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Technical Considerations on the Use of the 100mV Cathodic Polarization Criterion

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ABSTRACT

The 100mV cathodic polarization criterion is being used more extensively on piping in the oil and gas industry which has prompted a discussion on the limits of its use. This paper summarizes the technical literature on the validity of this criterion with respect to elevated temperature, sulfate reducing bacteria, mill-scale, type of metal, mixed metal structures, stress corrosion cracking, soil moisture, and AC corrosion.

Keywords: 100mV, cathodic polarization criterion, cathodic protection, elevated temperature, mill-scale, SRB, SCC, AC corrosion, mixed metal structures, soil moisture.

BACKGROUND

The 100mV cathodic polarization criterion, which was first proposed by Ewing[1] more than 65 years ago, has been validated through theoretical and empirical investigations[2] over the intervening years, and was incorporated into the original NACE corrosion control standard for underground and submerged piping (RP0169) as well as other standards.[3,4,5,6,7,8] Furthermore, in the reinforced concrete industry it has been the defacto standard for the protection of reinforcing steel in atmospherically exposed concrete structures on a worldwide basis for over 30 years. Not only is this criterion applicable to ferrous metal structures but also to other metals such as copper and aluminum.

It is only relatively recently however, that its application has become widespread in the petroleum industry. The reason for this arises from the pipeline industry reaction to the emphasis in the RP0169-1992 standard on "consideration" of voltage drops in the pipe-to-soil potential measurement for valid interpretation of the –850mV$_{cse}$ potential(with respect to a saturated copper-copper sulfate reference) criterion with the current applied. When IR drop "consideration" was rigorously applied to field data it was found that protection levels were often sub-criterion and, in lieu of automatically installing additional cathodic protection capacity, measurements were conducted to determine if the 100mV cathodic protection criterion was satisfied. In many cases the 100mV cathodic protection criterion was indeed satisfied thus relieving the owner/operator from remedial expenditures that would otherwise have been needed.

As application of the 100mV cathodic polarization criterion has increased, questions as to the limits of its validity have arisen, especially in regard to the factors that are known to limit the effectiveness of the –850mV$_{cse}$ potential criterion. This paper is a literature summary of the factors that need to be considered, and that was carried out in preparation of a state-of-the-art report on the 100mV cathodic polarization criterion by Task Group 211. The first draft of this report was distributed to members of STG 05 and STG 35 for review and comment in April 2006.

KINETIC THEORY

The success of the 100mV cathodic polarization criterion depends fundamentally on a combination of the cathodic protection mechanism, as first explained by Mears and Brown in 1938, and the anodic and cathodic polarization characteristics in a typical corrosion cell on a underground or immersed structure.

Mears and Brown[9] indicated that for complete corrosion control the cathodes of all existing corrosion cells on a structure must be polarized cathodically to the most electronegative open circuit anode potential on the structure. Typically, as illustrated in Figure 1, corrosion cells on steel structures exposed to soils are under cathodic control, which means that the reduction reaction at the cathode is the charge transfer reaction that controls the corrosion rate. In a corrosion cell under cathodic control, the corrosion potential (E_{corr}) is relatively close in value to the open circuit potential of the anode ($E_{a,oc}$). Hence the negative shift in cathodic polarization required to equal or exceed $E_{oc,a}$ is relatively modest.

