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A Method For Determining Corrosion Rates From Linear Polarization Data*

By MILTON STERN*

Introduction

ORROSION TESTING by weightloss methods is generally a long, tedious affair which often does not produce completely satisfactory results. This is particularly true when the corrosion rate changes with time.

Several attempts to relate various electrochemical properties of a metal to corrosion rate have been described in the literature. Unfortunately, the techniques usually are more involved than weight-loss procedures and furthermore they may have no sound basis in theory. Recently, however, Skold and Larson and Simmons² have described empirical observations which appear to have promise as a practical method for measuring instantaneous corrosion rates by electrochemical means. They showed that the slope of the linear portion of the polarization curve of iron can be related to its corrosion rate. The method has some foundation in theory and may have rather wide applicability to many systems.

The purpose of this discussion is (a) to describe the theoretical basis which makes the method attractive, (b) to define the conditions where the technique appears to be most applicable, and (c) to provide supporting evidence.

Description of the Method

It is often found experimentally that the initial portion of a polarization curve is linear so that potential plotted as a function of applied current or current density approximates a straight line. The slope of this straight line, $\Delta E/\Delta I$, has units of resistance and for conveni-ence will be called the "polarization resistance." It is important to note that this is not a resistance in the usual sense. The nature of "polarization re-sistance" will be discussed in a later will be discussed in a later section.

Simmons,² in a study of polar organic inhibitors in crude oil-salt water systems, found that a qualitative relation existed between $\Delta E/\Delta I$ and the corrosion rate. He reported that all inhibitors which exhibit good weight-loss suppression give high values of "polari-zation resistance." The converse was zation resistance." The converse was also true. In addition, simultaneous measurement of $\Delta E/\Delta I$ and weight change as a function of time showed that "polarization resistance" increases as inhibition proceeds reaching a maximum when the sample apparently stops corroding.

Skold and Larson¹ initially conducted polarization measurements to calculate corrosion rates from "breaks" in polarization curves by a method described by Schwerdtfeger and McDorman.³ This

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approach was abandoned for reasons described in their paper. They found in their studies of steel and cast iron in natural waters that a linear relation existed between potential and applied cathodic and anodic current density at low values of applied current density. "Polarization resistance" was higher for samples having a low corrosion rate than for samples exhibiting high rates. Fortunately, their conditions were such as to give corrosion rates which varied over several orders of magnitude. A plot of corrosion rate versus "polarization resistance" on logarithmic scales gave a straight line with a negative slope. This empirical data was used to determine changes in corrosion rate with time for various systems.

Theoretical Basis for the Method

Stern and Geary,⁴ in a discussion of the shape of polarization curves for corroding systems controlled by activation polarization,⁽¹⁾ showed that a linear relationship is expected in the region where the polarized potential is close to the corrosion potential. For these con-ditions, the following equation was derived.

$$\frac{\Delta E}{\Delta I} = \frac{\beta_{a}\beta_{c}}{(2.3)(I_{corr})(\beta_{a} + \beta_{c})} \qquad (1)$$

where $\Delta E/\Delta I$ is the polarization resistance, the constants β_e and β_a are the slopes of the logarithmic local cathodic and anodic polarization curves, and Icorr is the corrosion current. This equation applies only when ΔE is small.⁽²⁾ Thus, it is seen that the "polarization resistance" is inversely proportional to the corrosion current Four tional to the corrosion current. Equation (1), however, does not consider the influence of concentration polarization which undoubtedly played an important Skold and Larson¹. Thus, it is neces-sary to determine whether the polarization curve for corroding systems controlled by concentration polarization exhibits a linear section and whether the slope of this linear section is related to corrosion rate. To accomplish this, it is first convenient to consider concentration polarization on a non-corroding electrode and then introduce the additional complexity arising when the electrode corrodes.

