LOCALIZED CORROSION IN MATERIALS
FOR GEOTHERMAL POWER

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FINAL REPORT

A. R. Troiano and R. F. Hehemann

Case Western Reserve University
Department of Metallurgy and Materials Science
Cleveland, Ohio 44106

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ABSTRACT

The influence of 16 different geothermally related environments on a number of potentially useful steels was examined for both general and localized corrosion and at ambient and 150°C.

Variation in chloride concentration of 1-20 percent generally demonstrated only minor aggressiveness in acidified solutions. In general, the presence of H₂S raised the corrosion rate. However, very low concentrations (10ppm) indicated higher rates than in saturated brines. This is rationalized on the basis of the inability to develop a semi-protective film at the low H₂S concentration.

The corrosion rate for the Cr-Mo steel was unexpectedly high at ambient, but improved substantially at 150°C. The Ni-Cu-Cb steel consistently demonstrated excellent resistance in all environments, except the 10ppm H₂S at ambient. At 150°C there were no exceptions to its superior performance

Maximum pit depth studies, analyzed statistically, indicated that the Ni-Cu-Cb alloy was the most resistant to localized attack. A "clean" (low inclusions) Mn-C and a clean vacuum melted steel ranked well. A comparison of two almost identical Mn-C steels one "clean" and one "dirty" clearly indicated the deleterious influence of inclusions on the tendency for localized corrosion. The profiling of a protected section of a creviced or pitted sample helped to delineate the nebulous line of demarcation between general and localized corrosion in these low alloy steels.

Table of Contents

	page
Abstract.....	i
Table of Contents.....	ii
Introduction.....	1
Literature Review.....	5
Key Corrosive Species.....	16
Materials and Method.....	24
Results and Discussion.....	30
a. Weight Loss.....	30
b. Linear Polarization.....	34
c. Pitting and Crevice.....	35
d. Autoclave Tests.....	37
e. Quantitative Pitting.....	40
Summary.....	47
References.....	49
Acknowledgements.....	57
Tables.....	58
Figures.....	104
Appendix.....	141

HYDROGEN SULFIDE STRESS CORROSION CRACKING IN MATERIALS FOR GEOTHERMAL POWER

Introduction

The rapidly growing demands for energy in the past decade has emphasized the need for increased various sources of energy. Geothermal fluid is one that holds promise and is in fact being utilized to a limited extent already in the USA. The two general areas of geothermal fluid usage are electric power generation and direct applications such as space heating, agricultural stimulation and general process heat.

Development of U.S. liquid dominated geothermal resources is in the early stages, but power plants using this type of resource are already operational for example at Weirakei, New Zealand and Cerro Prieto, Mexico. There are numerous geothermal resource areas in the United States. Some have been designated as Known Geothermal Resource Areas (KGRA's) with potential for extraction of thermal or electrical energy. Seven such liquid dominated KGRA's are Salton Sea, California; East Mesa, California; Heber, California; Mono-long Valley, California; Baca, New Mexico; Beowawe, Nevada; Raft River. Idaho.

A major problem associated with the development of

geothermal energy is the highly corrosive nature of the brine from which steam is flashed.⁽¹⁻³⁾ The high corrosiveness of the brine arises from the combination of elevated temperatures (up to 350°C), the presence of high salt contents, dissolved carbon dioxide and hydrogen sulphide, and substantial amounts of calcium sulphate, calcium carbonate and silica. The volumes of fluid involved in geothermal applications are generally too large for chemical inhibitors to be economically effective. Thus, materials selection appears to be a realistic route to corrosion control. Availability of durable and cost effective materials for processing geothermal fluids has, therefore, a definite impact on the development of geothermal energy.

Another intrinsic difficulty arises from scale formation. Scaling tendencies of a given resource depend on its temperature and the concentration of relatively minor concentration species. As the brine cools, it becomes supersaturated in solids, notably the salt content of the brine and minor components as silica, calcium, carbonate, sulphate and heavy metal ions. Precipitation of these solids in solution or on equipment surfaces can cause erosion as well as set up occluded cells with attendant high localized corrosion.

Uniform and localized corrosion are the two main types of corrosion that are usually encountered. However,

the former can be accommodated by judicious choice of materials and appropriate design (i.e. wall thickness, prevention of galvanic coupling, use of protective coating, etc.). Localized corrosion, on the other hand, is much more difficult to control. These forms of attack involve pitting, crevice corrosion, stress corrosion cracking, blistering associated with hydrogen uptake as well as erosion and corrosion fatigue. One way of working with geothermal fluid involves the use of special alloys which have adequate corrosion resistance. This is a costly approach and may involve relatively scarce alloying elements. The low thermal grade of some geothermal resources precludes the high capital cost of a plant built with specialty materials.

Hydrogen sulphide is frequently present in hot brines, although usually only in parts-per-million concentration. The sulphide induced failure mechanisms imposes severe limitations on the use of high strength alloys in geothermal systems, much the same as it does in sour oil and natural gas wells.⁽⁴⁻¹⁰⁾

A recent report⁽¹¹⁾ provides excellent guidelines for the use of structural materials in these environments. Experience at Weirakei, Cerro Prieto and Raft River indicates that copper base and aluminum base alloys have high uniform corrosion rates. In addition, these materials are

also susceptible to localized attack. Therefore, it has been concluded that these materials are unsuitable for use in these liquid dominated resources.

Low alloy constructional steels, on the other hand, can serve for down hole applications provided that oxygen free conditions exist. In particular, these steels exhibit relatively low corrosion rates and are relatively free of localized attack in air free bore water at elevated temperatures. In addition, the low cost, availability and ease of fabrication of low alloy constructional steels make them attractive materials for down hole components such as casing, tubing, etc. However, there are strength level limitations in sour environments.

The ferritic and austenitic stainless steels, on the other hand, suffer from pitting and crevice corrosion both in the relatively low salinity and low H_2S brines encountered at Raft River as well as in the high salinity sour brines characteristic of Weirakei and Cerro Prieto. The stainless steel function quite satisfactorily for many components under the steam dominated conditions encountered at the Geysers provided that the steam remains relatively dry and free of oxygen.⁽¹²⁾

Both evaluation and control of corrosion phenomena in geothermal systems is complicated by the variability of the environment; for example, the broad range of chloride

content and of pH between sources. In addition, the nature of the corrosion problem also varies among different components of the system. For example, flashing removes the non-condensable gases but concentrates the dissolved solids in the remaining brine. This increases pH which would tend to reduce corrosive attack but it also increases the tendency for scale formation and susceptibility to localized attack since scales provide unpredictable sites for nucleation of pits and crevices. Steam condensate, on the other hand, tends to be particularly corrosive as a result of its low temperature, high concentration of acidic gases and the difficulty in avoiding oxygen contamination. It is difficult to simulate the brine chemistry, and therefore, the laboratory tests in simulated geothermal fluids need to be verified by testing under field conditions. It is apparent that no single environment can suffice for a complete evaluation of geothermal environments.

Literature Review

Fundamentals of General and Localized Corrosion

The basic electrochemical condition for uniform dissolution of a metal in an electrolytic solution is the continuous and fast exchange between the anodic and cathodic sites. But this is rather an ideal behavior since the

exchange is hindered by the electrochemical heterogeneity both of the metal and of the solution, and so permanent anodic and cathodic areas are set up, and it follows that the metal dissolution is localized. This type of localized corrosion occurs under conditions where the access of electrolyte is restricted due to a special geometry of the corroding material (i.e., riveted plates, threaded joints, gasket etc.), or due to the existence of some deposits (i.e., corrosion products, scales etc.). Such cases where corrosion takes place under conditions of restricted diffusion are generally known as "Occluded Cell Corrosion", in which the chemical composition of the corroding solution inside the occluded cavities would be different from the chemical composition of the bulk of the solution. Pitting, crevice, intergranular corrosion and SCC are the typical examples of the localized corrosion phenomenon.

Localized corrosion is common in materials that rely on the integrity of a protective or passive film for corrosion resistance. However, other materials such as constructional steels some of which develop moderately protective films, are also susceptible to this kind of attack. Pitting and crevice corrosion are similar in the sense that both are often associated with the localized breakdown of a passive film on the metal surface.

Electrochemical methods enable us to determine that

potential which characterizes the tendency of the given metal for pitting in a given solution. The breakdown potential⁽¹³⁾ E_b , characterizes the resistance of metals to pitting corrosion and therefore, E_b can be considered as a measure of susceptibility. The more positive E_b , the more resistant is the material to pitting.

Pourbaix⁽¹⁴⁾ distinguishes between two characteristic potentials, namely the "breakdown potential, E_b ", determined by measuring the polarization curve from negative to positive potential and the "protection potential, E_p " ($E_b > E_p$) obtained when the measurements are performed in the reverse direction. At the breakdown potential, a sudden and pronounced increase in current density occurs, the passive film ceases to be protective and pitting corrosion takes place. On the other hand, the protective potential is one below which the steel stops corroding. Thus a knowledge of breakdown potential and protective potential for a given steel in a given solution enables us to predict the corrosion behavior of this steel.

However, the applicability of electrochemical methods to the determination of pitting and crevice resistance has been questioned for many years.⁽¹⁵⁻²³⁾ Conflicting results have been reported with the use of different test methods and different alloy compositions within the austenitic and ferritic stainless steel classifications.⁽²⁴⁻²⁷⁾

Only limited data are available on the pitting and crevice corrosion resistance of constructional materials particularly with respect to geothermal environments. Syrett et al⁽²⁸⁾ have studied the pitting resistance of engineering materials in geothermal brines found in Imperial Valley of California and this study shows excellent correlations between field exposure and laboratory test data with the electrochemical measurements of the breakdown and protection potentials.

It has since long been known that the S content has a deleterious effect on steel from a corrosion point of view.⁽²⁹⁻³²⁾ Excellent reviews of the literature⁽³³⁻⁴²⁾ are available on the importance of nonmetallic inclusions for the initiation of localized attack.

Wranglen⁽⁴³⁻⁴⁵⁾ cites that localized attacks are initiated at sulphide inclusions in carbon and stainless steels. In stainless steels, the sulphide inclusions are usually less noble than the surrounding passive surface and they are therefore selectively dissolved which results in micropits. On the other hand, in carbon steel and Ni, the sulphide inclusions are usually more noble than the surrounding matrix which is therefore attacked preferentially. Regions containing FeS, MnS, CaS and especially mixed sulphide-oxide inclusions are most susceptible to preferential attack. Data presented by Szklarska-Smialowska^(46,47) show that inclusions of FeS are much more

detrimental than inclusions of MnS in spite of the lower solubility of FeS in aqueous solutions. Wranglen⁽⁴⁴⁾ pointed out that the greater effect of FeS can be explained by (1) the higher solubility of FeS in the matrix of the steel and (2) the higher electrical conductivity of FeS. The effect of FeS upon corrosion of steel has been well known within the oil industry ("sour" oil wells with high concentration of H_2S).

Wranglen⁽⁴⁵⁾ attributes the variation of corrosion attack of different steels in the same structure to the morphology and composition of the inclusions. The number and degree of active sites are dependent on melting practice, processing and heat treatment. Wranglen⁽⁴⁴⁾ also pointed out that the steel contains both active and inactive sulphide sites and the active sites are surrounded by a matrix containing a fine dispersion of submicroscopic sulphides. Since the small particles of sulphide have higher solubility than large ones, the anodic areas as a result of hydrolysis of metal ions tend to become acid, thus facilitating the dissolution of sulphides with the formation of H_2S and HS^- ions. He suggests that the corrosive effect of sulphides is due in part to this increase in $S^{=}$, HS^- , and H_2S activity in the solution as the sulphide dissolves. The reason why sulphide ions, $S^{=}$ and HS^- , are activators which greatly accelerates localized corro-

sion is apparently related to their high electric polarization and consequent strong contact adsorption on metal surfaces.⁽⁴⁸⁾

In contrast to the evidence cited by Wranglen, Ek-lund⁽⁴⁹⁾ stated that only a small proportion of the inclusions present have any influence on selective attack in the steel. He, however, recognized that the influence of sulphides on corrosion depends significantly on their composition, the presence of oxide and duplex inclusions (CaMn) S and the nature of the surrounding matrix.

The origin of selective attack in unalloyed steels is still the subject of much controversy. Wallwork and Harris⁽⁵⁰⁾ studied the morphology of localized attack in several low carbon steels where inclusions may play only a minor role. According to them, pitting especially for the more severe pits was not usually associated with inclusions. They also observed that corrosion rate and morphology of the pits varied from steel to steel and attributed this to the variations in steels arising from different melting practices, and not specifically to the inclusions.

