Cathodic protection criteria— A critical review of NACE Standard RP-01-69*

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NACE Recommended Practice RP-01-69, "Control of External Corrosion on Underground or Submerged Metallic Piping Systems," contains criteria for the cathodic protection (CP) of steel structures in natural soil and water environments and these criteria have been widely accepted both by the owners of cathodically protected structures and by CP practitioners. Despite this, it has become increasingly apparent that many of the criteria as stated in the standard are in serious error with the fundamental science and in conflict with other standards and the interpretation of some regulatory agencies. Recent studies, which have appeared in the literature. further confirm that the criteria require revision to ensure that only polarized potentials are used in the criteria and, furthermore, that potential measurements are corrected for IR drop error.

Introduction

PERHAPS NO OTHER ISSUE pertaining to the application of cathodic protection (CP) is subject to as much controversy and discussion as are the various protection criteria that are either in common use or contained in industry standards. Despite the existence and acceptance of some standards, there remains no single universal criterion nor is there total agreement between the criteria, their application, and their scientific validity. There are several principal reasons for this situation:

- 1. The exact potential criterion for protection of a particular structure under specific conditions cannot be readily determined in practice.
- 2. The scientific evidence to support the criteria is often misunderstood, misinterpreted, or completely lacking.
- 3. Difficulties are encountered in measuring structure parameters for comparison to the criteria.

Since a criterion is a standard used to judge the performance of a CP system, it is, therefore, often assumed that all corrosion activity has been halted whenever the criterion has been achieved. CP, however, is more loosely defined in NACE literature as "a technique to reduce corrosion of a metal surface by passing sufficient cathodic current to it to cause its

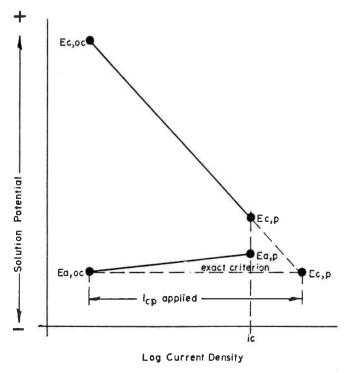


FIGURE 1 — Typical polarization diagram for a corrosion cell.

anodic dissolution rate to become negligible." This definition is contrasted with the more rigorous scientific explanation put forward in 1938 by Mears and Brown that states that "for CP to be entirely effective, the local cathodes on a corroding specimen must be polarized to the potential of the unpolarized local anodes" (Figure 1).2

For a single corrosion cell, the corrosion current is produced by the existence of a potential difference between the cathode (Ec.oc) and the anode (Ea.oc). Under equilibrium conditions a specific corrosion current density ic flows that results in a potential shift at both the anode and cathode owing to polarization. The potential difference between the polarized cathode potential (Ec,p) and the polarized anode potential (Ea,p) is equal to the total IR drop in the corrosion cell. Superimposing an external cathodic current onto this corrosion cell will cause the potential of the cathode to shift more electro-

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negatively. If a sufficient current density is applied to polarize the cathode to a potential (Ec,p) the difference in potential between it and the open circuit potential of the anode (Ea,oc) is reduced to zero at which point the net corrosion current is zero and corrosion is halted. The exact potential criterion, therefore, for a corroding structure in an aqueous electrolyte is the open circuit potential of the most electronegative anode that exists on the structure. In practice for an existing structure this cannot be easily determined, thus necessitating the development of alternative criteria. The need for applicable criteria was recognized for many years and addressed through the pioneering efforts of numerous investigators. The criteria established in NACE Standard RP-01-69 for metallic piping systems originally published in 1969 and later revised in 1972, 1976, and 1983 have been widely adopted by the pipeline industry and regulatory agencies.3 Despite the general acceptance of these criteria, there is a wide variation in their interpretation and usage. A re-examination of the criteria is warranted, not only with respect to the early investigations but also regarding the results of more recent studies and methods presently employed to measure the appropriate data.

