpretations related to SCC. Such information may have to be used as a first-round guide in the selection of candidate materials for service in what may appear to be a similar environment. One cannot state apriori that the final choice will be among these materials, for testing must be performed in the actual environment. This is especially true for geothermal brines. Information available on chlorides is related largely to sea water compositions, boiling MgCl_2 solution, and to a lesser extent various other (noncontaminated) chlorides. Neither the pH nor the oxidizing potential is usually controlled or specified. Other constituents such as H_2S and CO_2 that are present in the brines are most likely absent.

Very little information is available on SCC in geothermal brines -- and different brines may be expected to behave differently -- and since chloride-containing solutions are one of the most aggressive environments causing SCC, the need for extensive preliminary screening of materials is obvious. Using the information available in the literature and consulting with experts in industry and other laboratories, we have selected a number of Ti-, Fe-, Ni-, and Co-base alloys as possible candidate materials for SCC experiments in our laboratory and in the field. Most of the materials have been received.

b) Laboratory SCC Experiments (R. B. Shroyer and A. Goldberg)

Since the most likely candidates for the turbine wheel and nozzle will be Ti-base alloys, emphases are on testing such alloys. A number of Ti-base alloys were tested for their susceptibility to SCC in simulated Niland brine (16.4 NaCl-3 KCl-8.1 CaCl₂-bal H₂O in w/o) at 105°C. The solution was continuously purged with argon and maintained at a pH of 3. Bent beam, notched specimens supported in a constraining jig (constant strain) and measuring 13.0 mm wide by 100 mm long by approximately 1.3 mm thick were used. In the previous quarterly we pointed out the possible difficulty of screening Ti-base alloys for SCC under fixed strain conditions. Results of this quarter indicate that this is indeed the case.

A number of samples were exposed as follows: A notch 125 mm deep was milled in the center of the tension side of each sample using a diamond-tip scribe. The sample was then loaded in the constraining jig, immersed in the test solution and finally the notch was hand scribed lightly to expose fresh metal surface below the oxide. Samples were removed and examined following various intervals of about 100 to 200 hours. Following macro and micro examination for cracks and pitting, the samples were replaced in the test cells and rescribed each time. Table 2.5 lists the alloys tested and the total exposure time. No evidence of any cracking was detected. Pitting was observed in only one alloy, Ti-5Al-6Sn-2Zr-2Mo-0.25Si, and it

TABLE 2.5 EXPOSURE OF Ti-BASE ALLOYS TO 4-POINT BENT BEAM LOADING IN SIMULATED NILAND BRINE AT 105°C, pH of 3, PURGED CONTINUOUSLY WITH ARGON

Alloy	Exposure, Hours	
	Outer Fiber to 90% Yield	Plastic Requirements
Ti-8Al-1Mo-1V	451	458
Ti-6Al-2Sn-2Zr-2Mo-0.25Si	458	451
Ti-5Al-5Sn-2Zr-2Mo-0.25Si	451	451
Ti-6Al-4V	451, 1370	451, 1370
Ti-6Al-6V-2Sn	458	451
Ti-3Al-8V-6Cr-4Mo-4Zr	458	451

was undoubtedly due to the initially poor surface condition of the as-received material. The material was evidently deeply pitted from pickling, and it may be that such pits were not completely removed on polishing (320 grit) the specimens prior to testing. This pitting was first observed following 309 hours of exposure. In addition, some very slight pitting was observed along an edge of one of the Ti-6Al-4V specimens. In both cases, pitting did not appear to increase with further exposure.

In order to provide conditions that might be more likely to lead to SCC, all these specimens were additionally strained in small increments in the test cells following each examination after further exposures. Again, no SCC could be detected. The sum of the incremental strains was in the range of 10 to 15%, which was calculated using the bent beam formula for the outer fiber strain. Maximum total exposure was 2275 hours for two Ti-6Al-4V specimens. The remaining samples listed in Table 2.4 were exposed for total lengths of time ranging between 1128 and 1363 hours. These tests were then discontinued.

