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First Annual Report

Phase II

LOCALIZED CORROSION IN MATERIALS
FOR GEOTHERMAL POWER

by

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ABSTRACT

Ten different commercially available steels were examined for general and localized corrosion in 14 different environmental conditions. The chloride concentration was varied from 1 to 24 percent. In general, the influence of chloride was minor and seemed slightly more aggressive at 1 than at 5 or 24 percent. The brines were examined with and without saturated H_2S . Saturation with H_2S increased the general corrosion rate but appeared to reduce crevice attack in the acid solutions. Selected brines were examined in both acid and neutral conditions. As anticipated, a neutral brine with or without H_2S greatly reduced all forms of attack. Tests at $150^\circ C$ exhibited greater attack than at ambient.

A relatively new alloy, Ni-Cu-Cb, consistently demonstrated good resistance to both general and localized attack. Typical economical N80 grade steels clearly demonstrated the strong dependence of localized attack on inclusion variables and offer great promise in the minimized and/or controlled inclusion condition. The Cr-Mo steels surprisingly did not look good at ambient but did exhibit substantial improvement at $150^\circ C$.

The laboratory tests gave higher weight loss values for similar steels recently tested in a well; although in our neutral brines without saturated H_2S , the difference was not significantly larger.

TABLE OF CONTENTS

	Page
Abstract.....	i
Table of Contents.....	ii
Introduction.....	1
Literature Survey	
Localized Corrosion.....	6
Key Corrosive Chemical Species in Geothermal Fluids.....	16
Experimental Procedures.....	23
Results and Discussion.....	29
Summary Conclusions.....	40
Acknowledgements.....	42
References.....	43
Figures.....	50
Micrographs.....	64
Tables.....	66
Alloy Composition.....	69
Heat Treatments.....	70
Weight Loss Tables.....	72

INTRODUCTION

The rapidly growing demands for energy in the past decade coupled with high prices has emphasized the need for various sources of energy. Geothermal fluid is one such source which holds great 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 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 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. Typical chemical process industry corrosion control practices involve a combination of materials selection and chemical inhi-

bition. The volumes of fluid involved in geothermal applications are generally too large for chemical inhibitors to be economically effective. Secondly, one must anticipate that any chemical added to the geothermal fluid for corrosion control might have to be removed to satisfy environmental requirements. Thus, materials selection appears to be the most profitable route to corrosion control when large volumes of geothermal fluids are involved. Availability of durable and cost effective constructional materials for processing geothermal fluids has, therefore, a definite impact on the development of geothermal energy.

Another intrinsic difficulty arises from scale formation when the energy is extracted from the brine. 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 which is potentially disastrous for the efficient operation of a geothermal energy plant. This reduces the efficiency and raises cost.

Uniform and localized corrosion are the two main types of corrosion that are usually encountered in materials used in geothermal environment. 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 insidious and 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 specialty alloys which have adequate corrosion resistance. This is a costly approach and may involve relatively scarce alloying elements such as Mo, Co, Ni and Cr. In addition, 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 a part-per-million concentration. The sulphide induced failure mechanisms imposes severe limitations on the use of high strength alloys in geothermal systems, as has been the case in sour natural gas industry.⁽⁴⁻¹⁰⁾

A recent report⁽¹¹⁾ has documented corrosion experience in geothermal environments and 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 these materials are unsuitable for use in these liquid dominated resources.

Low alloy constructional steels, on the other hand, hold promise for down hole applications provided that oxygen free conditions are maintained. In particular, these steels exhibit low corrosion rates

and are nearly 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.

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 steels 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)

Many different types of materials are necessary to meet the requirements of a complete geothermal power system. For the most part, materials suitable for casing, tubing, etc., may not serve for much of the rest of the installation, such as well head fittings, valves, pumps, bolts and ancilliary equipment. Different kind of corrosion problems are encountered in different components. Accordingly, a major factor in the economic exploitation of geothermal resources would be the cost effective selection of materials that have sufficient resistance to corrosion to maintain component integrity.

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 within a given well or field as a function of time or operating conditions

as well as between various 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 very 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 an evaluation of geothermal environment.

LITERATURE ON LOCALIZED CORROSION

The fundamental 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 very common with materials such as stainless steels, Ti base and Ni base alloys, that rely on the integrity of a protective or passive film for corrosion resistance. However, other materials such as constructional steels which develop moderately protective films, are also susceptible to this kind of attack. Cl^- is the main initiator of localized attack, and the presence of H_2S increases the severity of localized corrosion.

