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by

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The Utility of Linear Polarization Method For The Determination of The Corrosion Rate*

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This work presents the situation of the up-to-date knowledge concerning the linear polarization method and its application to the determination of corrosion rates. This method has proved to be very practical and useful. The method has the advantage of greater general applicability and greater ease of use, gives quickly a numerical value of corrosion rates and can be conducted remotely, leaving the corroding specimen undisturbed in its environment.

In addition it is shown that the constant of Stern and Geary Equation can be substituted by the variation of corrosion potential with pH, below pH 7. An approximate constant for the Stern and Geary Equation is suggested for a system of unknown β constants or of unknown variation of corrosion potential with pH.

1. INTRODUCTION

A reliable and accurate method of determining corrosion rates in a relatively short time without disturbing the system by the measuring method is higly desirable. Weight-loss determinations on the specimen supply only average rate data over the interval of the test. The rate determinations by chemical analysis of the corrosion environment are also subject to this limitation. The determination of corrosion rates by measuring the

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increase in electrical resistance of a wire or ribbon specimen is also subject to some limitation.

It is evident that these methods are not always adequate for the continuous measurement of corrosion rate. A method for the measurement of corrosion rate is available in "linear polarization method" or "polarization resistance method" which is described by Stern [1,2].

The purpose of the present study is to examine the general aspect of the linear polarization method and to indicate the extend to which the method is applicable for the determination of corrosion rate.

2. THE LINEAR POLARIZATION METHODS

2.1. *Generality*

Different electrochemical methods for the measurement of corrosion rate were described in 1962 by Phelps [3]. A comparative review of electrochemical methods of assesing corrosion and their use in the research work on corrosion and in industry including the thermodynamic interpretation of potential current polarization curves has been published in 1965 by M. Pourbaix [4,5]. The principles involved in analyzing the corrosion situation according to electrochemical methods have been described in 1968 by Steigerwald [6]. Therefore the present report will merely be focused on the linear polarization method.

The polarization resistance, or linear polarization-method has received considerable attention in recent investigations. This method based on polarization resistance, was first described in 1955 by Simmons [7] and in 1957 by Skold and Larson [8]. Skold and Larson found empirically that a plot of polarization resistance versus corrosion rate on logarithmic scales for various steel and cast iron samples in fresh water gave a straight line relationship with a negative slope; polarization resistance was defined as the slope of the linear portion of the polarization curve obtained in potential region very close to the corrosion potential.

Stern and Geary [1] have presented in 1957 a theoretical analysis of the shape of polarization curves for both reversible electrodes and corroding electrodes. For a corroding system controlled by activation polarization the following linear relationship is expected between the potential (E) and the applied current (I) in the region where the polarized potential is close to the corrosion potential as is shown below:

$$\Delta E = \frac{\beta a \quad \beta c}{2.3 \ I_{corr} \ (\beta a + \beta c)} \Delta I$$

or

$$\frac{\Delta E}{\Delta I} = \frac{\beta a \quad \beta c}{2.3 \ I_{corr} \ (\beta a + \beta c)} \tag{1}$$

Where Δ E is the difference in the applied potential of a corroding electrode produced by the anodic or cathodic polarizing current ΔI; the constants βa and βc are the anodic and cathodic Tafel slopes respectively.

In the derivation of this Stern and Geary Equation [1,2], it is considered an electrochemical system the potential of which is determined by two intersecting activation polarization curves whose slopes are βa and βc. If current from an external source is applied to such a system, then the following relation applies:

$$I = I_{corr} \left[10^{-\frac{\Delta E}{\beta c}} - 10^{+\frac{\Delta E}{\beta a}} \right] \tag{2}$$

For small values of overvoltage where $10^{-\frac{\Delta E}{\beta c}}$ may be approximated by $1 - \frac{\Delta E}{\beta c}(2.3)$ and $10^{+\frac{\Delta E}{\beta a}}$ may be approximated by $1 + \frac{\Delta E}{\beta a}$ (2.3), equation (2) reduced to:

$$I = I_{corr} \left(1 - 2.3 \frac{\Delta E}{\beta c} - 1 - 2.3 \frac{\Delta E}{\beta a}\right) \qquad (3)$$

Rearranging of this equation and taking ΔI instead of I they obtain equation (1).

As it is shown by M. Pourbaix [9], the error coming from this approximation is not big.

Stern and Geary Equation applies only when ΔE is small. Linear dependance of potential on applied current is expected only when the polarization ΔE is less than 10 mV.

When the corrosion rate of a system is controlled by concentration polarization of the reduction reaction, βc becomes infinite and equation (1) reduces to:

$$\frac{\Delta E}{\Delta I} = \frac{\beta a}{2.3\ I_{corr}} \qquad (4)$$

Stern and Weisert [10] discussed possible errors in the method and gave to the equation (1) the following form:

$$\log \frac{\Delta E}{\Delta I} = \log \frac{\beta a \quad \beta c}{2.3\ (\beta a + \beta c)} - \log I_{corr} \qquad (5)$$

Thus a plot of the "polarization resistance" $\frac{\Delta E}{\Delta I}$ versus the corrosion current I_{corr} on logarithmic scales should yield a straight line with a slope of –1. If one assignes given values to the two β constants, a plot of equation (5) may be illustrated by *Figure* 1, taken from Stern and Weisert's work. This *Figure* shows the relationship assuming both constants equal to 0.1 V. The measurements of a polarization resistance permits a direct determination of a corrosion current from such a calibration curve. To use this method the β values must be known and they must remain constant.