Concentration polarization occurs at a cathode when the reaction rate or the applied cathodic current is so large that the substance being reduced cannot reach the cathode at a sufficiently rapid rate. The solution adjacent to the electrode surface becomes depleted of the reacting ions, and the rate then is con-

- (i) For systems where the local anodic and cathodic polarization curves are logarithmic in nature.
- (3) The expected range of the linear relation between E and I and the deviation from linearity for various potential values are described in the appendix.

Abstract

Abstract A method for determining corrosion rate from electrochemical polarization data obtained in the region of the corrosion potential is described. The technique has oundation in theory, is supported by ex-perimental evidence, and appears to have widespread application. The advantages and limitations of the method are dis-cussed. It would appear that the use of linear polarization measurements can supply valuable information regarding: (1.) Studies of the effect of environment variables on corrosion rate. These in composition, velocity, and temperature, (2.) Evaluations of in-hibitors in controlling corrosion, (3.) Comparison of the corrosion rates of va-rious alloys of similar composition in a given environment, and (4.) Determina-tion of changes in corrosion rate with ine, including studies of underground structures as well as materials in aque-ous solutions. It also may be possible to use this focatings in service which cannot be in-

It also may be possible to use this method in evaluating the condition of coatings in service which cannot be in-spected by visual methods. 2.3.5

trolled by the maximum rate at which the reacting species can diffuse to the surface. The electrode potential changes sharply in this region until a potential is reached where a new reaction proceeds. The change in potential caused by concentration polarization can be expressed in its most simple form as⁵

$$E_{conc} = 2.3 \, \frac{RT}{nF} \log \left(1 - \frac{I}{I_L} \right) \, (2)$$

where I_L is the limiting diffusion current or the current equivalent to the maxi-mum rate of diffusion of the reacting substance. By assigning arbitrary values

to the constants
$$(2.3 \frac{\text{RT}}{\text{nF}} = 0.059 \text{ volt,}$$

and $I_L = 100$ microamperes), the shape of the curve described by Equation 2 may be illustrated in Figure 1.

The series expansion of $ln(1 + X) = X - \frac{1}{2}X^3 + \frac{1}{3}X^3 - \frac{1}{4}X^4 + \dots$ can be used to estimate how concentration polarization varies with current for

small values of $\frac{I}{I_L}$. For this condition,

only the first term of the series is significant so that at 25 C

$$E_{conc} = -\frac{RT}{nF} \frac{I}{I_L} = -0.0256 \frac{I}{I_L}$$
(3)

Thus, when the applied current is small in comparison to the limiting diffusion current, concentration polarization approximates a linear function of current with a slope of 0.0256/IL. The plot of Equation 3 has been drawn on Figure 1 to illustrate the extent of its applicability.

When one considers a corroding electrode whose corrosion rate is controlled by concentration polarization, the situation is slightly different. The schematic

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Figure 2-with a la cathodic

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Figure 2—Polarization diagram for a corroding metal with a logarithmic anodic polarization curve and a cathodic polarization curve exhibiting concentration polarization.

polarization diagram for such a condition is illustrated in Figure 2 where the anodic polarization curve is considered logarithmic in nature. For such a system, the corrosion current is practically equal to the limiting diffusion current. It is well known⁶ that the applied cathodic current necessary to polarize such a corroding electrode to some given cathodic value is given by the following relationship:

$$I_{applied} = I_e - I_a \qquad (4)$$

where Ie and Ia are the local cathodic and anodic currents, respectively. Also, the equation for the change in anodic current, using the corrosion potential as reference, may be written

$$I_{a} = I_{corr} \left(10^{\frac{\varepsilon}{\beta_{a}}} \right)$$
 (5)

where e is the difference between the polarized potential and the corrosion potential. Since $I_c = I_{corr} = I_L$, substitution of Equation (5) into Equation (4) produces

$$I_{applied} = I_{L} - I_{L} \left(\frac{\varepsilon}{10^{\frac{\varepsilon}{\beta_{a}}}} \right) \qquad (6)$$