Cron⁽⁵¹⁾ studied the localized corrosion behavior of steel and related it to the size and spacing of the carbide phases. He suggested that the carbide becomes a cathodic site assisting the cathodic reaction and accelerating the

dissolution of the ferritic phase. Payer and Staehle⁽⁵²⁾ have investigated the dissolution behavior of carbides in aqueous environments and concluded that the dissolution of carbides is a function of potential, pH and anion present in solution. The stability of the carbides, according to them, could be related to the stability of corresponding metal and the nature and stability of carbide containing films that formed following dissolution of the carbides.

Gainer and Wallwork⁽⁵³⁾ examined the effect of alloying elements (such as Cr, Al, Ni and Cu) on pitting. According to them, small additions (<1 wt%) of chromium and aluminum segregate to nonmetallic inclusions in the steel and cause more active sulphides and duplex sulphide-oxide inclusions which result in increased anodic potential on the steel surface and thus increased activities. In addition, these elements also partition to the matrix and reduce the activity of the matrix. Thus, although Cr and Al considerably reduce the uniform corrosion, their additions lead to pitting. However, when the chromium content is sufficiently high (>12 wt%), it becomes beneficial in reducing pitting corrosion because of the formation of a protective film on the steel surface. Addition of copper and nickel also reduced the susceptibility to pitting and uniform corrosion.

The effect of different alloying elements on the sus-

ceptibility of Iron-chromium-nickel alloys to pitting corrosion has been discussed in Kolotyркиn's review article,⁽⁵⁴⁾ from which it appears that the tendency to pitting decreases as the concentration of nitrogen, nickel and especially chromium and molybdenum increase.

The influence of heat treatment, plastic deformation and applied stress on localized corrosion phenomena have received relatively little systematic attention. The role of metallurgical microstructure on general and localized corrosion in constructional steels is not well-documented. However, it is known⁽⁵⁵⁾ that fine structures with uniform carbide distribution such as tempered martensite are more resistant to SCC in hydrogenous environments than the more coarse structures such as ferrite-pearlite mixtures (normalized). There are a few recent studies^(35,56-58) concerning the influence of heat treatment and cold work on pitting in different austenitic stainless steel. From these studies it seems that plastic deformation which does not mechanically damage the passivating oxide film, does not affect pitting. Also, heat treatments leading to greater homogeneity of the material increase the resistance to pitting.⁽⁵⁴⁾

Nucleation of pits can be delayed by polishing. Most often the susceptible sites for pitting are grain boundaries which are especially inhomogeneous with regard to chemical composition and structure. Tomashov⁽⁵⁹⁾ found that the

value of the breakdown potential, E_b is shifted toward more positive potentials as the grain size is increased from .005 to 0.07mm. He proposed that fine grained steels should be more susceptible to pitting, since they contain more grain boundaries.

Although many notable contributions have been made towards understanding the effects of plastic deformation on the corrosion of metals,⁽⁶⁰⁻⁶²⁾ many questions remain unanswered. The relationship between heat treatment, plastic deformation and their effect on corrosion resistance of low carbon steel has been reported recently.⁽⁶³⁾ Certain treatments will promote precipitation and growth of iron carbides in a ferrite matrix of low carbon steel. These carbide particles are fractured during deformation creating separations at the carbide ferrite interface, which can act as crevices that allow corrosive substances to penetrate and concentrate and thus cause accelerated corrosion.⁽⁶⁴⁾

Influence of plastic deformation on corrosion behavior of iron and steel has been investigated by Green and Saltzman.⁽⁶⁰⁾ Plastic deformation increases the rate of oxidation reaction resulting in increased corrosion rates under deaerated conditions where the cathodic reaction is the activation controlled reduction of hydrogen ions. But in aerated neutral solutions, the corrosion

of iron and steel is controlled by the diffusion rate of dissolved oxygen in solution and is thus independent of metallurgical variables⁽⁶⁵⁾ such as plastic deformation, heat treatment and composition. The phenomenon of localized corrosion has been mostly in the case of alloys that passivate. Due to the complexity and unpredictable nature of this form of corrosion, the proposed theories are of limited help in explaining and predicting the observed phenomena. In the case of constructional steels the problem is further complicated by the simultaneous occurrence of uniform and localized corrosion.

Localized behavior in many aqueous corrosion processes occurs under conditions where the access of electrolyte is restricted, either because of special geometry of the corroding material or due to the formation of deposits, leading to conditions of restricted diffusion. However, this characterization is more true of crevice corrosion, where both environment and cleanliness of steel play a relatively minor role. In the case of pitting initiation the single most important factor seems to be the cleanliness of the steel which depends on the level of inclusion variables.

The powerful electrochemical methods unfortunately cannot be applied for determination of pitting tendency of nonpassivating metals or alloys such as low alloy and

carbon steels in aggressive environments. The measurement of the number, depth, width and shape of the pits in a suitable standard solution seems to be the only direct method of evaluating extent of pitting in these cases.

It has long been considered that even a semi-quantitative analysis of pit initiation and growth is essentially a statistical problem.⁽⁶⁶⁻⁷⁰⁾ One consequence of this statistical behavior is that the total area examined becomes a highly significant variable in the translation of laboratory studies to full scale components. Extreme value statistics⁽⁶⁷⁾ have been used in predicting the deepest pit and thus useful life in terms of failure by perforation.

Aziz⁽⁶⁸⁾ has detailed a statistical analysis of maximum pit depth data for aluminum. Pit depth distribution curves as a function of time consisted of two superimposed curves. A "J" shaped curve resulted from pits which initiated but ceased to grow after a certain period of time and a "bell-shaped" curve which resulted from pits that initiated and continued to propagate. The maximum pit depths obtained on each of replicate samples were analyzed by the statistical theory of extreme values using the appropriate probability paper. He demonstrated that the maximum pit depth is linear with the logarithm of the exposed area. This provides a method of extrapola-

ting pitting data on small samples obtained in the laboratory to large field installations and also allows the extraction of more information from a limited number of pit depth measurements.

Eldredge⁽⁶⁷⁾ has considered the application of extreme-value statistics in predicting the perforation in oil well tubing as measured by relatively crude caliper surveys. For the purpose of analysis, he developed a graphical method known as the Pit Depth Rank Chart. This is essentially a plot of maximum pit depth versus rank of pitting intensity.

Key Corrosive Chemical Species Present in Geothermal Fluids

Geothermal fluids are complex mixtures of corrosive chemical species whose characterization is difficult. The key species are hydrogen ions, chloride ions, H_2S , CO_2 , carbonate and bicarbonate ions, NH_3 , ammonium and sulphate ions. Typical concentrations of key corrosive chemical species in fluids from seven "Known Geothermal Resource Areas" (KGRA's) are shown in Tables 1 and 2.⁽¹¹⁾ From these tables it is apparent that there is a wide variation in the chemistry of the different geothermal resources and accordingly these variations make it difficult to define typical concentrations of key species.

Although concentrations of species vary in different geothermal resource areas, some generalizations about the

corrosive effects of these key species on constructional materials can be made.

A. a) Effect of Hydrogen Ion (pH):

The uniform corrosion rate of low carbon and low alloy steels increases rapidly with the lowering of pH. The critical pH below which rapid corrosion can occur is in the range of 5 to 7. This is illustrated in Figure 1, for relatively low temperature degassed sea water.⁽⁷¹⁾ On the other hand, pH has little effect on the pitting susceptibilities of stainless steels at low temperature. Neither pitting potentials nor corrosion potentials are affected significantly over the pH range of major interest (4 to 9) for geothermal systems.⁽²⁾

b) Effect of Chloride Ion:

The chloride concentration in KGRA fluids falls in the region of 3 to 15% (as NaCl); chloride concentration below 3% (NaCl) has little effect on the uniform corrosion rate of mild and low alloy steels but chloride concentrations as high as 10 to 30% (as NaCl) give higher corrosion rates (Figure 2).⁽⁷²⁾

Chloride ions give rise to local breakdown of the film that protects many metals. As a result of localized penetration of this film; pitting, crevice corrosion and SCC occur. Stainless steels become prone to localized attack as the chloride concentration increases. Although both

pitting and crevice corrosion are encountered in geothermal brines with stainless steels, the latter is often the more severe problem since stainless steels are frequently used in complex equipment where crevice attack is more readily initiated.

The minimum concentration of chloride ions necessary for initiating pitting corrosion in a given solution of unaggressive anions can be measured. The minimum concentration of Cl^- ions for localized corrosion attack on Fe-Cr and Fe-Cr-Ni alloys in 1N H_2SO_4 are given in Table 3⁽⁷³⁾ where it appears that the minimum Cl^- concentration increases with chromium content up to 25%. The "Critical pitting potential (E_p)" is known to be a function of the nature and concentration of aggressive ions i.e. Cl^- , and temperature. This is difficult to measure and different authors report different values for the same system. Vetter and Strehblow⁽⁷⁴⁾ determined the critical pitting potential of iron for Cl^- , Br^- , I^- and ClO_4^- , independent of pH. The Cl^- concentration versus dependence of E_p was developed by them as, $E_p = -0.29 - 0.125 \log [\text{Cl}^-]$, which is very similar to the Nernst equation.

The dependence of critical pitting potential on the chloride ion concentration is shown in Figure 3 for 304 stainless steel, from which it is evident that this steel becomes more susceptible to localized corrosion as the

chloride concentration increases.⁽¹⁵⁾ Figure 4 shows the variation of corrosion and pitting potentials with chloride concentration,⁽¹¹⁾ from which it appears that steels should be immune to pitting in deaerated chloride solutions since the corrosion potential is more active than the pitting potential. As the chloride concentration increases the difference between E_p and E_{corr} is gradually reduced.

c) Effect of H_2S :

Presence of hydrogen sulphide can promote the rate of general corrosion in low alloy steels.⁽⁷⁵⁾ In the presence of H_2S , an FeS layer may form on the steel and if part of this layer flakes off, the localized attack is intensified due to galvanic coupling. Also, the adsorption of sulphide ions on the steel surface catalyzes anodic dissolution.

Stainless steels, on the other hand, are generally resistant to corrosive attack in sea water containing H_2S and NH_3 .⁽⁷¹⁾ However, H_2S may cause pitting of 316 stainless steel in acidic solutions by retarding the formation of passive layers and initiating localized attack in the regions of low pH.⁽⁷⁶⁾

d) Effect of Sulphate ($SO_4^{=}$):

If the Cl^- concentration is low, sulphate becomes the main aggressive ion that promotes the uniform corrosion of low alloy constructional steels. But, its effect is less

aggressive than Cl^- in promoting a localized type of attack. Sulphate can inhibit the pitting of stainless steels in chloride solutions.

e) Effect of Oxygen:

The introduction of small amounts of oxygen can greatly accelerate the uniform corrosion rate of mild steel as illustrated in Figure 5. (71)

The uniform corrosion rate of most stainless steels is low in geothermal fluids; but many are subject to severe pitting and crevice corrosion in the presence of small quantities of oxygen. With oxygen present in the geothermal fluid, the reduction of oxygen becomes an important cathodic reaction, and with the formation of oxygen differential cells, the nucleation and growth of new pits or the accelerated growth of existing ones would be intensified further.

f) Effect of Co_2 and NH_3 :

Presence of Co_2 indirectly affects corrosion by the buffering action of the aqueous species such as H_2Co_3 , HCo_3^- and Co_3^{--} . H_2Co_3 increases the uniform corrosion rate of mild steel in acidic solutions (pH 3 to 5), due to acceleration of the hydrogen evolution reaction. (77)

H_2Co_3 , therefore, would not have as adverse an effect on localized corrosion as H_2S . No direct evidence for the effect of Co_2 on the pitting susceptibilities of stainless steels have been found in the literature.

Not enough information is available on the effect of NH_3 on the general and localized corrosion of engineering materials used in geothermal systems. Data⁽⁷¹⁾ shows that the uniform corrosion rate of mild steels is increased by the presence of NH_3 in degassed sea water. NH_3 absorbed in the condensate tends to neutralize the acidity produced by CO_2 and H_2S , but the amount of acidic species present in most geothermal sources are much larger than that of NH_3 .

g) Effect of Scales:

Scales or solid deposition can significantly influence the material's performance. Goldberg and Owen⁽⁷⁸⁾ studied pitting corrosion and scaling of carbon steel in geothermal brines. They found that the corrosion product (Fe_3O_4) was covered with scales deposited from brine. These scales consist of heavy metal sulphides dispersed in an Fe-rich, amorphous silicate matrix. Although scale deposits may protect from uniform corrosion, localized variations of thickness, density, and composition, as well as presence of cracks and voids may yield conditions favorable for pitting. The scales are porous and contain many fine micro-cracks.^(79,80) These cracks can expose fresh metal to the brine if the corrosion product is ruptured.