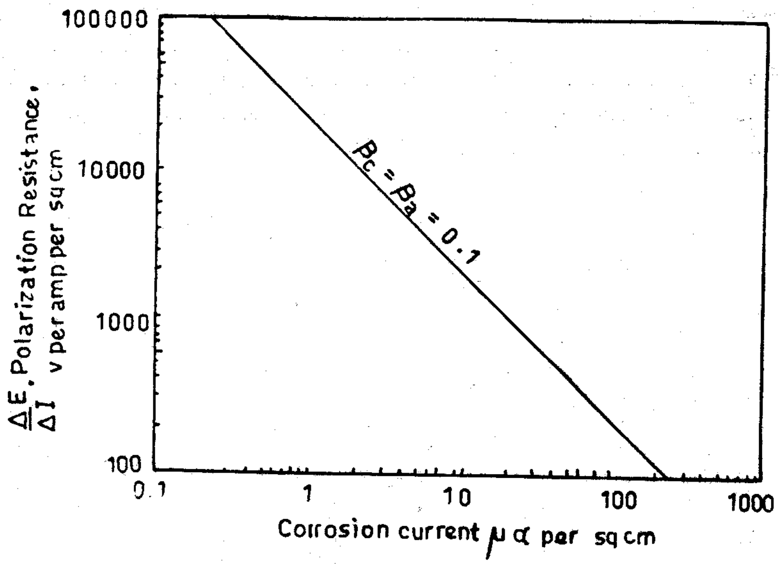

Figure 1– Calculated Relation Between Polarization Resistance and Corrosion Current for a System with Equal Cathodic and Anodic β values of O. 1 V. (M. Stern and E. D. Weisert) [10]

The study of Stern and Weisert [10] of available data on activation polarization kinetics [11] reveals that the range of experimental values of β for various electrochemical reactions is rather limited. In general β values range from 0.03 to 0.18 V. Actually, β values as low as 0.03 V are quite rare and generally apply to the hydrogen over voltage on materials like platinum and palladium. Most practical engineering materials exhibit larger values of β for hydrogen evolution. β Values as high as 0.18 V are also rare for activation overvoltage. Most β values lie between 0.06 and 0.12 V.

Stern and Weisert have illustrated on a figure a variety of bonds, the total width of which describes all systems where βc varies from 0.06 to 0.12 V. *Figure* 2 is taken from their work. The following systems fall between these lines: nickel in hydrochloric acid, iron in dilute hydrochloric acid containing sodium chloride, steel in sulfuric acid, cast iron in high conductivity waters, and cast iron in natural and synthetic waters. As is shown by Phelps [3] data obtained by Evans and Koehler [12] for aluminium in various acids and by Schwerdtfeger and Manuele [13] for steel in 3 percent sodium chloride solution also fall on or within the lines.

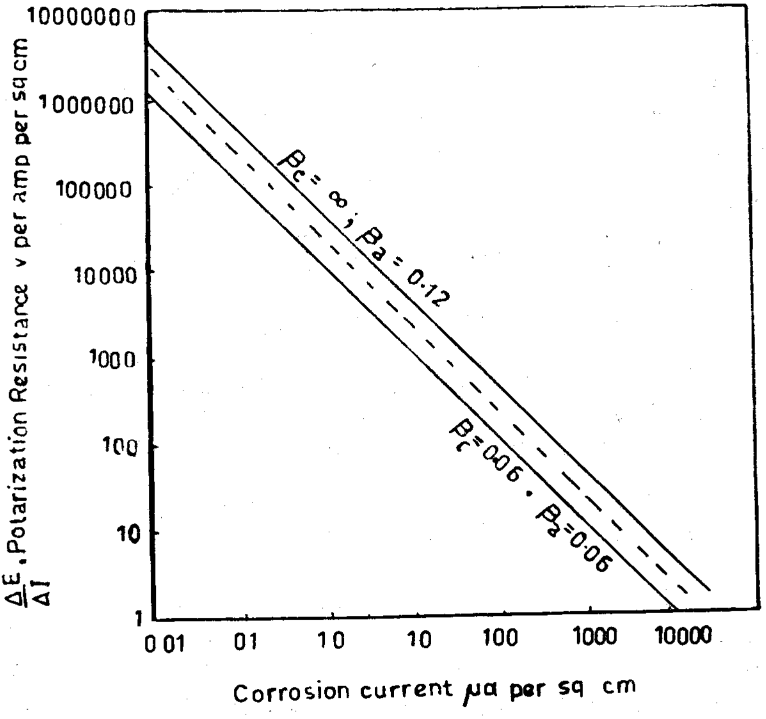

Figure 2. Calculated Relation Between Polarization Resistance and Corrosion Current for the systems with Various Cathodic and Anodic β Values. (M. Stern and E. D. Weisert) [10], and the Curve with the Value of B=0.026 V, Dashed Curve, (see text).