For small values of ε , that is where the polarized potential is close to the corrosion potential, expansion of the exponential and rearrangement yield

$$\epsilon = -\frac{\beta_a}{2.3 I_L} I_{applied}$$
(7)

$$\frac{\Delta E}{\Delta I} = -\frac{\beta_a}{2.3 I_L} = -\frac{\beta_a}{2.3 I_{corr}}$$
(8)

Therefore, a corroding electrode con-



3-Potential as a function of applied current for the system described in Figure 2. Figure 3-

trolled by concentration polarization also produces a linear polarization curve, the slope of which is related to the corrosion current.⁽³⁾ Figure 3 shows the cathodic polarization curve of the system illustrated in Figure 2 calculated from Equations (4) and (5). The arbi-trary constants for the calculation are $I_{\rm L} = 100$ microamperes, $\beta_{\rm a} = 0.1$ volt, and $E_{corr} = -0.1$ volt.

Equation (8) applies only when the anodic polarization curve intersects the cathodic curve close to the limiting diffusion current so that Ie may be considered a constant. If this is not true, such an equation cannot be simply derived. This does not mean necessarily that under such circumstances quasilinear behavior will not be observed, but the inverse relation between "polarization resistance" and corrosion current described by Equation (8) does not apply.

For example, consider a system with the same cathodic polarization curve illustrated in Figure 2 and an anodic curve of similar slope intersecting at 0.02 volt where Ie is not a constant. This is equivalent to moving the anodic curve of Figure 2 upward. Figure 4, which shows the cathodic polarization curve for such a system calculated in the manner described previously, reveals that quasi-linear behavior does exist. Furthermore, the slope of this portion of the polarization curve is greater than that shown in Figure 3 where the corrosion rate is greater. Thus, qualita-

tively, $\frac{\Delta E}{\Delta I}$ increases as $I_{corrosion}$ de-

creases. This is important since it is believed that the real value of this approach at the present time lies not in direct calculation of corrosion rates from equations such as (1) and (8), but rather in an empirical determination such as used by Skold and Larson.¹

There are several reasons for adopting this attitude. First, the constants required to apply Equation (1) or (8) are not available for many real systems. Secondly, the constants may not remain constant as environmental conditions change. Also, it is possible that the local

(3) Equation (8) can be derived directly from Equation (1) since the conditions selected are equivalent to considering β_e infinite. Thus,

$$\lim \frac{\beta_{a}\beta_{c}}{(2.3) (I_{corr}) (\beta_{a} + \beta_{c})} = \frac{\beta_{a}}{(2.3) I_{corr}}.$$

$$\beta_{c} \to \infty$$

Figure 4—Potential as a function of applied current for a corroding system similar to that shown in Figure 2 except that the anodic curve is moved upward to produce a corrosion potential of 0.02 volt.

anodic polarization curve is not loga-rithmic in nature since concentration polarization may play a role in anodic polarization, or the anodic curve may actually be linear as described by Petrocelli⁷ for dissolution of aluminum in alkaline solutions. In addition, an IR drop may be included in the polarization measurements. This would not distort the linear shape of the pertinent portions of the polarization curve but would, of course, increase the value of ΔE

 $\frac{-1}{\Delta I}$. This resistance error, which was

recognized by Skold and Larson,^t is evident in their empirical relationship between $\frac{\Delta E}{\Delta I}$ and corrosion rate. If the

corrosion rate is inversely proportional to "polarization resistance" as indicated by Equations (1) and (8), then a plot of these two parameters on logarithmic scales should give a straight line with a slope minus one. The slope of the line drawn by Skold and Larson' is greater than this for data obtained in 3000 ohmcm water. Their data in low resistance solutions lie close to the theoretical slope.

