

A STUDY OF THE EFFECTS OF TEMPERATURE AND OXYGEN CONTENT ON THE CORROSION OF SEVERAL METALS

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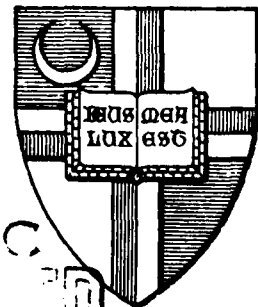
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ABSTRACT

The corrosion rates of stainless steels 304 and 316, mild steel, nickel, monel, inconel and brass were investigated by electrochemical polarization techniques in 5% aerated and deaerated HCl solutions. It was found that the corrosion rates of the stainless steels increased by an order of magnitude while the corrosion rate of mild steel decreased by an order of magnitude when oxygen was removed from the test solutions. Corrosion rates were only slightly reduced for nickel, monel, inconel and brass in deaerated solutions. Increasing temperatures between 20°C and 80°C caused the accelerated corrosion of nickel and monel, however, had little effect on brass and inconel.

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OBJECTIVE

Techniques for accelerating the corrosion rates of metals are extremely important for long term prediction of corrosion behavior. Many different tests have been used. Salt spray chambers and immersion in boiling chloride solutions are but two techniques in common practice. Unfortunately, their results most often are not applicable for practical predictions. It is desirable therefore that some type of universal corrosion acceleration test be developed so that the useful life of a metal in a specific environment might be accurately predicted.

Corrosion is defined as the destructive attack of a metal by chemical or electrochemical reaction with its environment, and since corrosion is a chemical process, the basic laws governing all chemical reactions must apply to its behavior. Chemical reaction rates are affected by temperature, pressure and the concentration of the substances involved in the reaction. In general, the rate of a chemical process is increased as the temperature is increased according to Arrhenius' Law:

$$\text{Log } K = A - \frac{C}{T}$$

where A and C are constants, T is absolute temperature and K is the reaction rate. One technique for accelerating corrosion then, would be to increase the temperature of the reacting surface.

Some corrosion mechanisms involve a reaction of the metal surface with oxygen. The corrosion resistance of stainless steels

for example, is dependent on the fact that oxygen combines with components in the alloy to form a tough, protective oxide film on the metal surface. Therefore, the amount of oxygen available to the corroding metal will also affect the rate of corrosion. Thus corrosion rates of certain metals may be accelerated by the removal of oxygen from their environments. The primary purpose of this investigation is to determine to what extent the corrosion rates of the various metals tested are affected by temperature and oxygen concentration.

It must be realized that in addition to the general corrosion or dissolution of a metal, there are many other types of metal deterioration. Stress corrosion, crevice corrosion, hydrogen embrittlement, fatigue corrosion, etc. are all other mechanisms of metal deterioration and are certainly important in the prediction of service life. For this report, however, general corrosion is the only type considered. The fundamentals must be understood before the complexities can be handled.

Hopefully the results of this investigation will identify which metals can and which metals cannot have their general corrosion rates accelerated by temperature elevation and/or removal of oxygen from their environments. Ideally this report is but the first step in a program to design useful accelerated corrosion testing procedures.

INTRODUCTION

Any study involving corrosion must be based on a reliable method for measuring corrosion rates. For years, the most common method was determination of weight loss of a metal sample in a specified environment for a specified duration. This method yields corrosion rates averaged over the entire length of the test and needless to say, is very time consuming. Furthermore, true corrosion rates may be altered by the periodic removal of samples for cleaning and weighing in an attempt to obtain a time history of the corrosion process.

Corrosion rates have also been determined by chemical analysis of the aqueous solution containing the electrodes. In addition to producing only an average figure for corrosion rate, this method is not always accurate because of the insolubility of some of the corrosion products.

ELECTROCHEMICAL TECHNIQUES

The fact that corrosion is an electrochemical process as first suggested by Whitney (16) over sixty years ago, has led to additional methods for determining corrosion rates. It has been shown by several investigators (1)(5)(6)(13) that the weight loss calculated from Faraday's Law from electrochemical measurements made on the surface of a corroding electrode are comparable to actual weight losses measured by the conventional techniques. Anodic and cathodic polarization curves have been

used in several ways to predict instantaneous corrosion behavior. When using polarization curves, however, it must be assumed that the mechanism of the electrochemical process occurring is not altered by the application of the polarization current.

Schwerdtfeger and McDorman (6) used electrochemical techniques to measure corrosion rates in aqueous media. Their method consisted of determining the amount of externally applied current necessary to reduce the corrosion rate to zero. This they accomplished by noting the potential at "breaks" in the anodic and cathodic polarization curves and considering the currents at these "breaks" to be equivalent to the I_a and I_c values required in the calculation of the corrosion current from the relation:

$$i_{\text{corr}} = \frac{I_a I_c}{I_a + I_c}$$

I_a - the polarization current with the specimen cathodic at which the anodic action ceases
 I_c - the polarization current with the specimen anodic at which the cathodic action ceases

Figure 1 illustrates this method.

Stern and Geary (9) pointed out that experimental evidence for "breaks" in polarization curves is doubtful, and in most cases, polarization data is best plotted using smooth curves. When Skold and Larson (7) attempted to employ this method they found that data collection was extremely time consuming and the "breaks" in the polarization curves were not defined sharply enough to allow accurate calculation of corrosion rates.

Stern proposed a method for calculating corrosion rates by the extrapolation of polarization curves from the Tafel region to the corrosion potential to obtain the local action current. Using the relation:

$$E_{\text{corr}} = B \log \frac{i_{\text{corr}}}{i_0}$$

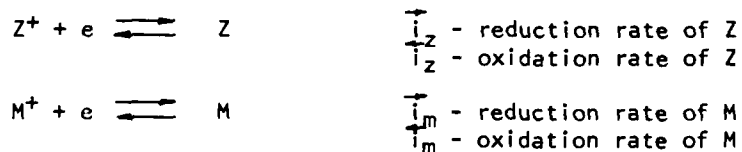
E - activation overvoltage
 B - slope of the Tafel curve
 i_0 - exchange current
 i_{corr} - corrosion current

For a value of E_{corr} , i_0 and B are obtained from the polarization curve and i_{corr} can be calculated as shown in Figure 2.

POLARIZATION RESISTANCE

Both Butler and Armstrong (15) in 1934 and Skold and Larson (7) in 1957 gave experimental evidence demonstrating that the initial slope of the polarization curves is constant. Stern and Geary (9) provided the theoretical explanation for this behavior.

Consider an activation controlled corroding electrode system composed of anode M and cathode Z. The reactions occurring are



Each reaction has its own exchange current and Tafel slope so that the steady state potential of the corroding metal occurs where the total rate of oxidation equals the total rate of

reduction:

$$\vec{i}_z + \vec{i}_m = \vec{i}_z + \vec{i}_m \quad (1)$$

The corrosion rate is defined as the rate of oxidation minus the rate of reduction:

$$\vec{i}_m - \vec{i}_m \text{ or } \vec{i}_z - \vec{i}_z \quad (2)$$

The corrosion current can be defined as the total rate of oxidation minus the total rate of reduction:

$$i_x = (\vec{i}_z + \vec{i}_m) - (\vec{i}_z + \vec{i}_m) \quad (3)$$

When the corrosion potential is far removed from the equilibrium potential, \vec{i}_m is small compared to \vec{i}_m and \vec{i}_z is small compared to \vec{i}_z . Therefore, the corrosion current can be expressed as

$$i_x = \vec{i}_z - \vec{i}_m \quad (4)$$

Using the Tafel relationship

$$E = -B_z \log \frac{\vec{i}_z}{i_{\text{corr}}} \quad (5)$$

i_{corr} is analogous to i_0 for a corroding system and B_z and i_{corr} are constants depending on temperature. E is activation overvoltage.

$$E = B_m \log \frac{\vec{i}_m}{i_{\text{corr}}} \quad (6)$$

$$\vec{i}_z = i_{\text{corr}} (10^{-E/B_z}) \quad \text{and} \quad \vec{i}_m = i_{\text{corr}} (10^{+E/B_m}) \quad (7) \quad (8)$$

substituting:

$$i_x = \hat{i}_z - \hat{i}_m = i_{\text{corr}} (10^{-E/B_z} - 10^{+E/B_m}) \quad (9)$$

If $10^{-E/B_z}$ and $10^{+E/B_m}$ are expanded into a series of the form

$$a^x = 1 + \frac{x \ln a}{1!} + \frac{(x \ln a)^2}{2!} + \dots$$

$$10^{-E/B_z} = 1 - \frac{E(2.3)}{B_z} + \frac{E(2.3)^2}{B_z} \frac{1}{2} - \dots$$

$$10^{+E/B_m} = 1 + \frac{E(2.3)}{B_m} + \frac{E(2.3)^2}{B_m} \frac{1}{2} + \dots$$

$$i_x = i_{\text{corr}} (2.3) E \left[-\frac{1}{B_z} - \frac{1}{B_m} + \frac{2.3E}{B_z} - \frac{2.3E}{B_m} \right] \quad (10)$$

If $B_z = B_m$ or to first approximations

$$i_x = -i_{\text{corr}} 2.3E \left[\frac{B_m + B_z}{B_m B_z} \right] \quad (11)$$

$$E = \frac{-i_x}{2.3 i_{\text{corr}}} \left[\frac{B_m B_z}{B_m + B_z} \right] \quad (12)$$

$$\frac{dE}{di} = \frac{1}{2.3 i_{\text{corr}}} \left[\frac{B_m B_z}{B_m + B_z} \right] \quad (13)$$

Since B_m , B_z and i_{corr} are constants, the relationship between E and the applied current is linear and the slope of the curve, called polarization resistance, $\frac{dE}{di}$, is constant.