As pointed out by Stern and Weisert [10], if no information exists concerning β values of a given system, the corrosion rate can only be determined by factor of 2. When the Tafel slopes βa and βc of the system are known, the band can be narrowed and then a simple measurement of polarization resistance will provide a calculated corrosion current with an accuracy of about 20 percent. When the β values change due to concentration polarization, as is very common in practical systems, corrosion current can be estimated only with an accuracy of 40 percent.

A very similar technique for the measurement of corrosion rates of metals in solutions containing air, such as natural water, sea water, etc. has been developed in 1958 by Engell [14]. But this method is limited to cases where concentration polarization is controlling the system.

2.2. *Different technique in the application of the linear polarization method*:

The linear polarization methods have been applied using both direct current and alternate current techniques.

D. c. techniques have been applied in different ways as follows.

2.2.1. *Three electrode technique with conventional reference electrode*:

Skold and Larson [8] and the other investigators [12, 24-36] used a third electrode, used as reversible reference electrode. All these "three electrode methods" require a potential measuring circuit with high impedance. In addition the standard reference electrodes (calomel, silver/silver chloride, normal hydrogen, etc.) are not sufficiently robust for field use, and the necessity of a complicated electronic equipment is also a drawback if the technique is to be applied under plant conditions.

2.2.2. *Three electrode techniques with reference electrode made of the same metal to be tested*:

For the simplification of the measuring equipment, use of a reference electrode made of the same metal to be tested is appealing. This technique has been applied by Neufeld [15] and Annand [16].

Using a reference electrode made of a metal similar to the metal to be tested (mild steel, 99.5 % Al and 18/8/Ti stainless steel) a simple method of applying this technique under plant conditions for corrosion monitoring has been applied by Neufeld [15], using 18/8/Ti stainless steel electrode as an auxiliary electrode. The control circuit system used was the simple constant current type.

The sensitivity and the speed of response of this technique to rapid changes in the corrosion rate has been demonstrated by comparing polarization resistance data with potential-time curves for 99.5 % Al and 18/8/Ti stainless steel. The processes of film breakdown and repair are shown to be accompanied by corresponding variations in corrosion rate.

Annand [16] has used three idential steel electrodes made from a sandblasted SAE 1020 steil coupon. One of the three electrodes was designated as reference electrodes and was never polarized. The Other two were designated as test and auxiliary electrodes.

2.2.3. *Two electrodes technique:*

In 1962 Seyl [17] and Marsh [18] have developed a new system which eliminates the reference electrode and thus necessitates only two electrodes. The conventional polarization resistance method has been modified by Marsh [18] to eliminate the need for reference electrode. In the system of Marsh two more-or-less identical electrodes are made of the metal to be studied. A technique [18, 19] and instrumentation has been described using two electrodes in such a way that one is first polarized in the anodic direction and the other in the cathodic direction by an impressed 20 mV potential. The potential span is then reversed and the resulting reverse current is made average with the previously mentioned current. The average current is related to the corrosion rate through equation (1) by an empirically derived constant.

In 1966 Annand [16] has used both a 2–electrode and 3–electrode technique in parallel experiments, utilising identical steel electrodes. Annand's research reveals that the 3–electrode technique is preferable to the 2–electrode one because even though 2–electrode measurements show a qualitative relation to the corrosion rate in the system investigated, they exhibit variations which are directly related to the actual rate of corrosion of a particular electrode, and therefore these measurements are not so reliable correlated to the actual corrosion rate of identical electrode as are the 3–electrode measurements.*

A d.c. technique has been developed in 1968 by Retel [21] for the determination of direct corrosion current and instantaneous corrosion current.

2.2.4. *The alternative technique*:

An a. c. technique was first applied in 1963 by Schwenk and Bühler [22]. A reciprocal proportionality was found between the corrosion rate and the polarization impedance with a frequency depending of proportionality factor.

Another a.c. technique has also been suggested in 1967 by Prazàk and Barton [23].

A special a. c. technique has also been developed in 1967 by Rowlands and Bentley [24] for the rapid determination of changes in corrosion rates, using a square-wave generator in conjunction with an oscilloscope.

The electrical circuits to produce polarization diagrams for different linear polarization techniques are given by M. Pourbaix [9].

3. APPLICATION OF LINEAR POLARIZATION METHODS

Linear polarization methods have been used by a number of investigators in acidic and in alkaline media as well as in neutral salt solutions for the following metals:

3.1. Aluminium
3.2. Steel
3.3. Tin
3.4. Molybdenum and cobalt
3.5. Nickel
3.6. Silver, copper and zinc

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* As will be shown later [20], the polarization resistance data obtained with 3 – identical steel electrodes are not so reliably corelated to the actual corrosion rate of identical electrode as are the 3 electrode measurements used a third electrode as reversible reference electrode.