Following the inability of introducing SCC using fixed strain techniques, we have initiated the use of the constant strain rate tensile deformation-to-failure technique for screening the Ti-base alloys. Two environmental brine cells were designed and have been built for such tensile testing. Tensile specimens of several Ti-base alloys are presently being machined for these tests, (Ti-4Al-3Mo-1V, Ti-6Al-2Sn-4Zr-6Mo, Ti-15V-3Cr-3Al-3Sn, Ti-3Al-8V-6Cr-4Mo, Ti-6Al-4V ELI, Ti-6Al-4V and, finally, Ti-8Al-Mo-1V as a material which should show susceptibility to SCC). The alloys will be tested in different heat-treated conditions. Details of the testing system and specimens will be presented in the following quarterly with the expected experimental results.

As alternatives for the turbine wheel, we will examine several non-Ti-base alloys. These are, MP35N, Haynes 25, Inconel 718, PH 13-8, and PH 15-7. All but MP35N are on hand. These will be heat treated to various strength levels and will be tested in the form of U-bend specimens until the constant strain-rate-to-failure units are available (for the non-Ti-base alloys).

c) Field Tests (A. Goldberg, R. E. Garrison)

In the previous quarterly, we described the technique to be used for preliminary screening of materials for SCC in the geothermal field. This involved adapting the wear plate holder to accommodate three constrained strip specimens which are to be exposed with the wedge wear plates to the impinging expanded brine. Two of the specimens will overlap in contact with each other to provide conditions for crevice corrosion. Some 300 strip specimens are now available for such exposure. These consist primary of Ti-base alloys.

Field systems for the constant strain rate-to-failure SCC tests and for the erosion fatigue tests are still in the very preliminary design stages.

2.3 General Corrosion Tests (A. Goldberg and H. De Coursey)

In addition to the nozzles and turbine wheel we will be concerned with corrosion of the turbine case, the turbine exhaust system, effluent reinjection lines and well casings. We will, therefore, examine a number of materials that may be considered as candidates for these components. Results of the corrosion studies for the Industrial Support Program will provide useful information which must, however, be taken with some caution since the corrosion behavior in the modified brines may be quite different than that behavior indicated from results obtained in "raw" brine. We are, therefore, planning to examine various materials exposed to the effluent from the modified brines.

Three 102-mm diameter elbows just downstream from the three nozzle-wearplate test stations at the LLL field unit will serve as test specimens. We are presently in the process of ordering materials which will be fabricated into these elbows. We will examine typical API steels, a series of Cr-Mo steels, stainless steels, and commercial purity and slightly alloyed Ti materials. Along any given cross section, the elbow will be subject to a continuous variation in erosion/corrosion conditions which should become more damaging from the inner to the outer radius. Turbulence of the flow will also vary on passing from inlet to outlet. Thus, the elbow specimen should offer excellent screening for a wide range of flow conditions of the chemically modified brines.

3. Industrial Support Program

3.1. Evaluation of Corrosion and Erosion Failure

a) Introduction

An important aspect of the Industrial Support Program is surveillance of corrosion problems. This involves the repeated inspection of plant components in service, the analysis of failures, and the recommendation for replacement parts and/or design modification.

We completed the analysis of pitting corrosion failures of a wellhead casing and surface pipe which was described in the previous quarterly. Two additional failed parts -- pressure sensing tubing from Magmamax Well No. 3 and an elbow from the SDG&E Geothermal Test Loop Facility -- are presently being analyzed. The UCID, in which we discuss potential problems related to the separator drums, 0.316 L stainless steel claddings, is in press. This report was summarized in the previous quarterly.

b) Pitting Corrosion of Carbon Steel Pipe Material (A. Goldberg and L. B. Owen)

In the previous quarterly we described some preliminary metallographic observations on sections of a wellhead casing pipe and surface pipes that were perforated by pitting corrosion. The analyses of these pipes have been completed and a paper will be written on this work. An extended abstract has been submitted to the Electrochemical Society for presentation at their October 1976 meeting.

The pipes had been used in connection with various field activities at the Sinclair No. 4 well, where an acidic ($\text{pH} \sim 5.5$), reducing brine is produced at a temperature of 200°C . At depth, the dissolved-solids content of the brine is about 25 w/o. However, as the brine flows to the surface, flashing occurs so that salinities reach 30 w/o at the wellhead. The brine consists primarily of Na, K, and Ca chlorides, with minor constituents including transition metals, Si, CO_2 , and H_2S . It is likely that during intermittent operation of the well over a period of several months, metal surfaces had been exposed to atmospheric oxygen. Furthermore, surface pipes were inadvertently flushed with oxygenated irrigation water on at least one occasion. Perforated pipe sections totalling about 4 m in length were sent to LLL for analysis.