B. Influence of Temperature:

Not much data is available on the influence of tempera-

ture on the corrosion of constructional steels in geothermal brines. However, Shannon⁽⁷²⁾ reports a decrease in corrosion rate of low carbon steels with increasing temperature (100°C to 250°C range) in simulated geothermal fluids at a constant Co_2 partial pressure. This observation could be explained in terms of the formation of more protective magnetite films, as well as an increase in pH of the solution at constant Co_2 partial pressure with increasing temperature. A different source reports an increase in corrosion rate of carbon steel with increasing temperature in an environment having high chloride concentration in the absence of Co_2 .⁽⁸¹⁾ This is illustrated in Figure 6.

Temperature has a substantial effect on susceptibility to localized corrosion. Generally, pitting increases as the temperature increases. Figure 7^(2,82) shows that increasing the temperature drastically affects the pitting potential but the corrosion potential is relatively constant.

The influence of temperature on the breakdown potential of pure iron has been investigated by only a few people. One study⁽⁸³⁾ indicated that the breakdown potential of pure iron in a relatively alkaline low chloride solution became more noble with increasing temperature following an initial decrease between 25°C and 125°C. This is illus-

trated in Figure 8.

Pitting susceptibility in stainless steels increases with increasing temperature (Figure 9) by shifting the pitting potential towards more active values.⁽⁸⁴⁾ An initial rapid decrease in pitting potential is often followed by a much slower decrease or nearly constant value at higher temperatures. This study suggested that pitting resistance might be improved in the temperature range of 102-250°C, and that little difference exists between the pitting and corrosion potentials in high chloride fluid at elevated temperatures.

C. Effect of Flow Rate

Localized uncontrolled flashing of geothermal steams can cause high flow rates in the system which will produce bubbles of non-condensable gas, causing impingement attack. Also the entrained solids in the stream can cause erosion-corrosion.

The influence of flow rates on corrosion in mild steel⁽⁷¹⁾ is shown in Figure 10 for sea water at 250°F, from which it is evident that in the range of 5-7 ft./sec., the corrosion rate is low but beyond this range the corrosion rate increases rapidly.

Materials and Methods

I. Corrosion Rate from Weight Loss Measurements

Materials and Treatments

Table 4 gives the compositions of the low alloy constructional steels examined for general corrosion. All these alloys were about .100" thick and received in the hot rolled condition.

Test specimens were cut from plate into $1\frac{1}{2}$ " x 1" coupons with a $\frac{3}{16}$ " diameter hole in the top center for mounting on a glass rod. Heat treatment was performed in a purified nitrogen atmosphere at controlled temperatures, subsequently quenched and tempered. The heat treating temperatures and times for each steel are given in Table 5. All specimens were surface ground and stress relieved. All samples were polished to a 600 grit finish, washed with water, rinsed with methanol, air dried and weighed. The early crevice corrosion samples were prepared by placing a teflon disc on one side of the samples and wrapping them crosswise with rubber bands according to ASTM Standard G 48-76. (85)

Environments

In view of the wide variation in geothermal brines no attempt was made to simulate any specific geothermal environment. The first test environment was the standard NACE

solution for sour environments, which is a deaerated aqueous solution of 5% NaCl, 0.5% acetic acid, saturated with a continuous flow of H_2S .⁽⁸¹⁾ The NACE solution was modified later to examine the influence of H_2S and chloride concentration as well as pH levels.

Ambient Temperature Tests

Samples were mounted on a glass rod in a dessicator so that no two samples touched. The glass rods were supported in grooves cut in a cylindrical stand made of glass and then the unit was immersed in the environment. The test procedure involved deaeration with nitrogen both before and after the specimens were introduced, and maintaining a continuous flow of H_2S throughout the entire test period. The test set up used at ambient temperature is shown in Figure 11.

Elevated Temperature Tests

High temperature autoclaves were used for 300°F temperature tests approximating downhole temperatures.

The test procedure involved mounting the specimens on a glass rod placed in a teflon holder. A maximum of four specimens were tested per run. The recommended procedure of continuous bubbling of H_2S ,⁽⁸⁶⁾ employed for tests at ambient temperature was not possible for the autoclave tests because of the pressure. Rather, the test solution was purged with N_2 for four hours followed by

saturation of H_2S by bubbling for two hours. A schematic is shown in Figure 12.

The specimens were exposed to the environment for 10 days unless otherwise specifically noted. At the conclusion of the tests, the samples were chemically cleaned in a 10% H_2SO_4 (by weight) solution containing Rodine as an inhibitor to remove adherent corrosion products; then washed with water, rinsed with methanol, air dried and weighed. The composition of the cleaning solution and the cleaning conditions are given in Table 6. General corrosion rates were determined in terms of $mg/dm^2/day$ from the weight loss and total surface area of each specimen.

II. Corrosion Rate from Polarization Resistance

This method uses polarization data obtained in the region of the corrosion potential. It has been demonstrated⁽⁸⁷⁾ that for iron and steel in media of varying corrosiveness, the polarization potential is a straight line function of the applied anodic or cathodic currents at low current density. Since the slope, $\Delta E/\Delta I$, has units of resistance, this term is often called polarization resistance. Originally developed by Stern and Geary,⁽⁸⁸⁾ this technique has been widely used to study different corroding systems.⁽⁸⁹⁻⁹²⁾

The specimens for these tests were one cm^2 plates with a wire spot-welded to their backs and otherwise prepared the same as the weight less specimens. The three

electrode technique was employed using a working electrode, a cylindrical platinum counter electrode, a luggin capillary connected to a saturated calomel reference electrode, and a gas inlet (see Figure 13). The environment was a deaerated aqueous solution of 5% NaCl and 0.5% acetic acid. Polarization resistance was measured from the plot of over-voltage versus applied anodic and cathodic current. Corrosion rates were calculated from the Stern-Geary relation.⁽⁸⁸⁾ The reported corrosion rates are the average of consecutive cathodic and anodic values.

III. Modified Crevice Corrosion Tests

For these tests the specimens were cut into 2" x 1½" coupons with a 3/16" diameter hole in the top center for mounting the specimens on a glass rod. They were cut so that the longitudinal direction of the specimens were parallel to the rolling direction. Prior to test, the specimens were abraded with 240 grit paper to provide a uniform surface finish free of scale and dirt. The edges were then treated in a solution containing HF, HNO₃ and distilled water to eliminate the edge inclusion effect. Finally the specimens were polished to a 600 grit finish, rinsed in water, dipped in acetone, air dried and weighed.

As stated earlier, the ASTM⁽⁸⁵⁾ crevice corrosion test specimen configuration was first employed. It proved to give erratic results, largely because of the unequal and variable pressure the rubber bands placed on the teflon.

Accordingly, a new test method developed at ARMC⁽⁹³⁾ was introduced. This involves two cylindrical TFE-fluorocarbon crevice blocks fastened to the test specimen by passing a sleeved bolt through a $\frac{1}{4}$ " diameter hole in the center of the specimen and positioning a block on either side of the specimen as shown in Figure 14. The sleeve avoided metallic contact between the bolt assembly and the specimen. The crevice blocks measured 0.75 inch in diameter and 0.25 inch thick, with 12 radial slots .063 inch wide and 0.03 inch deep cut in one side. A torque of 80 oz.-in. was applied on the bolt using an adjustable torque screwdriver.

The test environment selected initially was the standard NACE solution because it could provide a basis of comparison with the extensive literature employing this environment. However, it was felt that the standard NACE environment was not entirely relevant to geothermal sources, since the dissolved gases observed in most geothermal brines are predominantly carbon dioxide with smaller amounts of H_2S . So more generally relevant environments were employed for the modified crevice corrosion test.

These environments were prepared by mixing controlled amounts of CO_2 , H_2S and N_2 through a gas flow meter (see Figure 15). The tests were conducted using two different gas mixtures containing N_2 , CO_2 and H_2S in a volumetric ratio of N_2 to CO_2 of approximately 65-35, with H_2S at 2%

volume (20,000 ppm) and 10 ppm by volume.

IV. Pit Depth Measurements

Materials

Five of the more promising alloys selected from the early screening in terms of general corrosion were selected for the pit depth study. These are indicated on the appropriate figures and their analyses are given in Table 4.

Procedure

As indicated in the Literature Survey, it is recognized that pitting is a statistical phenomenon. Therefore, it becomes necessary to determine the distribution of the number of pits as a function of the depth of each pit. This has been accomplished by means of a surface profiling technique. Two sophisticated instruments were employed for this purpose.^(94,95) Their operation is quite intricate so a description of their analytical features and the details of their operation are best considered separately in an Appendix. However a general schematic layout can be seen in Figures 16 and 17.

Briefly, the technique involves surface profile measurements with the aid of the Proficorder and Profilometer. These instruments function to measure "roughness" and thus afford a comparison among materials in terms of extent of pitting. Since pits are distributed throughout

the total area of the specimen and the tracing pattern is linear, in order to obtain a distribution of pit depth, traces are run in many different directions on each specimen. Analysis is based on Proficorder charts for quantitative depth and Profilometer peak counts for depth distribution.

Results and Discussion

Ambient Temperature Test

General Corrosion Rates From Weight Loss Measurements

Ambient temperature tests were conducted in brines containing 1, 5 and 24% NaCl, and acidified with 0.5% acetic acid. The results of general corrosion rates on the basis of measured weight losses for ten days exposures in deaerated brines and brines with and without H₂S are presented in Tables 7-12, with some observations on surface appearance after exposure.

Chloride Concentration

The influence of chloride on the general corrosion rates in sour environments has been open to some question, particularly for low alloy constructional type steels. It appears from Tables 7-12 that the 24% NaCl generally exhibited similar or lower rates of corrosion, while there was no consistent pattern between the 1 and 5% chloride environ-

ments. For example, the Ni-Cu-Cb alloy exhibited mdd values of 18, 16 and 18 respectively in the 1, 5 and 24% NaCl environments without H_2S and 35, 38 and 52 mdd respectively saturated with H_2S . Other comparisons such as with alloy V-1551 and $2\frac{1}{4}Cr-1Mo-.19C$ are equally relevant.

The general inhibitive influence of chlorides above 5% can account for the reduced corrosion in these constructional type steels,⁽⁹⁶⁾ and is consistent with studies on the influence of chloride on sulphide stress cracking (SCC) of constructional steels where the susceptibility to SCC was the same or even slightly improved at the higher chloride concentrations.⁽⁹⁷⁾

Hydrogen Ion Concentration (pH)

The pH may vary widely in different sources and even within the same source, with time. However, the CO_2 which is the primary source of acidification can be lost in the condensate. Thus, indicated values of pH 5-6 may not always reflect true down-hole values. This leads one to suspect that many of the sources are more acid than indicated. General corrosion rates in neutral solutions containing 5% NaCl, deaerated, and with and without saturated H_2S are presented in Tables 14 and 15. Comparison of these with previous ones clearly reveals that the acidification of the brines substantially increases the corrosion rate of these steels, regardless of the presence of H_2S . Steel

#28, a low carbon-manganese alloy, provides a good example where in the neutral brine (Table 14) it exhibits a corrosion rate of 8 mdd (1.5 mpy) and at pH 3 (Table 9) the rate is virtually doubled at 16 mdd (2.9 mpy). In the presence of H_2S , the rate also doubled but at a higher level.

Hydrogen Sulphide (H_2S)

In general, the influence of H_2S on these types of steels accelerates corrosion. In the presence of H_2S , a weakly adherent film of iron sulphide will form which offers no real basic protection against corrosion. Alloy #28 presents a good example of the increased corrosion induced by H_2S . In a neutral brine without H_2S the rate was 8 mdd (1.5 mpy) as indicated above and saturated with H_2S it was 78 mdd (14.3 mpy). In the acid brine the corresponding rates were 2.9 mpy and 22.5 mpy respectively.

Duration of Test

Tables 15 and 16 give the corrosion rates obtained after 30 days exposure for several of the more promising materials as compared to the usual 10 day exposure. It is clear that in the acid environment without H_2S (Table 16), the 10 and 30 day runs give essentially the same rate. In short, a true steady rate is attained under these conditions. However, in the presence of saturated H_2S (Table 16), the rate has definitely decreased during the period

from a 10 to 30 day exposure. Presumably this effect would level out with longer exposures.

The inference is strong that the iron sulfide film which will thicken with time is providing a measure of protection to general corrosion. Although the iron sulphide film may partially shield the steel from the environment, it would be a mistake to consider this film protective largely because of its fragility and poor adherence,

Alloy Evaluation

In the neutral 5% chloride solution all the alloys examined exhibited excellent corrosion resistance with rates in the range of 1-2 mpy. However, in the same environment saturated with H_2S the rates increased substantially and varied between approximately 4.5 and 29 mpy, depending on the analysis (compare Tables 14 and 15).