The -0.850 V criterion

The criterion, used most often for steel structures exposed to a soil or water electrolyte, is the -0.850 V potential referenced to a Cu:CuSO₄ electrode (CSE). In the current NACE standard this criterion is stated as follows:

"A negative (cathodic) voltage of at least 0.85 V as measured between the structure and a saturated copper-copper sulfate reference electrode contacting the electrolyte. Determination of this voltage is to be made with the protective current applied."⁴

One of the difficulties in applying this potential criterion is rooted in the requirement that the measurement be taken with the current applied. Because of this requirement, it follows that all measurements will contain an IR drop measurement error that will vary in magnitude depending on such factors as current magnitude, electrolyte resistivity, and reference electrode position. This essentially means that the measured potential of a structure contains an IR drop error usually of unknown magnitude, and, therefore, the exact polarized potential of the structure is not determined. In Figure 2, assuming the equipotential surfaces each are 100 mV, then with the reference electrode located at grade, the voltmeter reading would indicate approximately 350 mV more negative than the exact polarized potential of the pipe. A voltmeter

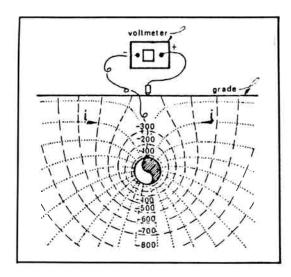


FIGURE 2 — Illustration of IR drop error inherent in structure/soil potential measurement with CP current applied.

reading of -0.850 V, therefore, would apparently satisfy the NACE criterion, yet the polarized potential of the pipe would only be -0.500 V. The -0.850 V criterion as stated in the standard is, therefore, meaningless without an IR drop correction. Although the preface to the NACE criteria states that "consideration should be given to voltage (IR) drops...for valid interpretation...", there is no guidance as to what constitutes "consideration" nor any suggestion that a correction be made in respect to this inherent measurement error.

R. J. Kuhn first postulated in 1933 that the potential needed to stop corrosion "is probably in the neighborhood of $-0.850~\rm V$." This criterion received little by way of scientific verification until the work of Schwerdtfeger and McDorman was published in the early 1950s. They recognized that the theoretical and experimental foundation for the $-0.850~\rm V/CSE$ criterion had not been stated and set out by experimentation to validate a potential criterion. In their study, potentials of steel electrodes were measured in 20 air-free soils, ranging in pH from 2.9 to 9.6 and in resistivity from 60 to 17.800 ohm-cm. The results are shown in Figure 3 in which the measured potentials of the steel samples are plotted vs the soil pH.

Also shown in this figure is the theoretical hydrogen electrode potential vs pH. Considering that the cathodic reaction in deaerated soils is the reduction of hydrogen, then at the point of intersection of these two curves the potential difference between the steel anodes and the hydrogen electrode (cathode) would be zero. The intersecting potential was approximately -0.770 V to a saturated calomel electrode (SCE), which is about -0.850 V to a saturated copper-copper sulfate electrode. Schwerdtfeger and McDorman then polarized the metal electrodes electronegatively to -0.770 V/SCE and maintained this potential over a period of 60 days during which time the steel electrodes "lost negligible" weight. They, therefore, concluded that "referred to the copper-copper sulfate electrode, the protective potential of approximately $\,-\,0.850\,\,\mathrm{V}$ is in agreement with the practice for CP used by many corrosion engineers, in those cases where the measurements are free of IR drop external to the electrical boundary of the corrosion circuit." The most important aspects of their experimental conclusions are that the corrosion was "negligible" but not necessarily zero, and the potential was measured free of IR drop. These findings were also verified by Ewing.7

A more recent study, conducted by Barlo and Berry, employed corrosion cells modeled after those used by

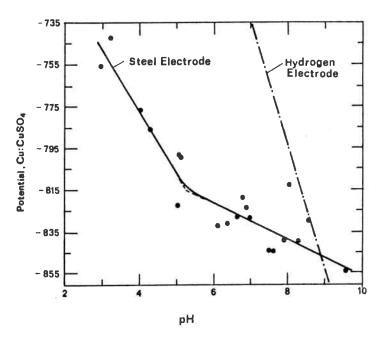
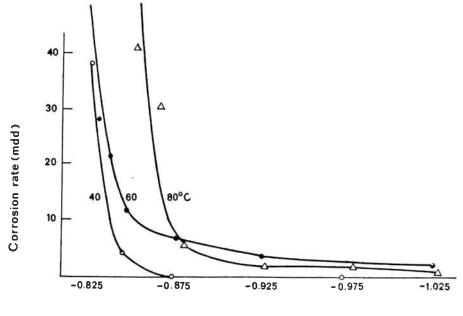


FIGURE 3 — Relation between the potential of steel in air-free soils, and the pH values of the soils.