Suppose the corroding electrode is concentration controlled rather than activation controlled. The change in potential resulting from concentration polarization is (14)

$$E_c = 2.3 \frac{RT}{nF} \log\left(1 - \frac{i}{i_1}\right) \quad i_1 - \text{limiting diffusion current} \quad (14)$$

Expanding the log term in a series of the form

$$\ln(1+a) = a - \frac{1}{2} a^2 + \frac{1}{3} a^3 - \dots$$

$$\log\left(1 - \frac{i}{i_1}\right) = \left[-\frac{i}{i_1} + \frac{1}{2} \frac{i^2}{i_1^2} - \dots \right] \frac{1}{2.3}$$

$$E_c = \frac{RT}{nF} \frac{i}{i_1} \quad (15)$$

Thus when the applied current is small compared to the limiting diffusion current, the concentration curve is linear and inversely dependent on the limiting diffusion current. Figure 3 shows the concentration polarization curve and the extent of its linear range.

Now consider a corroding electrode system where the cathodic reaction is controlled by concentration polarization and the anodic curve is logarithmic. In this case the corrosion current is almost equal to the limiting diffusion current. See Figure 4. The applied current necessary to polarize the electrode to some given cathodic value is related to local anodic and cathodic

current by:

$$i_c = i_a + i_{\text{applied}} \quad (16)$$

Using the Tafel relation again

$$E = B_a \log \frac{i_a}{i_{\text{corr}}} \quad (17)$$

$$i_a = i_{\text{corr}} (10^{E/B_a}) \quad (18)$$

and since $i_c = i_l = i_{\text{corr}}$, substituting:

$$i_{\text{applied}} = i_l - i_l (10^{E/B_a}) \quad (19)$$

expanding $10^{E/B_a}$:

$$10^{E/B_a} = 1 + \frac{E(2.3)}{B_a} + \frac{1E(2.3)^2}{2B_a} + \dots \quad (20)$$

$$i_{\text{applied}} = i_l - i_l (1 + \frac{E(2.3)}{B_a} + \dots) \quad (21)$$

$$i_{\text{applied}} = i_l \frac{(-2.3)E}{B_a} \quad (22)$$

$$E = - \frac{i_{\text{applied}} B_a}{i_l (2.3)} \quad (23)$$

$$\frac{dE}{di} = - \frac{B_a}{i_l} = - \frac{B_a}{i_{\text{corr}}} \quad (24)$$

Therefore, a corroding electrode controlled by concentration polarization also has a linear polarization curve with constant slope dependent on corrosion current.

This reasoning applies only when the anodic polarization curve intersects the cathodic curve near the limiting diffusion current so that i_c can be considered constant. If the anodic polarization curve intersects the cathodic curve where i_c is transient, Stern has shown (11) that quasi-linear behavior exists and $\frac{dE}{di}$ increases as i_{corr} decreases.

A third type of polarization, polarization resistance, may also be included in polarization measurements. While this will not affect the linearity of the polarization curve, it will increase the $\frac{dE}{di}$ value. For metals having low corrosion rates cell resistances are large compared to the solution resistances and the error resulting from the IR drop is negligible. However, for metals having high corrosion rates, cell resistances are low and IR drop through the solution may be an appreciable part of the measured polarization resistance.

Because polarization resistance is inversely proportional to corrosion current it can be used as a relative measure of corrosion rate. This has been done by several investigators in the past few years on a variety of systems (1)(3)(13)(17)(5).

Stern and Weisert showed (13) that for most corroding systems the corrosion rate can be estimated to within a factor of two by measurement of polarization resistance even without any knowledge of the electrochemistry of the system. If some

knowledge of the system is available, a better estimate can be obtained.

Polarization curves need not be logarithmic in order to apply polarization resistance techniques. If i_a and i_c are logarithmic functions of potential, when they are similar in value, their difference approximates a linear function of potential (13). In some systems, current may not be a logarithmic function of potential as in regions where both activation and concentration polarization are occurring. However, if only a small range, 5 mv, is considered, the local polarization curves will often approximate logarithmic behavior sufficiently to produce linear polarization resistance characteristics.

The foregoing relationships have been derived for low values of applied current, and potentials differing only slightly from equilibrium potentials. It is now important to determine over what range the linear portion of the polarization curve actually does extend.

When an electrode is polarized by an external current equation (16) applies:

$$i_{\text{applied}} = i_c - i_a$$

Using the Tafel relationship for this case,

$$E_a = B_a \log \frac{i_a}{i_{\text{corr}}} \qquad E_c = -B_c \log \frac{i_c}{i_{\text{corr}}} \qquad (25)$$

$$i_a = i_{\text{corr}} 10^{E/B_a} \quad i_c = i_{\text{corr}} 10^{-E/B_c} \quad (26)$$

Recognizing that $i_c = i_a$ at the corrosion potential and assuming that $B_a = B_c$ so that $B = 2.3B_a = 2.3B_c$, substitution yields:

$$i_{\text{applied}} = i_{\text{corr}} (10^{-E/B} - 10^{E/B}) \quad (27)$$

$$i_{\text{applied}} = (e^{-E/B \ln 10} - e^{E/B \ln 10}) \quad (28)$$

$$i_{\text{applied}} = -i_{\text{corr}} (e^{-E/B \ln 10} - e^{E/B \ln 10}) \quad (29)$$

$$i_{\text{applied}} = -2i_{\text{corr}} \sinh^{-1} \left[\frac{E \ln 10}{B} \right] \quad (30)$$

$$E = \frac{-B}{\ln 10} \sinh^{-1} \left[\frac{i_{\text{applied}}}{i_{\text{corr}}} \right] \quad (31)$$

Expanding $\sinh^{-1} \left[\frac{i_{\text{applied}}}{i_{\text{corr}}} \right]$ into a series of the form:

$$\sinh^{-1} (a) = a - \frac{1 \cdot a^3}{2 \cdot 3} + \frac{1 \cdot 3 \cdot a^5}{2 \cdot 4 \cdot 5} - \frac{1 \cdot 3 \cdot 5 \cdot a^7}{2 \cdot 4 \cdot 6 \cdot 7} + \dots$$

$$E = \frac{-B}{\ln 10} \left[\frac{i_{\text{applied}}}{2i_{\text{corr}}} - \frac{i_{\text{applied}}^3}{2i_{\text{corr}}^3} \frac{1}{6} + \dots \right] \quad (32)$$

$$E = \frac{-B}{2 \ln 10} \frac{i_{\text{applied}}}{i_{\text{corr}}} + \frac{B}{48 \ln 10} \left[\frac{i_{\text{applied}}}{i_{\text{corr}}} \right]^3 \quad (33)$$

$$\frac{dE}{di} = \frac{-B}{2 \ln 10} \frac{1}{i_{\text{corr}}} + \frac{B}{48 \ln 10} \frac{3(i_{\text{applied}})^2}{(i_{\text{corr}})^3} \quad (34)$$

Since the first term on the right produces the linear inverse relationship between $\frac{dE}{di}$ and i_{corr} , the following terms represent

the error.

$$\text{error} = \left[\frac{B}{48 \ln 10} \frac{i_{\text{applied}}}{i_{\text{corr}}} \right]^3 - \dots$$

This is an alternating series and the error introduced by using only the first term is bounded by the absolute value of the first neglected term:

$$\text{error} \leq \left| \frac{B}{48 \ln 10} \frac{i_{\text{applied}}}{i_{\text{corr}}} \right|^3$$

For given values of error and B ratios of $\frac{i_{\text{applied}}}{i_{\text{corr}}}$ can be calculated and substituted into equation (31) to find the value of E below which the polarization curve is linear. It can be seen from figure 5 that for most systems, 10 mv is the limiting value.

TEMPERATURE EFFECTS

One would normally expect the corrosion rate to increase as temperature increases since this is the case for most chemical processes. Temperature is usually related to reaction rate constants by an equation of the Arrhenius form:

$$\text{Log } K = A - \frac{C}{T}$$

If such a relationship exists, a plot of the reciprocal temperature versus the log of the reaction rate produces a straight line from which activation energy can be calculated. The data of Butler and Carter (1) shows considerable curvature when plotted in this manner.

This may indicate that for the corrosion of stainless steels, the metals used by Butler and Carter, more than a simple activation process is involved in the corrosion mechanism.

EQUIPMENT

Figure 6 shows a diagram of the experimental apparatus used for this project. The equipment consisted of [1] an Evenvolt power supply whose constant dc voltage was varied from 0 to 25 volts by means of [2], a rheostat which functioned as a voltage divider. [3] is a control that varied resistance from 0 to 100,000 K ohms and [4] is a Leeds and Northrup pH meter with the capability of a 200 mv expanded scale. [5] is a standard calomel electrode filled with saturated KCl solution and [6] is a salt bridge filled with the electrolyte of the standard polarization cell [9] as described by Green (19). [8] is a platinum electrode through which the current is applied and finally, [7] is the working electrode, the metal sample under test. This experimental arrangement is not unique, but is one that is commonly used in polarization studies.

Current is applied to the working electrode by the dc power supply and is varied by means of the voltage divider and the variable resistance controls. The varied resistance is kept several orders of magnitude above the resistance of the cell so that the current applied will be constant and will not be affected by changes in the resistance of the cell. Potential across the cell is read on the pH meter and applied current is read directly from the ammeter [10], a Hewlett Packard voltmeter with eleven dc current

scales ranging from 1.5 ua full scale deflection to 150 amps full scale deflection.

EXPERIMENTAL PROCEDURE

Sample Preparation: Metal specimen approximately 1.5 cm by 2.5 cm were cut from sheet samples and fastened to conducting wire by means of epoxy. The polishing technique used on the surface of each specimen to be exposed was as follows. Fifty hand strokes in one direction were followed by fifty strokes perpendicular to the direction of the first with 0 emery paper. This sequence was repeated and then the same procedure was duplicated using 00 emery paper. The samples were then degreased in acetone. A one square centimeter area was marked and the remainder of the sample was coated with a polystyrene-toluene mixture which dried to a hard nonconductive film. Compositions of the metals used are shown in Table I.