Perhaps the most important reason for considering that an empirical de-termination of the quantitative relation between "polarization resistance" and corrosion rate is necessary, lies in the ٨F

act that determination of
$$\frac{\Delta L}{\Delta I}$$
 depends

heavily on the judgment which an in-vestigator uses to determine the extent of the linear polarization curve. An in-sufficient number of experimental points and scatter in the data of a few milli-volts often will tend to extend the apparent linear portion of a polarization curve to higher potentials resulting in inaccurate values of polarization re-sistance.⁽⁴⁾ As described in the appendix, truly linear dependence of potential on applied current is expected only for about the first 10 millivolts of polarization.

Experimental Observations

Equation (1) applies to any system whose potential is determined by two

⁽⁴⁾ When concentration polarization is involved, the measured "polarization resistance" will tend to be too high, whereas if only activa-tion polarization occurs, the measured "polarization resistance" will be low. This occurs because of the different shapes of concentration polarization and activation polarization when plotted on a linear scale.

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Figure 5—Potential as a function of opplied cathodic current density for various bi-electrodes.

intersecting logarithmic polarization curves. Therefore, in addition to corroding electrodes, reversible electrodes also can be described by this equation simply by substituting exchange current for corrosion current.

A reversible electrode system was selected for experimental verification primarily because an obvious, well behaved system was readily available.

system was readily available. Some earlier work⁸ showed that titanium and Type 316 stainless steel in uitrate containing solutions of ferrous and ferric chloride exhibit potentials very close to the reversible ferric-ferrous potential of the solution. In addition, it was found that the exchange current density for the reaction Fe⁺⁺ + $e \rightleftharpoons Fe^{++}$ was markedly different when it occurs on the surface of the two metals. Also, it was shown⁹ that the exchange current density on bi-electrodes (couples) made of these two materials could be represented by the following equation.

$i_{o(T1+316)} = f_{316} i_{o(316)} + f_{T1} i_{o(T1)}$

where f_{316} and f_{T1} represent the fraction of the couple area occupied by Type 316 stainless steel and titanium, respectively; $i_{0(310)}$ and $i_{0(T1)}$ are the exchange current densities for the individual materials; and $i_{0(316+T1)}$ is the exchange current density of the bi-electrode. Bi-electrodes are formed by electrically coupling different areas of the two metals. Thus, the use of bi-electrodes with various area fractions of titanium and Type 316 stainless provides an ideal system for obtaining surfaces with a range of exchange current densities which vary from the low value on titanium itself to the high value on stainless steel. This permits an experimental check of the inverse relationship between "polarization resistance" and exchange current as predicted by Equation (1). ⁽⁶⁾

The samples, procedures, and equipment were exactly the same as those described previously⁹ except that in this case, it was necessary to get many accurate points on a polarization curve in the potential region from 0 to 15 millivolts. This was accomplished, without reducing the impedance of the potential measuring system, by using an Applied Physics Corporation Model 31 vibrating reed electrometer as a null point indicator in series with a precision potentiometer. The electrometer has a four-inch 0- to 1-millivolt scale which permits potential measurement to better than 0.01 millivolt. Six samples, contained in the same polarization cell, were used to produce the bi-electrodes. They are designated at Ti(5), Ti(10), Ti(50), 316(0.9), 316(2), and 316(5) where the prefix indicates the material, and the number in parentheses approximates the surface area in square centimeters. Inasmuch as exact areas along with the measured exchange current densities have been published previously⁹ this information will not be repeated here.

Figure 5 shows the low potential cathodic polarization region for various bi-electrodes which were selected to give a range of exchange current densities between the values which apply to titanium and 316 stainless steel. The exchange current densities, calculated from the preceding equation are included on the figure.⁽⁹⁾ In those cases where the bi-electrode exchange current density was actually determined,⁸ the agreement between measured and calculated values was good. Figure 6 illustrates the inverse relation between "polarization resistance" and exchange current density as predicted by Equation (1). When these data are plotted in this manuer, it is important to note that "polarization resistance" should be zero when the exchange current density is infinite.