Potential (volts, Cu: CuSO₄)

FIGURE 4 — Relationship between the potential and the corrosion rate of mild steel in 3% NaCl solution at 40, 60, and 80 C.¹⁰

Schwerdtfeger and McDorman and involved six different soils both under aerated and deaerated conditions.⁸ They concluded that "in the absence of moderately elevated temperatures and anaerobic bacteria, potentials more negative than about -0.850 V appear adequate for protection in most cases." In this study, potential measurements were taken with the current interrupted to determine the polarized potential free of IR drop. Furthermore, CP was considered to be effective when the general corrosion rate was reduced to less than 1 mpy (5 mdd) (25 μ m/y).

There is now substantial scientific corroboration for a -0.850 V/CSE criterion providing that this criterion is interpreted as a polarized potential free of IR drop with the expected corrosion rate to be negligible but not zero. The -0.850 V criterion as stated in the standard, however, does not stipulate that the potential should be a polarized potential, and, therefore, the standard is in serious disagreement with the fundamental science.

Though the -0.850 V criterion has now been verified for both aerated and deaerated conditions at room temperature it does not necessarily have validity under some other conditions. In the presence of sulfate reducing bacteria, for instance, the potential criterion may have to be increased to -0.950 V.⁹ Also, at higher temperatures of 40 and 60 C, it may not be possible to reduce the corrosion to a negligible value, even at polarized potentials as negative as -1.025 V/CSE as indicated in Figure 4.¹⁰

Testing of steel coupons in electrolytes having various pH values has indicated that sufficient protection could not be obtained at a polarized potential of -0.850 V/CSE in a solution having a pH of 3.5 under stagnant and stireed conditions. Figure 5 illustrates the effect of solution pH on the corrosion rate of mild steel as a function of the polarized potential.

It should also be noted from Figure 5 that the corrosion rate of mild steel in a solution at pH 6 under stagnant conditions was not reduced to zero at a polarized potential of $-0.850~\rm V$, thus verifying previous findings. A more recent investigation confirms this limitation of the $-0.850~\rm V$ criterion. This study, based on measurements at 87 locations on an existing pipeline, indicated that the polarized potentials ranged from $-0.55~\rm to$ $-1.50~\rm V/CSE$ while the IR drop in the measured potential ranged from $-0.24~\rm to$ $-9.05~\rm V$. Accord-

ingly, a criterion based on a potential measurement with the current applied is not indicative of the polarized potential. These same investigators also concluded that a more adequate potential criterion would be a polarized potential of $-1.00\ \text{V/CSE}$ since considerable attack was observed even at polarized potentials of $-0.90\ \text{to}-0.95\ \text{V}$. Toncre as a result of recent studies concluded that "a more realistic definition of adequate CP on a buried pipeline would be $-1.0\ \text{V}$." 13

Not only is the standard at odds with the science, but it is also not in accordance with the practice of many CP users and practitioners who routinely assume that a polarized potential of -0.850 V/CSE is the correct value. Other publications and standards also disagree with the NACE standard. The British Standards Institution's Code of Practice for Cathodic Protection considers a metal/electrolyte potential equal to or more negative than -0.850 V/CSE to be valid for iron or steel in aerobic environments only and more importantly define the structure/electrolyte potential as one taken with the "reference electrode in contact with the electrolyte at a point sufficiently close to (but without actually touching) the structure to avoid error because of the voltage drop associated with any current flowing in the electrolyte."14 Von Baeckmann and Schwenk in their handbook on CP caution that when applying potential criteria to electrochemical protection the "potentials have to be determined at the phase boundary metal/corrosion medium" otherwise "substantial errors can arise if the reference electrode is far from the metal surface." ¹⁵ Even more significant is the recent compliance order issued by the US Department of Transportation that considers "that a violation of the 850 mV criterion exists if a pipeline under CP has a voltage less than 850 mV after the IR drop has been con-