Aeration: Conditions of aeration were maintained by bubbling oxygen through the test solution by means of the special adapter on the polarization flask. Bubbling was initiated at least fifteen minutes prior to the tests and was continued throughout the course of each run. Deaerated conditions were induced by bubbling nitrogen through the electrolyte in the same manner. An oxygen test indicated that nitrogen bubbling through the solution

reduced the oxygen content from 0.64 to 0.30 ppm after fifteen minutes of bubbling at 20°C.

Data Acquisition: The sample was introduced into the polarization flask about five minutes after the completion of its surface preparation and the system was allowed to stabilize for five minutes. Polarization was begun with zero or close to zero applied current being the first reading. Current was incrementally increased with subsequent readings of applied current and cell potential being taken after two minute stabilization periods.

Samples were run in triplicate with at least one particular sample being repeated in order to check reproducibility. If reproducibility was not obtained within reasonable limits, or if the polarization resistances of the three specimen were not in agreement, the tests were repeated.

RESULTS AND DISCUSSION

Polarization resistances for the seven metals considered are given in Table II. Figure 7 illustrates the graph of ΔE vs ΔI obtained for nickel at 20°C in a deaerated solution, however, it is typical of the results for all the data taken. Data for the various metals differs only in the equilibrium potentials and the range over which linearity of the ΔE vs ΔI curve extends.

Equilibrium potentials are a function of many variables among which are the internal structure of the metal, external connections to the system and surface condition. While these potentials have very little importance alone, it is interesting to note that different samples of the same metal exhibited different equilibrium potentials, but these individual samples tended to repeat their equilibrium potentials to within 5 mv on subsequent runs under the same conditions. It has been noted before that equilibrium potentials have no direct relationship to corrosion rate, but it is reassuring to discover that sample preparation techniques were sufficient to produce surface conditions consistent enough to repeat initial potential readings.

The range of linearity of the polarization resistance curves was dependent on conditions of temperature and oxygen content as well as the type of metal under study. In general, except for mild steel, linearity extended over a minimum range of 10 mv. For the stainless steels, nickel and monel the range of linearity increased to as much as 40 mv with increasing temperature and oxygen content. Inconel and brass both began at 20° C with ranges of linearity on the order of 40 mv and then decreased as temperature and oxygen content increased. In the case of brass at higher temperatures, ranges of linearity persisted for only 5 mv. Mild steel was somewhat different from the other metals in that its polarization resistance curve remained linear for only 5 mv at 20° C and decreased to the point for which all the variables could no longer be measured with the existing apparatus. For this reason, polarization resistances for mild steel are not reported for all conditions tested.

It was shown previously that the range of linearity is primarily a function of B. For this reason and by using Figure 5, a general idea of the B values for the metals under the conditions to which they were exposed, can be obtained. B values for the stainless steels, nickel and monel range from about 0.06 to 0.22, increasing with temperature. This agrees with Stern and Weisert (13) who indicate that for activation

controlled systems, the group to which the stainless steels generally belong, B values are found largely between 0.06 and 0.12. Actually Stern and Weisert indicate that B values greater than 0.18 are unusual for activation controlled reactions, however, the data with which they worked was restricted primarily to room temperatures.

Inconel and Brass have B values between 0.22 and 0.03, decreasing with temperature. The B values of mild steel would be 0.03 and less.

The stainless steels were by far the easiest metals on which to experiment. They were consistently stable while in the electrolytic solution and quickly reached equilibrium. Brass and Inconel were the most difficult to handle. Tests were run several times before reproducibility could be obtained, and the specimens often required quite some time to reach an equilibrium potential. Bubbles were sometimes formed on the surfaces of these metals. While bubbles were also observed on nickel and steel, they were neither as frequent nor as plentiful.

EFFECT OF OXYGEN

Figure 8 illustrates the effect of oxygen on the polarization resistances of the metals tested. As can be predicted from theory, mild steel and stainless steels 304 and 316 are

most affected by the presence of oxygen. For the stainless steels, polarization resistance increases or corrosion rate decreases by an order of magnitude in oxygen saturated solutions. This is to be expected since the protective oxide film on the surface of the stainless steels cannot be formed without the presence of oxygen. Mild steel on the other hand shows a decrease in polarization resistance or an increase in corrosion rate in aerated solutions. In the case of steel, the effect of oxygen is to combine with the iron to form ferrous and ferric oxides which are not protective in the initial stages, and thus to accelerate the dissolution of the steel.

The corrosion rates of nickel, monel, inconel and brass show oxygen dependence to a much smaller extent. In each case the corrosion rate is slightly accelerated by the presence of oxygen, thus leading to the conclusion that oxide films are not the source of protection on these metals. Similar observations have been reported in the literature (26).

STAINLESS STEELS

Figure 9 shows the variation of polarization resistance with temperature for stainless steels 304 and 316 in the 5% HCl solution. In the same figure the results of Butler and Carter (1) for the same metals in 5% H_2SO_4 are shown.

While the experimental results fall generally within the same range as those of Butler and Carter, it will be noticed that they slope in opposite directions. If the technique described in the appendix is used to calculate approximate corrosion rates, a plot of temperature vs calculated corrosion rates can be drawn as in Figure 10. Figure 11 shows temperature vs measured corrosion rates taken from the literature (1)(25). Again it is obvious that the temperature effect on corrosion rates as determined by this experiment does not agree with that established by previous investigators. The results of this experiment indicate that there is a decrease in the corrosion rates of stainless steel 304 and 316 with increasing temperature. A minimum rate for stainless steel 316 is reached at 60°C. Previous work has shown by weight loss measurements that between 25°C and 70°C in 5% H₂SO₄ solutions the corrosion rate increases with temperature in deaerated solutions. Since the initial corrosion rates of stainless steels are generally accepted to be activation controlled, increasing temperature would most certainly have the effect of increasing corrosion rate. This leads to the observation that the experimental conditions were such that parameters other than temperature must have entered and had the controlling influence on the system. The most obvious explanation for the apparent discrep-

ancy between the experimental results and the work cited from the literature is the oxygen content of the test solution. It can be seen from figure 8 that the corrosion rates of the stainless steels are affected by the presence of oxygen more than any of the other metals tested. From this observation it can be deduced that these metals would be the most sensitive to the oxygen content of the test solution. It has been determined (33) that the solubility of oxygen in sea water increases as the temperature is increased up to 80°C and then decreases with further temperature increase. A similar relationship might be expected for the HCl test solution so that the amount of oxygen dissolved in the test solution would have increased with increasing temperature. Unfortunately, the assumption was made that N₂ bubbling continuously through the test solution would remove most of the oxygen. Further investigation has disclosed that this assumption is invalid. This technique would only have tended to keep the oxygen level constant for all tests at a particular temperature. Dissolved oxygen content would still increase with increasing temperature, and increasing amounts of oxygen in the test solution would have the effect of increasing polarization resistances or decreasing corrosion rates as temperature is increased. This is exactly what is shown in figures 9 and 10.

The minimum corrosion rate experienced by stainless steel

316 can most likely be explained as the point at which the oxygen lost its controlling influence and another mechanism became dominant. This type of behavior has been observed by other experimenters in recent work (30)(31).

NICKEL AND MONEL

The relationships between temperature and polarization resistance for nickel and monel are illustrated in figure 12. Both metals show a decrease in polarization resistance with increase in temperature. Using the previously described technique, corrosion rates can be calculated and plotted as in figure 13. Corrosion rates, as expected, increase with temperature. Figure 13 also presents weight loss data from other sources (26)(33) for comparison with the experimental results. The fact that the experimental results do not fall within the same range as results from the literature should not be surprising. Both sets of data from the literature do not entirely agree as to the range or slope of the curves, and it must be remembered that these data represent weight loss figures averaged over some length of time, not initial corrosion rates as do the results of this experiment. Surface preparation is also a very important factor in determining corrosion rate, and no attempt has been made to duplicate surface preparation of samples used in the literature. The most important observation

is that all sets of figures show that corrosion rate is increased as temperature is increased.

If polarization resistance is plotted against the reciprocal of the absolute temperature, figure 14 results. Since neither curve is a straight line, it must be concluded that activation is not the controlling factor in the corrosion of nickel and monel. Cheng (23) states that the corrosion of nickel in degassed HCl is controlled by both transport and phase boundary reaction. This statement tends to support the nonlinearity of the curves in figure 14.

INCONEL AND BRASS

Figure 15 illustrates the relationships found between polarization resistance and temperature for inconel and brass. Temperature appears to have little or no effect on the polarization resistance of either brass or inconel. Calculated weight loss figures are plotted in figure 16 along with weight loss data from the literature for brass (33). Corrosion rates from the literature are somewhat lower and show the slightly more pronounced influence of temperature. Considering that these results were obtained under different conditions using different techniques (see figure 16) comparison of the experimental results with the literature shows reasonable agreement.

Other investigators have noted that consistent corrosion rates are difficult to obtain with brass as either a function of temperature or chloride ion concentration (35). Correlations with length of exposure time have been more successful. This investigator can confirm the fact that brass is an unpredictable metal with which to work in electrolytic solutions.

Very little work appears to have been done on inconel in the past. For this reason, no weight loss data are presented for comparison with the experimental results. Cheng (23) states that at higher temperatures chromium sulfides are formed in inconel depleting the alloy matrix of its protective chromium. For this reason, corrosion rates increase with temperature. However, in the temperature range used for this work no such relationship is visible.

If their basic composition are considered, nickel, monel and inconel should behave similarly. However, in these experiments inconel was quite different from either monel or nickel. This may possibly be explained by the fact that under the conditions of the tests, nickel and monel were both in their passive states while inconel remained in its active state. Small differences in the quantities and natures of the trace alloying elements would account for such behavior. Metals when in their passive

states are more noble than when in their active states and thus exhibit more stable behavior.

Brass is composed primarily of copper and zinc. Zinc is extremely active in chloride solutions and no doubt accounts for the instability encountered in the electrochemical system of brass.

CONCLUSIONS

Several useful conclusions can be drawn from the results of this experiment. Although the temperature relationships on steel and the stainless steels were obscured as the result of a false assumption, some beneficial conclusions can still be made.