3.1. *Aluminium*:

Evans and Koehler [12] were highly successful in applying this method to the determination of corrosion rate of aluminium alloys in acid media and in deaerated food media. They have obtained Tafel type cathodic polarization curves for aluminium alloys in dearated acids and various food media. The overvoltage intercept method was found to give corrosion currents equivalent to the measured rates of hydrogen evolution. The overvoltage intercept method [3,10,12] involves extrapolation of the cathodic Tafel overvoltage curve to the corrosion potential to obtain the corrosion current. Using suitable values for the Tafel slopes β in the Stern and Geary Equation, the polarization resistance method likewise gave corrosion current in good agreement with measured rates of hydrogen evolution. Corrosion rates of aluminium in a variety of dearated food media are reported in this work of Evans and Koehler. Corrosion currents were determined by both the overvoltage-intercept and the polarization-resistance methods. The plot of polarization resistance vs. corrosion current according to Stern and Geary Equation is represented on logarithmic cales showing that the currents determined by the overvoltage intercept method fall on corresponding lines.

The use of a square-wave generator in conjunction with an oscilloscope has been applied by Rowlands and Bentley [24] for the corrosion changes of aluminium brass in seawater and in seawater containing 0.01 % sodium dimethyl dithiocarbamate for which the corrosion characteristic had previously been investigated, (See above, 2.2.4).

The corrosion rate of buried aluminium tubes was studied by Jones and Lowe [25] with the polarization method and with the polarization resistance method. The exact determinations of β 's values from the E/log I plot for aluminium was impossible. The author has suggested $\beta a = \beta c = 0.1$ V as a reasonable estimate for soils. The polarization break method [13] was compared with the polarization resistance method, with the results that the polarization resistance method appeared to be the most useful available method for measuring corrosion rate of buried metal specimens.

A method using a reference electrode made of a metal similar to the metal to be tested has been applied by Neufeld [15] for aluminium (99.5 %) in a 3 % sodium chloride solutions without and with addition of hydrochloric acid to give a 2 percent solutions (using 18/8/Ti stainless steel electrode as an auxiliary electrode, (see, above 2.2.2).

3.2. *Steel:*

Using a reference electrode made of a metal similar to the metal to be tested a polarization resistance technique has been applied by Neufeld [15] for mild steel using 18/8/Ti stainless steel electrode as an auxiliary electrode in propionic, formic, acetic and hydrochloric acid in water and in Tees Valley water, and for 18/8/Ti stainless steel in 10 % sulfuric acid without and with addition of potassium chromate to give a 5 % solution. Polarization resistance data were compared with weight-loss measurements for the mild steel. The results have shown that corrosion velocity in an unknown corrodent can be estimated within a factor of two, (see, above 2.2.2).

Butler and Carter [26] have stated that this method is applicable for stainless steel (AISI 304, 316 and 317) in sulfuric acid solutions, using the electrical circuit for producing polarization diagram potentiostatically. The results of this study showed that, polarization resistance had an excellent correlation ($r = 0.98$) with weight-loss in determinations made in corrosion tests conducted under similar conditions.

A linear polarization technique has been applied by Jones and Greene [27] to studies of corrosion rates of type 304 L stainless steel in oxygen saturated 1N H_2SO_4, and by Greene and coworkers [28] for carbon steel implanted in tigh muscle of a dog.

This method has been applied by Doruk [29] to the investigation of the effect of alternating stress on the polarization of mild steel in sulfuric acid solutions.

The corrosion rates of 316 steel in 70 % sulfuric acid has been determined by Clerbois [30], who compared the result so obtained with the results of the weight-loss measurement, (See discussion).

The corrosion rates of different austenitic and ferritic stainless steels in the active state in 1 N sulfuric acid at room and boiling temperatures have been determined by Schwenk and Bühler [22], using d.c. and a.c. techniques. In all cases a reciprocal proportionality was found between the corrosion rate and the polarization impedance with a frequency dependent proportionality factor, (See above, 2.2.4).

Annand [16] has studied the behavior of sandblasted SAE 1020 steel in both NaCl solutions and in two phase NaCl/hydrocarbon systems containing nitrogen, air, H_2S, CO_2 and mixtures of these gases. They have used three identical steel electrodes. One of these electrodes was never polarized and considered as reference electrode. The other two electrodes were used as test-and auxiliary electrodes and were used for both the three-electrodes and two electrodes technique. Annand has also used calomel as a reference electrode and platinum as auxiliary electrode for comparing the results. Weight-loss measurements have been made in similar conditions, showing that the precision of polarization resistance measurements themselves is comparable to that of weight-loss measurements. The 3–electrodes-technique was found preferable to the 2–electrodes-technique, (See, above 2.2.3).

Using instantaneous corrosion-rate-meter* the effectiveness of various corrosion inhibitors and their synergistict effects have been studied by Marsh and Schachl [19], exposing prerusted steel (cold rolled mild steel rod of 1020 steel) elecrodes alternately to oil (kerosine) and to 3 percent NaCl in a bottle held in an oscillating rack, and the effect of mercaptobenzothiazole sodium salt and of sodium nitrite on clean steel in aerated static 3 percent NaCl solution. The relative effectiveness of the inhibitor has been estimated from the corrosion rate of electrodes as measured by the "Rate meter". Inhibitors highly effective under widely different conditions have been discovered by this technique, (See above 2.2.3).