In view of all the research findings both past and present, it is apparent that the $-0.850~\rm V$ criterion, as stated by the NACE standard RP-01-69 (1983 Revision), is clearly in error. The $-0.850~\rm V/CSE$ criterion, to be correct, should be stated as a polarized potential measured free of external IR drop with a clear understanding that corrosion activity may not be completely arrested, especially in the presence of elevated temperatures, low solution pH, and anaerobic bacteria. Measurement of polarized potentials is possible using available technology and techniques. 17

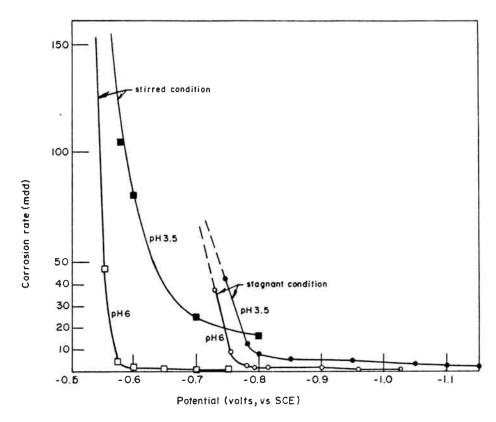


FIGURE 5 — Relationship between the corrosion rate of mild steel and potential in 3% NaCl solution having a pH of 3.5 and 6.0 under stagnant and stirred conditions.

Potential shift criteria

The two potential shift criteria in common use are stated in the NACE standard as follows:

"A minimum negative (cathodic) voltage shift of 300 mV, produced by the application of protective current. The voltage shift is measured between the structure surface and a stable reference electrode contacting the electrolyte. This criterion of voltage shift does not apply to structures in contact with dissimilar metals."

"A minimum negative (cathodic) polarization voltage shift of 100 mV measured between the structure surface and a stable reference electrode contacting the electrolyte. This polarization voltage shift is to be determined by interrupting the protective current and measuring the polarization decay. When the current is initially interrupted, an immediate voltage shift will occur. This voltage reading after the immediate shift shall be used as the base reading from which to measure polarization decay."

Verification of the -0.850 V/CSE criterion by Schwerdt-feger and McDorman was conducted with steel samples exposed to deaerated soils. In high-resistivity, well-aerated soils that are relatively porous, steel can exhibit corrosion potentials in the -0.3 to -0.4 V range and the polarizing of the steel structure to the -0.850 V criterion can require large CP currents at a corresponding increase in cost. Sudrabin has reported that the ratio of required protective current to corrosion current increases with increasing media resistivity. ¹⁸ On large bare structures exposed to well-aerated, high-resistivity soils, it has been considered uneconomical to attain an absolute potential criterion such as -0.850 V. Investigations by Ewing revealed that steel exposed to aerated soils (sandy

loam) required approximately 8 times the current than when exposed to clay soil.¹⁹ Of greater interest, however, is that he discovered in all cases tested that protection was achieved with less than -0.1 V polarization. Logan also confirmed that in some circumstances protection is polarized to -0.85 V.20 Ewing further stated that "in well drained and rather dry soil, the protective potential was about -0.7 V/CSE."²¹ The theoretical validity for the 0.10 V shift criterion for mild steel exposed to both seawater and groundwater has been demonstrated by Schwenk and Von Baeckmann and confirmed by tests conducted by Barlo and Berry who concluded that "the 100 mV polarization criterion appears to be the most generally applicable criterion in the soils studied."22,23 Accordingly the 100 mV electronegative, polarized potential shift appears to be valid although it is questionable whether it is necessary to measure this shift only as a potential decay since methods are now available which can be used to determine a true polarized potential free of IR drop. There is no significant difference, therefore, between measuring a polarization decay as opposed to measuring a polarized potential shift with respect to the initial structure corrosion potential.