- 1) The corrosion rates of stainless steels 304 and 316 are greatly increased (an order of magnitude) by the removal of oxygen from their environment.
- 1a) The effect of oxygen concentration in the environment of stainless steels 304 and 316 is to have a greater influence on corrosion rates than temperature in the 20°C to 80°C range.
- 2) Removal of oxygen from the environment of mild steel decreases its corrosion rate by an order of magnitude.
- 3) Removal of oxygen from the environments of nickel, monel, brass and inconel tends to reduce corrosion rates but only slightly.
- 4) The corrosion rates of nickel and monel can be accelerated by increasing temperature.
- 5) The corrosion rates of brass and inconel are relatively unaffected by temperature changes between 20°C and 80°C.

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TABLE I							
	Mild Steel	S.S. 304	S.S. 316	Monel 400	Inconel 625	Nickel 200	Admiralty Brass
C	0.05	0.046	0.042	0.15	0.04	0.03	---
Mn	0.28	1.45	1.84	0.95	0.03	0.27	---
P	0.005	0.025	0.021	---	---	---	0.03
S	0.020	0.007	0.020	0.012	0.009	0.005	---
Si	0.012	0.062	0.32	0.08	0.21	---	---
Cu	0.015	0.13	0.20	31.88	0.03	0.01	72.6
Ni	0.006	8.96	12.65	65.52	60.21	99.56	---
Cr	0.011	18.17	17.70	---	22.68	---	---
Mo	0.001	0.11	2.18	---	9.26	---	---
Fe	bal	bal	bal	1.39	3.44	0.05	0.06
Al	---	---	---	0.002	0.17	---	---
Ti	---	---	---	---	0.24	---	---
Cb+Ta	---	---	---	---	3.66	---	---
Zn	---	---	---	---	---	---	bal
Sn	---	---	---	---	---	---	0.85
Pb	---	---	---	---	---	---	0.07
density	---	7.44	7.58	8.03	8.05	8.52	7.87

TABLE 11

	Mild Steel	S.S. 304	S.S. 316	Nickel	Monel	Inconel	Brass
20°C aerated	---	46.2	28.2	66.8	251	46.5	115
20°C deaerated	2.4	0.23	3.27	83.5	441	79.4	356
40°C deaerated	.8	39.2	40.1	51.0	250	74.0	357
60°C deaerated	---	62.5	74.4	30.5	132	85.7	400
80°C deaerated	---	387	38.7	11.5	37.5	76.0	354

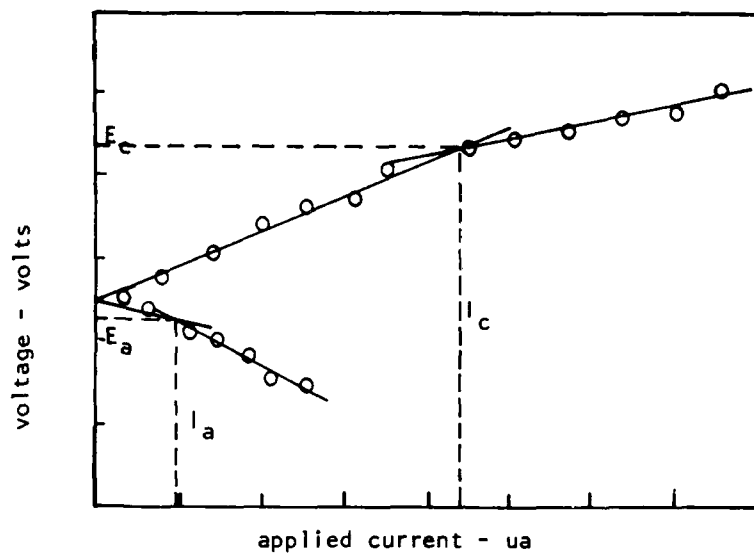


Figure 1 Polarization curves illustrating the method of Schwerdtfeger and McDorman (6)

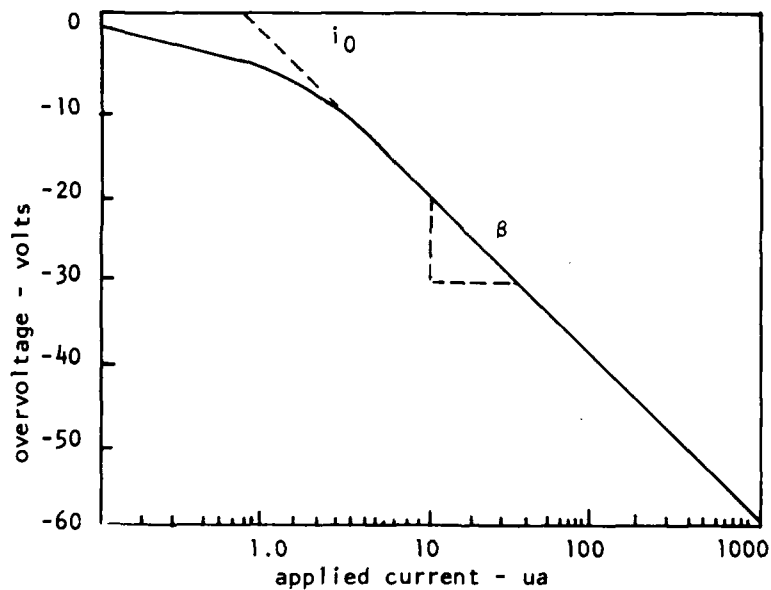


Figure 2 Polarization curves illustrating the method of Stern (9)

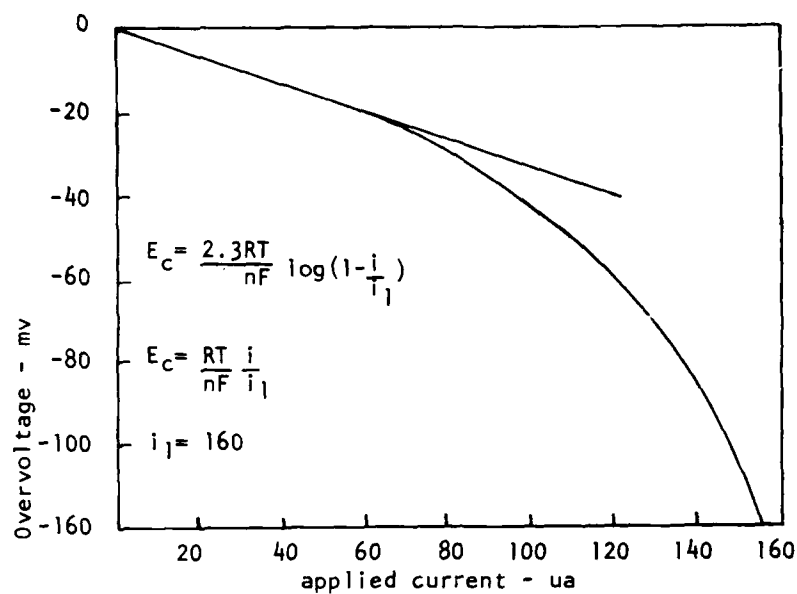


Figure 3 Concentration polarization curve showing the extent of linearity (11)

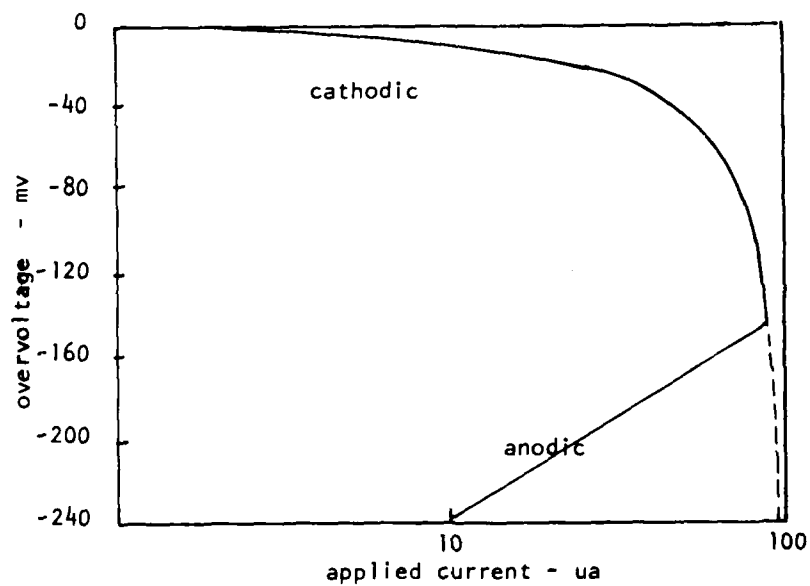


Figure 4 Polarization diagram where cathodic curve is logarithmic and anodic curve intersects near the limiting diffusion current (11)

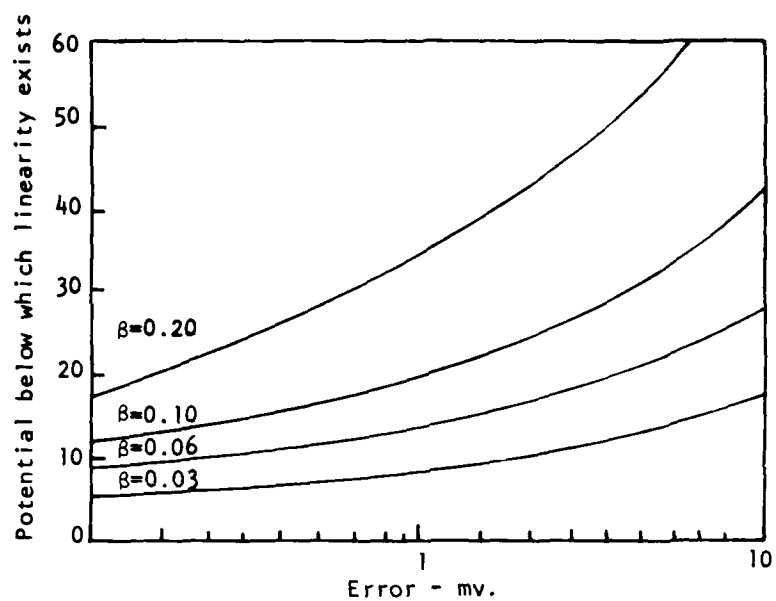


Figure 5 Error in linear polarization behavior as a function of β values and overvoltage (11)