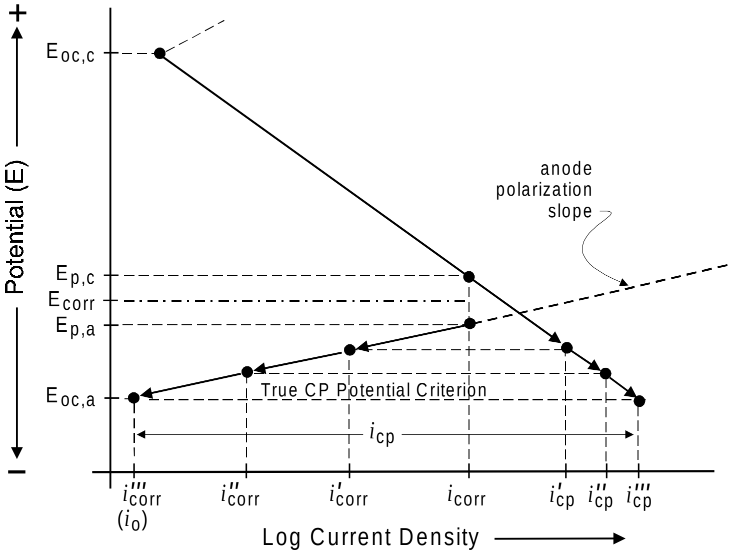

FIGURE 1 – Cathodic Protection for a Corrosion Cell Under Cathodic Control

Even if the cathodic polarization shift does not result in a polarized potential equal to or more negative than $E_{oc,a}$, which would produce a zero corrosion rate, the corrosion current density (i_{corr}) is nevertheless reduced logarithmically as the cathodic protection current density is increased. Moreover, the results of a number of investigations[10,11,12,13] into the slope of the anode polarization line has indicated a range between 30 and 60mV per decade of current, which would result in a corrosion rate reduction by a factor of 2150 and 46, respectively for a 100mV polarization shift from the corrosion potential.

EMPIRICAL EVIDENCE

A number of studies have been conducted using the 100 mV criterion on steel in a wide range of soil types and conditions that indicates for relatively neutral pH soil conditions, in the absence of sulphate reducing bacteria, the corrosion rate is reduced to less than 25 microns/yr (1 mpy). Clause 6.2.2.2.2 of RP0169-2002 cautions however that *"In some situations, such as the presence of sulphides, bacteria, elevated temperatures, acid environments, and dissimilar metals,"* the criteria may not be sufficient. These studies also show that there are some conditions under which the 100mV cathodic polarization criterion may be insufficient or invalid.

Elevated Temperature

As with the –850mV$_{cse}$ criterion, the 100mV cathodic polarization shift criterion might also be insufficient at elevated temperature. Barlo and Berry[14] conducted tests on steel samples in aerated soils obtained from Ohio (4OH-21% moisture) and California (9CA-13% moisture) at both room temperature and 60ºC. The results, depicted in Figure 2, shows that in both soils require more polarization was required to reduce the corrosion rate to less than 1 mpy, although there was some uncertainty in the data for the California soil.

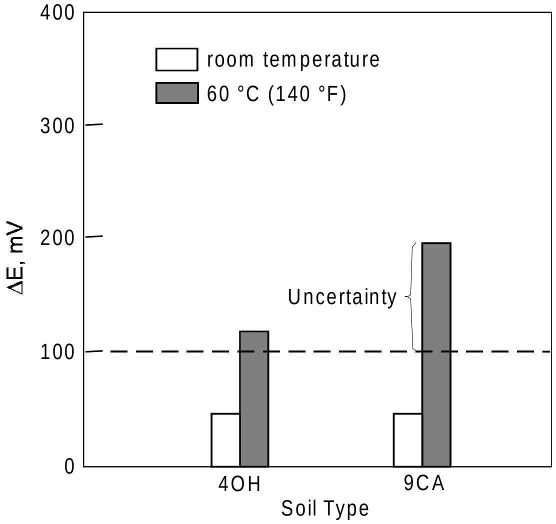

FIGURE 2 – The Effect of Temperature on the Minimum Requirements to Prevent Pitting and General Corrosion Relative to the Level of Cathodic Polarization

In an attempt to quantify the long term cathodic polarization required for mild steel, tests were conducted in a soil leachate by Zdunek and Barlo. The results of this research, illustrated in Figure 3, also indicate that more than 100mV of cathodic polarization is required at temperatures greater than

30ºC (95ºF), although the polarization requirements did not increase with increasing temperature beyond this temperature.

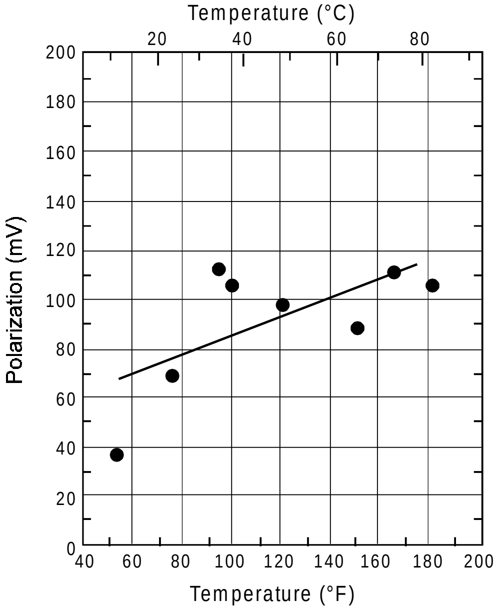

FIGURE 3 – Effect of Temperature on the Level of Polarization for 25 µm/y (1 my) Corrosion Rates

It is also interesting to note that as the temperature decreases from 30ºC the amount of polarization required diminishes significantly.

