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THE EFFECT OF SWEEP RATES ON LINEAR POLARIZATION RESISTANCE MEASUREMENTS

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RESEARCH REPORT

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ABSTRACT

A study of Linear Polarization Resistance Measurements for silver metal immersed in a solution of AgNO₃ and HNO₃ to determine the effect of varying potential sweep rates has been made.

Results indicate that for the system under investigation the Polarization Resistance is a non-linear function of potential sweep rate.
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CHAPTER I
INTRODUCTION

The word corrosion denotes destruction of metal by chemical or electrochemical action\(^1\). The rate at which this destruction occurs is a function of the environment surrounding the metal, individual material properties and physical loading placed on the system. With the greatly increasing costs of production and the advent of new processes requiring higher temperatures and pressures, the losses due to corrosion have become extremely expensive. For this reason a need exists for a quick and accurate method of measuring corrosion rates within a particular system.

In the past the most used method for determining the corrosion rate within a system was to periodically shut the system down and inspect it for damage. Other methods include placing metal coupons at selective points in the system and periodically checking for corrosion by measuring weight loss of the samples. These methods do work but require long periods of time to determine corrosion rates. This is impractical because it identifies a corrosion problem after significant damage is done and the corrective action is limited to replacing damaged components.

During the past fifteen years, electronic methods that allow for the measurement of corrosion currents have been developed. These methods, called Polarization methods, have been used to measure corrosion rates in many systems.
CHAPTER II
RESEARCH OBJECTIVE

The research objective is to determine the effect of Potential Sweep Rate on Linear Polarization measurements.
CHAPTER III
THEORY

Ohms Law states that when a conductor of resistance, R, carries a current I, a potential difference V, must be present across the ends of the conductor. When a metal undergoes corrosion in the presence of an electrolyte, a potential difference exists between points located on the surface of the metal resulting in a current flow between these points. This current is called the corrosion current. The current flows from the anode to the cathode.

Electrons are released at the anode as a result of an electrochemical reaction, which takes place at the metal-electrolyte interface. The reaction at the interface consists of a metal atom being oxidized to a metal ion which goes into solution with the electrolyte. The reverse reaction occurs at the cathode, or the electrons may be picked up by a Hydrogen ion to form a Hydrogen molecule, which is then released to the atmosphere as a gas.

The amount of metal released at the anode is directly proportional to the corrosion current. Michael Faraday showed in the early nineteenth century that (Faraday's Law):

\[ \text{Weight of metal reacting} = KIT \]

where I is in amperes, t in seconds and K is a constant called the electrochemical equivalent (a physical property of the material). As a result of Faraday's Law the corrosion rate can be determined by measuring the corrosion current.
Under actual corrosion conditions the anodes and cathodes are dispersed throughout the material and it is not possible to directly measure the current flowing between them. It has been shown that there is a direct relationship between the corrosion voltage and the effect of an externally applied current on the metal surface. The development of the theory of polarization measurements is based on this physical relationship.

There are two generally accepted methods for measuring corrosion current. They are the Tafel Extrapolation Method and the Linear Polarization Method.

The Tafel Extrapolation Method has been used to verify the Mixed-Potential Theory developed by Wagner and Traud. Stearn and Geary have studied this method and found it fundamentally sound from an electrochemical viewpoint and suitable for both anodic and cathodic polarization measurements. Their development of this method is as follows. In the case of a noncorroding electrode system consider a substance Z in a solution containing its ions $Z^+$. At equilibrium the rate of oxidation of Z is equal to the rate of reduction of $Z^+$.