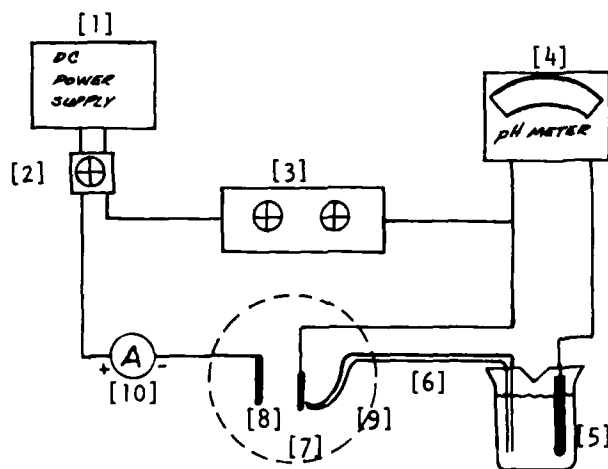


Figure 6 Schematic of experimental apparatus

FIGURE 7
TYPICAL POLARIZATION RESISTANCE CURVE
NICKEL 20°C 5% HCl

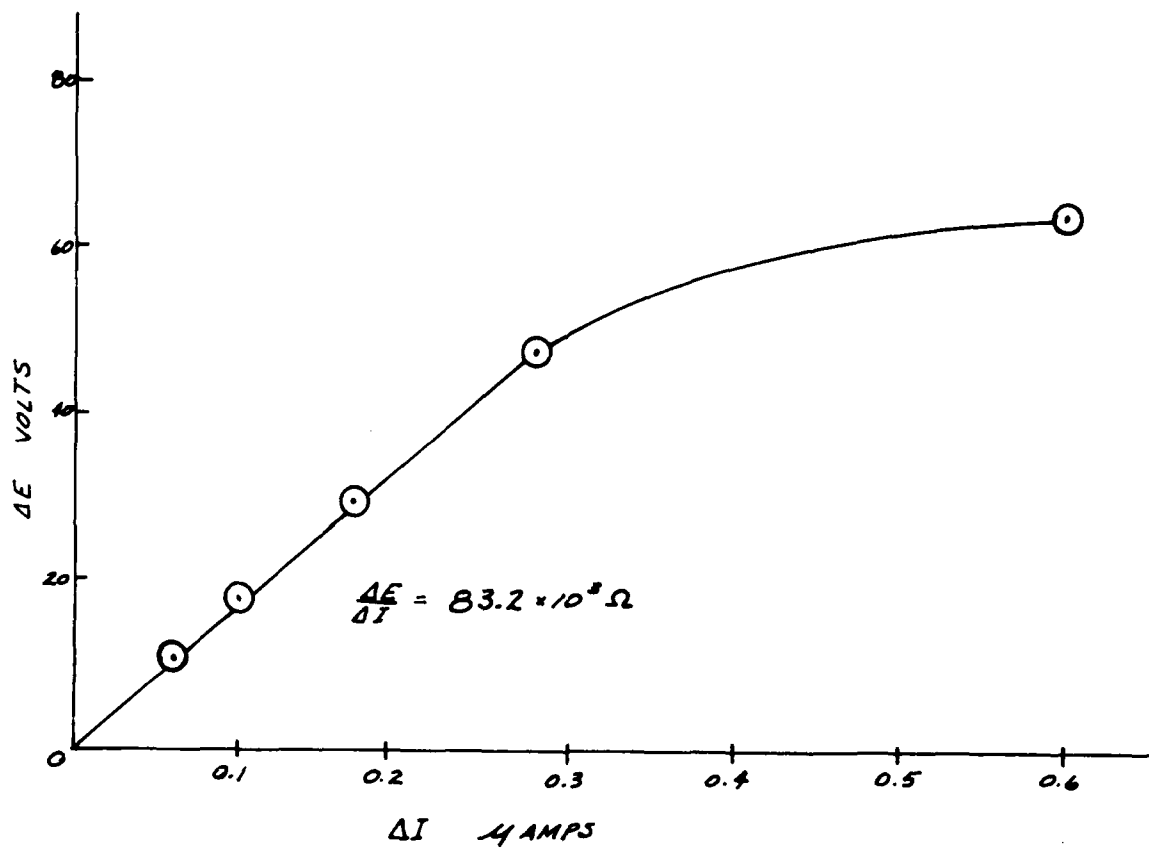


FIGURE 8
VARIATION OF POLARIZATION RESISTANCE
WITH OXYGEN CONTENT
 5% HCl 20°C

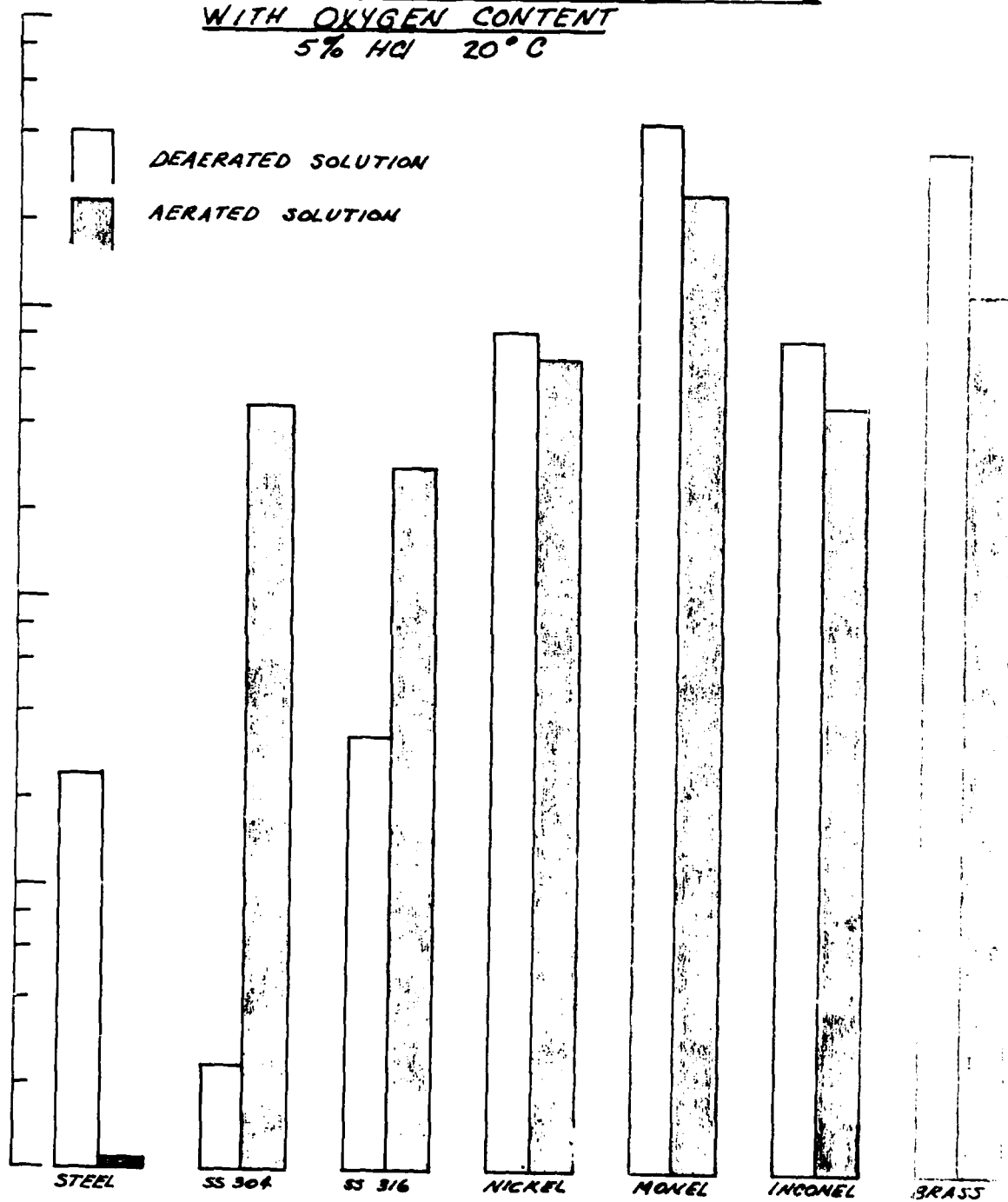


FIGURE 9
TEMPERATURE VS POLARIZATION RESISTANCE