Mill-scaled Steel

Most laboratory testing on criteria has been done using steel coupons with a cleaned surface. Barlo and Berry[15] conducted tests on mill-scaled steel samples at both room temperature and at 60ºC. In both cases as illustrated in Figures 4 & 5, there were some soils that required more than 100mV of cathodic polarization, albeit with some uncertainty in the data.

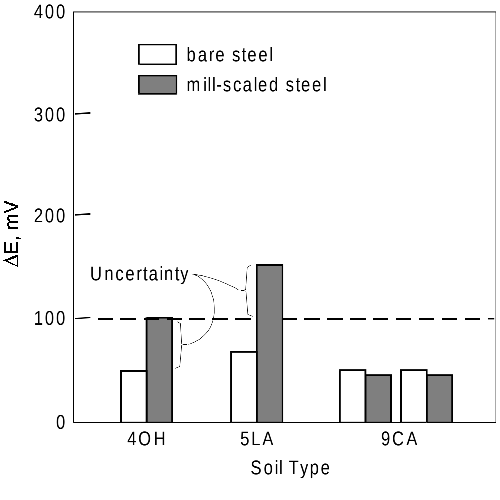

FIGURE 4 – The Effect of a Mill-scaled Surface Condition on the Minimum Polarization Levels Required to Prevent General Corrosion Relative to Non-Mill-scaled Steel

In both an aerated Ohio soil(4OH - 21% moisture) and an aerated Louisiana soil(5LA-14% moisture), the mill-scaled steel samples required more polarization than the bare steel samples. This was not the case for two samples in California soil(9CA-13% moisture), but these latter tests were run under deaerated conditions.

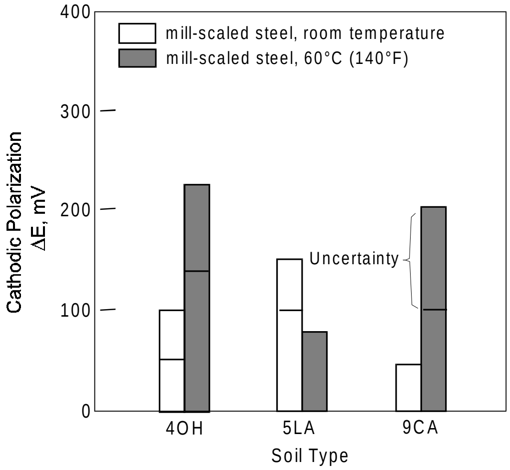

FIGURE 5 – The Effect of Temperature on the Minimum Level of Cathodic Polarization to Prevent General Corrosion on Mill-scaled Steel Relative to Room Temperature

When the temperature was increased to 60ºC, the cathodic polarization requirements increased substantially for the deaerated California soil (9CA-13% moisture) and for the aerated Ohio soil at 21% moisture content.

The foregoing results are particularly relevant to the cathodic protection of the external surface of storage tank bottoms, since these surfaces are typically bare and mill-scaled, are sometimes heated, and the 100mV criterion is often applied to minimize the cathodic protection current required. It is not unusual for the bottoms of heated above ground storage tanks to fail from external corrosion in the presence of a cathodic protection system being operated with respect to the 100mV cathodic polarization criterion.

Soil Moisture Content

Another field study[16] conducted in 14 field sites located in Australia, Canada, and the US, to evaluate the effectiveness of all the criteria in the RP0169-83 standard, also evaluated the average minimum polarization shift needed as a function of soil moisture. The result of this assessment is graphically summarized in Figure 6.

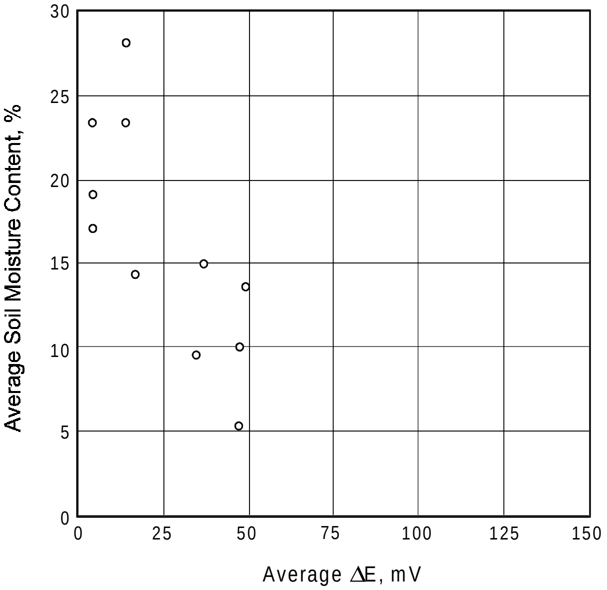

FIGURE 6 – Effect of Soil Moisture on the Average Minimum Polarization for Protection

It is interesting to note that in moisture conditions greater than 5%, that 50mV of cathodic polarization was adequate for all sites. Furthermore the steel coupons at these sites would normally be at soil ambient temperature, which would be less than the room temperatures during the laboratory studies.