$$Z^+ + e \rightarrow Z$$

The reaction rate and current flow are directly related according to Faraday's Law. If $i_z$ is defined as the current in the forward (Reduction) direction and $i_z$ as the current in the reverse (Oxidation) direction, the electrode equilibrium may be expressed in the form

$$i_{oz} = \dot{i}_z = \ddot{i}_z$$ \hspace{1cm} (1)

where $i_{oz}$ is commonly called the exchange current. When the reaction rate is controlled by a slow step requiring an activation energy, the
dependence of current on overvoltage may be expressed as

\[ i_z = i_{oz} \exp(-n/\beta_z') \]  \hspace{1cm} (2)

\[ i_z = i_{oz} \exp(-n/\beta_z'') \]  \hspace{1cm} (3)

where the overvoltage, \( n \), is the difference between the potential of the reaction being studied, and \( \beta_z' \) and \( \beta_z'' \) are constants. For a system with a symmetrical energy barrier at the electrode interface, \( \beta_z'' \) is equal to \( \beta_z' \). Therefore, equations (2) and (3) may be written as

\[ n = -\beta_z \log \frac{i_z}{i_{oz}} \]  \hspace{1cm} (4)

\[ n = +\beta_z \log \frac{i_{oz}}{i_z} \]  \hspace{1cm} (5)

where \( \beta_z = 2.3\beta_z' = 2.3\beta_z'' \).

For a physical description of the terms in equations (4) and (5) consider an electrode in a solution containing its ions as shown in Figure 1.

Where \( i_x \) is the external current generated when the electrode is polarized to some overvoltage \( n \) and is equal to the net difference between \( i_z \) and \( \dot{i}_z \). Equation (6) shows this relationship.

\[ \dot{i}_x = \dot{i}_z - \dot{i}_z \]  \hspace{1cm} (6)

It is evident that \( \dot{i}_x \) approaches \( \dot{i}_z \) as \( n \) becomes large in the negative direction and \( \ddot{i}_x \) approaches \( -\dot{i}_z \) as \( n \) becomes large in the positive direction. Substituting into equations (4) and (5) one obtains the Tafel Equation:\n
\[ n = \pm \beta_z \log \frac{i_x}{i_{oz}} \]  \hspace{1cm} (7)
Figure 1. Electrode Reaction.
This equation does not consider concentration polarization or resistance drop effects.\textsuperscript{5} The important factor here is that the equation is in terms of measurable quantities \( n \) and \( i_x \).

In the case of a corroding electrode system two co-existing electrochemical reactions now appear; the previously discussed oxidation reduction system, \( Z^+ + e^- \rightarrow Z \), and the oxidation reduction system of the metal, \( M^+ + e^- \rightarrow M \). Each of these systems 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. Thus at the steady state corrosion potential,

\[
\dot{i}_Z + \dot{i}_m = \dot{i}_Z + \dot{i}_m
\]

where \( \dot{i}_m \) is the rate of reduction of \( M^+ \) and \( \dot{i}_m \) is the rate of oxidation of metal \( M \), and \( \dot{i}_Z \) and \( \dot{i}_Z \) are the rates of reduction and oxidation of species \( Z \), respectively. Since the corrosion rate by definition is \( \dot{i}_m - \dot{i}_m \), it is evident that the rate may also be defined as \( \dot{i}_Z - \dot{i}_Z \) at the corrosion potential. As shown earlier \( \dot{i}_Z - \dot{i}_Z = i_x \) therefore one may now determine the corrosion current by measuring \( i_x \) and \( n \) and extrapolating the experimental data back to the corrosion potential. This is shown in Figure 2 where \( n \) is the overvoltage referenced to the equilibrium potential of the \( Z \) reaction and \( i \) is the applied current. \( \beta_a \) and \( \beta_c \) are the Tafel Constants for each reaction. Values of \( \beta_a \) range from 0.06 to 0.12 volt/decade while \( \beta_c \) remains constant at 0.12 volt/decade.\textsuperscript{6}

There are several disadvantages with this method. The first being that it requires the sample to be polarized several hundred millivolts
resulting in comparatively large currents. The end result being damage to the sample under test. It requires several hours for each test and can only be used in systems containing one reduction process.