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. Due to this momentary breakdown of this film, a rapid anodic metal dissolution takes place at the exposed area and oxygen reduction takes place on adjacent surfaces, which supplies a high electrochemical driving force. Water or hydrogen ions may also serve as the oxidizing agent, but the driving force is lower. Once the growth starts, the pit or crevice area becomes acidic and Cl^- ions are transported into the area. Both these effects accelerate the pit or crevice growth and thus the process becomes autocatalytic in nature.

As the corrosion within the crevice or pit increases the rate of oxygen reduction on the adjacent surface also increases and this cathodically protects the external surface. So during pitting and crevice corrosion, attack is localized in the shielded area, while the remaining surface suffers little or no attack.

The tendency of a metal or alloy toward pitting can be estimated by⁽¹³⁾

- (a) Determination of critical potentials for pitting.
- (b) Determination of minimum concentration of Cl^- ions in solutions causing pitting.
- (c) Determination of the critical temperature for localized corrosion in a standard solution.
- (d) Measurement of the number, depth, width, and shape of the pits in a standard solution.

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 of different metals and alloys to pitting corrosion in aggressive environments. The more positive E_b , the more resistant is the given 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 using potentiokinetic methods, and the "protection potential, E_p " ($E_b > E_p$) obtained when the measurements are performed in 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⁾

Limited data are available on the pitting and crevice corrosion resistance of constructional materials used in geothermal environment.

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 test data, laboratory exposure test data and the electrochemical measurements of the breakdown potential (E_b) and protection potential (E_p).

It should be emphasized that the values of E_b and E_p are often dependent on the nature of steel, its heat treatment and surface condition, and on the potential scan rate. The potential scan rate is defined as the rate at which the applied potential linearly increases with time. The potential scan rate strongly influences the time necessary to conduct potentiodynamic pitting test. Given sufficient time (or a low enough scan rate), pits may be initiated at potentials more active than E_b , but never at potentials more active than E_p .

It has since long been known that 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 non-metallic inclusions for the initiation of localized attack, particularly for stainless steels.

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. Re-

gions containing FeS, MnS, CaS and especially mixed sulphide-oxide inclusions are most susceptible to preferential attack. Data presented by Szklarska-Smialowska^(46,47) shows 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 stimulating effects 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 both the melting practice and heat treatment used in manufacturing the steel.

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^{2-} , HS^- , and H_2S activity in the solution as the sulphide dissolves. The reason why sulphide ions, S^{2-} and HS^- , are activators which greatly

accelerates localized corrosion in much the same way as Cl^- ions 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, Eklund⁽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 he related this 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. As the carbide (lamellar or spheroidal) spacing is reduced, the dissolution rate is increased due to increased interfacial energy. Preferential dissolution of carbides can create sites for

stress concentration and thus increases the possibility of crack initiation.

Payer and Staehle⁽⁵²⁾ have investigated the dissolution behavior of carbides in aqueous environments and they think 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⁾ have studied the effect of alloying elements (such as Cr, Al, Ni and Cu) on pitting corrosion by examining the potential distribution on the surface of low alloyed mild steels. According to them, small additions (<1 wt%) of chromium and aluminum segregate to non metallic 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 toward corrosion. Thus, although Cr and Al considerably reduce the uniform corrosion, their additions lead to intense pitting attack. However, they believe that when the chromium content is sufficiently high (>12 wt%), it is 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 susceptibility of Iron-chromium-nickel alloys to pitting corrosion has been discussed in Kolotyrkin'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. More recently, the effect of alloying elements on the breakdown potential, E_b has been studied. The elements which have beneficial effects on pitting (such as Cr, Mo, Ni etc.), would shift the E_b to more positive values while elements (such as C, Ce, Nb etc.) having detrimental effects shift the E_b value to more negative ones.

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 well known from the work at Case⁽⁵⁵⁾ that fine structures with uniform carbide distribution such as tempered martensite are more resistant to SCC in hydrogenous environments than the more coarse structure such as ferrite-pearlite mixtures (normalized). However, in order to evaluate the relative resistance of normalized structures versus tempered martensitic structure to localized corrosion, further study is necessary. 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. On the other hand, heat treatments leading to

greater homogeneity of the material should increase the resistance to pitting.

Resistance of a metal to pitting is higher, the better the homogeneity of the surface.⁽⁵⁴⁾ The nucleation of the pit 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. The effect of grain size on the susceptibility to pitting in chromium-nickel steels has been studied by Tomashov, et al⁽⁵⁹⁾. He 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 steels composed of smaller grains should be more susceptible to pitting, since they contain more grain boundaries with heterogeneous inclusions.

Influence of plastic deformation on corrosion behavior of iron & steel has been investigated by Green & 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⁽⁶¹⁾ such as plastic deformation, heat treatment and composition.