There is little if any empirical or scientific support for the -300 mV shift criterion. Significant cost savings were, however, successfully demonstrated by Van Nouhuys by using a -0.3 V potential shift criterion in high-resistivity soils. Although he used a remote electrode method (e.g., placed 300 ft (91 m) from the structure) conventional use of the 300 mV criterion involves determining the difference between the measured pipe potential before and after CP current is applied with the reference located on the soil surface directly above the pipe. The potential difference measured by either of these methods will contain a voltage drop component of varying magnitude, depending on the current density and soil resistivity. Figure 6 illustrates the typical potentials measured with a reference on the surface when executing the -0.3 V shift test.

When the CP current is applied at "t1," there is an im-

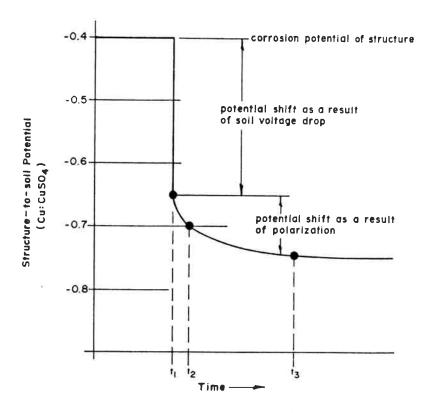


FIGURE 6 — Typical structure-to-soil potential change with respect to time.

mediate potential shift to -0.65 V caused by the voltage drop in the soil between the reference and the pipe from the protection current. At time " t_2 ," at a potential of -0.70 V, the -0.3 criterion would be satisfied even though the amount of polarization is only 0.05 V. The difficulty in applying this criterion to bare structures in well-aerated, high-resistivity soils is that these are the precise conditions that are apt to produce the largest IR drop. This criterion, therefore, does not directly address the most important parameter of CP, which is polarization, and hence its validity is suspect unless the IR drop component in each measurement is quantified.

At time "t₃" in Figure 6, the 0.1 V polarization potential shift is satisfied. This latter criterion is more valid than the 300 mV shift criterion since it deals only with polarization, and by definition the IR drop must be eliminated from the measurement. The fact that the 0.3 V shift criterion has been effective in some instances is probably attributable to the coincidental inclusion of a significant amount of polarization shift. The necessity for the shift criterion to include a significant polarization potential shift is echoed by Sudrabin and Ringer who concluded that "a pipe potential change (say 200 or 300 mV) criterion will not be reliable if the protective potential does not exist in the electrolyte at the anode-cathode junction of a local cell."25 Accordingly, as the proportion of the -0.3 V shift caused by the soil path voltage drop increases, then the effectiveness of the criterion will proportionately decrease. Peabody cautions that the 0.3 V criterion "will not provide complete protection but is a useful practical tool when used in connection with bare structures or nonpolarizable structures in the absence of dissimilar metals and stray direct currents."26 Even Van Nouhuuys, who appears to have been a major proponent of the 300 mV shift criterion, acknowledges its limitations in that the "degree of protection is not sufficient to suppress all types of galvanic cells."27 Rather, he goes on to explain that adherence to the 300 mV criterion was "the first logical step in evolving as nearly a leak-proof system of CP as experience and economics will permit."

Owing to the fact that there is no scientific justification for the 300 mV criterion, which must be corrected for the IR drop in any event, and that the 100 mV polarized potential shift is a perfectly acceptable criterion, it is obvious that the 300 mV criterion as stated in the standard is as meaningless as it is unnecessary.

E Log I criterion

The potential criteria discussed to this point are generally applied universally without a great deal of regard for the particular environmental circumstances. Issues such as cost of protection to achieve a particular criterion or ease of measurement of the criterion are often more paramount considerations than is the validity or interpretation of the individual criterion. It is often claimed, however, that the E log I criterion will provide a more accurate standard, not only because the method is considered scientifically fundamental but also because onsite testing must be conducted which, therefore, considers the effect of the specific environmental conditions. The E log I criterion in the standard is stated as follows:

"A structure-to-electrolyte voltage at least as negative (cathodic) as that originally established at the beginning of the Tafel segment of the E-log-l curve. This structure-to-electrolyte voltage shall be measured between the structure surface and a stable reference electrode contacting the electrolyte at the same location where voltage measurements were taken to obtain the E-log-I curve."