On the average, in all the various environments the Ni-Cu-Cb exhibited the lowest corrosion rates, generally less than 9 mpy and often less than 4-5 mpy. This alloy is a very low carbon precipitation hardening fine grained steel. The beneficial effects of copper in ranges above .20% on atmospheric corrosion have long been appreciated.⁽⁹⁸⁾ However, to the best of our knowledge there has not been any evaluation of this type of copper containing alloy in this class of aggressive environments. Both #28 and #80 steels generally exhibited good resistance to corrosion in

all the brines. Both of these steels are essentially economical low-carbon, 1.5% manganese steels (typical N80 grades) with only residual amounts of other alloying elements and low sulphur. The only difference between the two steels was that #28 had employed rare earth (REM) additions in the deoxidation process and was a substantially "cleaner" steel.

Most of the other steels exhibited a more or less mixed response and generally a somewhat higher corrosion rate in the various test environments. The higher alloy steels containing chromium were somewhat surprising indicating high corrosion rates for 4135 and $2\frac{1}{4}\text{Cr}-1\text{Mo}-.19\text{C}$ in almost all environments. Rates in the acidified H_2S environments varied from 495 mdd (90 mpy) to 723 mdd (130 mpy). Even in the neutral H_2S environment rates of 111 and 160 mdd (10-30 mpy) were observed (Tables 8 and 14). This behavior is not only contrary to expectations but does not agree with results obtained in a test well.⁽⁹⁹⁾ However, the well tests were conducted at the higher well temperature and substantially lower H_2S concentrations.

General Corrosion Rates by Linear Polarization

Examination of Table 17 reveals that the corrosion rates by linear polarization yield substantially higher values than by weight loss measurements. However, those alloys which appeared promising in the weight loss tests

also generally indicated better corrosion resistance by linear polarization.

The literature clearly indicates that the corrosion behavior is strongly dependent upon the type and rate of formation of the corrosion product films.⁽⁹⁹⁻¹⁰⁰⁾ The weight loss specimens invariably had a corrosion product film whose thickness depended on the corrosion rate. On the other hand, the linear polarization specimens were essentially film free, undoubtedly related to the fact that a complete test involved approximately only one hour of exposure. It is felt that the weight loss method gives more realistic values, although the linear polarization values appear to rank order the alloys more or less in the same sequence.

Pitting and Crevice Corrosion

As stated earlier, the ASTM crevice corrosion test specimen configuration was employed initially. The weight loss tables (Tables 7-14) have a column indicating the loss of weight with the teflon artificial crevice. It is important to realize that these numbers are not even a semi-quantitative measure of localized corrosion. The severe limitations of this approved technique were detailed earlier. Any serious consideration of localized corrosion will be developed later in this report employing more quantitative methods.

However, a few brief comments may have some broad general relevance. A cursory examination of Tables 7-14 reveals that acidification of the brines increased the susceptibility to localized attack and the introduction of H_2S (saturation) into the acidified brines of varying chloride concentrations seemed to reduce the tendency to crevice corrosion. On the other hand in the neutral solutions, H_2S did not appear to have any influence on localized attack. None of the alloys suffered any localized attack in the neutral solutions either with or without H_2S (Tables 13 and 14).

Most of the alloys exhibited some pitting in the acidified brines with 1 and 5% NaCl; but with 24% NaCl alloys Ni-Cu-Cb, 1551 and #4 did not indicate any pitting and/or crevice attack. These alloys were very "clean" (low inclusion count), and alloys 1551 and #4 in particular both possessed extremely low S contents (Table 4) which minimized the formation of sulphide inclusions. The same general behavior was apparent in the same solutions saturated with H_2S . Alloy #28 also showed little or no pitting in all environments while alloy #80, essentially the same composition, behaved poorly in terms of pitting and crevice attack. In fact, it frequently displayed surface "cracks" particularly in the H_2S environments, quite consistent with the strong hydrogenating power of H_2S .

Severe localized attack and even cracks are apparent in Figure 18 of the as-corroded surface of steel #80. A comparison of this with the corresponding surface (Figure 19) for steel #28 of essentially the same composition clearly demonstrates the difference in behavior between a "clean" and "dirty" steel.

No systematic study was conducted on the types of inclusions in these materials. However, they can be classified mostly as MnS inclusions⁽¹⁰¹⁾ and/or complex variations, possibly modified by the REM treatment. Steel #80 contained elongated inclusion stringers of rolled-out entrapped slag inclusions. These are not only nucleation sites for localized corrosion but also responsible for hydrogen induced fissures which occur even without applied stress and develop mainly parallel to the steel surface or sometimes in a step-wise pattern.⁽¹⁰²⁾ A similar comparison can be made with several other steels, but steel #80 is an extreme example of a "dirty" steel and does not necessarily reflect the performance potential of this analysis.

Elevated Temperature Tests

The corrosion rates at 150°C in both acid and neutral brines with and without H₂S saturation are given in Tables 18-23. As expected, the higher temperature raised the general corrosion rate and intensity of localized attack. It should be noted that these autoclave tests were in a

closed system so that the H_2S concentration was saturated only initially and also there was some increase in the pH.

The higher temperature tests produced variations in the relative responses of the different steels. Most interesting was 2½Cr-1Mo-.19C steel which in the absence of H_2S exhibited relatively improved performance as compared to ambient temperature tests. The Ni-Cu-Cb steel still maintained its relatively good corrosion resistance.

In general, the elevated temperature increased localized attack. Results indicate that localized corrosion was slightly sensitive to variations in chloride concentration. For example in the acidified brine of 5% NaCl without H_2S , alloys Ni-Cu-Cb and #4 exhibited good resistance to localized corrosion, while in the same solution with 1% NaCl both materials exhibited susceptibility. The behavior of the other steels for the most part was erratic and generally indicated some localized attack. As anticipated, steel #80 displayed the same problems as it did at ambient temperatures; the result of its poor quality.

Acidification generally increased the susceptibility to localized attack with the exception of alloy 4.5Cr-.46Mo-.10C (a last minute addition to the series). This material demonstrated good resistance to localized corrosion in these environments. Introduction of H_2S into the acidified brine of both 1 and 5% NaCl increased the susceptibility to pitting in most materials. Again, the addition of

H₂S, as with acidification, did not seem to destroy the relatively good resistance of 4.5Cr-.46Mo-.10C steel. On the other hand, in the neutral solution, H₂S did not appear to have any influence on localized corrosion (Tables 22 and 23).

Modified Crevice Corrosion Test

The new type of crevice corrosion tests were conducted at ambient temperature in more relevant environments containing controlled concentrations of nitrogen, carbon dioxide and hydrogen sulphide. Tables 24 and 25 give the corrosion rates obtained after 10 days exposure for the more promising materials. A cursory examination of these tables reveals that steel Ni-Cu-Cb again headed the list of corrosion performance. This alloy exhibited excellent corrosion resistance with rates in the range of 2.2-2.4 mpy. However, for the other four materials out of the five selected the corrosion rates varied between 3.84 and 5.86 mpy. Most of the alloys exhibited a slight tendency towards crevice attack but none of them suffered from obvious pitting. The photo of Figure 19 for steel #28 is quite representative of the as-corroded surface of steels Ni-Cu-Cb, #80, V-1551 and 4135. Apparently there is no qualitative evidence of severe pitting.

Quantitative Pitting Tests

This section represents an attempt to quantify pitting susceptibility. The approach is aimed at the evaluation of the deepest pit encountered since it is the single most determining factor in the perforation of geothermal well casing and tubing. A direct determination of this value is virtually ruled out because of the statistical nature of pitting corrosion in terms of both origin and propagation.

The results of the series of experiments conducted with the Proficorder are presented in Figures 20 to 30 depicting surface profiles. The environmental conditions are numbered for convenience and their description is included in Table 26. Table 27 gives the peak counts on as-polished specimens, the reference base. The peak counts for each alloy in all eight environments at each depth cut-off appear in Tables 28 to 35. A compilation of the maximum pit depth as read from the chart along with the ratio of these values to the uniformly corroded depth are listed in Table 36.

Initially, the surface profiles and peak counts were determined for as-polished specimens (Figure 20 and Table 28) which serve as the datum line. For the case of Environment #1 (1% NaCl, 2% Vol. H_2S , $N_2 + CO_2$, ambient temperature), the chart records (Figure 21) show clearly that Ni-Cu-Cb has relatively higher resistance to pitting com-

pared to other materials. Steels #28 and V-1551 also exhibit relatively better performance than either #80 or 4135M. While #80 shows a few very deep pits, alloy 4135M exhibits a larger number of deeper pits. This fact is clearly evident if we examine the ratio of maximum pit depth to the uniformly corroded depth (Table 36). The largest ratio (1.280) is obtained in the case of 4135M and next largest (0.913) occurs in #80 steel indicating their localized corrosion sensitivity Ni-Cu-Cb (0.829) shows a larger ratio than either #28 (0.749) or V-1551 (0.448). However, this is the result of its very low general corrosion rate.

The studies with the Profilometer confirm the observations based on Proficorder charts. There is close agreement between results obtained separately by each of the techniques. The deepest pit for #80 read from the chart (Figure 6) is 120 microinches and for 4135M 200 microinches which agrees fairly well with the observations based on Profilometer counting (Table 28) which indicated a range between 100 and 250 microinches. There is also good agreement in relative magnitudes between the two methods in terms of the number of pits above a certain cut-off value of depth.

Chloride Ion Concentration: In general, higher chloride ion concentration increases the pitting tendency. This

is apparent if we compare Proficorder data for 1% Cl^- and 5% Cl^- by referring to Figures 21 and 22 in conjunction with Table 36. The Profiles in Figures 26 and 27 also show this trend. Excepting Ni-Cu-Cb, all other alloys exhibited lower values of maximum pit depth in 5% NaCl than in 1% NaCl. The case of Ni-Cu-Cb which seems to be exhibiting larger values of maximum pit depth in 5% NaCl may be mainly the result of statistical variations. This is suggested by an analysis of the Profilometer peak counts for the case of 1% NaCl and 5% NaCl solutions (both 2% Vol. H_2S and 10 ppm H_2S environments) by referring to appropriate Tables.

Hydrogen Ion Concentration (pH): Acidification enhances pitting as is indicated by the data for the standard NACE solution versus 5% NaCl solution both with and without H_2S (Figure 29). Lower values of pH significantly increase pitting tendencies.

Sulfide Ion Concentration: Unexpectedly, the Proficorder and Profilometer studies clearly indicate that H_2S at the 10 ppm level is more aggressive in promoting pitting corrosion than at higher H_2S levels. For instance, if we examine Proficorder data for 1% NaCl, 2% Vol. H_2S and 1% NaCl, 10 ppm H_2S (Table 36) for all alloys there is at least a three-fold increase in the value of maximum pit depth in the 10 ppm H_2S level. This is also evident from

the relevant Profilometer peak counts. (Tables 28 and 33) where all the alloys have a finite number of peaks with depths greater than 500 microinches in the 10 ppm H_2S and none in 2% Vol. H_2S . This is illustrated again by comparison of Proficorder and Profilometer data for 2% Vol. H_2S and 10 ppm H_2S in 5% NaCl solution, although the difference is less pronounced in this case.

Temperature: Generally, the pitting tendency seems to be less at elevated temperatures. Values of maximum pit depths for the standard NACE solution at ambient temperature are approximately equal to the value at $150^{\circ}C$ (Table 36). Again, comparing Profilometer data (Tables 30 and 32, specimens in 1% NaCl, 10 ppm H_2S exhibit less pitting attack at the elevated temperature. Explanation for this unexpected behavior may reside in the fact that the gas mixture is not bubbled continuously in the autoclave tests. Thus, some or most of the H_2S may be consumed during the test.

Exposure Time: This is a significant test variable. The literature^(68,69) indicates that different exposure times have been utilized to examine the propagation of pits and their depth with the help of extreme-value statistics. Here, most of the tests involved exposure for 10 days. Proficorder and Profilometer studies on 30 day exposure

specimens are revealing. Proficorder charts (Figure 23 versus Figure 24) exhibit totally different patterns especially in the case of 4135M and to a lesser extent #80 steel. On closer examination, it becomes evident that in the 30 day exposures, shallower pits have reduced growth and deeper pits continued to grow. The question as to why the chart record for 4135M in the 30 day run exhibits characteristics akin to passivating alloys may be at least partially answered if we take into account the influence of general corrosion. Those shallow pits that have ceased to grow would have been levelled by the uniform corrosion process and only the deeper pits that continue to grow show up. It is noteworthy that steel Ni-Cu-Cb and to a lesser extent #28 and V-1551 exhibit a stabilized pitting pattern while #80, has reduced intensity of pitting when subjected to corrosion for a longer time period. These facts become self-explanatory if we consult Table 36. Profilometer studies (Tables 30 and Table 31A) help clarify the foregoing observations. Specifically, the peaks obtained for 4135M indicate the following: Number of peaks having depths greater than 5 microinches is about 400 in a 10 day exposure and is only about 150 in a 30 day period. On the other hand, the number of peaks greater than the 500 microinch depth range is only 5 in 10 days and is about 25 in 30 days exposure. In order to get a statistical "feel" of the pit distribution, ten tracings were conducted

on specimens of Ni-Cu-Cb, #80 and 4135M alloys with 30 day exposures. This result (Table 31B) indicates a quite reasonable consistency in the number of pits at a given depth "cut-off".