In recent years much attention has been given to the morphology of pits and to the conditions leading to the formation of pits of different shapes. However, it is not clear what conditions must be

fulfilled to realize the formation of pits of a particular shape. It appears that the shape of the pit depends upon the conditions existing within the pits and consequently, upon the composition of the aggressive solution, properties of the given metal as well as its composition and structure.

KEY CORROSIVE CHEMICAL SPECIES PRESENT IN GEOTHERMAL FLUIDS

Geothermal fluids are complex, variable 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 we can notice that there is a wide variation in the chemistry of the different geothermal resources and, accordingly these variations make it difficult to define typical or representative 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.⁽⁶²⁾ 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 concentration as high as 10 to 30% (as NaCl) gives higher corrosion rates,⁽⁶³⁾ as illustrated in Figure 2.

Chloride ions give rise to local breakdown of the film that protects many metals from uniform attack. As a result of localized penetration of this film, pitting, crevice corrosion and SCC take place. 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⁽⁶⁴⁾ from which one can see that the minimum Cl^- concentration increases with chromium content up to 25%.

For metals which show passivity, there exists a potential above which pitting can initiate in the presence of chlorides or other aggressive anions. This potential is called the "Critical pitting potential (E_p)" which 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⁽⁶⁵⁾ determined the critical pitting potential E_p 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⁾

For practical applications, measurements of both corrosion and pitting potentials are necessary in making predictions regarding localized attack. Figure 4 shows the variation of corrosion and pitting potentials with chloride concentration⁽¹¹⁾ at 25°C , from which one can see 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 in acidic environment can promote the rate of general corrosion in low alloy steels.⁽⁶⁶⁾ In the presence of H_2S , FeS layer can form on the steel surface and if part of this layer flakes off, the localized attack at this surface is in-

tensified due to galvanic coupling action between Fe and FeS. Also, the adsorption of sulphide ions on the steel surface catalyses the anodic dissolution rate.

Stainless steels, on the other hand, are generally resistant to corrosive attack in sea water containing H_2S and NH_3 .⁽⁶²⁾ 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.⁽⁶⁷⁾

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 solution.

e) Effect of Oxygen:

The introduction of small amounts of oxygen can greatly accelerate the uniform corrosion rate of mild steel. This is illustrated in Figure 5 for gas-free sea water steam.⁽⁶²⁾

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 & 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 $\text{CO}_3^{=}$. 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.⁽⁶⁸⁾ 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⁽⁶²⁾ 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 is an aspect of geothermal fluid chemistry that influences the material's performance. Goldberg and Owen⁽⁶⁹⁾ 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 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 favorable conditions for pitting. The scales are porous and contain many fine micro-cracks.^(70,71) These cracks can expose fresh metal to the brine if the corrosion product is ruptured. Thus, these types of scales can permit access and entrapment of the brine favoring the formation of crevices and shallow pits.

B. Influence of Temperature:

Not enough experimental data is available on the influence of temperature on the uniform corrosion rate of constructional steels in geothermal brines. However, Shannon⁽⁶³⁾ reports a decrease in corrosion rate of low carbon steels with increasing temperature (in the 100°C to 250°C range) in simulated geothermal fluids at a constant CO₂ partial pressure. This observation could be explained in terms of formation of more protective magnetite films, as well as an increase in pH of the solution at constant CO₂ partial pressure with increasing temperature. On the contrary, an increase in corrosion rate of carbon steel with increasing temperature has been reported in an environment having high chloride concentration in the absence of CO₂.⁽⁷²⁾ 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^(2,73) 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⁽⁷⁴⁾ showed 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 illustrated in Figure 8.

Data is available on the temperature dependence of pitting in stainless steels. Pitting susceptibility increases with increasing temperature (Figure 9) by shifting the pitting potential towards more active values.⁽⁷⁵⁾ 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. Because of these high flow rates, bubbles of non-condensable gas would be produced, causing impingement attack. Also the entrained solids in the stream can cause erosion-assisted corrosion.

The influence of flow rates on corrosion in mild steel⁽⁶²⁾ is shown in Figure 7 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.

EXPERIMENTAL PROCEDURES

This study is concerned primarily with the localized mode of attack and is concentrated on pitting and crevice corrosion in constructional steels and corrosion resistant alloys in environments relevant to geothermal resources. However, in many instances, particularly with constructional type steels, the line of demarcation between localized and general corrosion is quite nebulous. In view of this fact, due consideration has been given to both types of corrosion phenomena for evaluation of corrosion resistance in geothermal type fluids. Uniform corrosion rates have been measured by:

- (1) Weight loss (in terms of mdd).
- (2) Polarization resistance.

a) Corrosion Rate from Weight Loss Measurements

Materials and treatments

A wide range of commercially available low alloy constructional steels have been examined for assessment of general corrosion rates. Their compositions are listed in Table 4. All these alloys are about .100" thick and in the hot rolled condition.