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* A Product Magna, Santa Fe Springe, California.

A polarization resistance method has been applied by Legault and Walker [31], for AISI C–1011 steel in sodium chloride solution with sodium nitrite as inhibitor, to the determination of corrosion rate changes for the evaluation of corrosion inhibitors, and to the study of synergistic effects in corrosion studies, which would have been enormously difficult by any other method.

The corrosion rate of buried steel was studied by Jones and Lowe [25] with the polarization and with the polarization resistance method. I_{corr} by Tafel extrapolation was found in good agreement with the data obtained by polarization resistance for buried steel.

Kobayashi and Nagayama [32] have determined corrosion rates of mild steel in 1 per cent sodium chloride solution containing various quantities of sodium silicate.

Using of a.c. technique the corrosion rate of mild iron (Weichblech -Fe) and of tempered steel (härtbarer Stahl) has been determined by Pražàk [33] at 40°C for the following systems: mild iron in 10 % H_2SO_4, tempered steel in 10 % H_2SO_4 without and with addition of 1 % thiourea; in 1N H_2SO_4 without and with addition of 1 % thiourea; in 0.2 N HCl without and with addition of 1 % oxyquinolin –5–sulfonic acid; and in 1 N HCl.

Corrosion rates of mild steel in alkaline lithium bromide solution and in inhibited with lithium chromate were studied by Cohen and Jelinek [34]. The results were compared with weight-loss measurements, and the polarization resistance method was found to be applicable to the corrosion evaluation of mild steel in alkaline bromide solutions.

The polarization resistance method has been applied to the study of the anticorrosion properties of paints in demineralised water and in 1 N NaCl solutions by Bureau [35], who showed that the polarization resistance is a suitable indirect measure for the corrosion rates of painted steel.

3.3. *Tin*:

Butler and Carter [36] have stated that the method is applicable for tinplate grape fruit juice using an electrical circuit of conventional design for producing an increase in steps by polarizing current.

3.4. *Molybdenum and Cobalt:*

Linear polarization method has been applied by Greene and Co-workers [28] to laboratory studies of corrosion rates of molybdenum, cobalt-and carbon steel specimens implanted in tigh muscle of a dog. A good agreement was found between the total weight-loss calculated from linear polarization data and direct weight-loss measurements.

3.5. *Nickel:*

Other investigators have presented data showing that the method is applicable for nickel in hydrogen-saturated or nitrogen saturated hydrochloric acid, as has been cited in the work of Stern and Weisert [10].

3.6. *Silver, Copper and Zinc:*

Using of a.c. technique, corrosion rates of silver, copper and zinc have been determined by Prazàk [33] (at 20°C) for the following systems: Silver in 0.1 N H_2SO_4 with addition of various amount of $Fe_2(SO_4)_3$; copper in 1 N H_2SO_4 and in 0.1 N H_2SO_4 with addition of various amount of $Fe_2(SO_4)_3$; zinc in 1 N H_2SO_4 and in 1 N $NH_4OH + 0.01$ M H_2O_2.

4 DISCUSSIONS

4.1. *Determination of polarization admittance:*

The Stern and Geary Equation [1] can be given in the following form:

$$I_{corr} = B \frac{\Delta I}{\Delta E} \tag{6}$$

Where

$$B = \frac{\beta a \quad \beta c}{2.3\ (\beta a + \beta c)} \tag{7}$$

Because I_{corr} is proportional to the "polarization admittance [16], $\frac{\Delta I}{\Delta E}$, (the inverse of polarization resistance) this form is more practical of use.

Figure 3 and 4 are typical complete continuous linear polarization curves [20]. From the slopes of these simple curves polarization admittances can be determined. Note that the relationship between overvoltage and current is no longer linear beyond 7 mV (*Figure* 3).