Additional support for this kind of analysis can be obtained from the data of Bonhoeffer and Jena¹⁰ who studied the electrochemical behavior of 11 different types of iron in sulfuric acid solutions. These authors compared "polarization resistance" and corrosion current for these materials and showed that the corrosion rate decreases as "polarization resistance" increases. Their plot of "polarization resistance" versus corrosion current appears to be hyperbolic in nature. Figure 7 illustrates their data" plotted in the same manner as Figure 6 and shows the inverse relation between "polarization resistance" and corrosion current. Since it is most likely that activation polarization controls corrosion rate under the conditions of their test, Figure 7 supplies additional confirmation of Equation (1) and indicates that such electrochemical measurements can supply a valuable screening method.

General Features of the Method

"Polarization resistance," as used here, is not a resistance in the usual sense of the term. The linear dependence of potential on current only exists because the difference between two logarithmic functions of current (Equation (4)) approximates a linear function when the logarithmic functions are of the same order of magnitude.

"Polarization resistance" measured by either anodic or cathodic polarization should be identical. This not only results from the derivation of Equations (1) and (8) but also is observed experimentally.⁸ Skold" has confirmed this, but reports that the extent of the linear relation observed during anodic polarization is smaller than that observed during cathodic measurements.

The extent of the linear relation described by Equation (1) is dependent upon the beta values of the individual anodic and cathodic polarization curves. It is possible to analyze Equation (1) mathematically to show the amount of polarization which can occur for systems with various beta values while maintaining a linear relation within various error limits. To do this, it is necessary to assume that the anodic and cathodic beta values are equal. While this is not necessarily the case for many real systems, it provides a valuable guide in interpretation of experimental data. Such an analysis is presented in the appendix and shows that the maximum error in potential (designated by e) can be described by Equation (9).

$$e = \frac{\beta I^3}{48 \ln 10 I^3_{\text{corr}}}$$
(9)

In the region where current approximates a linear function of potential, the value e is the maximum deviation of potential from linearity at any current. For a reversible electrode, the corrosion current in Equation (9) would be replaced

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⁽⁶⁾ Actually, one may compare either "polarization resistance" to exchange and corrosion current or "polarization resistance per unit area" to exchange or corrosion current density. The use of corrosion current density only serves to compare samples of different size under the same conditions and has no direct relation, in this case, to the actual anodic or cathodic current densities which exist during corrosion.

^(*) The Ti(10) electrode exhibited a lower exchange current density than the other titanium samples. This is not considered serious for present purposes, since actual experimental values for each electrode have been used to calculate the exchange current current of bi-electrodes.

⁽⁷⁾ One point which appeared abnormal has not been included.



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Figure 6—Polarization resistance as a function of the reciprocal of the exchange current density for various bi-electrodes.

by the exchange current. Using Equation (9) and the known relation between potential and applied current in the linear region (see appendix), it is possible to calculate the value of polarized potential below which a linear relation is expected within any given error. This is shown in Figure 8 for a variety of beta values and reveals that a system with anodic and cathodic beta values of 0.1 can be polarized for about 10 millivolts with a maximum deviation from linearity of 0.1 millivolt, or it may be polarized 21 millivolts with a maximum deviation from linearity of 1.0 millivolt.

The use of the "polarization resistance" for measuring corrosion rates has one particularly important advantage. The potential range investigated is close to the corrosion potential and the applied currents are generally smaller than the corrosion current. Thus, the nature of the surface is not changed significantly, and the reactions which proceed during polarization are those which actually occur during the corrosion process. This is not necessarily the case when a corroding surface is markedly polarized, since under such conditions, the subsequent corrosion rate may be affected for some time after polarization has been discontinued.

The following is a list of situations where it appears that the use of linear polarization measurements can supply valuable information.

1. Studies of the effect of environment variables on corrosion rate. These include changes in composition, velocity, and temperatures.

2. Evaluation of inhibitors in controlling corrosion.

3. Comparison of the corrosion rates of various alloys of similar composition in a given environment.

4. Determination of changes in corrosion rate with time, including studies of underground structures as well as materials in aqueous solutions.