Test specimens were made by cutting the plate materials into $1\frac{1}{2}$ " x 1" coupons and drilling a $\frac{3}{16}$ " diameter hole in the top center for mounting the specimens on a glass rod. Heat treatment of all samples was then performed in a purified nitrogen atmosphere at controlled temperature. They were quenched for martensite and given a single temper. The specific heat treating temperatures and times for each constructional steel are given in Table 5. The heat treated

samples were then surface ground to remove scales and finally stress relieved. Prior to testing, all of the samples were polished up to 600 grit finish, washed with water, rinsed with methanol, air dried and weighed. The crevice corrosion samples were prepared by placing teflon discs on the samples and wrapping them crosswise with rubber bands according to ASTM Standard G 48-76.⁽⁷⁶⁾ Duplicate samples of each alloy, one with the teflon disc and one without, were employed in both ambient and elevated temperature tests.

Environments

As mentioned earlier, geothermal environments vary widely and no one solution can serve for total evaluation of general corrosion rates. In view of this fact, no attempt has been made to simulate specific geothermal environments. Rather, the primary 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 ⁽⁷⁷⁾. The NACE solution was modified later to examine the effects of varying chloride concentration and pH levels on corrosion rates.

Ambient Temperature Tests

Desiccators were employed to contain the solutions for tests conducted at ambient temperature. Samples were mounted on a glass rod so that no two samples touched each other. This was accomplished by wrapping a rubber band around the glass rod between two samples.

The glass rods were supported in grooves cut in a cylindrical stand made of glass and then the entire stand was completely im-

mersed into the solution contained in the desiccator. The test procedure involved deaeration of the solution 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.

Since the available tank H_2S had approximately 300 ppm oxygen, it was necessary to purify it. This was done by bubbling H_2S over scrap iron wire immersed in a flask containing the test solution. The purified H_2S was then bubbled into the desiccator saturating the test solution. This was followed by releasing H_2S through an outlet valve into a 20% NaOH solution which acted as a neutralizing agent. As a further safety precaution a backup of soda lime was employed. The soda lime gave a good indication of the saturation of NaOH with H_2S and therefore provided knowledge of when fresh NaOH solution was required.

Elevated Temperature Tests

High temperature, high pressured autoclaves were used for elevated temperature tests. All tests were conducted at 300°F. The purpose of these tests was to approximate the downhole well temperature.

The test procedure involved mounting the specimens on a glass rod and then placing this rod in a teflon holder contained in a 1000 ml beaker. A maximum of four specimens were tested per run. The test solution was poured into the beaker completely immersing the specimens. The beaker was placed at the bottom of the autoclave

and the autoclave top was closed. Care was taken to avoid contact of the specimens with one another or the inlet tube when the top was closed. The recommended procedure of continuous bubbling of H_2S ⁽⁷⁷⁾ employed for tests at ambient temperature was not possible for the high temperature tests conducted in autoclaves. Rather, the test solution was purged with N_2 for four hours followed by bubbling H_2S for two hours. The autoclave was then sealed, the desired temperature was set and the test begun. The set-up used for the high temperature tests is shown in Figure 12.

The test specimens were exposed to the environment for 10 days. 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. Crevice corrosion specimens were visually examined with a microscope to define the area of attack.

Corrosion Rate from Polarization Resistance

This method uses polarization data obtained in the region of corrosion potential to determine the corrosion rate. It has been demonstrated⁽⁷⁸⁾ 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⁽⁷⁹⁾, this technique has been widely used to study different corroding systems⁽⁸⁰⁺⁸³⁾, and is based on the following equation:

$$\frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3 (I_{corr}) (\beta_a + \beta_c)} \quad 1)$$

where $\Delta E/\Delta I$ is the polarization resistance, β_a and β_c are the slopes of the logarithmic local anodic and cathodic polarization curves, and I_{corr} is the corrosion current which is equivalent to the rate of corrosion by Faraday's law. Assuming that anodic and cathodic beta values of 0.12 volt represent the average of all corrosion systems⁽⁷⁹⁾, equation 1 reduces to:

$$\frac{\Delta E}{\Delta I} = \frac{0.026}{I_{corr}} \quad 2)$$

The specimens for linear polarization tests were one cm² plates of the materials listed in Table 4, with a wire spot-welded to their backs. They were mounted in "Quick Mount" and then polished up to 600 grit sand paper to reduce all scratches. The samples were then washed with distilled water and degreased with methanol. In order to insure against edge effects, stop-off lacquer was applied around the perimeter of the metal and "Quick-Mount" interface. 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. The polarization cell is shown in Figure 13.