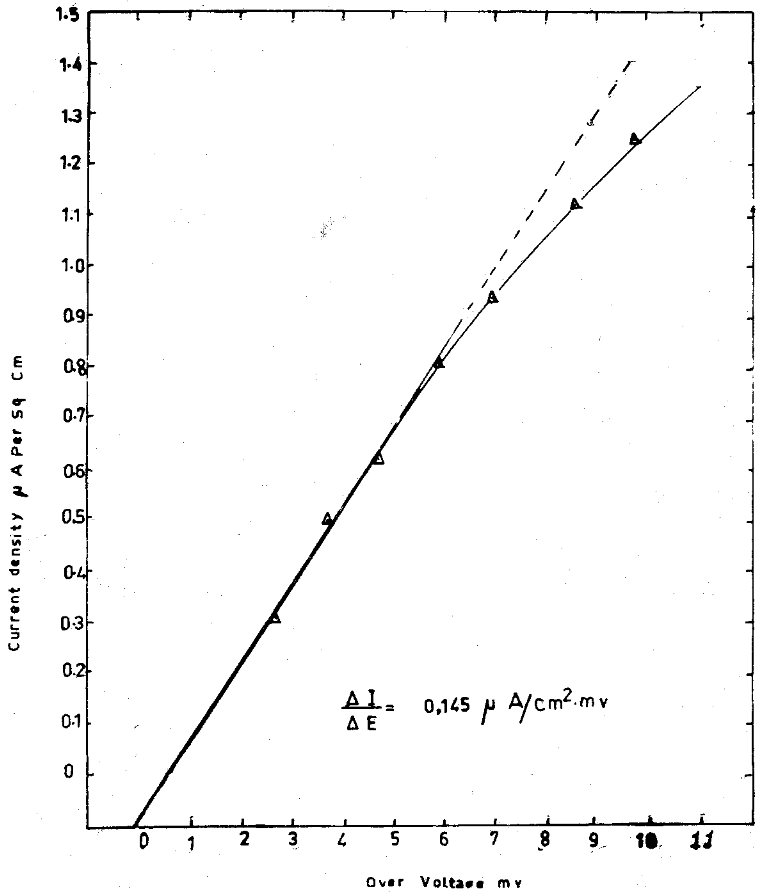

Figure. 3. Linear polarization cuve, for mild steel exposed to air saturated Brussel water.

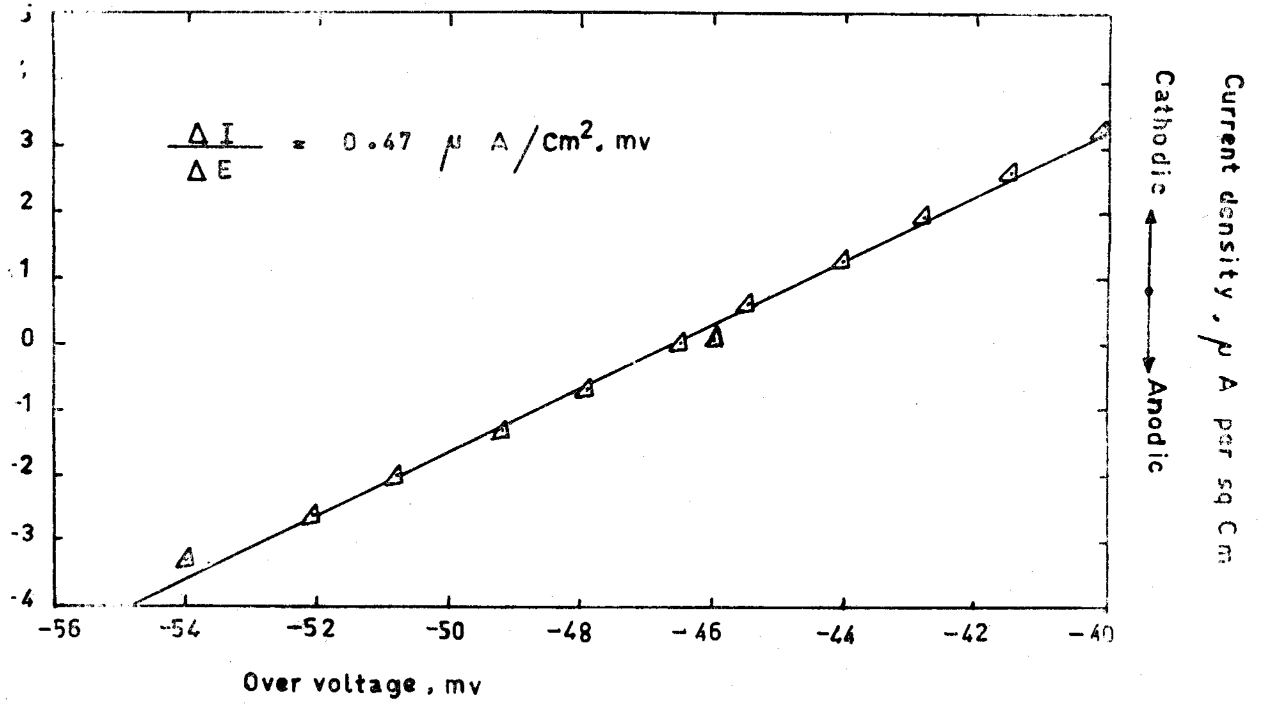

Figure 4. Anodic and cathodic linear polarization curve for mild steel exposed to air saturated Brussel water using 3 - identical electrodes.

4.2. *Determination of the Constants*:

The polarization admittance is proportional to the corrosion rate, and the proportionality constant is a function of the slopes of the linear E /log I polarization curves. If the value for the constants of Tafel slopes for the anodic and cathodic reactions, βa and βc are available [11], corrosion rate can be calculated directly from equation [1] or [6]. In cases where great precision is not required, available value [11] for these constants can be used for calculations of corrosion rates. If more accuracy is required, the constants can be derived from running the full polarization curves. But the linearity in the experimental curves is often obscured. Therefore the slopes can not be estimated for each system to be studied. Once the proportionality constant is agreed upon for a particular system, corrosion rate comparisons between numerous investigations or applications should be relatively reliable.

The constant B has been determined by Clerbois [30] from the variation of corrosion potential with pH, according Röschenbleck [37] Equation.