Alloy Evaluation:

A qualitative examination of the data obtained in Profilometer charts (Figures 21 to 30) and Profilometer peak counts (Tables 23 to 30) indicates that Ni-Cu-Cb tops the list of pitting resistant steels examined. A more quantitative treatment of a statistical nature was attempted. Unfortunately, it developed that the standard deviation was high and very nearly equal to the statistical mean depth. Simply, this means that based on these data, the statistical mean depth was not a valid quantity in evaluating the pitting tendencies of these alloys. The prime reason for this resides in the limitation of the Profilometer, which can not obtain peak counts above 500 microinches. This instrument can undoubtedly be extended to provide peak counts of greater depth and allow a valid statistical analysis. This has been planned for the future.

However, it is possible to obtain a ranking of these alloys based on the maximum pit depth data of Table 36. This is accomplished by assigning the value "1" to the minimum value occurring in the set and progressively higher

ratings in order. Table 37 summarizes the material-environment combinations along with the cumulative rank. This provides an acceptable level of information for ranking the alloys for pitting resistance, where Ni-Cu-Cb tops the list, followed closely by #28 and V-1551, and 4135M and #80 exhibit relatively high susceptibility.

The overlapping effect of general corrosion prohibits a distinction of pitting corrosion with reference to the sample surface prior to testing. In order to delineate this "original" surface, the part of the sample under teflon in the crevice corrosion test specimen can be effectively utilized. Proficorder traces with this background in the "Total" mode (see Appendix) are depicted in Figure 30. This provides a base reference surface for localized corrosion. The uniformly corroded depth assessed from the chart compares well with the mpy values. For example, Ni-Cu-Cb has an mpy value of 45.8 and when converted to the depth of general corrosion for a 10 day period, it will be about 0.00125". This is almost exactly the value (0.0012") obtained from the Proficorder Chart.

The next stage in this study will involve the application of extreme value statistics as described earlier in this report. Also, it is planned to extend the range of the Profilometer to its limits. This will allow a more complete statistical analysis. All this is contingent on continued support.

Summary

1. In acidified brines general corrosion rates were higher than in near neutral brines.
2. Chloride concentrations in the range of 1-5% were slightly more aggressive than at higher concentrations, particularly in acidified brines.
3. Exposure at 150°C increased the corrosion rate in the acidified brines with or without H₂S.
4. In general the presence of H₂S raised the corrosion rate. However, the very low H₂S concentration (10 ppm) brines demonstrated higher corrosion rates than saturation concentrations of H₂S. Presumably, this was the result of the inability to develop a substantial FeS semi-protective film.
5. The corrosion rate for the Cr-Mo steel (4135M) was unexpectedly high at ambient, but improved substantially at 150°C exposure, particularly in the absence of H₂S for both acid and neutral environments.
6. The Cu-Ni-Cb consistently demonstrated good general corrosion resistance in all environments except the 10 ppm, pH 4.5 environment. At 150°C this alloy was superior in all environments.
7. A new type of crevice corrosion test gave much more consistent results than the recommended standard ASTM configuration.

8. Pitting studies, analyzed statistically and utilizing the criterion of maximum pit depth indicated that the Ni-Cu-Cb alloy was the most resistant to localized attack. A manganese-carbon alloy (#28) and a special vacuum melted steel (V-1551) ranked next. The Cr-Mo steel (4135M) was surprisingly susceptible. Steel #80, a type similar to #28, but of poor quality (many inclusions) was by far the worst.
9. The more acid environments increased pitting in all alloys as did the 10 ppm H₂S environment.
10. The low chloride concentrations (~1%) were the most aggressive in terms of pitting.
11. Increased exposure time from 10 to 30 days yielded pitting patterns resembling those of passivating alloys; that is fewer but deeper pits. This was most evident with the Cr-Mo steel (4135M).
12. The difference in localized corrosion between ambient and 150°C exposures was minimal.
13. A quantitative comparison of the pitting tendencies of the two similar Mn-C steels clearly demonstrated the difference between a "clean" and "dirty" steel.
14. Profiling a protected section of a creviced or pitted sample aided in delineating the nebulous line of demarcation between general and localized corrosion in low alloy steels.

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TABLE 1 Typical Concentrations of Key Corrosive Chemical Species in Fluid from Seven Known Geothermal Resource Areas.

RUSA	Temperature °C and location	Properties of the Geothermal Resource						Fluid Description	Comments
		Concentration of Key Species in the Fluid (ppm)							
		pH	Cl	Total CO ₂	Total H ₂ S	Total NH ₃	SO ₄		
Salton Sea, Ca.	250 (bore-hole)	5.2	115,000	1,000	10-30	500	20	unflashed well-head fluid	These data are the results of extensive analyses of several wells, so they are representative of the resource. Variations occur; CO ₂ concentrations as high as 10,000 ppm have been measured.
East Mesa, Ca.	100-200 (bore-hole)	5.7	11,000	800	1	61	70	unflashed well-head fluid	The data are for well 6-1, which has received the most study. It may not be typical of the field. Higher pH (6.5) and lower Cl ⁻ and CO ₂ have been measured at other wells. The fluid also contains about 9 ppm Fe.
Heber, Ca.	100-200 (bore-hole)	7.1	9,000	100	<1	13	152	unflashed well-head fluid	These data are from two separate analyses of fluid from the well (Well 1). The fluid also contains about 4 ppm Fe.
Mono-Lang Valley, Ca.	175 (bore-hole)	6.5	277	180	14	0.1	96	unflashed well-head fluid	These data are for well Sedgwick 4. It is the only well for which H ₂ S concentrations were measured. Results of analyses of other species in fluids from other wells in the area agree with the results for this well.
Bore (Yellow Caldera) N.M.	171 (well-head at 110 psig)	6.0	3,770	120	6		50	flashed fluid	These data represent the results of three similar analyses of flashed fluid from well Bore 11. They are not representative of values in the unflashed fluid.
Geopline, Nev.	132 (well-head)	9.3	50	200	6	3	89	flashed fluid	These data are representative of wells Geopline 1, 2, and 4. Data for H ₂ S, CO ₂ , NH ₃ , and pH are not representative of the unflashed fluid.
Geft Stiver, Id.	146 (bore-hole)	7.2	200	60	0.1	2	61	unflashed fluid	These data are for well BRCE 1 which is well characterized. Well BRCE 2 has a similar composition. Well BRCE 3 has a similar composition except for Cl ⁻ , which is about 3 times higher.

TABLE 2 Typical Composition of Non-Condensable Gases in Seven Known Geothermal Resource Areas.

RGRA	Concentration of Noncondensable Gases	Composition of Noncondensable Gases (volume % of gas)							
		CO ₂	H ₂ S	NH ₃	N ₂	Ar	H ₂	He	CH ₄
Salton Sea, Ca.	0.2-0.3 vol % of steam	80.-90.	0.3	-	c	-	-	-	0.5
East Mesa, Ca.	no data available								
Weber, Ca.	0.2 wt % of total flow	1.4-9.5	-	-	70-92	1.0	1.8-3.8	<0.01	2.9-15
Mono-Long Valley, Ca.	0.87 wt % of steam	98.2	1.7	-	-	-	-	-	-
Baca (Valles Caldera), N. M.	1.72 vol % of steam 4.10 wt % of steam	(47,390) ^a	(567)	(6)	(109)	-	(4)	-	(6)
Geopline, Nev.	0.19 wt % of steam	97.6	0.93	1.06	-	-	-	-	0.39
Raft River, Id.	1.6 vol % of total flow	7.2 ^b	0.022	-	90.16	1.89	0.148	0.049	0.369

^aunits are ppm in steam

^bMeasured oxygen concentration was 0.459 vol % of gas. Sample was probably contaminated with air.

^cbalance is N₂ + Ar

TABLE 3 Minimum Concentration of Cl^- Necessary
to Start Pitting on Fe-Cr and Fe-Cr-Ni
Alloys in 1N H_2SO_4

Alloy	Cl^- (N)
Fe	0.0003
5.6 Cr-Fe	0.017
11.6 Cr-Fe	0.069
20 Cr-Fe	0.10
24.5 Cr-Fe	1.0
29.4 Cr-Fe	1.0
18.6 Cr-9.9 Ni-Fe	0.10

TABLE 4
Composition of Steels Tested

STEEL	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	Al	Co	V	N	Ti
Ni-Cu-Co	.03	.48	.010	.014	.25	.02	1.39	.06	1.18	-	.048	-	-	-
#28	.11	1.44	.010	.007	.21	.08	.30	.06	.20	.038	.001	-	-	-
#80	.12	1.50	.010	.008	.21	.07	.25	.06	.20	.052	.001	-	-	-
#4	.27	1.54	.006	.006	.18	.40	-	.11	-	-	-	.006	-	-
#10	.29	1.41	.009	.007	.18	.006	-	.17	-	-	-	.063	-	-
Y	.27	1.44	.009	.020	.17	-	-	-	-	-	-	-	-	-
H1 Phos	.08	.38	.105	.024	.44	1.11	.13	.04	.36	-	-	.033	-	-
V-1551	.28	.007	.001	.004	.013	.73	-	1.57	.98	-	.048	.049	-	.065
4135 Modified	.33	.86	.013	.015	.28	1.08	-	.83	-	.067	.054	-	.014	-
2 1/2 Cr-Mo-.19 C	.19	.55	.013	.008	.22	2.20	-	1.00	-	-	-	-	-	-

TABLE 5

Heat Treatment

MATERIAL	QUENCHED	TEMPERED
4135 modified #4 #10 Ni-Cu-Cb #28 #80 y V-1551 2¼ Cr-1Mo-.19C	1650°F 10 Minutes Oil Quench	1250°F 1 Hour Water Quench
High Phos	1750°F 10 Minutes Oil Quench	1250°F 1 Hour Water Quench

Samples were stress relieved @ 1100°F/10 minutes/air cooled after grinding.

TABLE 6

Composition of Cleaning Solution

H ₂ So ₄	:	100 gms
Rodine	:	0.3 c.c.
Water	:	to make 1000 c.c.
Cleaning Temp.	:	100°F.
Cleaning time	:	30 minutes

TABLE 7

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TEST AT AMBIENT TEMPERATURE**

**Environment: Aqueous solution of 1% NaCl and 0.5% CH₃COOH
pH: 3.15 - 4.30**

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	18 (N)	NA
#80	24 (N)	32 (C)
#28	34 (N)	65 (C)
Y	35 (N)	37 (C)
H1 Phos	56 (N)	43 (mc)
#4	117 (N)	118 (mc)
#10	118 (N)	98 (mc)
V-1551	166 (N)	88 (N)
2½ Cr-1Mo-.19C	389 (N)	280 (C)
4135 Modified	495 (N)	344 (C)

KEY TO TABLE:

N - No pit or crevice

C - Deep crevice

mc - Minute crevice

NA - Corrosion rate not available

* mpy = 0.1832 x mdd

TABLE 8

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TEST AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 1% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH: 3.15 - 4.30

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample with Teflon
Ni-Cu-Cb	35 (N)	39 (N)
#28	119 (N)	116 (mc)
V-1551	140 (N)	144 (N)
#80	177 (Tp + Cr)	160 (P + Cr)
Y	256 (P + Cr)	209 (P + Cr)
H1 Phos	357 (P + Cr)	288 (P + Cr)
#4	388 (N)	309 (N)
4135 Modified	518 (N)	396 (Cr)
#10	526 (N)	402 (N)
2½ Cr-1Mo-.19C	723 (N)	593 (mc)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

P - Distributed deep pits

Cr - Cracks on the surface

Tp - Tiny pits

* mpy = 0.1832 x mdd

TABLE 9

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TESTS AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH
pH: 2.30 - 4.40

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
#28	16 (N)	16 (C)
Ni-Cu-Cb	20 (N)	21 (C)
#80	20 (N)	24 (C)
V-1551	26 (N)	23 (C)
Y	47 (Tp)	44 (Tp)
2½ Cr-Mo-.19C	83 (N)	67 (mc)
Hi Phos	92 (N)	61 (mc)
4135 Modified	100 (N)	83 (C)
#4	137 (N)	99 (N)
#10	153 (N)	57 (N)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