The environment selected for this test was a deaerated aqueous solution of 5% NaCl and 0.5% acetic acid. Prior to placing the specimens in the electrolytic cell, the test solution was purged with nitrogen for one hour. This purging continued throughout the entire test period.

Initially, the specimens were allowed to reach their open-circuit or corrosion potential, which took about one hour. The working electrode was then polarized first cathodically and then anodically by scanning the potential by 5 mv steps up to 20 mv. Polarization resistance was measured from the plot of over-voltage versus applied anodic and cathodic current. Corrosion rates were then calculated using equation 2. The reported corrosion rates are the average of the consecutive cathodic and anodic values.

Crevice Corrosion Tests

Crevice corrosion specimens were cut from the plate materials into 2" x 1½" coupons with a 3/16" diameter hole in the top center for mounting the specimens on a glass rod. The specimens were cut so that the longitudinal direction of the specimens was parallel to the rolling direction of the original plate material. The heat treatment of all the specimens is indicated in Table 5. Prior to the 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 in order to eliminate the edge inclusion effect. Finally the specimens were polished up to 600 grit finish, rinsed in water, dipped in

acetone, air dried and weighed.

The ASTM⁽⁷⁶⁾ crevice corrosion test specimen configuration was employed for all the data presented here. This method involves two teflon discs, one on each side of a flat specimen, held against the surface by two rubber bands at right angles to each other. As indicated later in the text, this technique left much to be desired.

Accordingly, as this is being written a new test method developed at ARMCO⁽⁸⁴⁾ is being 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 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 - ins was applied on the bolt using an adjustable torque screwdriver.

RESULTS AND DISCUSSION

Coupons of ten commercially available low alloy constructional steels are under examination for weight loss and evidence of pitting and crevice corrosion. Two types of tests using synthetic fluids are being conducted. One series at ambient temperature and the other in high pressure autoclaves at 150°C.

Ambient Temperature Tests

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 calculations of general corrosion rates on the basis of measured weight losses for ten day exposure tests in deaerated brines with and without saturation of H_2S are presented in Tables 7-12, with some observations on the appearance of materials 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 an examination of Tables 7-12 that the most aggressive chloride concentration is near 1% where the environments containing 5 and 24% NaCl generally showed similar or lower rates of corrosion. 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 with saturated H_2S . Other comparisons such as with alloy 1551 are even more relevant.

The inhibitive influence of chlorides above 1% can account for the reduced corrosion in these constructional type steels.⁽⁸⁵⁾ This behavior could be explained by Cl^- adsorbing on the metal surface. This adsorption would be expected to increase with increasing Cl^- concentration up to a certain point after which more Cl^- would have little effect. This 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. (86)

Hydrogen Ion Concentration (pH)

Another important parameter under examination here involves the influence of pH on corrosion, a variable which may be widely different in different sources and even within the same source with time. However, in this connection it should be recognized that the CO_2 , commonly found in geothermal brines and which is the primary source of acidification can be lost in the condensate. Thus, indicated values of pH 5-6 may not reflect true down-hole pH. This leads one to suspect that many of the sources are more acid than indicated.

Values of pH 2.4-4.4 and 5.8-7.4, typical of acid and neutral NaCl solutions were examined. General corrosion rates of the materials in neutral solutions containing 5% NaCl, deaerated and with and without saturated H_2S are presented in Tables 13 and 14. Examination of these tables and comparison with previous ones clearly reveals that the acidification of the brines substantially increases the corrosion rate of the low alloy constructional steels tested in this program, regardless of the presence of H_2S . Steel #28, a low carbon-manganese economical alloy, provides a good example of this effect, where in the neutral brine (Table 13) 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 uniform corrosion. Alloy #28, discussed above 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 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. At this time it is important to note that these observations with respect to the influence of H_2S have considered only environments saturated with H_2S . Current studies are now employing lesser and more probable concentrations of H_2S and will be considered in the next report.

Duration of Test

Tables 15 and 16 give the corrosion rates obtained after 30 days exposure for the more promising materials as compared to the more standard 10 days adopted in this study. It is clear that in the acid environment without H_2S (Table 15), the 10 and 30 day runs give essentially the same rate. In short, a true steady rate is being measured in the 10 day runs under these conditions. However, in the presence of saturated H_2S (Table 16), it appears that the rate has definitely decreased during the period from a 10 to 30 day exposure. It is not known what additional time of exposure beyond 30 days would do to the rate. Presumably this effect would level out.