A relationship between the corrosion current, the inverse of the polarization resistance and the variation of the corrosion potential with pH has been found by Röschenbleck [37]. When the anodic reaction is the dissolution of a metal and the cathodic reaction is the reduction of hydrogen:

$$I_{corr} = -\frac{\left(\frac{dI}{dE}\right)_o \left(\frac{dE_o}{dpH}\right)}{2.3} \quad (8)$$

Where I_{corr} is the corrosion current, Eo is the corrosion potential and $(dI\ /\ dE)_o$ is the reciprocal of the polarization resistance at the corrosion potential. This relationship is applicable below pH 7.

From equation [6] and [8] one can drive for the constant B the following expression:

$$B = -\frac{1}{2.3} \quad \frac{dE_o}{d\,pH} \quad (9)$$

Using this expression, the constant B can be calculated, when the value of the variation of the corrosion potential with pH is available.

The variation of the corrosion potential with pH for chromium [38, 39], chromium - iron alloys [38, 39] (25. 6 % Cr) and iron [38, 39] have been determined by Röschenbleck, who stated a linear relationship between the potential and the corresponding pH. The slopes of these curves for these three metals are 47.0, 51.4 and 54.2 mV respectively per unit pH.

The constant B has been calculated by Clerbois [30] using the Equation of Röschenbleck (9) and the data of Röschenbleck for iron [38, 39]. Clerbois has also calculated the constant B from the weight-lost data and the polarization admittance which is determined by himself experimentally. The accordance between them is excellent.

Succesful use of the polarization resistance method depends on proper evaluation of the constants β in the Stern and Geary Equation, but fortunately this is not usually much of a problem, as is shown below:

The effect of pH on the corrosion potential of iron has been studied by many investigators [38 – 44]. The reported values of the potential variation per unit pH are comprised between -0.045 and -0.059 V. The variation of corrosion potential with pH in a variety of airfree acid media for carbonyl-and electrolytic iron was found -0.058 V by Jena and Bonhoffer [40], -0.059 V by D'ans and Breckheimer [41], -0.0559 V by Stern [42]. The data has been found by Felloni [43] -0.051 and -0.047 V in the solutions of HCl and in H_2SO_4 respectively. Hurlen deduced [44] the following expression for the variation of corrosion potential with pH, in solutions of negligible ferrous iron content;

$$\frac{d\,E_{corr}}{d\,pH} = -\frac{4}{5}\,2.303\,\frac{RT}{F} \qquad (10)$$

in acid media and:

$$\frac{d\,E_{corr}}{d\,pH} = -\frac{2}{5}\,2.303\,\frac{RT}{F} \qquad (11)$$

in alkaline media. Evans and Koehler [12] have found the data –0.0632 V for aluminium alloys in citrate buffer solutions (at 37.8°C). A general summary of data up to 1938 was provided by Gatty and Spooner [45]. An explanation of the effect of pH on the corrosion potential is suggested by Uhlig [46], who stated that the observed iron potential is a result of surface anode and cathode potentials polarized by local action currents.

The variation of corrosion potentials dEo/dpH with pH, for some industrially important metals and alloys has been collected in table I. As can be observed the values of dEo/dpH are comprised between –0.045 and –0.063 V for different metals and alloys. If the value of dEo/dpH is available for the metal to be tested, this value can be used for the calculation of the constant from equation (9). Calculated values of these constant B, from the values of variation of corrosion potentials with pH for different metals and alloys have been given in the last line of the table I. If the variation of the corrosion potential with pH is unknown, one can admit –0.059 V per pH for the value of dEo/dpH for the calculation of an approximate value of the constant B. One thus obtains:

$$B = -\frac{1}{2.3}\frac{dEo}{dpH} \cong -\frac{-0.059}{2.3} \cong 0.026 \ \text{V} \qquad (12)$$

with this constant, equation [6] can be express as follows:

$$I_{corr} = 0.026 \frac{\Delta I}{\Delta E} \qquad (13)$$

Our investigation on the corrosion rate for mild steel [20] in Brussel water using 3– electrode technique with conventional reference electrode and 3– identical electrodes are shown that the proposed value of the Constant B = 0.026 V is a good correlation factor between the polarization admittances and the corrosion currents. The accordance of these corrosion currents with the weight-loss measurements carried out in similar conditions are exellent.

The value of the constant B for iron can be calculated from the expression of Hurlen [44]:

$$B = -\frac{1}{2.3}\left[-\frac{4}{5}\ 2.3\ \frac{RT}{F}\right] = 0.0205\ \mathrm{V} \qquad (14)$$

in acid media and

$$B = -\frac{1}{2.3}\left[-\frac{2}{5}\ 2.3\ \frac{RT}{F}\right] = 0.0103\ \mathrm{V} \qquad (15)$$

in alkaline media.

The curve with the value 0.026 V falls in the middle of the band in *Figure 2* of Stern and Weisert [10]. This is illustrated as the dashed curve in *Figure 2.* That is to say, without any information at all concerning the β value of a given system, corrosion rate can only be determined within a factor of one. The limit in *Figure 2* is extended at the upper side to $\beta a = 0.12$ and $\beta c = \infty$, that is, to the cathodic limiting diffusion current with the highest value of $\beta a = 0.12$ and at the other side to the smallest values of the constant of βa and *βc* for practical engineering metals. These values are 0.06 V for both βa and βc.