A continuous layer of corrosion product was found on brine-exposed surfaces. Within this layer, numerous bowl-shaped pits were observed. Microhardness measurements of the corrosion product in the pits gave reproducible values on the Mohs scale and falls within the range of 5.5 to 6.5 reported for Fe_3O_4 . The presence of Fe_3O_4 was confirmed by x-ray diffraction; no other phases were detected. This is also consistent with the observed characteristic light grey, microscopic, as-polished appearance of Fe_3O_4 . The formation of Fe_3O_4 can be ascribed to the oxidation of ferrous ions and/or hydroxides by water and O_2 . However, significant amounts of O_2 should also have resulted in the formation of Fe_2O_3 [or $\text{Fe}(\text{OH})_3$]. The absence of the ferric state suggests that the ingestion of O_2 was minimal. The presence, however, of even trace quantities of O_2 in chloride solutions greatly increases the tendency toward pitting. It is possible that any ferric products formed during previous shutdowns were reduced to a lower state of oxidation during flow of the highly reducing brine.

In the surface pipes, most of the pits were less than 0.5 mm deep. Although several pits penetrated the entire 7.2-mm-thick pipe wall, only one pit of intermediate depth (~ 1 mm) was found. In the well casing, however, several pits within the 1-mm to 7.2-mm range were found. Penetration of wedge-like intrusions of corrosion product into the metal substrate was common, especially within the pits. This suggests that corrosion may have been assisted by a wedging stress-corrosion-cracking mechanism made possible by the intrusion of low-density corrosion products. Etching revealed that the pearlite in the steel was usually preferentially attacked and that the dissolution of ferrite grains appeared to occur at a slower rate. Figures 3.1 and 3.2 show examples of corrosion attack of pearlite and ferrite in the wellhead and surface pipes, respectively. In each case, an example is given where pearlite appears to be preferentially attacked and another example where the attack seems to be random. (Other microstructural features of surface and pitting corrosion were presented in the previous quarterly.) Throughout the pipe, the corrosion product itself had been partially dissolved and replaced by scale consisting of iron-rich amorphous silica with entrained galena (PbS) and some chalcopyrite (CuFeS_2). Thick scale-rich deposits were observed in the pits that had perforated the pipe.

Corrosion rates had been greatly accelerated by the introduction of atmospheric oxygen during shutdown intervals. With brine flowing through

the system, pitting may have been promoted by crevice-type corrosion resulting from variations in scale-deposit thickness along the surface of the corrosion product. Such variations would affect transport and local concentration of species participating in the corrosion process. Since scale thickness increased with pit depth, the process was self-perpetuating. At some small critical pit depth, the rate of pitting increased catastrophically, ultimately resulting in wall penetration. When the pipe was breached, brine erupted violently through the orifice. As a consequence, the corrosion product was eroded and replaced by a thick deposit of siliceous scale.

c) Penetration of Elbow at SDG&E Test Loop Facility (A. Goldberg)

A 152-mm (6-in.) diameter elbow, located next to and downstream from the control valve for the first stage flash drum, had been perforated along the outer radius following approximately 150 hours of intermittent operation of the SDG&E Geothermal Test Loop Facility. The brine, flowing at $\sim 180 \text{ Mg}\cdot\text{h}^{-1}$, was supplied from Magmamax No. 1 well. The elbow had been badly eroded as revealed by extensive gouging. The perforation was patched by welding on to the outside surface a plate measuring 240 x 150 mm. The gouges were filled with weld metal. The elbow was made of A-106 plain carbon steel. The repaired elbow was not put in use and, instead, sent to LLL arriving on June 7. Analysis of the elbow which will include radiography and metallography, has been initiated.

d) Failure of Down-Hole Pressure Sensing Tubing (A. Goldberg)

Pressure sensing tubing which had been submerged for approximately one month in Magmamax No. 3 (reinjection) well was removed on May 27, 1976. The tubing measures approximately 2.5 mm O.D. by 0.8 mm I.D. and is reported to be E-Brite 26-1 (26 Cr-1Mo ferritic stainless). Sections from the tubing where it had broken off at the 396-m (1300-ft) depth level in the well and at the 209-m level at the takeup reel were received at LLL. Analysis of these sections have been initiated. Preliminary observations are: Corrosion is observed throughout the lengths of both sections, with variations in the degree of pitting; where pitting is rather severe, the tubing is brittle and easily cracks on bending; where pitting was barely

perceptible, considerable ductility (by bending) is exhibited; microscopic examination shows that the tubing is in a sensitized condition.