The inference is strong that the iron sulphide film which will

thicken with time is providing a measure of protection to general corrosion. There can be no doubt that the presence of H_2S results in a more aggressive environment as indicated earlier. 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 13 and 14).

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.⁽⁸⁷⁾ However, to the best of our knowledge there has not been any evaluation of this type of copper containing alloy in these types of aggressive environments. Both #28 and #80 steels generally exhibited good resistance to corrosion in all the brines with #28 showing up some what better than #80. 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 steel was that #28 had employed

rare earth (REM) additions in the deoxidation process and was a substantially "cleaner" steel.

In recent years, attention has been focused on the number, size, type and distribution of inclusions relative to both general and localized corrosion. "Cleaner" steels are usually less susceptible to corrosive attack all other things equal. Sulphides in particular, as well as silicates and oxides are the primary culprits. Steel #28 is a good example of the action of a "clean" steel as compared to its counterpart which had a large number of inclusions. However, the presence of inclusions primarily influence localized corrosion, to be considered in the next section

Most of the other steels exhibited a more or less mixed response and generally a somewhat higher corrosion rate in the various test environments. Particularly surprising was the poor showing of the higher alloy steels containing chromium. The corrosion rates for 4135 and $2\frac{1}{4}$ Cr-1Mo-.19C exhibited the highest corrosion rates in almost all environments indicating corrosion rates in the acidified H_2S environments 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.⁽⁸⁹⁾ However, the well tests were conducted at the higher well temperature and substantially lower H_2S concentration.

General Corrosion Rates by Linear Polarization

Linear polarization techniques present an alternative method to weight loss measurements for the determination of general corrosion rates. Examination of Table 17 reveals that the corrosion rates by this method yield substantially higher values than obtained by weight loss measurements. However, it is significant that those alloys which appeared promising in the weight loss tests also more or less indicated better corrosion resistance in the linear polarization resistance method.

The literature clearly indicates that the corrosion behavior, as expected, is strongly dependent upon the type and rate of formation of the corrosion product films.⁽⁸⁷⁻⁸⁸⁾ The weight loss specimens (10 day exposure) 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 run involved approximately only one hour exposure. We feel 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 in the section on experimental procedures, the ASTM specimen configuration was employed. It proved to give erratic results, largely because of the unequal and variable pressure the rubber bands placed on the teflon resulting in crevices of variable and

and non-reproducible geometry. This ruled out any attempt at even a semi-quantitative evaluation of the susceptibility of the various alloys and consequently negated any use of the profilometer in these studies. Hopefully, the new crevice method (Fig. 14) currently being employed will allow some meaningful results to be obtained. Thus, these crevice study data should be interpreted only in broad terms.

Most of the weight loss tables have a column indicating the loss of weight with a teflon artificial crevice. It is important to realize that these numbers are not even a semi-quantitative measure of localized corrosion. The reason is simply that in the low alloy types of steels the general and localized corrosion overlap to the extent that in some circumstances it is not possible to distinguish between them. However, the accompanying comments do have a general broad relevance to localized corrosion.

A cursory examination of Tables 7-14 reveals that at ambient temperature the localized corrosion in these steels is relatively insensitive to variations in the chloride concentration in sharp contrast to the behavior of austenitic stainless steels. Also, as might be expected, the acidification of the brines increased the susceptibility to localized attack. In addition, the introduction of H_2S (saturation) into the acidified brines of varying chloride concentrations generally inhibited 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. In fact none of the alloys suffered any localized attack in the neutral solutions either with or without

H₂S (see Tables 13 and 14).

Most of the alloys exhibited good resistance to pitting in the acidified brines with 1 and 5% NaCl; but with 24% NaCl, only alloys Ni-Cu-Cb, 1551 and #4 did not show some 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 the sulphide inclusions.

The Ni-Cu-Cb and 1551 steels closely followed by #4 exhibited very good resistance to pitting and crevice attack in all three acid environments saturated with H₂S. Here again, as indicated above, the steels are relatively clean (Tables 8, 10 and 12). 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 H₂S environments. This is quite consistent with the strong hydrogenating power of H₂S.