C - Deep crevice

Tp - Tiny pits

* mpy = 0.1832 x mdd

TABLE 10

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TEST AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH: 2.30 - 4.40

MATERIAL	CORROSION RATE (mdd) *	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	38 (N)	42 (N)
#28	123 (N)	115 (N)
H1 Phos	158 (Cr + Tp)	142 (Cr + Tp + mc)
Y	162 (Cr + p)	135 (Cr + p)
#80	166 (Cr + p)	158 (Cr + p)
V-1551	178 (N)	159 (N)
#4	233 (N)	195 (mc)
#10	266 (N)	230 (mc)
4135 Modified	367 (Tp)	294 (mc)
2½ Cr-1Mo-.19C	389 (N)	308 (mc)

KEY TO TABLE:

N - No pit or crevice   mc - Minute crevice
p - Distributed tiny pits   Cr - Cracks on the surface
Tp - Tiny pits

* mpy = 0.1832 x mdd

TABLE 11

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TEST AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 24% NaCl and 0.5% CH₃COOH
pH: 2.40 - 3.80

MATERIAL	CORROSION RATE (mdd) *	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	18 (N)	27 (C)
V-1551	42 (N)	32 (N)
#10	67 (N)	32 (pT)
#80	72 (N)	53 (C + pT)
#4	80 (N)	50 (N)
H1 Phos	109 (N)	71 (mc)
Y	121 (N)	70 (C + pT)
2½ Cr-1Mo-.19C	133 (p)	95 (mc + pT)
#28	134 (N)	123 (mc + pT)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

C - Deep crevice

pT - Tiny pits under the teflon

p - Distributed tiny pits

* mpy = 0.1832 x mdd

TABLE 12

GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TEST AT AMBIENT TEMPERATURE

Environment: Aqueous solution of 24% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH: 2.40 - 3.80

MATERIAL	CORROSION RATE (mdd) *	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	52 (N)	69 (N)
#28	111 (N)	97 (N)
V-1551	119 (N)	115 (N)
#80	210 (P + Cr)	164 (P + Cr + mc)
Y	219 (P)	166 (P)
H1 Phos	228 (P + Cr)	180 (P + Cr)
#4	255 (N)	192 (N)
#10	262 (N)	222 (N)
2½ Cr-1Mo-.19C	427 (N)	348 (N)

KEY TO TABLE:

N - No pit or crevice   mc - Minute crevice
P - Distributed deep pits   Cr - Cracks on the surface
* mpy = 0.1832 x mdd

TABLE 13

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TESTS AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl
pH: 6.0 - 7.4

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
#80	5 (N)	4 (N)
Y	5 (N)	4 (N)
2½Cr-1Mo-.19C	6 (N)	7 (N)
#28	8 (N)	7 (N)
#4	9 (N)	9 (N)
V-1551	9 (N)	8 (N)
Ni-Cu-Cb	10 (N)	7 (N)
#10	11 (N)	11 (N)
4135 Modified	11 (N)	11 (N)

KEY TO TABLE:

N - No pit or crevice

* mpy = 0.1832 x mdd

TABLE 14

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE IN
TEN-DAYS TESTS AT AMBIENT TEMPERATURE**

**Environment: Aqueous solution of 5% NaCl, Saturated with H₂S
pH: 5.8 - 7.4**

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	26 (N)	29 (N)
V-1551	47 (N)	35 (N)
#28	78 (N)	87 (N)
Y	78 (Tcr)	77 (Tcr)
#80	104 (Cr)	100 (Cr)
#4	111 (N)	92 (N)
2½Cr-1Mo-.19C	111 (N)	108 (N)
#10	150 (N)	101 (N)
4135 Modified	160 (N)	128 (N)

KEY TO TABLE:

N - No pit or crevice   Cr - Cracks on the surface
Tcr - Some tiny cracks on the surface

* mpy = 0.1832 x mdd

TABLE 15

**COMPARISON OF GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN 10 AND 30 DAYS TESTS AT AMBIENT TEMPERATURE**

**Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH
pH: 2.3 - 4.4**

MATERIAL	CORROSION RATE (mdd)*	
	10 Days	30 Days
#28	16 (N)	20 (N)
Ni-Cu-Cb	20 (N)	16 (N)
#80	20 (N)	23 (N)
V-1551	26 (N)	29 (N)
4135 Modified	100 (N)	184 (N)

KEY TO TABLE:

N - No pit or crevice

* mpy = 0.1832 x mdd

TABLE 16

**COMPARISON OF GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN 10 AND 30 DAYS TESTS AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH: 2.3 - 4.4

MATERIAL	CORROSION RATE (mdd)*	
	10 Days	30 Days
Ni-Cu-Cb	38 (N)	17 (N)
#28	123 (N)	79 (N)
#80	166 (p + Cr)	124 (p + Cr)
V-1551	178 (N)	123 (N)
4135 Modified	367 (Tp)	272 (P)

KEY TO TABLE:

N - No pit or crevice

Tp - Tiny pit

p - Distributed tiny pits

Cr - Cracks on the surface

P - Distributed deep pits

* mpy = 0.1832 x mdd

TABLE 17

**COMPARISON OF CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
AND LINEAR POLARIZATION AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH
pH: 2.3 - 4.4

MATERIAL	CORROSION RATE (mdd)*	
	Weight loss (10 da)	Linear Polarization
#28	16	130
Ni-Cu-Cb	20	130
#80	20	110
V-1551	26	520
2½ Cr-1Mo-.19C	83	390
H1 Phos	92	130
4135 Modified	100	260
#4	137	390

*mpy = 0.1832 x mdd

TABLE 18

GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)

Environment: Aqueous solution of 1% NaCl and 0.5% CH₃COOH
pH: 3.1 - 5.2

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	213 (N)	201 (mc)
4135 Modified	230 (N)	217 (mc)
V-1551	262 (N)	232 (C)
2½ Cr-1Mo-.19C	273 (Tp)	272 (mc)
#28	412 (N)	380 (C)
#4	415 (N)	370 (C)
#80	536 (p)	454 (p + mc)

KEY TO TABLE:

N - No pit or crevice
C - Deep crevice
mc - Minute crevice

Tp - Tiny pits
p - Distributed Tiny pits
* mpy = 0.1832 x mdd

TABLE 19
GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)

Environment: Aqueous solution of 1% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH:

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	229 (N)	207 (C)
V-1551	232 (p)	253 (C + p)
2½ Cr-1Mo-.19C	247 (p)	223 (C + p)
4135 Modified	300 (p)	260 (C + p)
#4	360 (N)	310 (C)
#80	380 (p)	322 (p + C)
#28	383 (N)	331 (C)

KEY TO TABLE:

N - No pit or crevice
C - Deep crevice

p - Distributed Tiny pits
* mpy = 0.1832 x mdd

TABLE 20

GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH
pH: 3.0 - 5.8

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
2½ Cr-1Mo-.19C	81 (N)	93 (C)
4.5 Cr-.46Mo-.10C	134 (N)	118 (N)
Ni-Cu-Cb	274 (N)	206 (N)
V-1551	284 (N)	269 (mc)
#4	293 (N)	267 (N)
#80	298 (Tp)	248 (mc + Tp)
#10	386 (p)	440 (mc + p)
H1 Phos	428 (N)	390 (mc)
4135 Modified	450 (N)	410 (pT)
Y	622 (N)	520 (mc)
#28	669 (N)	598 (mc + p)

* mpy = 0.1832 x mdd

KEY TO TABLE:

N - No pit or crevice
C - Deep crevice

mc - Minute crevice
Tp - Tiny pits

P - Distributed tiny pits
pT - Tiny pits under the teflon

TABLE 21

GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)

Environment: Aqueous solution of 5% NaCl and 0.5% CH₃COOH, Saturated with H₂S
pH: 2.4 - 5.2

MATERIAL	CORROSION RATE (mdd) *	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	124 (N)	125 (mc)
#28	182 (N)	170 (mc + Tp)
V-1551	221 (N)	244 (C)
High Phos	234 (Cr)	196 (mc + Tp)
4.5 Cr-.46Mo-.10C	244 (N)	196 (N)
#10	256 (Tp)	244 (mc + Tp)
Y	308 (p)	269 (mc + p)
#80	414 (Tp)	323 (mc + Tp)
2½ Cr-1Mo-.19C	430 (p)	424 (p + C)
4135 Modified	508 (N)	437 (C)
#4	715 (N)	652 (mc)

KEY TO TABLE:

N - No pit or crevice   mc - Minute crevice   p - Distributed tiny pits
C - Deep crevice   Tp - Tiny pits   * mpy = 0.1832 x mdd

TABLE 22

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)**

**Environment: Aqueous solution of 5% NaCl
pH: 5.4 - 6.3**

MATERIAL	CORROSION RATE (mdd) *	
	Sample W/o Teflon	Sample with Teflon
V-1551	8 (N)	9 (N)
Ni-Cu-Cb	12 (N)	7 (N)
2½Cr-1Mo-.19C	12 (N)	13 (N)
4.5Cr-.46Mo-.10C	16 (N)	18 (mc)
Y	23 (Dp)	21 (mc + Dp)
H1 Phos	23 (N)	23 (mc)
#10	24 (Tp)	26 (mc)
#4	24 (N)	24 (mc)
4135 Modified	25 (N)	24 (mc)
#28	36 (N)	50 (N)
#80	41 (N)	56 (mc)

KEY TO TABLE:

N - No pit or crevice
mc - Minute crevice

Tp - Tiny pits
Dp - Few deep pits

* mpy = 0.1832 x mdd

TABLE 23

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS AUTOCLAVE TESTS (150°C, 60 psig)**

**Environment: Aqueous solution of 5% NaCl, Saturated with H₂S
pH: 5.4 - 6.6**

MATERIAL	CORROSION RATE (mdd)*	
	Sample W/o Teflon	Sample With Teflon
Ni-Cu-Cb	10 (N)	9 (N)
V-1551	13 (N)	11 (mc)
#4	14 (N)	15 (N)
Y	14 (p)	15 (mc)
2½Cr-1Mo-.19C	15 (N)	14 (mc)
H1 Phos	15 (N)	12 (N)
4135 Modified	15 (N)	11 (N)
4.5Cr-.46Mo-.10C	21 (N)	21 (mc)
#10	25 (p)	17 (Tp + mc)
#80	27 (N)	27 (N)
#28	31 (N)	28 (N)

KEY TO TABLE:

N - No pit or crevice   mc - Minute crevice
p - Distributed tiny pits   Tp - Tiny pits
* mpy = 0.1832X mdd

TABLE 24

GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS TEST AT AMBIENT TEMPERATURE

Environment: Aqueous solution of 1% NaCl with a
63:35:2 volumetric ratio of N₂:CO₂:H₂S
pH: 4.50

MATERIAL	CORROSION RATE (mdd)*	
	Sample w/o Teflon	Sample with Teflon
Ni-Cu-Cb	12 (N)	12 (mc)
#28	21 (N)	22 (mc)
#80	26 (N)	24 (mc)
V-1551	31 (N)	17 (mc)
4135 Modified	32 (N)	28 (mc)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

*mpy = 0.1832 x mdd

TABLE 25

**GENERAL CORROSION RATES OBTAINED BY WEIGHT-LOSS TECHNIQUE
IN TEN-DAYS TEST AT AMBIENT TEMPERATURE**

Environment: Aqueous solution of 5% NaCl with a
63:35:2 volumetric ratio of $N_2:CO_2:H_2S$
pH: 4.40

MATERIAL	CORROSION RATE (mdd)*	
	Sample w/o Teflon	Sample with Teflon
Ni-Cu-Cb	13 (N)	14 (mc)
#28	22 (N)	20 (mc)
#80	23 (N)	19 (mc)
4135 Modified	29 (N)	26 (mc)
V-1551	31 (N)	19 (mc)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

*mpy = 0.1832 x mdd

TABLE 26
ENUMERATION OF ENVIRONMENTS.

IDENTIFICATION	ENVIRONMENT
#1	1% NaCl solution with 2%Vol. H ₂ S and N ₂ , CO ₂ in the ratio 63:35, pH: 4.5, Ambient temperature, 10 day exposure.
#2	5% NaCl solution with 2%Vol. H ₂ S and N ₂ , CO ₂ in the ratio 63:35, pH: 4.4, Ambient temperature, 10 day exposure.
#3	Standard NACE solution saturated with H ₂ S, pH: 2.3-4.4, Ambient temperature, 10 day exposure.
#4	Standard NACE solution saturated with H ₂ S, pH: 2.3-4.4, Ambient temperature, 30 day exposure.
#5	Standard NACE solution saturated with H ₂ S, pH: 2.4-5.2, Elevated temperature (150°C), 10 day exposure.
#6	1% NaCl solution with 10 ppm H ₂ S and N ₂ , CO ₂ in the ratio 64:36, pH: 5.3, Ambient temperature, 10 day exposure.
#7	5% NaCl solution with 10 ppm H ₂ S and N ₂ , CO ₂ in the ratio 64:36, pH: 5.2, Ambient temperature, 10 day exposure.
#8	1% NaCl solution with 10 ppm H ₂ S and N ₂ , CO ₂ in the ratio 64:36, pH: 5.5, Elevated temperature (150°C), 10 day exposure.