Sulfate Reducing Bacteria

Just as the –850mVcse polarized potential criterion needs to be more electronegative in the presence of sulfate reducing bacteria, it also appears to be the case for the 100mV cathodic polarization criterion as shown in Figures 7 & 8. These results were obtained by Barlo and Berry[17] from laboratory tests on bare steel samples (Figure 7) and mill-scaled steel samples (Figure 8) in two deaerated Texas soils (8TX at 10% and 19% moisture) and a deaerated California soil (9CA- 13% moisture). For the bare steel samples in the California soil and one Texas soil (8TX-19% moisture), more than 200mV of cathodic polarization was necessary to mitigate corrosion.

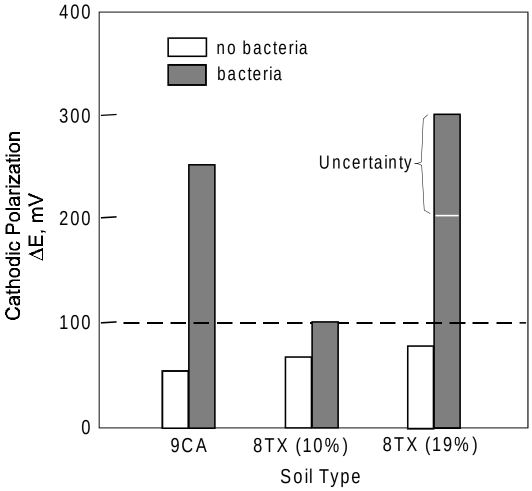

FIGURE 7 – The Effect of Anaerobic Bacteria on the Minimum Levels of Cathodic Polarization to Prevent General Corrosion Relative to the Criterion for Bare Steel at Room Temperature

When the same tests were repeated with the same soils but with mill-scaled steel samples approximately 300mV of cathodic polarization was required at room temperature.

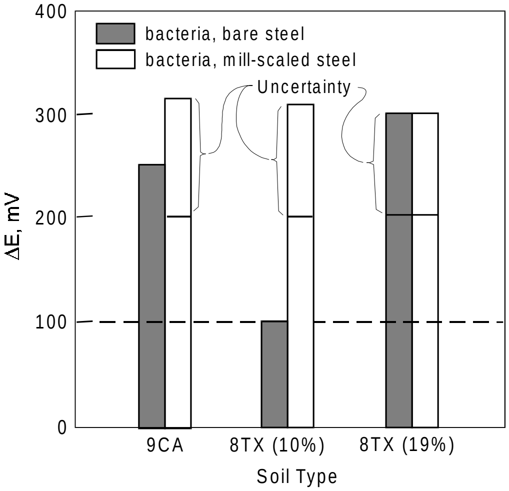

FIGURE 8 – The Effect of a Mill-Scaled Steel Surface Condition on the Minimum Levels of Cathodic Polarization Required to Prevent General Corrosion in the Presence of Anaerobic Bacteria

Consideration for Stress Corrosion Cracking (SCC)

When the 100mV of cathodic polarization criterion is applied the resulting polarized potential is normally less negative than –850mV$_{cse}$, otherwise the latter criterion would have been used. Clause 6.2.2.3.2 of the NACE RP0169-2002 standard cautions against using potentials less negative than -850mV$_{cse}$ when *"operating pressures and conditions are conducive to stress corrosion cracking"*. The polarized potential range for carbonate/bicarbonate induced SCC widens with increasing temperature as shown in Figure 9. At room temperature of about 21ºC, the potential range is from about –550mV$_{cse}$ to –700mV$_{cse}$. For susceptible pipelines in ambient temperature conditions, polarized potentials within this range should be avoided.