Figure 15 is a low magnification photo (4X) of the as-corroded surface of steel #80. The severe localized attack and even the "cracks" are visible. The photomicrographs of Figs. 16 and 17 of the corroded surface of steels #28 and 80 allow a comparison of the attack in these two steels of virtually the same composition. Clearly, steel #28 shows little or no pitting while 80 is severely attacked. The origin of this difference in behavior becomes more understandable by a metallurgical comparison demonstrated by the photomicrographs of Figs. 18 and 19 showing polished and etched

cross-sections of the two steels rather than the corroded surfaces. It is quite evident that the localized corrosion and pitting in particular is directly related to the inclusion variables. Apparently steel #28 has a few small well-distributed spherical inclusions approximating the ideal situation.

No systematic study has been conducted on the type of inclusions in these materials. However, they probably are a type of MnS inclusion or some complex variation, possibly modified by the REM treatment. The structure of steel #80 clearly shows the elongated inclusion stringers of rolled-out entrapped slag inclusions. These are not only nucleation sites for localized corrosion but also present ideal locations, not necessarily at the surface, for hydrogen blistering. Although, these blisters are not real brittle fracture cracks, for all practical purposes they are no different except they can occur even in the lowest strength materials. Thus, employing low yield strength steels significantly does not provide immunity as it does for SCC.

A similar comparison can be conducted with several other steels, but we hasten to point out that steel #80 is an extreme example of a "dirty" steel and does not necessarily reflect the performance potential of this analysis. Although it does provide a dramatic example of the influence of inclusions on localized attack, unfortunately it does not allow us to evaluate the influence of rare earth additions (steel 28) on essentially the same analysis. This should be done! The Japanese have made great progress in the control of

inclusions and related localized attack, particularly in line pipe, by specific deoxidation practices involving additions such as Cb, rare earths (REM), etc.

Tests at 150°C

The corrosion rates at 150°C in the acid brine with and without H₂S saturation are given in Tables 18 and 19. As expected, the higher temperature increased the corrosion rate and intensity of localized attack. It should be noted that these autoclave tests were in a closed system so that the H₂S concentration was saturated only initially and also there was some increase in the pH approaching neutral.

The higher temperature tests produced some dramatic variations in the relative responses of the different steels. Most interesting were the 2½ and 4.5% Cr plus Mo steels, which in the absence of H₂S exhibited relatively improved performance as compared to ambient temperature tests. Also, the poor performance of steel #28 was unexpected. The Ni-Cu-Cb steel still maintained its relatively good corrosion resistance. On the other hand, in the H₂S brine of the two Cr plus Mo steels only the 4.5% Cr alloy survived. However such steels as Ni-Cu-Cb and #28 again headed the list of corrosion performance much the same as at ambient temperature.

In general, the elevated temperature also increased the local-

ized attack. In the brine without H_2S , both the 4.5% Cr and the Ni-Cu-Cb alloys exhibited good resistance to localized corrosion. The addition of H_2S did not seem to destroy their relatively good resistance. 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 temperature; the result of its poor quality. Again, as indicated earlier in this report, the crevice tests should be interpreted only in very broad terms. The new type of test (see Experimental Procedures) currently employed should allow a more relevant comparison.

SUMMARY CONCLUSIONS

A number of significant conclusions become evident at this stage of the program. There has always been some consideration of "in-situ" versus laboratory tests and the extent to which they may agree. Our results here indicate higher corrosion rates than recent tests in a well with several similar steels.⁽⁹⁰⁾ Of course, the environments were quite different. In the environment close to neutral pH that we examined, our rates were higher but not substantially so. This does not consider such other variables as chloride and H_2S concentration as well as temperature. Also, the longer exposure times of the "in-

situ" tests may have allowed a greater build-up of semi-protective films.

A relatively new and moderately priced steel, Ni-Cu-Cb, with approximately 1% each of Ni and Cu and no carbon has shown consistently good corrosion and localized attack resistance in all 14 different conditions examined. The Cr-Mo steels were surprisingly poor at ambient temperature but did look better in the elevated temperature tests. The economical carbon, 1.5% Mn steels (N80 type) show real promise in resistance to localized attack if the inclusions are minimized and/or controlled. A comparison of two very similar N80 type steels one "clean" and one "dirty" clearly demonstrated this.

It now becomes evident that in terms of general corrosion and more particularly pitting, the single most important factor is the cleanliness of the steel. Indeed, within the realm of feasible cost, this is more important than composition involving substantial amounts of expensive alloying elements. In short, the problem becomes primarily metallurgical not corrosion. In fact, "clean" steels become even less sensitive to aggressive variations in the environment.

A characterization of the tendency for crevice corrosion is a more difficult problem. It is well known that the development of some type of occluded cell is a necessary requisite. These cells can result from discontinuities of geometrical design factors such as threads, bolts, welded joints, etc. However, more subtle factors can also be involved such as discontinuities or cracks in scales or corrosion product films. Here both environment and cleanliness of

the steel will play some role but not as controlling as in the case of pitting.