TABLE 27
NUMBER OF PEAKS ON AS-POLISHED SPECIMEN

DEPTH CUT-OFF (LOWER) μ IN.	TRACING DIRECTION			
	LONGITUDINAL		TRANSVERSE	
	I	II	I	II
5	220	200	880	950
10	96	97	400	400
25	16	18	60	50
50	0	0	0	0
100	0	0	0	0
250	0	0	0	0
500	0	0	0	0

TABLE 28

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL			TRANSVERSE		
			I	II	III	I	II	III
Ni-Cu-Cb	2.2	5	215	205	200*	430	510	501*
		10	130	150	145*	340	390	390*
		25	50	48	50*	190	238	240*
		50	20	15	16*	100	94	92*
		100	4	1	2*	25	2	2*
		250	0	0	0*	0	0	0*
		500	0	0	0*	0	0	0*
#80	4.8	5	232	300		645	490	
		10	140	185		520	450	
		25	75	98		337	270	
		50	32	34		146	124	
		100	7	7		18	32	
		250	0	0		0	4	
		500	0	0		0	0	
4135 MOD.	5.7	5	401	348		630	748	
		10	262	200		510	566	
		25	159	105		365	376	
		50	80	36		228	175	
		100	14	6		85	36	
		250	0	0		0	0	
		500	0	0		0	0	

ENVIRONMENT: 1% NaCl solution with 2% Vol. H_2S and N_2, CO_2 in
 (#1) the ratio 63:35, pH:4.5, Ambient temperature,
 10 day exposure.

*Check for reproducibility on Set II

TABLE 28 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
#28	3.9	5	612	575	572	546	467	554
		10	427	290	314	321	290	328
		25	150	116	108	100	115	118
		50	32	35	22	15	26	26
		100	2	0	0	3	0	1
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0
V-1551	5.7	5	825	736	750	915	735	792
		10	628	525	520	692	500	573
		25	326	318	246	410	250	310
		50	100	175	114	135	88	122
		100	4	24	8	5	15	11
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0

ENVIRONMENT: #1

TABLE 29

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
Ni-Cu-Cb	2.6	5	335	300	297	304	332	314
		10	285	234	243	253	254	254
		25	110	112	62	102	140	105
		50	36	43	28	20	46	35
		100	7	4	0	0	4	3
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0
4135 MOD.	4.7	5	594	495	397	544	410	488
		10	407	396	294	376	301	355
		25	210	190	163	160	146	174
		50	66	68	90	64	50	68
		100	5	15	27	12	9	14
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0
#80	3.6	5	400	368	345	308	417	368
		10	271	265	258	210	258	252
		25	142	150	141	90	155	136
		50	68	67	73	44	43	59
		100	8	28	12	18	0	13
		250	0	4	0	6	0	2
		500	0	0	0	0	0	0

ENVIRONMENT: 5% NaCl solution with 2% Vol. H₂S and N₂, CO₂ in
 (#2) the ratio 63:35, pH:4.4, Ambient temperature,
 10 day exposure.

TABLE 29 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
#28	3.4	5	373	372	390	358	288	356
		10	245	241	238	236	180	228
		25	120	125	121	137	100	121
		50	37	38	45	60	56	47
		100	12	2	6	10	12	8
		250	0	0	0	2	0	0
		500	0	0	0	0	0	0
V-1551	3.5	5	484	340	254	451	307	367
		10	282	196	160	290	238	233
		25	136	101	80	147	126	118
		50	36	36	35	48	60	43
		100	0	0	7	2	7	3
		250	0	0	3	0	0	1
		500	0	0	0	0	0	0

ENVIRONMENT: #2

TABLE 30

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS			
			LONGITUDINAL		TRANSVERSE	
			I	II	I	II
Ni-Cu-Cb	7.0	5	530	460	489	525
		10	400	340	350	395
		25	200	170	206	240
		50	67	69	108	118
		100	12	11	36	25
		250	0	2	1	3
		500	0	0	0	0
#80	27.8	5	390	350	400	390
		10	290	280	346	320
		25	160	140	250	200
		50	60	57	165	120
		100	18	17	60	48
		250	4	7	14	10
		500	2	4	5	0
4135 MOD.	58.6	5	440	340	500	500
		10	350	290	420	430
		25	245	190	345	346
		50	135	115	265	250
		100	60	60	145	130
		250	15	25	19	18
		500	2	10	4	0

ENVIRONMENT: Standard NACE solution saturated with H_2S , pH:
 (#3) 2.3-4.4, Ambient temperature, 10 day exposure.

TABLE 30 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					AVER.
			I	II	III	IV	V	
#28	21.1	5	492	500	510	580	500	516
		10	395	405	421	506	340	413
		25	232	279	240	224	166	228
		50	112	170	114	77	80	111
		100	23	54	42	20	19	32
		250	4	0	0	0	0	1
		500	2	0	0	0	0	0
V-1551	28.6	5	587	688	610	589	695	634
		10	424	545	388	444	463	453
		25	250	334	265	256	240	269
		50	124	151	119	128	130	130
		100	31	32	26	30	31	30
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0

ENVIRONMENT: #3

TABLE 31 A

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS			
			LONGITUDINAL		TRANSVERSE	
			I	II	I	II
Ni-Cu-Cb	3.2	5	377	580	600	650
		10	215	305	405	425
		25	85	85	150	115
		50	30	20	32	35
		100	13	4	4	4
		250	0	0	0	0
		500	0	0	0	0
#80	18.5	5	560	320	520	455
		10	465	280	470	427
		25	380	232	380	360
		50	300	175	275	260
		100	155	85	155	145
		250	20	25	30	18
		500	4	15	9	0
4135 MOD.	49.8	5	145	185	124	123
		10	130	150	114	120
		25	120	122	107	111
		50	109	105	104	107
		100	57	66	50	47
		250	48	36	40	43
		500	30	21	35	35

ENVIRONMENT: Standard NACE solution saturated with H_2S , pH:
 (#4) 2.3-4.4, Ambient temperature, 30 day exposure.

TABLE 31 A (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
#28	14.4	5	655	640	616	671	632	643
		10	560	575	525	594	540	559
		25	446	426	428	460	394	431
		50	318	314	315	332	306	317
		100	157	135	141	130	146	142
		250	0	0	2	11	0	4
		500	0	0	0	0	0	0
V-1551	40.9	5	212	184	242	280	231	230
		10	165	140	194	243	210	190
		25	136	130	138	196	129	146
		50	97	91	120	125	83	103
		100	68	65	51	90	50	65
		250	33	41	17	33	14	28
		500	7	20	8	15	3	11

ENVIRONMENT: #4

TABLE 31 B

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS										
			LONGITUDINAL										
			I	II	III	IV	V	VI	VII	VIII	IX	X	AVER.
Ni-Cu-Cb	3.2	5	390	465	372	460	392	367	420	340	440	460	410
		10	240	230	206	285	210	270	270	198	260	295	246
		25	100	75	70	115	86	110	90	92	75	106	92
		50	30	22	30	40	23	43	23	38	17	36	30
		100	8	5	10	4	0	20	2	16	2	2	7
		250	0	0	0	0	0	0	0	0	0	0	0
		500	0	0	0	0	0	0	0	0	0	0	0
#80	18.5	5	555	573	480	600	525	600	510	560	590	515	550
		10	505	530	410	517	440	522	455	512	573	455	492
		25	420	427	341	410	358	435	370	410	455	363	399
		50	284	320	248	303	266	346	300	296	350	248	297
		100	163	160	133	160	133	220	156	146	200	120	159
		250	35	20	19	10	12	20	26	17	11	16	19
		500	7	4	6	2	0	0	4	0	0	5	3
4135 MOD.	49.8	5	160	163	162	137	132	150	175	175	141	119	151
		10	153	130	143	121	115	132	153	149	126	107	132
		25	144	122	126	115	109	130	130	146	121	105	125
		50	121	117	122	110	96	118	115	140	111	95	115
		100	84	64	67	48	60	72	72	89	55	52	66
		250	45	47	55	41	49	50	46	60	44	45	48
		500	33	35	30	35	40	30	32	35	37	43	35

ENVIRONMENT: #4

TABLE 32

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS			
			LONGITUDINAL		TRANSVERSE	
			I	II	I	II
Ni-Cu-Cb	22.8	5	627	735	600	700
		10	531	610	508	657
		25	302	345	330	425
		50	105	174	155	216
		100	9	40	28	37
		250	0	0	0	0
		500	0	0	0	0
#80	75.2	5	419	406	328	338
		10	390	372	305	320
		25	305	287	252	256
		50	225	200	200	186
		100	132	115	136	127
		250	33	45	65	52
		500	2	2	32	22
4135 MOD.	93.1	5	750	730	451	500
		10	588	676	407	430
		25	474	490	324	330
		50	326	310	220	225
		100	162	150	90	100
		250	1	0	6	4
		500	0	0	0	0

ENVIRONMENT: Standard NACE solution saturated with H_2S , pH:
 (#5) 2.4-5.2, Elevated temperature ($150^\circ C$),
 10 day exposure.

TABLE 32 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
#28	33.2	5	403	486	360	438	400	447
		10	360	367	321	366	276	338
		25	225	246	231	210	173	217
		50	121	145	172	101	90	126
		100	60	56	91	43	57	61
		250	17	10	26	4	18	15
		500	7	0	6	0	0	3
V-1551	40.4	5	810	884	847	910	937	878
		10	658	740	712	815	826	750
		25	417	482	448	600	580	505
		50	190	203	200	270	291	231
		100	36	30	43	23	48	36
		250	7	1	3	0	0	2
		500	0	0	0	0	0	0

ENVIRONMENT: #5

TABLE 33

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					AVER.
			I	II	III	IV	V	
Ni-Cu-Cb	8.2	5	630	631	645	650	620	635
		10	560	595	628	595	600	596
		25	430	503	514	490	528	493
		50	274	326	340	310	270	304
		100	147	134	140	160	132	143
		250	8	8	8	6	4	7
		500	3	0	0	1	2	1
4135 MOD.	4.3	5	295	235	276	265	306	275
		10	210	173	181	190	215	194
		25	103	123	90	116	128	112
		50	48	110	45	70	105	76
		100	22	72	27	38	55	43
		250	22	21	16	28	32	24
		500	15	2	10	6	12	9
#80	5.6	5	366	331	340	325	358	344
		10	340	320	312	320	345	327
		25	286	295	260	280	305	285
		50	225	272	221	230	278	245
		100	160	181	175	170	186	174
		250	61	72	74	65	80	70
		500	4	15	10	8	3	8

ENVIRONMENT: 1% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.3, Ambient temperature, 10 day exposure.

TABLE 33 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVG.
#28	6.5	5	435	388	520	500	450	459
		10	383	380	510	460	410	429
		25	337	322	450	390	362	372
		50	285	277	340	330	318	310
		100	196	205	207	210	230	210
		250	62	81	25	34	28	46
		500	8	8	0	0	2	4
V-1551	2.9	5	160	195	190	185	180	182
		10	155	100	100	120	117	118
		25	143	56	74	95	88	91
		50	126	40	60	78	69	75
		100	115	30	42	50	45	56
		250	76	12	22	34	27	34
		500	30	2	4	10	3	10
4.5 Cr- 0.46 Mo- 0.10 C	4.3	5	614	501	514	500	540	534
		10	500	435	447	345	420	429
		25	396	409	393	268	308	355
		50	268	340	305	190	230	267
		100	130	212	165	70	150	145
		250	10	15	16	2	1	9
		500	0	1	0	0	0	0

ENVIRONMENT: #6

TABLE 34

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					AVER.
			I	II	III	IV	V	
Ni-Cu-Cb	10.3	5	360	291	294	321	353	324
		10	315	226	250	220	285	259
		25	258	140	208	132	154	178
		50	195	100	157	66	65	117
		100	114	60	125	35	26	72
		250	32	29	38	26	2	25
		500	0	0	0	0	0	0
4135 MOD.	4.2	5	475	411	520	451	425	456
		10	381	362	430	348	309	366
		25	220	233	248	217	180	220
		50	151	167	156	139	100	143
		100	68	70	45	57	40	56
		250	4	3	2	5	1	3
		500	0	0	0	0	0	0
#80	5.6	5	645	495	544	507	578	554
		10	491	330	415	495	384	423
		25	210	178	202	183	160	187
		50	64	79	64	46	35	58
		100	5	35	10	9	4	13
		250	2	10	8	3	1	5
		500	0	0	0	0	0	0

ENVIRONMENT: 5% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.2, Ambient temperature, 10 day exposure.