This criterion refers to the curve relating the structure potential to applied cathodic current (Figure 7); which is sometimes called a Britton curve. The potential (Ep) at which the potential curve departs from the linear portion of the curve (Tafel Slope) is considered by the standard as the protective potential criterion. The significance, however, of the break in the polarization curve is subject to a wide variation of opinion and interpretation. Krehn and Wilhelm found that, where the corrosion activity is under CP, the intersection of the two straight lines extrapolated from the two portions of the curve denotes the minimum current density (ip) required for protection.²⁸ In an aqueous solution containing 500 ppm of sodium chloride, however, the minimum current density defined by

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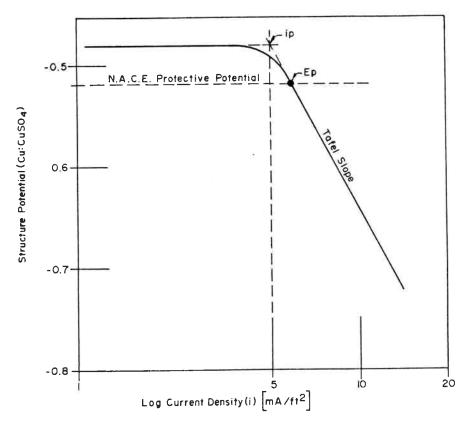


FIGURE 7 — E Log I (Britton) curve for steel in contact with water containing 500 ppm sodium sulfate.²⁰

this technique was found to be less than required to achieve full protection. Schwerdtfeger and McDorman, by noting the breaks plotted both on linear and logarithmic scales and then applying the minimum current, were able to protect steel in four of the five soils tested.²⁹ Moreover, when these currents were applied for a period of time (60 day) the steel potential polarized to at least -0.85 V/CSE. These results, which support the intersection of the extrapolated slopes on the E log I curve as the minimum current required for CP, arose from laboratory experimentation only.

Attempts by Riordon and Sterk to apply this method in the field led them to conclude that "the conventional E log I method is not accepted by the authors as a satisfactory indicator of current requirements for well casings."30 Schwerdtfeger later disputed their conclusions after replotting their field data.31 This difference of opinion based on the same data demonstrates a basic problem with E log I criterion that is the inherent difficulty in interpreting the data. Kubit reiterated this difficulty by emphasizing that the one most important factor in using this criterion is "experience," which suggests that a considerable degree of judgement is required to interpret the data.32 The use of this criterion on a bare pipeline in wellaerated, high-resistivity soil led Sudrabin and Ringer to conclude that "the actual current requirements for the control of corrosion are greater than that indicated by an apparent break in the potential-log current relationship."33 Furthermore, Dabkowski has reported that the E log I curve breakpoints (intersection) are "indicative of a current level where the average applied current density to the casing is equal to the casing corrosion current density rather than an indicator of when an adequate CP level is achieved for local corrosion cells."34

In well-aerated electrolytes where the primary cathodic polarization reaction is the reduction of oxygen, a distinctive Tafel slope will not be present since the reaction rate is dependent on the rate of diffusion of oxygen to the structure. Under these circumstances, the polarization curve would typically appear as in Figure 8 for which there is no Tafel

slope for the aerated (O_2 saturated) condition. Holler confirmed that a Tafel slope break in the potential/current curve was not obtained in extremely aerated conditions.³⁶

Despite the lack of agreement on the application of the E log I criterion and the reservations expressed concerning its usage, this criterion is in common use as a method for determining the current required for protection of well casings. Conventional application of this criterion, however, does not agree with the NACE standard, which considers the technique a potential criterion rather than a minimum current criterion. Conservative use does, however, consider the current at the potential (Ep) of Figure 7 as the nominal design current for the CP system.

In obtaining the test data, the potentials measured must be corrected for IR drop error so that only polarized potentials are plotted, and the current must be applied in steps separated by equal-time increments.³⁷ For the E log I criterion to be a useful standard then, it should be stated in a manner that recognizes it as a minimum current criterion not a potential criterion. Furthermore, limitations in its application for structures in aerated environments and instruction on measurement techniques and data interpretation should be integral parts of this standard.