In view of the above, the orientation of this study has already been changed. The number of steels under examination has been reduced to 4 or 5 and mostly of the more economical variety. Also, more attention will be focused on controlled inclusion variables involving basic metallurgical melting practices.

As indicated in the text, a new type of crevice corrosion test will hopefully give more reproducible results. And finally, a more relevant environment is now in use. This involves the mixing thru flow meters of controlled CO_2 and H_2S . It is felt that the standard NACE environment with saturated H_2S is not relevant to the problem although initially it has provided a basis of comparison with the extensive literature employing this environment.

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Figure 1. Effect of Seawater pH on the Corrosion of 1010 Mild Steel. (62)

Figure 2. Average Corrosion Rate of Carbon Steels as a Function of Salinity. (63)

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. (65)

Figure 5. Effect of Dissolved Oxygen on Corrosion Rate of 1010 Mild Steel in Seawater at 250°F. (62)

Figure 6. Corrosion rate of A212B Carbon Steel in Deaerated 4M NaCl as a Function of Temperature and pH. (72)

Figure 7. Pitting and Corrosion Potentials of Steel as a Function of Temperature in Heber Geothermal Fluid. (73) 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. (74)

Figure 9. Pitting Potentials and Corrosion Potentials of Stainless Steels in 4M NaCl as a Function of Temperature. (75)

Figure 10. Effect of Velocity on Corrosion Rate of Mild Steel in Sea Water. (62)

Figure 11. Ambient Temperature Setup

Figure 12. Elevated Temperature Setup

Figure 13. The Apparatus for Linear Polarization Measurements

Figure 14. Crevice Block Assembly

Fig. 15. Steel #80
As-Corroded Surface
Localized Corrosion
and "Cracks".
X4

Fig. 16. Steel #28
As-Corroded Surface
Few Small Pits.
X150

Fig. 17. Steel #80
As-Corroded Surface
Small and Typical Large
Elongated Pits.
X150

Fig. 18, Steel #28
Cross Section of Specimen
of Fig. 16, Metallurgical
Polish and Etch, Well
Distributed Small Round
Inclusions,
X150

Fig. 19, Steel #28
Cross Section of Specimen
of Fig. 17, Metallurgical
Polish and Etch, Elongated
Slag Stringers and a Few
Small Inclusions,
X150

TABLE 1 Typical Concentrations of Key Corrosive Chemical Species in Fluid from Seven Known Geothermal Resource Areas. (11)

KGRA	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 ²⁻		
Bulton Sea, Ca.	250 (bore-hole)	5.2	115,000	1,000	10-30	300	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.	180-200 (bore-hole)	5.7	11,000	800	3	41	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.
Huber, Ca.	180-200 (bore-hole)	7.1	9,000	180	~2	13	152	unflashed well-head fluid	These data are from two separate analyses of fluid from the well Howlin 1. The fluid also contains about 4 ppm Fe.
Hono-Lua Valley, Ca.	175 (bore-hole)	6.5	227	180	14	0.1	96	unflashed well-head fluid	These data are for well Radogenous 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.
Baca (Valles Calders) N.M.	171 (well-head at 110 psig)	6.8	3,770	128	6	-	59	flashed fluid	These data represent the results of three similar analyses of flashed fluid from well Baca 11. They are not representative of values in the unflashed fluid.
Bourne, Nev.	132 (well-head)	9.3	50	209	6	3	89	flashed fluid	These data are representative of wells Vulcan 2, 3, and 4. Data for H ₂ S, CO ₂ , NH ₃ , and pH are not representative of the unflashed fluid.
Reft River, Id.	146 (bore-hole)	7.2	780	60	0.1	2	61	unflashed fluid	These data are for well ERGE 1 which is well characterized. Well ERGE 2 has a similar composition. Well ERGE 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. (11)

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								
Heber, 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)
Beowawe, 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

^a units are ppm in steam

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

^c balance 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	Cb	V	N	Ti
Ni-Cu-Cb	.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 2½ 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-1Mo-.19C	83 (N)	67 (mc)
H1 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

C - Deep crevice

mc - Minute 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)
Hi 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)	23 (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 TEMPERATUREEnvironment: 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 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 + Tp)

KEY TO TABLE:

N - No pit or crevice

mc - Minute crevice

C - Deep crevice

Tp - Tiny pits

P - Distributed tiny pits

pT - Tiny pits under the teflon

* 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 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

C - Deep crevice

Tp - Tiny pits

p - Distributed tiny pits

* mpy = 0.1832 x mdd