3.2. Corrosion Testing

a) Introduction

It is expected that in the surveillance of materials problems during the operation of the SDG&E Geothermal Test Loop Facility, especially during its early stages of operation, failures of some plant components will take place. Unacceptable corrosion rates of other components will become evident. Replacement of these components, but with different materials, will eventually have to be made. To assure that the proper substitute material is specified, a knowledge of the relative corrosion behavior of readily available structural materials in the geothermal, high salinity brines will be required. We must also address the choice of plant materials from an economical, long-range point of view, and toward this end a more extensive range of materials will have to be examined.

b) Corrosion Spools (A. Goldberg and H. DeCoursey)

Corrosion spools are presently being fabricated for insertion in one of the supply lines to the SDG&E Geothermal Test Loop Facility. These are 0.27-m diameter pipes, approximately 0.6 m in length, and are being made out of readily available "low cost" pipe materials. To date, grades Soo-90, SS 95, L-80, K-55, and B-Line are on hand (See Table 3.1). The spools have been designed so that information on pitting corrosion, crevice corrosion, and the corrosion attack of welds may be obtained.

c) Corrosion Coupons (A. Goldberg)

Corrosion racks have been designed for exposing corrosion coupons (3 x 25 x 50 mm) on a bypass loop located between Magmamax No. 1 well and the LLL Geothermal Field Test Unit. In addition to obtaining corrosion information on potential substitute plant materials, the choice of materials for corrosion coupons was selected to provide an understanding of the effect of alloying elements, especially Cr, Mo, and Ni, on the corrosion resistance of both nonstainless and stainless types of alloys. The various alloys we

TABLE 3.1 CORROSION SPOOLS FOR THE
SDG&E GEOTHERMAL TEST LOOP FACILITY
SUPPLY LINE

Grade	C	Mn	P	S	Si	Cr	Mo	Ni	Cu
Soo-90 ¹	.31	.75	.006	.010	.26	.95	.30	.00	.00
L-80 ²	.40	1.90	.04	.06	.35	--	--	.25	.35
B-Line ²	.26	1.15	.04	.05	--	--	--	--	--
A-53 ²	.30	1.20	.05	.06	--	--	--	--	--
SS-95 ²	.31	1.50	.04	.05	--	--	--	--	--
K-55 ²	.35	1.10	.04	.06	--	--	--	--	--

¹Actual Analysis

²Nominal composition, P and S maximum

have considered for exposure are listed in Tables 3.2 to 3.4. We will also expose several low strength Ti-base alloys such as Ti-Code 12, C.P. 30, and 75. In addition, we will expose some of the high strength alloys being considered for the turbine components. With but very few exceptions, all these materials are on hand; however, a number of these will have to be reduced in thickness and heat treated to the proper condition before exposure. We are giving priority to those alloys listed in Table 3.1 to obtain input for the

TABLE 3.2 SELECTED LIST OF ALLOYS TO STUDY
THE EFFECT OF Cr-Mo ADDITIONS
TO STEELS CONTAINING 2% Ni

	%Cr	%Mo	%Ni	Material Inventory
Low Plain Carbon Steel	0	0	0	On Hand
A204-Grade B	0	0.5	0	On Hand
SAE 4330	0.8	0.4	1.8	On Hand
A387-Grade 12	0.9	0.5	0	On Hand
Soo-90 (Modified 4130)	1	0.2	0	On Hand
A387-64 Grade D	2.2	1.0	0	On Hand
H-11	5	1.5	0	To be Delivered
502-1/2 Mo	5.6	0.5	0	On Hand
9Cr-1Mo	9.1	1	0	On Hand
410SS (Martensitic)	12	0	0.26	On Hand
405SS (Ferritic)	12	0	0.50	To be Delivered
422SS	12	1	0	To be Delivered
430SS	17	2	0.43	On Hand
18-2	18	2	0.25	On Hand
E-Brite	26	1	0.12	On Hand
29-4	29	4	0	On Hand
29-4-2	29	4	2	On Hand

development of an alloy which will show a minimum combined investment/
replacement cost for the expected life of a plant.