In the case that metal corrodes in a solution where the rate is controlled by the limiting diffusion current for oxygen, the cathodic β value would be expected to increase from a normal activation overvoltage value to a high value. In this case the value of the constant would be expected to increase from the approximate value of 0.026 V up to the 0.052 V, which corresponds the upper curve of Stern and Weisert in *Figure 2.*

Another effect on the constant B which causes the constant to increase up to 0.052 V is the exchange current of metals to be tested, which increase according to the system to be studied as is pointed out also by Pražák [33].

With the knowledge of the cathodic reduction and exchange current of the metal to be tested one can estimate an approximate value for the constant B.

If more accuracy is required for the value of the constant B, the variation of the corrosion potential with pH can be determined experimentally; this is more easy than to determine the Tafel constants of a system.

5. CONCLUSION

The general aspect of the investigations and applications of the polarization resistance method have been examined. The linear polarization method developed in recent years has been found very rapid and convenient for the determination of corrosion rates. The method has the advantage of greater general applicability and greater ease of use, gives numerical value of corrosion rate and can be conducted remotely, leaving the corroding specimen undisturbed in its environment. Extensive polarization data are not necessary, and do not need to be extended to potential differences higher than 7 or 10 mV.

In the application of the method, the length of the polarizing time must be very exactly reproduced in each measurement, so that the relative polarization values are actually a function of impressed current. In the determination of polarization resistance or polarization admittance (inverse polarization resistance) the slope of a complete continuous linear polarization curve *(figure 3 and 4)* must be preferred to a single measurement of polarization resistance, for the compensation on the uncertainty introduced by a change of the corrosion potential. The corrosion rate can also be determined from polarization data obtained potentiostatically, however, this method requires an expensive apparatus and fairly extensive data for accurate determination.

The constant of Stern and Geary Equation can be substituted below pH 7 by the variation of the corrosion potential with pH, $-\dfrac{d\,E_o}{2.3\,d\,pH}$. For system of unknown β constant or of unknown variation of the corrosion potential with pH, it is suggested an approximate constant for the Stern and Geary Equation:

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

which corresponds to,

$$\frac{dE_o}{d\ pH} = -\ 0.059\ \text{V}.$$

The polarization resistance method should be a valuable tool in future corrosion investigations and applications. This method is particulary useful, and sensitive and is applicable in situations where relative rather than absolute corrosion rates are required. Such cases would be: the evaluation of inhibitors, -the screening of different alloys for a particular service-, the determination of effects on corrosion of environmental variables, such as composition, temperature and velocity, the determination of changes in corrosion rate with time. The method is promising as a means for determining the corrosion rate of underground structures, such as a piling and pipelines, as well as uncoated structures in contact with aqueous solutions, corrosion in-vivo tests and studies under intense nuclear radiation.

The method can not be used in those cases where an oxidation process occurs which is different from the metal dissolution reaction.

Calibration is required if an IR drop is included in the measurement. An IR drop may result either from the use of a low conductivity electrolyte or from high resistance films on the metal surface.

In the last few years polarization resistance method has been used increasingly by many investigators so that the value of the method is apparently becoming more widely appreciated. The method will become even more important than at present as the simplicity of its implementation becomes more widely recognized [20].

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TABLE 1. The variation of corrosion potentials with pH , $\frac{d\ Eo}{d\ pH}$ (in volts per pH unit) for some metals, and the corresponding calculated values of B (in Volt).

METALS	Fe[38-45]	Cr[38,39]	Cr–Fe[38,39]	Al[12]	Co [45]	Ni[45]	Sb[45]	As[45]	W[45]
$\frac{d\ Eo}{d\ pH}$	–0.045 to –0.059	–0.047	–0.051	–0.063	–0.058	–0.045	–0.059	–0.059	–0.055
B	0.020 to 0.026	0.020	0.022	0.027	0.025	0.020	0.026	0.026	0.024

The marked number near–by the symbols of metals are the numbers of the references.

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ÖZET

Bu çalışma linear polarizasyon metodunun bu günkü durumunu ve bugüne kadar korozyon hızı tayinine uygulanmasını göstermektedir. Bu metodun çok pratik ve faydalı olduğu gösterilmiştir. Metodun genel bir uygulama alanı göstermesi ve uygulanmasının kolay olması büyük bir avantaj sağlamaktadır. Bu metotla kolaylıkla korozyon hızının büyüklügü bulunabilmekte, korozyona uğrayan maddeyi yerinden almaya lüzum kalmadan metodu uzaktan uygulamak mümkün olmaktadır.

Bu çalışmada ayrıca pH $= 7$ nin altında Stern ve Geary Denklemindeki sabitlerin yerine korozyon potansiyelinin pH la değişiminin kullanabileceği gösterilmiştir. β sabitleri ve korozyon potansiyelinin pH la değişimi bilinmeyen çözeltilerde kullanılmak üzere Stern ve Geary Denklemi için yaklaşık bir sabit teklif edilmiştir.

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