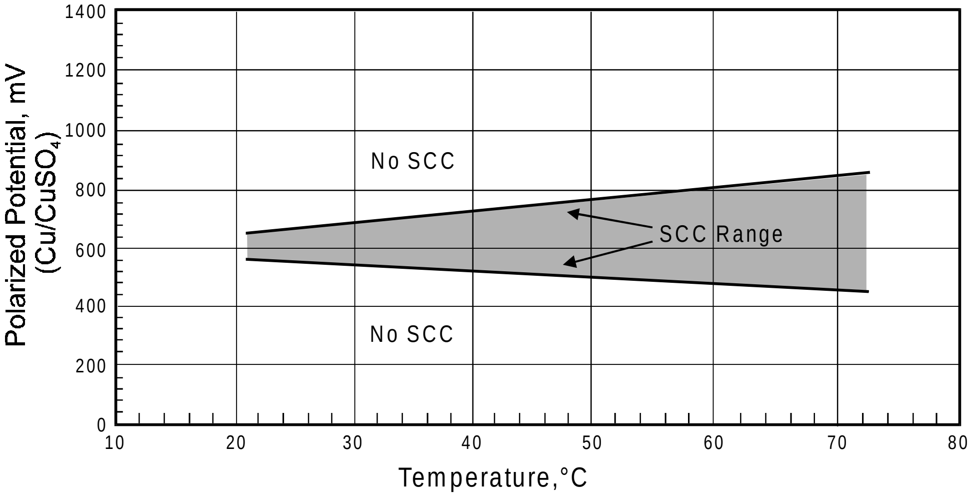

FIGURE 9 – SCC Range in Carbonate/Bicarbonate Environments

Beavers et al[18] have produced a flow chart for guidance in applying the 100mV cathodic polarization criterion to avoid the possibility of producing SCC, which includes consideration of a number of pertinent factors such as type of coating, surface preparation conditions prior to coating application, operating pressure, operating temperature, and soil/groundwater chemistry. This chart, based on accumulated experience from numerous SCC investigations in the laboratory and in the field is included as Figure 10.