STAINLESS STEEL

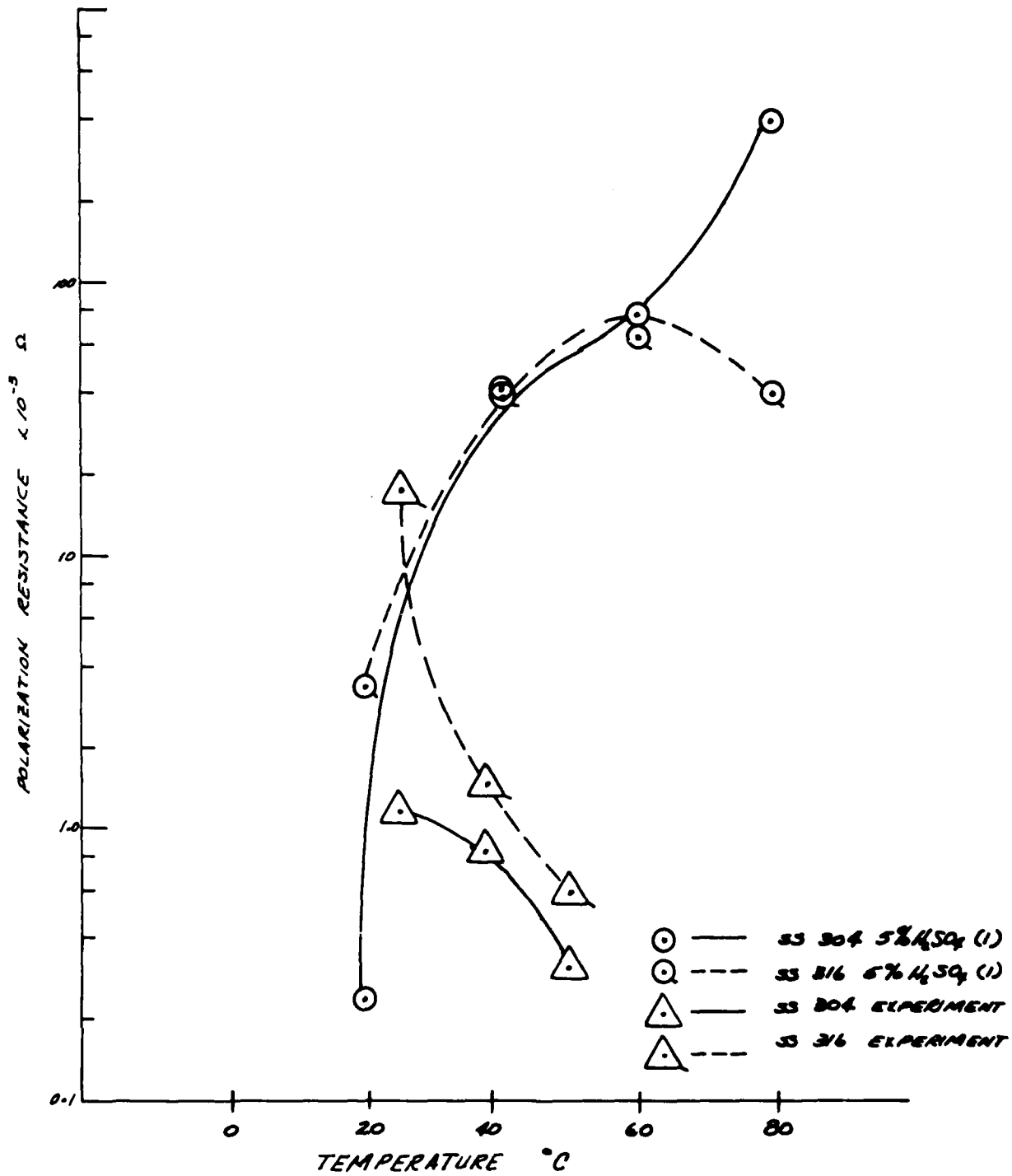


FIGURE 10
TEMPERATURE VS CORROSION RATE
STAINLESS STEEL

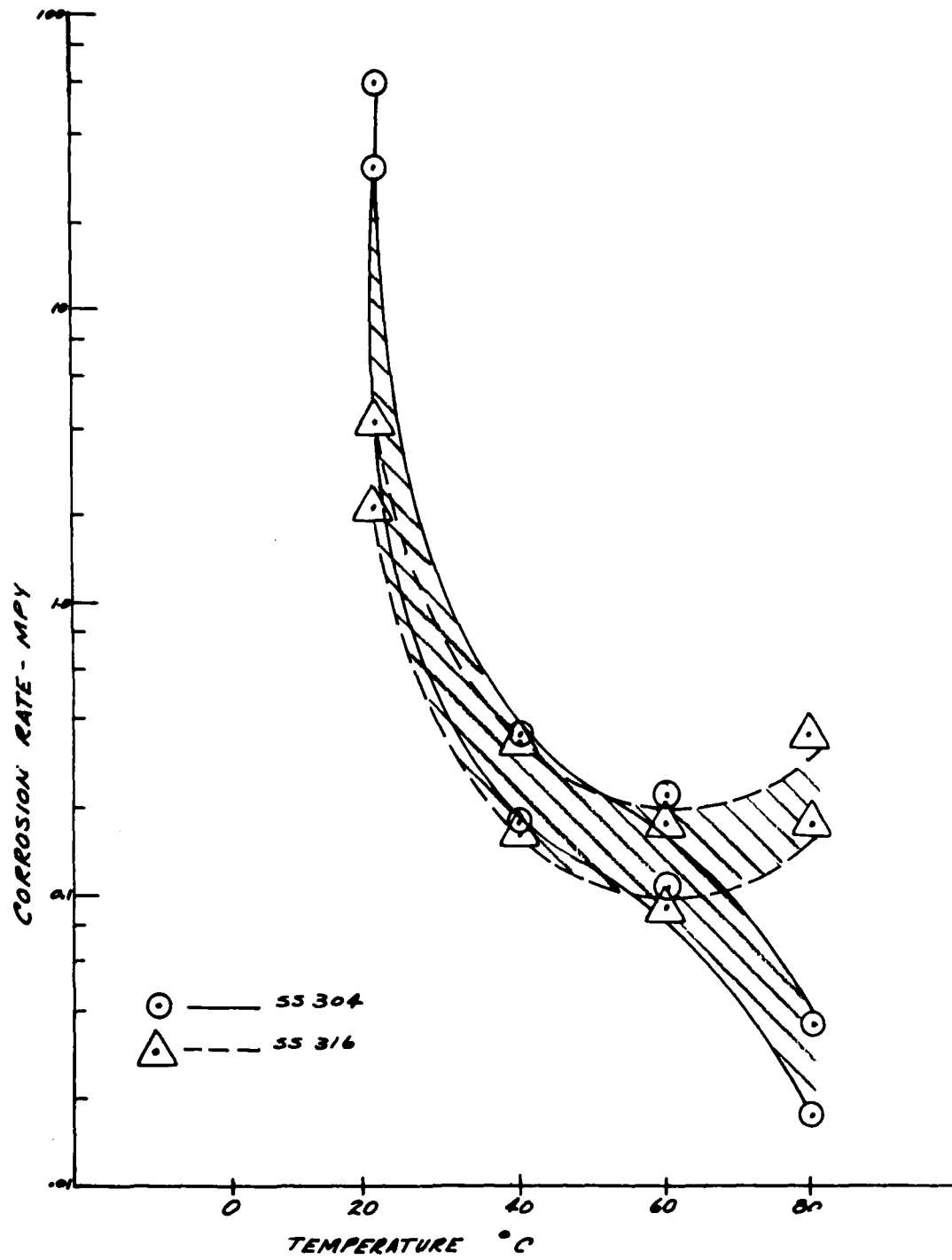


FIGURE 11
TEMPERATURE VS. CORROSION RATE
 STAINLESS STEEL
 RESULTS FROM THE LITERATURE

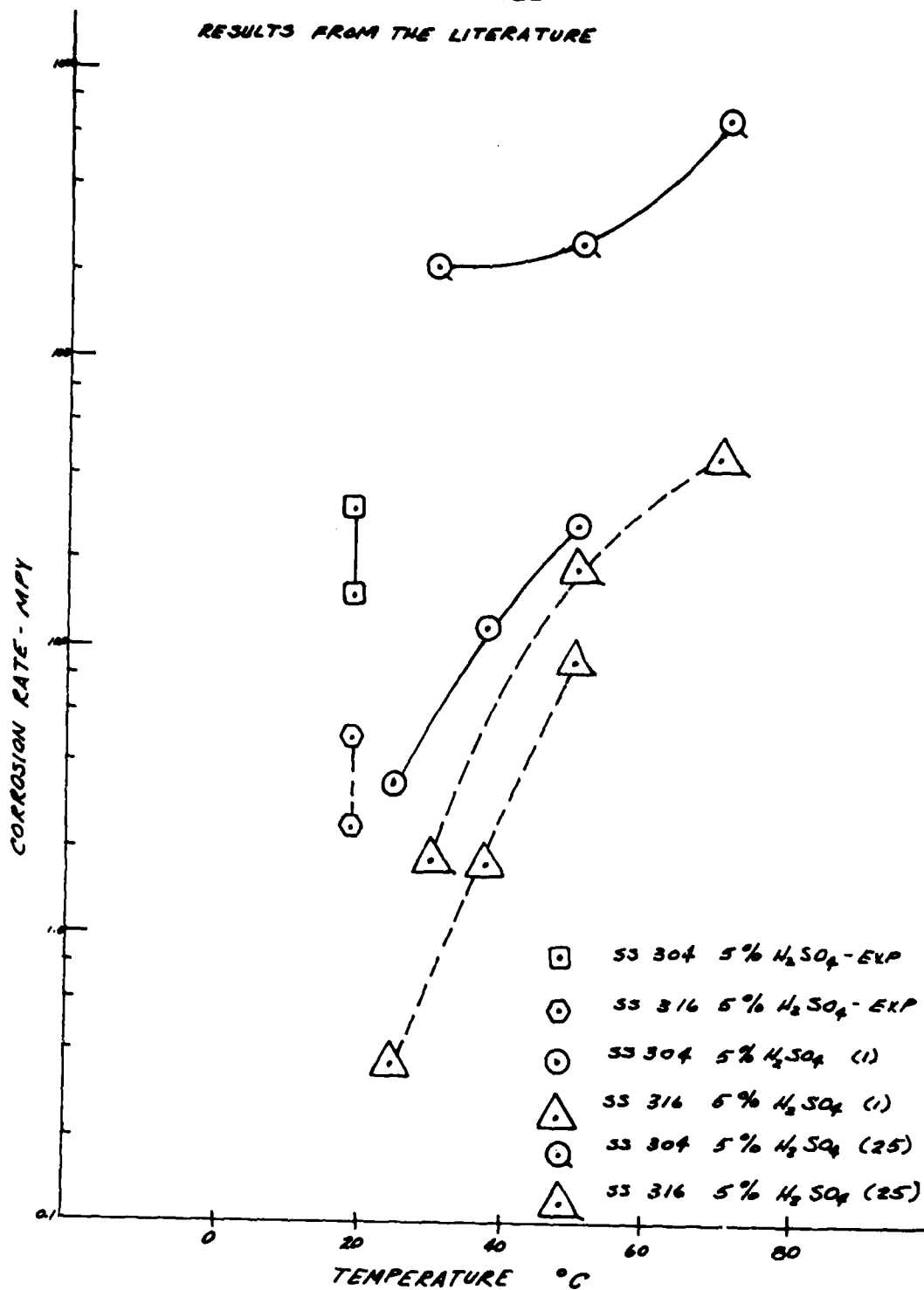
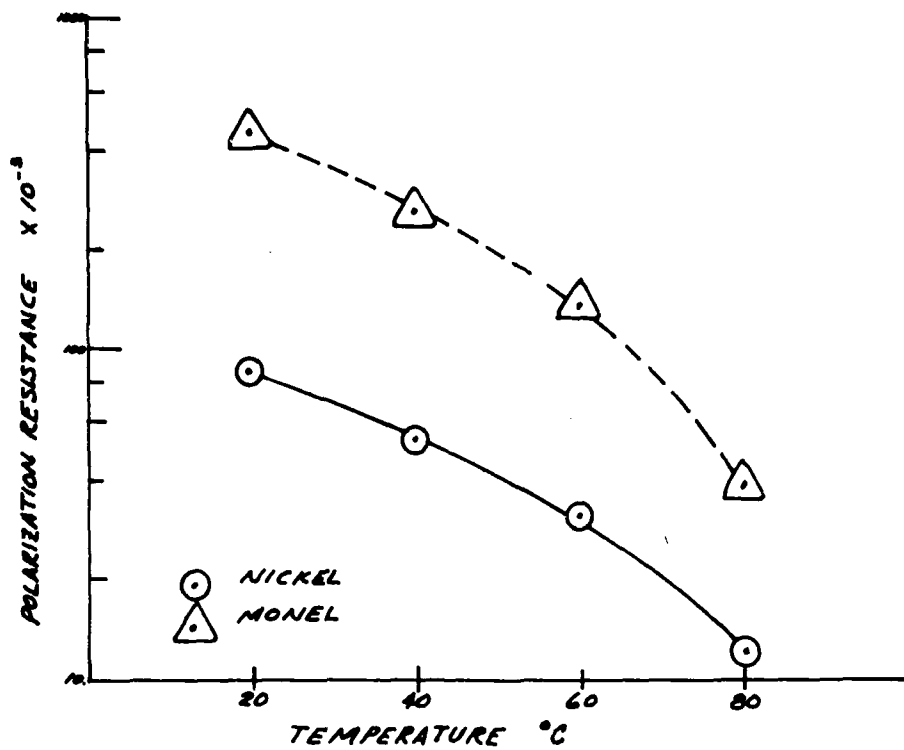