TABLE 34 (CONTD.)

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					AVER.
			I	II	III	IV	V	
#28	5.5	5	510	557	528	512	450	511
		10	335	391	395	395	388	381
		25	170	205	196	215	190	195
		50	72	86	60	84	75	75
		100	35	34	25	16	26	27
		250	10	0	6	4	14	7
		500	0	0	0	0	0	0
V-1551	4.2	5	600	485	514	435	588	524
		10	525	390	380	348	450	419
		25	310	254	279	230	286	272
		50	176	149	151	133	140	150
		100	73	60	50	50	43	55
		250	0	1	0	0	0	0
		500	0	0	0	0	0	0

ENVIRONMENT: #7

TABLE 35

PROFILOMETER PEAKS ON SPECIMENS SUBJECTED TO CORROSION

MATERIAL	MPY	DEPTH CUT-OFF μ IN.	NUMBER OF PEAKS					
			LONGITUDINAL					
			I	II	III	IV	V	AVER.
Ni-Cu-Cb	3.4	5	540	340	316	460	551	380
		10	224	172	190	260	192	208
		25	50	56	60	89	60	63
		50	15	11	20	22	12	16
		100	0	0	2	2	0	1
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0
4135 MOD.	3.0	5	176	184	168	196	181	181
		10	90	80	90	104	110	95
		25	38	36	40	25	45	37
		50	11	17	20	6	10	13
		100	1	3	2	1	2	2
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0
#80	5.2	5	416	503	465	470	390	449
		10	220	252	237	195	200	221
		25	100	118	75	98	82	95
		50	57	30	24	10	8	26
		100	18	1	4	0	0	5
		250	0	0	0	0	0	0
		500	0	0	0	0	0	0

ENVIRONMENT: 1% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.5, Elevated temperature (150°C), 10 day exposure.

TABLE 36

COMPARISON OF PROFICORDER MAXIMUM PIT DEPTH DATA

ENVIRON- MENT	MATERIAL	MPY	T_G^* (μ IN.)	T_P^{**} (μ IN.)	$R = T_P/T_G$
#1	Ni-Cu-Cb	2.2	60.3	50	0.829
	4135 Mod.	5.7	156.2	200	1.280
	#80	4.8	131.5	120	0.913
	#28	3.9	106.8	80	0.749
	V-1551	5.7	156.2	70	0.448
#2	Ni-Cu-Cb	2.6	70.1	75	1.070
	4135 Mod.	4.7	129.0	60	0.465
	#80	3.6	98.1	90	0.917
	#28	3.4	93.1	40	0.430
	V-1551	3.5	95.9	50	0.521
#3	Ni-Cu-Cb	7.0	479.5	120	0.250
	4135 Mod.	58.6	1605.5	200	0.125
	#80	27.8	761.6	600	0.788
	#28	21.1	578.1	250	0.432
	V-1551	28.6	783.6	140	0.179
#4	Ni-Cu-Cb	3.2	262.2	70	0.267
	4135 Mod.	49.8	4096.4	1500	0.366
	#80	18.5	1519.7		0.296
	#28	14.4	1183.6	260	0.220
	V-1551	40.9	3361.6	500	0.149

*Thickness of material corroded in 10 day period of exposure.

**Maximum pit depth read off from the Proficorder chart.

TABLE 36 (CONTD.)

ENVIRON- MENT	MATERIAL	MPY	T_G^* (μ IN.)	T_P^{**} (μ IN.)	$R = T_P/T_G$
#5	Ni-Cu-Cb	22.8	623.8	80	0.128
	4135 Mod.	7.0	467.4	200	0.428
	#80	75.2	2061.4	400	0.194
	#28	33.2	909.6	200	0.220
	V-1551	40.4	1106.8	140	0.126
#6	Ni-Cu-Cb	8.2	224.7	200	0.890
	4135 Mod.	4.3	117.8	550	4.670
	#80	5.6	153.4	775	5.052
	#28	6.5	178.1	260	1.460
	V-1551	2.9	79.5	650	8.176
#7	Ni-Cu-Cb	10.3	282.2	250	0.886
	4135 Mod.	4.2	115.1	240	2.085
	#80	5.6	153.4	400	2.608
	#28	5.5	150.7	250	1.659
	V-1551	4.2	115.1	200	1.738
#8	Ni-Cu-Cb	3.4	93.2	85	0.912
	4135 Mod.	5.2	142.5	215	1.509
	#80	3.0	82.2	25	0.304

*Thickness of material corroded in 10 day period of exposure.

**Maximum pit depth read off from the Proficorder chart.

TABLE 37

RANKING BASED ON PROFICORDER MAXIMUM PIT DEPTH DATA

MATERIAL	ENVIRONMENT							CUMULATIVE RANK
	#1	#2	#3	#4	#5	#6	#7	
Ni-Cu-Cb	3	6	10	5	7	12	15	58
4135 Mod.	12	4	12	24	12	20	14	98
#80	10	9	21	18	17	23	17	115
#28	7	2	15	16	12	16	15	83
V-1551	5	3	11	19	11	22	12	83

Figure 1. Effect of Seawater pH on the Corrosion of 1010 Mild Steel. (71)

Figure 2. Average Corrosion Rate of Carbon Steels as a Function of Salinity. (72)

Figure 3. Effect of Chloride Ion Activity on Critical Potential for Pitting. (15)

Figure 4. Pitting and Corrosion Potentials of Steel in Deaerated Chloride Solution at 25°C. (11) Pitting Potential Curve is Drawn from Equation by Vetter and Strehblow.

Figure 5. Effect of Dissolved Oxygen on Corrosion Rate of 1010 Mild Steel in Seawater at 250° F. (71)

Figure 6. Corrosion rate of A212B Carbon Steel in Deaerated 4M NaCl as a Function of Temperature and pH. (81)

Figure 7. Pitting and Corrosion Potentials of Steel as a Function of Temperature in Heber Geothermal Fluid. (82) Data at 25°C and 200°C are Average Value Taken from Ref. (2) Due to Lack of Other Data, Linear Relationships and Ranges are Assumptions.

Figure 8. Effect of Temperature on Breakdown Potentials of Pure Iron in 0.1N NaOH + 0.1M NaCl Solution. (83)

Figure 9. Pitting Potentials and Corrosion Potentials of Stainless Steels in 4M NaCl as a Function of Temperature. (84)

Figure 10. Effect of Velocity on Corrosion Rate of Mild Steel in Sea Water. (71)

Figure 11. Ambient Temperature Setup

Figure 12. Elevated Temperature Setup

Figure 13. The Apparatus for Linear Polarization Measurements

Figure 14. Crevice Block Assembly

Figure 15. Schematic of Linde Electronic Flow Controller.

Figure 16. Schematic of Proficorder System.

Figure 17. Schematic of Profilometer System.

Figure 18. Steel #80. As Corroded Surface.
Localized Corrosion & "Cracks".
(4X). Ten Days Exposure in NACE
Solution at Ambient Temperature.

Figure 19. Steel #28. As Corroded Surface
Few Small Pits. (150X). Ten
Days Exposure in NACE Solution
at Ambient Temperature.

Figure 20. Surface profile of a typical as-polished specimen.

Figure 21. Roughness Comparison, 1% NaCl solution with 2% Vol. H_2S and N_2 , CO_2 in the ratio 63:35, pH:4.5, Ambient temperature, 10 day exposure.

Figure 21. Roughness Comparison, 1% NaCl solution (contd.) with 2% Col. H₂S and N₂, CO₂ in the ratio 63:35, pH:4.5, Ambient temperature, 10 day exposure.

Figure 22. Roughness Comparison, 5% NaCl solution with 2%
 (contd.) Vol. H₂S and N₂, CO₂ in the ratio 63:35, pH:4.4,
 Ambient temperature, 10 day exposure.

Figure 23, Roughness Comparison, Standard NACE solution saturated with H_2S , pH:2.3-4.4, Ambient temperature, 10 day exposure.

Figure 24. Roughness Comparison, Standard NACE solution saturated with H_2S , pH:2.3-4.4, Ambient temperature, 30 day exposure.

Figure 24. Roughness Comparison, Standard NACE
(contd.) solution saturated with H_2S , pH:2.3-4.4,
Ambient temperature, 30 day exposure.

Figure 25. Roughness Comparison, Standard NACE solution saturated with H_2S , pH:2.4-5.2, Elevated temperature ($150^{\circ}C$), 10 day exposure.

Figure 25. Roughness Comparison, Standard NACE solution (contd.) saturated with H_2S , pH:2.4-5.2, Elevated temperature ($150^{\circ}C$), 10 day exposure.

Figure 26. Roughness Comparison, 1% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.3, Ambient temperature, 10 day exposure.

Figure 26. Roughness Comparison, 1% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.3, Ambient temperature, 10 day exposure.

Figure 27. Roughness Comparison, 5% NaCl solution with 10 ppm H_2S and N_2 , CO_2 in the ratio 64:36, pH:5.2, Ambient temperature, 10 day exposure.

Figure 27. Roughness Comparison, 5% NaCl solution
(contd.) with 10 ppm H₂S and N₂, CO₂ in the ratio
64:36, pH:5.2, Ambient temperature,
10 day exposure.

Figure 28. Roughness Comparison, 1% NaCl solution with 10 ppm H₂S and N₂, CO₂ in the ratio 64:36, pH:5.5, Elevated temperature (150°C), 10 day exposure.

Figure 30. "Total" Comparison, Ambient temperature, 10 day exposure.

Appendix

Proficorder

The Proficorder Linear Profile system is a versatile unit capable of producing a graphic representation of the linear profile of a sample. Essentially it consists of a Tracer/Piloter assembly and a Profiling Amplifier with an analog meter and a strip chart recorder.⁽⁹⁴⁾ The Proficorder is capable of deriving four surface texture characteristics. Those relevant to this study are total profile, waviness and roughness. A diamond stylus tracks over the surface of the sample. Vertical displacements of the stylus arm are relayed to the amplifier as electrical impulses which then actuates the recorder pen. A positive chart pen deflection indicates an upward stylus deflection and a negative deflection indicates a downward stylus movement. A range of vertical magnifications, from 0.00002 inches to 0.01 inches for full scale deflection are available. Width cut-off scale is also available from 0.003" to 0.300".

The total surface profile can be divided into two components, surface waviness and roughness. In the total mode (roughness plus waviness) the chart center line serves only as a convenient line of reference. The trace is arbitrarily positioned by the manual adjustment of the Tracer/Piloter head assembly. In the roughness mode the

Appendix cont'd

chart pen is automatically centered to the chart reference line.

Set Up and Operation: Initially, the apparatus is levelled following which the sample is mounted on a glass slide and also levelled. The glass slide with the specimen is rested firmly on the Alignment Fixture just below the stylus arm. The amplifier unit is switched on and the Tracer is brought down until the diamond stylus just touches the surface of the sample. Now, the Handwheel is turned until the Amplifier meter registers "zero" deflection. The Tracer is moved across the sample with the Manual Drive Handwheel and aligned in the direction of tracing by manipulation of Vertical Adjustment Handwheel and Tilt Adjustment Knob; starting with less sensitive range up to the range of the sensitivity desired. The mode of surface profile (roughness, etc.) is selected as well as the width cut-off. Range of vertical magnification is chosen by running the Tracer manually along the specimen so as to get the whole set of deflections within the full scale range of the analog meter. The length of tracking is fixed, the Tracer is brought back to the starting point and motor drive mechanism is engaged. Feed rate of chart paper is suitably selected and the Tracer, recorder pen

Appendix cont'd

and the chart feed are actuated by depressing appropriate buttons.

Profilometer

The Profilometer consists of a Tracer unit, a gated Piloter and an Amplimeter Peak Counter.⁽⁹⁵⁾ It is capable of making average roughness and peak-count measurements. A diamond stylus traces over the surface of the sample and senses the roughness of the surface generating signals which are transmitted to the Amplimeter for digital readout. This study is primarily concerned with the peak-count mode of operation. In this mode, the Profilometer displays the number of peaks which exceed a selected vertical range per unit of horizontal travel. Seven ranges are available, from 5 microinches to 500 microinches.

Set Up and Operation: As in the case of Proficorder, again the specimen is levelled. Stroke length of the Piloter is adjusted and the Tracer is fitted to the Piloter and the diamond stylus is brought to the surface. After the units are switched on, the range of depth and the width cut-off are selected the counter is set in the "operate" mode. The number of peaks is read off for each value of the depth "cut-off".