The Linear Polarization Method can now be developed from equations (4) and (5). Butler and Armstrong\(^7\) have shown that the overvoltage of a reversible electrode is a Linear function of applied current for values of overvoltage only slightly removed from the reversible voltage. Rearranging equations (4) and (5) and substituting into equation (6) yields

\[ i_x = i_0 z \left( 10^{-n/\beta_z} - 10^{+n/\beta_z} \right) \tag{9} \]

for small values of \( n/\beta_z \) where \( 10^{-n/\beta_z} \) may be approximated by \( (1- n/\beta_z)^{2.3} \) and \( 10^{+n/\beta_z} \) may be approximated by \( (1^+ n/\beta_z)^{2.3} \), equation (9) reduces to

\[ i_x = -2(2.3)(i_0 z) n/\beta_z \tag{10} \]

and

\[ \frac{d\eta}{dix} \bigg| _{n \to o} = \frac{-\beta_z}{(2)(2.3)(i_0 z)} \tag{11} \]

This development is for the non corroding electrode and as for the Tafel Method be extended to the corroding electrode. this yields

\[ i_x = -2.3 i_{corr} n \left( \frac{\beta_z + \beta_m}{\beta_z \beta_m} \right) \tag{12} \]

and

\[ \frac{d\eta}{dix} \bigg| _{n \to o} = \frac{-\beta_z}{(2.3)(i_{corr}) \left( \beta_z + \beta_m \right)} \tag{13} \]
Figure 2. Example of a Tafel Plot.
Here \( n \) is defined as the difference between the polarized potential and the corrosion potential. Figure 3 shows an example of Linear Polarization Plot.

This equation is more commonly written

\[
\frac{\Delta E}{\Delta I} = -\frac{1}{I_{\text{corr}}(2.3)} \frac{\beta_a \beta_c}{\beta_a + \beta_c}
\]

(14)

and is called the polarization resistance.

In this equation \( \Delta E \) is the overvoltage of the corroding electrode produced by the polarizing current \( \Delta I \). \( \beta_a \) and \( \beta_c \) are the slopes of the anodic and cathodic polarization curves in the Tafel region and \( I_{\text{corr}} \) is the corrosion current.

The polarization resistance is mainly controlled by \( I_{\text{corr}} \) and is relatively insensitive to change in beta values. Hence, it is possible to formulate a reasonable accurate approximation of equation (14).

Assuming that anodic and cathodic beta values of 0.12 volt represent the average or all corrosion systems equation (4) becomes

\[
\frac{\Delta E}{\Delta I} = \frac{0.026}{I_{\text{corr}}}
\]

(15)

This equation may be used to calculate the corrosion rate of a system without knowledge of its electrode kinetic parameters yielding corrosion rates differing by no more than a factor of 3 from actual rates.

The advantage of linear polarization are obvious. It permits rapid corrosion rate measurement without damage to the system under test.
Figure 3. Linear Polarization Plot.
CHAPTER IV
EXPERIMENTAL EQUIPMENT

The experimental setup centers around potentiostat/galvanostat. This instrument provides the capability to set and maintain a constant voltage across the sample and reference electrode. It features control by means of an internal potential source, as well as by external control potentials applied to the unit. The unit used was a Princeton Applied Research Corporation model number 371.

Current and voltage measurement were made using a Keithley Model 616 Digital Electrometer. This unit provides the capability to measure currents ranging from $10^{-1}$ to $10^{-11}$ amps.

A potentiometer was used to provide external voltage inputs during non-automated tests. During automated tests voltage scans were produced by a variable resistor driven by variable speed electric motor. Later tests used a variable frequency/amplitude signal generator.

Data was displayed and recorded on a X-Y recorder.