TABLE 3.3 SELECTED LIST OF ALLOYS TO STUDY
THE EFFECT OF Ni-Mo ADDITIONS TO STAINLESS
Fe- and Ni-Rich Alloys ($\approx 20\%$ Cr)

	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Mn</u>
Nitronic 33	18	3	0	14
21-6-9	21	6	0	9
AL-216	20	7	2.8	8.4
304 SS	18	10	0	2 max
316L and 316 SS	17	13	2.5	2 max
Nitronic 50	22	13	2.2	5
317L SS	18	14	3	2 max
IN 862	21	24	5	0.13
AL-6X	20	24	6.5	1.7
IN 800	21	32.5	0	0.75
20CB-3	20	34	2.2	2 max
IN 825	21.5	44	3	0.40
IN 718	19	52.5	3	0.2
IN 625	21.5	61	9	0.25

All of these materials are on hand, although some in limited quantities and sizes.

TABLE 3.4 MISCELLANEOUS MATERIALS ON HAND
WHICH SHOULD EXHIBIT ACCEPTABLE HIGH RESISTANCE TO CORROSION

	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Others</u>
Haynes 6B	30	2	1	2Fe, 3.8W, 58Co
IN 600	15.5	76	0	8Fe
IN 833	12	7	0	Fe Base
Hastelloy C-276	15	58	16	3.6W, 2.5Co, 18Fe
Hastelloy G	22	45	6.5	1W, 25Co, 21Fe 2Ta + Cb

d) Electrochemical Corrosion Tests (G. E. Harrer and A. Goldberg)

Equipment is being designed and assembled, and plans are being formulated to carry out several types of electrochemical corrosion measurements of numerous alloys in high-temperature, high-salinity geothermal brines. Measurements will be made at the LLL Geothermal Field Test Unit with brine at $\sim 220^{\circ}\text{C}$ and ~ 1.4 MPa (200 psi). Alloys to be tested are essentially those listed in the previous section 3.2.c; the corrosion electrodes and corrosion coupons will be from the same stock. The purpose will again be to provide screening for plant and substitute plant materials and to gain information which will provide input for alloy development of economical corrosion resistant alloys.

At the LLL Field Test Unit, tests will be conducted both in unmodified brine (with special attention to the effect of scaling on corrosion), and in brine modified chemically to reduce scaling (where the corrosion rates will probably be higher). The facility for corrosion tests in unmodified brine will be located sufficiently close to the wellhead (MagmaMax No. 1 well) so as to closely approximate conditions within the well. Scale buildup will be an important parameter in these tests. Provision will be made to preheat the test probe-electrode assembly to brine temperature with pressurized steam so that accurate measurements may be initiated at zero time without any prior scale buildup.

In addition to the field tests, a laboratory facility is being developed at LLL for preliminary testing of specimens and equipment concomitant to their use in the field. Two laboratory hoods equipped with all necessary service and venting facilities have been installed and are now in use. We have acquired the basic equipment and many accessories for laboratory electrochemical corrosion measurements. Tests in the laboratory will be confined to simulated brine, ambient pressures, and temperatures $< 110^{\circ}\text{C}$. To obtain information on the effect of (simulated) environmental variables beyond those available in the field, samples will be sent to ORNL for electrochemical measurement in their high temperature, high pressure laboratory autoclave. An informal cooperative working arrangement has been agreed upon between LLL and ORNL (John Griess and Franz Posey) for testing of samples, exchange of information, and loan of components.

Three basic types of measurements will be carried out in the Geothermal Field. The first, linear polarization resistance (LPR) measurements, will be carried out with a Petrolite Instrument, Model M-103 corrosion rate meter, together with an M-510SSE probe assembly inserted into the brine loop. Measurements of open-circuit corrosion potentials and current-vs-potential (polarization) behavior of materials will be made using a Petrolite "Potentiodyne" instrument and a suitable reference-electrode assembly that will withstand the severe environment of the Niland brine. Polarization and LPR measurements can in theory yield information on corrosion phenomena more rapidly and more completely than the weight-loss coupon technique, but few such measurements have ever been made under such harsh conditions as exist in the field.

The basic feasibility of the LPR technique will be tested using the single-probe test instrument and specimens acquired from Petrolite, as well as some fabricated at LLL. To date the LPR equipment has been tested successfully in the laboratory and the field test facility has been designed. If the field tests appear to give useful information, consideration will be given to carrying out tests with multiple probes using a multiple-ring instrument so that the large number of candidate alloys to be examined can be tested more quickly and economically.