Net protective current criterion

When the corrosion current flow from all structure anodic sites to the electrolyte is made zero by the application of a cathodic current, corrosion is halted. This criterion is expressed in the standard as:

"A net protective current from the electrolyte into the structure surface as measured by an earth current technique applied to predetermined current discharge (anodic) points of the structure."

This is an absolute criterion in the sense that there can be no corrosion when there is a net cathodic flow of current to all

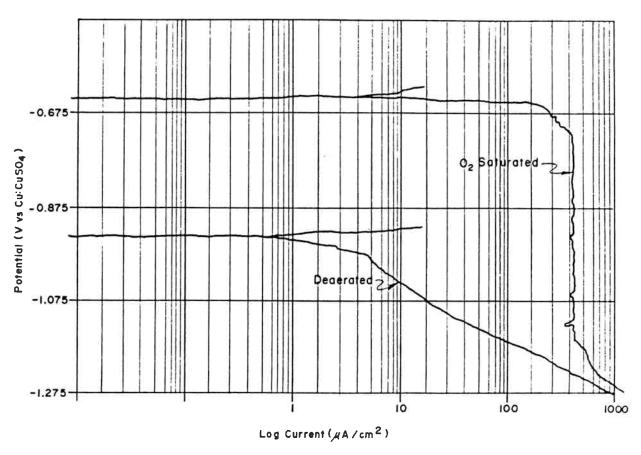


FIGURE 8 — Typical cathodic polarization curve for steel exposed to aerated and deaerated electrolyte.

anodic sites. Unfortunately, when the corrosion cells are small local action cells, there is no practical method to measure the net current flow, and, therefore, this criterion cannot be applied in practice even though it is fundamentally correct.

Summary

CP is a powerful technique for the prevention of corrosion on buried metal structures if it is properly applied. The measure of its success, however, depends principally on the interpretation of field data and on comparison to various criteria. It is imperative that the criteria be clearly stated and that these criteria are accurately linked to the fundamental science involved. There are several deficiencies in the present NACE standards that lead to misinterpretation of CP data, which promote scepticism in the minds of the users and practitioners, and encourage manipulation of the data to satisfy the requirements of regulatory agencies.

If the CP criteria are to properly serve the user and practitioner, they must address the underlying fundamental factor concerning CP which is polarization. As Mears and Brown have stated, "the local cathodes must be polarized to the potential of the unpolarized local anodes." Any criterion that does not concern itself with a polarized potential will be in error with the basic definition of CP and the intent of the RP-01-69 recommended practice that is to prevent corrosion. Over 40 y ago, Pearson emphasized the importance of determining the polarized potential when he stated, "it is clear that any measurement of the polarization of a buried structure must be made to differentiate between the effects of purely IR drop and the electrochemical results of the current flow. Only the latter is of any use in controlling the rate of corrosion."

The criteria in NACE standard RM-01-69 must be revised to reflect the basic principles of CP.⁴⁰ This can be accomplished primarily by eliminating the IR drop in the potential measurements so that emphasis is focused on a polarized

potential. Accordingly the existing criteria should be revised as follows:

- 1. The -0.85 V/CSE criterion should be a polarized potential criterion so that errors arising from soil path IR drop are eliminated. It should also be clearly stated that even under ideal environmental conditions, such as neutral pH and relatively low temperatures, corrosion is not necessarily fully arrested.
- 2. Consideration should be given to adopting a -1.00 V/CSE polarized potential criterion for circumstances where more complete corrosion prevention is desired.
- 3. The $-300\,\text{mV}$ shift criterion should be dropped in favor of the $-100\,\text{mV}$ shift criterion since the former criterion has not be scientifically substantiated and more importantly incorporates IR drop errors in its measurement.
- 4. The E log I criterion should be stated as a minimum current criterion rather than a potential criterion, and the method of conducting the test should be clearly defined. Moreover, the limitation of this technique in aerated environments should be also noted.
- 5. Because the net current flow criterion cannot be applied in practice, it should be removed from the standard.

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