FIGURE 12

TEMPERATURE VS POLARIZATION
RESISTANCE
NICKEL AND MONEL



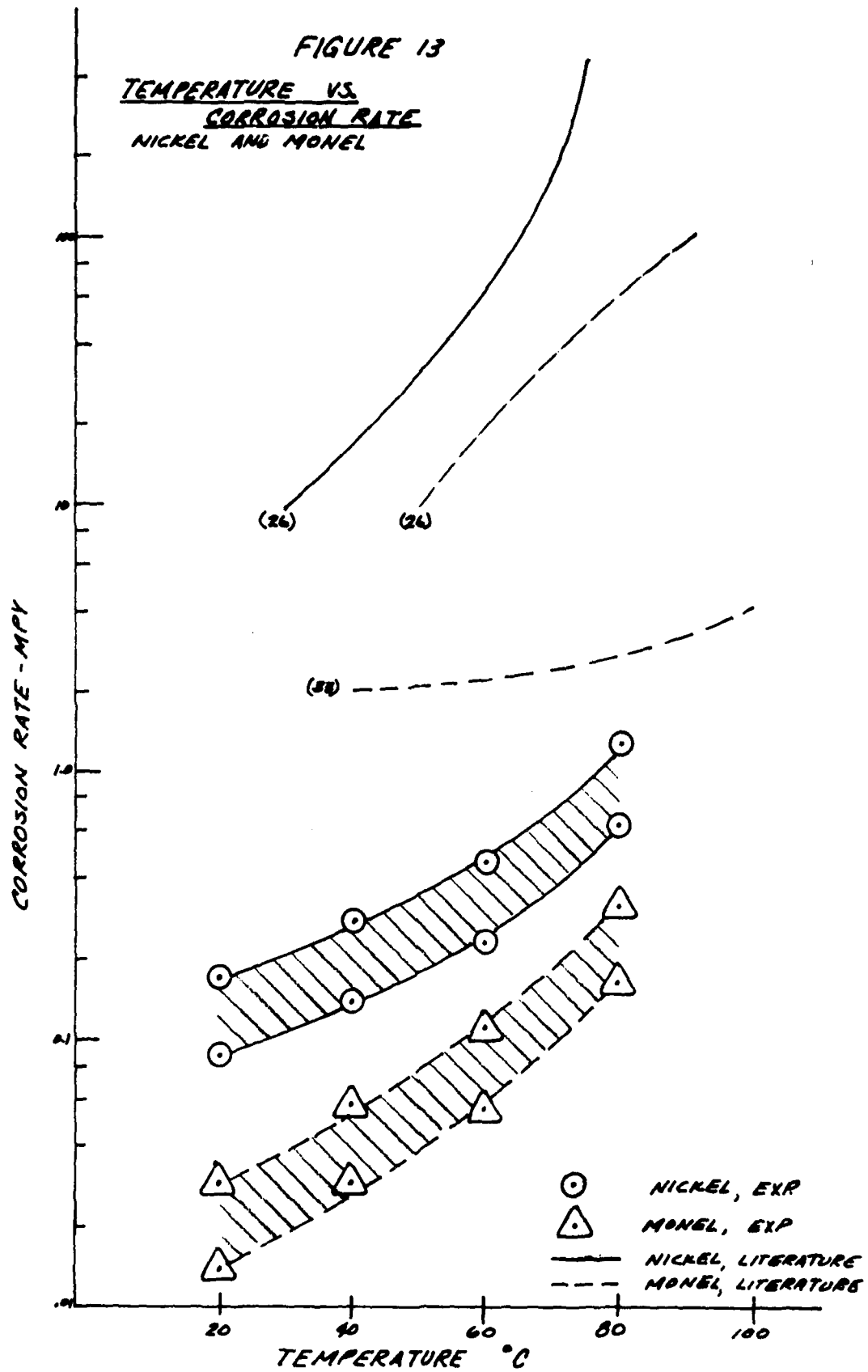


FIGURE 14

RECIPROCAL TEMPERATURE VS
POLARIZATION RESISTANCE

NICKEL AND MONEL

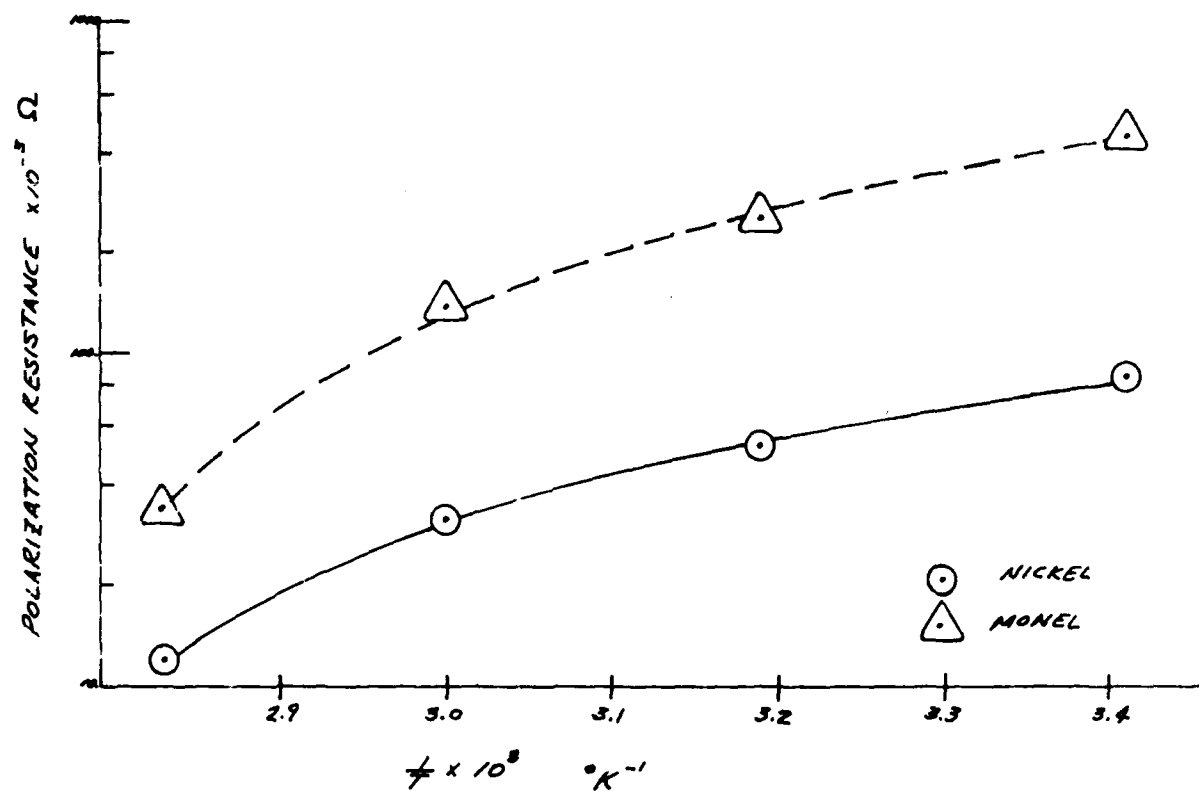


FIGURE 15
TEMPERATURE VS POLARIZATION
RESISTANCE
INCONEL AND BRASS

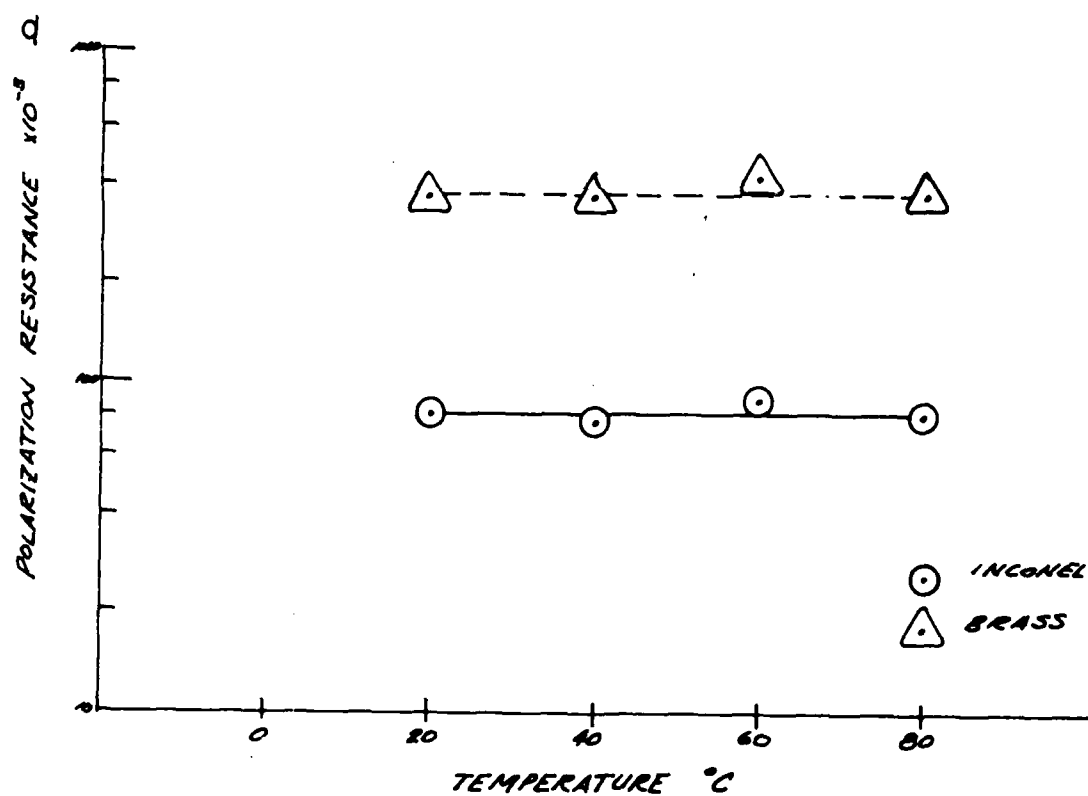
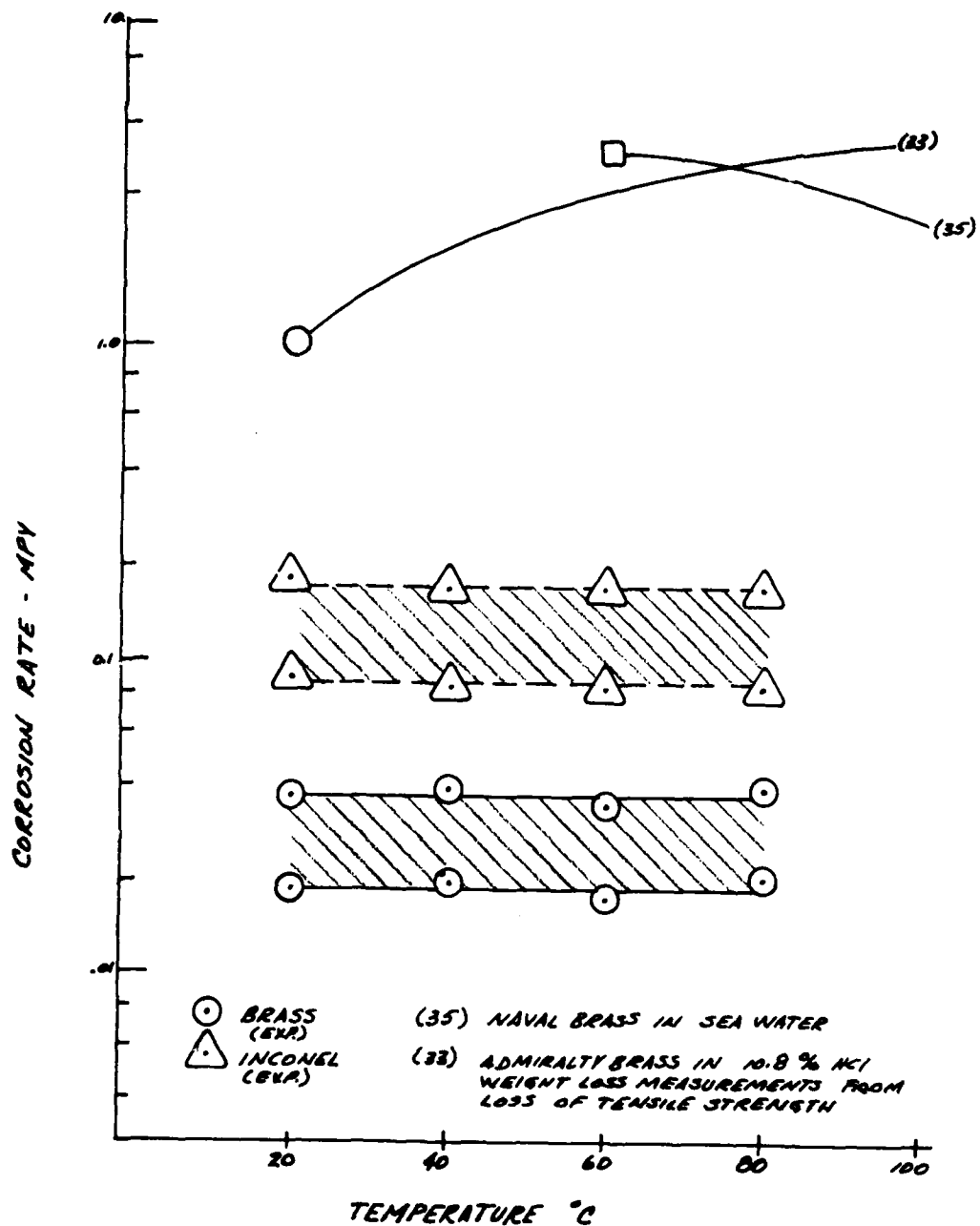


FIGURE 16
TEMPERATURE VS CORROSION RATE
 BRASS AND INCONEL
 LITERATURE AND EXPERIMENTAL



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APPENDIX

Calculation of Approximate Weight Loss from Polarization Resistance Measurements

It has been shown that polarization resistance is related to corrosion current by:

$$R = \frac{B_a B_c}{2.3(B_a + B_c) I_c}$$

If it is assumed that $B_a = B_c$, then,

$$R = \frac{B^2}{2.3(2B) I_c} = \frac{B}{4.6 I_c}$$

and

$$I_c = \frac{B}{4.6R}$$

Stern and Weisert (13) have indicated that most B values fall between 0.03 and 0.18 and for activation controlled reactions the range narrows to 0.06 to 0.12.

Faraday's Law states that the weight of a metal reacting is related to the amount of current passing through the metal and the time the current flows:

$$w = \frac{IMt}{Fj}$$

w - weight in grams
I - current in amps
t - time in seconds
F - Faraday, 96519 coulombs
j - valence
M - molecular weight in grams

Use of this relationship provides weight loss in units of gm/cm²sec. More common units of weight loss can be calculated by the use of simple conversion factors and densities.

$$\text{gm/cm}^2\text{sec} \times 8.64 \times 10^9 = \text{mgm/dec}^2\text{day} \quad (\text{mdd})$$

$$\text{mdd} \times 1.44/D = \text{mils/year} \quad (\text{mpy})$$