To carry out the polarization and corrosion-potential measurements, we will use a reference-electrode assembly being developed at ORNL by Griess and Posey. Some modification of the test facility will be required. The Potentiodyne instrumentation for the polarization field studies has been checked out satisfactorily in the laboratory.

e) Corrosion of Expansion Nozzles (A. Goldberg)

Scaling in chemically modified brine from Magmamax No. 1 well will be examined through the use of converging-diverging nozzles at the LLL Field Test Unit. These nozzles will contain a 330-mm long, 0.034 rad (2°) diverging nozzle which includes a 273-mm long expansion attachment that will experience a temperature drop of the order of 100°C . These nozzles will be exposed for periods ranging from a few hours to 48 hours, and they will provide the opportunity to study the effect of temperature and brine conditioning on corrosion.

Accordingly, a number of materials, typical of those listed in Tables 3.2 to 3.4, as well as some Ti-base alloys, will be fabricated into nozzle expansion attachments for combined scaling and corrosion tests. These nozzle inserts are presently being fabricated from 304SS, AISI 1018, AISI 4130, and Ti-6Al-4V.

Two nozzle expansion attachments which had been exposed for scaling studies, one at Sinclair No. 4 well and a second at Magmamax No. 3 (reinjection) well, have recently been examined for corrosion. The expansion attachment and mating nozzle throats were made of 304SS. Both diverging sections were about 655 mm long. The first nozzle was exposed for 5.75 hours to the brine and had experienced a temperature drop from 225 to 110°C from throat to exit along the diverging length. The expansion attachment had suffered considerable grain boundary corrosion attack. The second nozzle was exposed for three hours; the corresponding temperature drop was from 174 to 82°C. No significant corrosion was apparent for this nozzle.

Figure 3.3(a) shows a view of a polished transverse section taken from the Sinclair No. 4 well nozzle attachment about 70 mm from the exit end (approximately 120°C). A view of an etched transverse section near the throat of the same nozzle attachment (182°C) is shown in Fig. 3.3(b). Both views are at the same magnification. Penetration by intergranular corrosion was considerably greater at the higher temperature (and also where less scale had been deposited, which suggests that some of this difference may be due to the protective nature of the scale). It is clearly seen in Fig. 3.3(b) that the steel is in a sensitized condition and if it had been exposed under any significant load, it surely would have failed catastrophically in that period of time. Residual weld stresses and internal brine pressure may have, in fact, contributed to the observed corrosive attack. The second nozzle attachment, which did not show any corrosive attack, had not been sensitized (except slightly in the heat-affected weld zone). Both nozzles had been exposed to reducing brines.

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Fig. 2.1 Variable angle wear plate fixture. Nozzle insert (not shown) is set in the nozzle holder such that the flow of the expanded fluid is directed onto the wear plate. The wear plate is rotated about an axis perpendicular to the flow direction and fixed in position.

(a)

Scale

Corrosion product

Steel casing

200 X

(b)

Scale

Corrosion product

Steel casing

200 X

Fig. 3.1 Views showing corrosion attack into wellhead steel casing exposed to Niland geothermal brine: (a) general tendency for preferential attack of pearlite is indicated, (b) both pearlite and ferrite appear to be attacked at random. From wellhead at Sinclair No. 4.

(a)

As-polished

500 X

(b)

Electroetched in oxalic acid

500 X

Fig. 3.3 Type 304 SS nozzle with 4:1 expansion ratio, exposed 5h-45 min to brine from Sinclair No. 4 well: (a) near exit end of nozzle; $T \approx 120^{\circ}\text{C}$; average scaling rate $\approx 325 \mu\text{m}\cdot\text{h}^{-1}$, (b) near throat; $T \approx 182^{\circ}\text{C}$; average scaling rate $\approx 20 \mu\text{m}\cdot\text{h}^{-1}$; note preferential attack along sensitized grain boundary areas.

(a)

Scale

Corrosion
product

Steel pipe

500 X

(b)

Mixed scale/
corrosion product

Corrosion
product

Steel pipe

500 X

Fig. 3.2 Views showing corrosion attack into surface steel pipe exposed to Niland geothermal brine: (a) general tendency for preferential attack of pearlite is indicated, (b) both pearlite and ferrite appear to be attacked at random. From surface pipe at Sinclair No. 4 well.