A polarization cell was constructed using 250 ml pyrex beaker with a rubber lid. Three holes were located symmetrically in the rubber lid to accommodate three silver electrodes. The electrodes were cylindrical in shape and drilled and taped to allow attachment of a threaded steel rod to form a terminal for each electrode. The steel terminals were isolated from the electrolyte by placing a glass tube over each terminal, sealing the silver glass interface with a rubber "O" ring and inserting each electrode in the drilled hole in the rubber lid. Each
terminal was identified as either reference, sample or power to facilitate connection to test circuit. A .099 MOLAR solution of AgNO₃ and .001 MOLAR HNO₃ was used as an electrolyte. Figure 4 shows a sketch of the experimental set-up.
Figure 4. Schematic drawing of laboratory apparatus.
CHAPTER V
EXPERIMENTAL PROCEDURE

Since the purpose of the research was to determine the effect of the rate of change of polarization voltage on polarization resistance, it was necessary to insure that all other variables were held constant. The procedure is as follows:

1. The same electrolyte solution was used for all experiment runs.
2. The silver electrodes were cleaned using an Aqua Regia solution followed by a rinse in distilled water prior to each run.
3. The electrodes were allowed to come to equilibrium at zero current flow for 30 minutes prior to each run.
4. Data was taken at polarization potentials of +/- 10 MV going from cathodic to anodic region. Initially data was taken manually at 10 minute intervals with a ΔV of 0.2 MV to establish a baseline. All other data was recorded on X-Y plot using X-Y recorder.
CHAPTER VI
TEST RESULTS AND DISCUSSION

The results of the completed tests are shown in Figures 5 through 20 and are summarized in Table 1.

Figures 5 through 19 show the input voltage waveform along with the resulting linear polarization plot. The values of corrosion current vary from 3.89 µA at an applied voltage rate of 6 mV/sec to 0.520 µA at static applied voltage. Assuming that the actual corrosion current is that measured at static conditions the data shows a 13.4% difference at the highest sweep rate.

Figure 20 shows a plot of polarization resistance vs sweep rate for the system studied. This curve is essentially linear for sweep rates higher than 1 mV/sec but it becomes non linear at lower rates where the static value of polarization resistance is approached.
Figure 6. Input Voltage - 6 mv/sec.
Figure 7. Scan Rate - 2.8 mv/sec.
Figure 8. Input Voltage - 2.8 mv/sec.
Figure 10. Input Voltage - 1.55 mv/sec.
Figure 11. Scan Rate - 1.33 mV/sec.
Figure 12. Input Voltage - 1.33 mv/sec.
Figure 13. Scan Rate $-\cdot 903$ mv/sec.
Figure 14. Input Voltage - 0.903 mv/sec.
Figure 15. Scan Rate = 0.509 mV/sec.
Figure 16. Input Voltage - .509 mv/sec.
Figure 18. Input Voltage - 0.323 mv/sec.
Figure 20. Polarization Resistance Vs Sweep Rate.
<table>
<thead>
<tr>
<th>Rate (mv/sec)</th>
<th>$\Delta E/\Delta I$</th>
<th>$\Delta E/\Delta I^*$</th>
<th>$I_{Corr}$ (µa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.00</td>
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</tr>
<tr>
<td>Static</td>
<td>50.0</td>
<td>1.00</td>
<td>.520</td>
</tr>
</tbody>
</table>

* Normalized with respect to static value.
CHAPTER VII

CONCLUSIONS & RECOMMENDATIONS FOR FURTHER STUDY

The objective of this research was to determine the effect of varying potential sweep rates while making polarization resistance measurements. The results of the research show the following:

1. Rapid scan of voltage greatly changes the measured corrosion current.

2. Beyond a scan rate of 1 mv/sec, the change in measured corrosion current is small and linear. This gives promise of faster rates being feasible.

3. When scan rates greater than 1 cycle per second were attempted the response of the potentiostat/galvanostat was not fast enough to produce reliable data.

4. A stable measurement system can probably be built to measure corrosion currents at rates as high as 6 mv/sec.

Further study in the following areas are recommended:

1. Attempts should be made to extend measurements to higher sweep rates, including electronic differentiation.

2. Studies should be made of other more complicated systems such as iron in sea water or aluminum in a highly corrosive environment.
FOOTNOTES


BIBLIOGRAPHY