5. It also may be possible to evaluate the condition of coatings in service which cannot be inspected by visual methods.

While the use of linear polarization data to determine corrosion rates cannot be considered a universal approach, there is sufficient basis in theory along



CORROSION CURRENT" (CM2/Mo)

Figure 7---Polarization resistance as a function of the reciprocal of corrosion current for various iron samples in sulfuric acid (Bonhoeffer and Jena).

with supporting evidence to believe that the technique can find a useful place in corrosion studies.

Acknowledgment

The author would like to acknowledge the skillful assistance of E. A. Tomes who conducted the experimental measurements, and E. J. Bartolomei and N. Darroch who carried out many of the calculations. Dr. L. Cross assisted in the derivation of Equation (17).

APPENDIX

Since the use of polarization data to determine corrosion rates requires a measurement of the slope of the linear region of a polarization curve, it is necessary to know the approximate extent of the linear region. This is best described by indicating the potential change during polarization below which the polarization curve is linear within a given potential error. Consider a corroding system whose potential and corrosion rate are determined by two intersecting logarithmic polarization curves with equal beta values. When the metal is polarized by an external applied cathodic current, the following relation applies:

$$I_{applied} = I_{c} - I_{a} \qquad (10)$$

Since Ie and Ia are equal at the corrosion potential and are logarithmic functions of potential

$$I_{applied} = I_{corr} \begin{pmatrix} -\frac{\varepsilon}{\beta} + \frac{\varepsilon}{\beta} \\ 10 & -10 \end{pmatrix}$$
(11)

where ϵ is the difference between the polarized potential and the corrosion potential.

Rearranging gives

$$I_{applied} = -I_{corr} \begin{pmatrix} +\frac{\varepsilon}{\beta} \ln 10 & -\frac{\varepsilon}{\beta} \ln 10 \\ e & -e \end{pmatrix}$$
(12)

and

$$I_{applied} = -2 I_{corr} \sinh \frac{\epsilon}{\beta} \ln 10$$
 (13)

Therefore,

$$\varepsilon = \frac{\beta}{\ln 10} \sinh^{-1} \left(\frac{I_{applied}}{2 I_{corr}} \right) \quad (14)$$



Figure 8—The amount an electrode may be polarized and still exhibit linear polarization behavior as a function of the deviation from linearity for various beta values.

Using the series
$$\sinh^{-1} X = X - \frac{1 \cdot X^3}{2 \cdot 3}$$

+ $\frac{1 \cdot 3X^3}{2 \cdot 4 \cdot 5} - \frac{1 \cdot 3 \cdot 5X^7}{2 \cdot 4 \cdot 6 \cdot 7} + \dots,$
 $s = -\frac{\beta}{2 \ln 10} \frac{I_{applied}}{I_{corr}} + \frac{\beta}{48 \ln 10} \frac{I^3_{applied}}{I^3_{corr}} - \dots$ (15)

The first term on the right side of Equation (15) shows the inverse relation between $\frac{\Delta E}{\Delta I_{spplied}}$ and $I_{corr}^{(8)}$. Thus, the subsequent terms are the error (designated by e) in ε if only the first term is considered. Therefore,

$$e = \frac{\beta}{48 \ln 10} \frac{I^{s}_{applied}}{I^{s}_{corr}} - \dots$$
(16)

However, since the right side of Equation (15) is an alternating series, it can be shown that the error in using the first term of the series is bounded by the first neglected term.

Hence

$$e \leqslant \frac{\beta}{48 \ln 10} \frac{I^{3}_{applied}}{I^{3}_{corrosion}}$$
(17)

Thus, for given values of e and β , one may calculate the ratio of applied current to corrosion current and use this in Equation (11) or (14) to calculate ε which is the amount an electrode has been polarized. This value of potential shows how far one may polarize a surface and expect linear behavior within the error selected. This is the basis of Figure 8.

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