If weight losses are calculated for B values of 0.06 and 0.12, a band of probable corrosion rates in mpy can be obtained for comparison with other weight loss data. While this approximation is valid only for activation controlled reactions, it has been used for all the metals tested. It was assumed that since the plots of reciprocal temperature vs polarization resistance did not deviate greatly from linearity, the error introduced by considering these reactions to be activation controlled was not significant as far as estimation purposes are concerned.

TABLE A1

<u>°C</u>	<u>SS 304</u>		<u>SS 316</u>		<u>Nickel</u>		<u>Monel</u>		<u>Incone1</u>		<u>Brass</u>	
	<u>mdd</u>	<u>mpy</u>	<u>mdd</u>	<u>mpy</u>	<u>mdd</u>	<u>mpy</u>	<u>mdd</u>	<u>mpy</u>	<u>mdd</u>	<u>mpy</u>	<u>mdd</u>	<u>mpy</u>
B=0.06												
20	141.7	29.2	9.97	2.05	.412	.085	.077	.014	.432	.089	.054	.018
40	.832	.171	.813	.167	.672	.138	.137	.028	.463	.083	.053	.019
60	.522	.107	.438	.090	1.12	.231	.260	.053	.400	.082	.048	.017
80	.084	.017	.842	.173	2.98	.613	.914	.164	.451	.081	.054	.020
B=0.12												
20	283.5	58.3	19.4	4.10	.824	.169	.155	.028	.863	.178	.393	.036
40	1.66	.342	1.62	.334	1.34	.276	.274	.056	.926	.167	.392	.038
60	1.043	.215	.876	.180	2.25	.462	.519	.107	.800	.164	.349	.034
80	.168	.035	1.68	.347	5.96	1.23	1.83	.329	.902	.162	.395	.038

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13. ABSTRACT The corrosion rates of stainless steels 304 and 316, mild steel, nickel, monel, inconel and brass were investigated by electrochemical polarization techniques in 5% aerated and deaerated HCl solutions. It was found that the corrosion rates of the stainless steels increased by an order of magnitude while the corrosion rate of mild steel decreased by an order of magnitude when oxygen was removed from the test solutions. Corrosion rates were only slightly reduced for nickel, monel, inconel and brass in deaerated solutions. Increasing temperatures between 20°C and 80°C caused the accelerated corrosion of nickel and monel, however, had little effect on brass and inconel.		

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