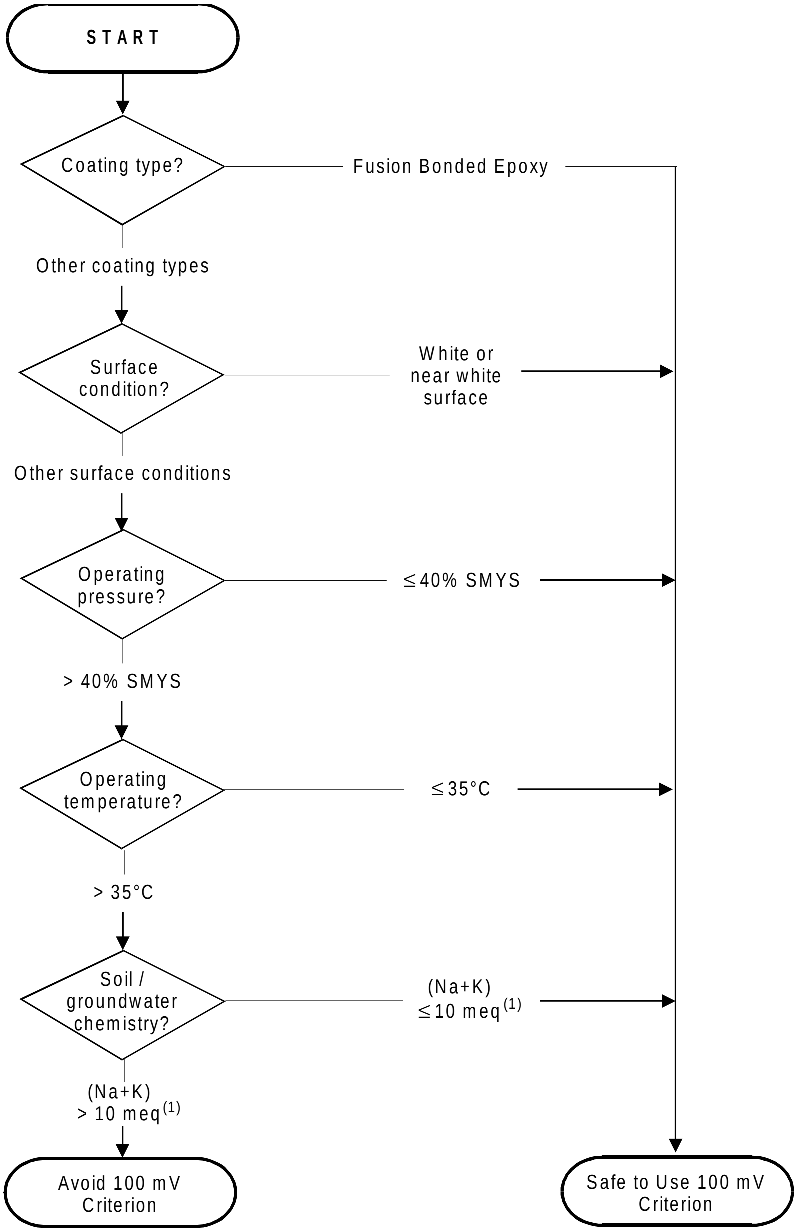

FIGURE 10 – Flow Diagram for Decision-making with Respect to the Use of the 100mV Polarization Criterion(2) to Avoid the Possibility of High-pH Stress Corrosion Cracking

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(1) Based on laboratory analysis of limited field data.

(2) The safe use of the 100mV cathodic polarization criterion in accordance with this chart does not guarantee that high pH SSC will not occur but only that it is extremely unlikely.

Mixed Metal Structures

For dissimilar metal piping Clause 6.2.5.1 of RP0169-2002[19] states *"A negative voltage between all pipe surfaces and a stable reference electrode contacting the electrolyte equal to that required for the protection of most anodic metal should be maintained"*. Hence for a steel-copper piping system the criterion would be a polarized potential of –850mV$_{cse}$ and implies that the 100mV cathodic polarization criterion cannot be utilized. Yet the slope of the anodic polarization curve for such a system should be no different than if it was a steel structure and therefore the relative reduction in corrosion rate when applying the 100mV criterion should not differ regardless of the cathode material.

However when compared to the Mears and Brown definition of cathodic protection, the corrosion potential of a mixed metal corrosion cell may not be close to the open circuit potential of the anode. As shown in Figure 11, as the cathode area increases relative to the anode area the corrosion potential moves farther away from the anode open circuit potential ($E_{a,oc}$).

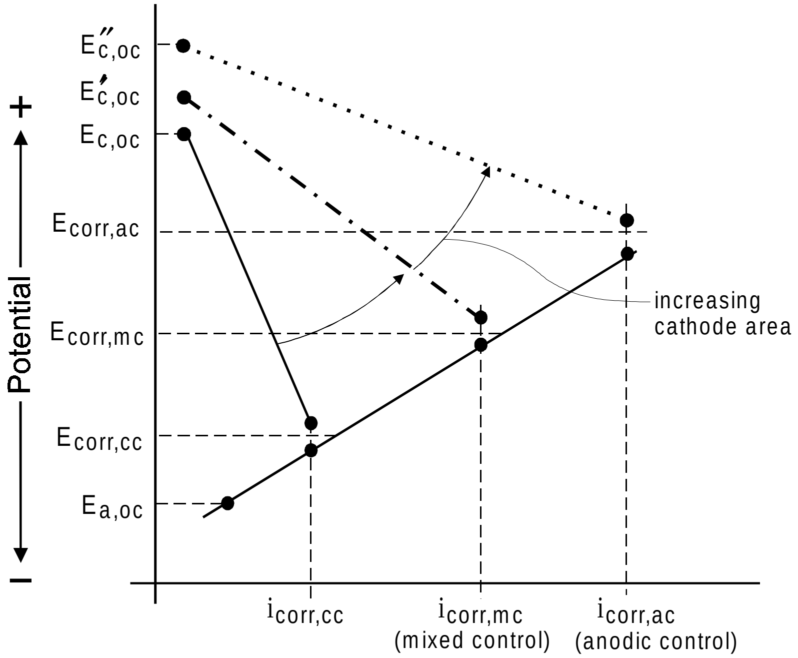

FIGURE 11 – Polarization Schematic Illustrating Effect on Corrosion Rate in a Mixed-Metal Corrosion Cell

It follows then if the cathode of the mixed metal couple is small in surface area compared to the anodic metal then the corrosion potential could indeed be close to the anode open circuit potential ($E_{a,oc}$) in which case the 100mV criterion would be reasonably effective. Even when the cathode has a large area and the corrosion potential of the mixed metal cell is not close to the anode open circuit potential the corrosion rate reduction may be similar because the anodic slope is the same. But in this latter case the resultant corrosion rate may be greater than the 25 microns/yr used to quantify the effectiveness of the criteria.

AC Corrosion

As with the any of the cathodic protection criteria the 100mV cathodic polarization criterion may not be completely effective in reducing corrosion rates to acceptable levels depending on the AC current density. However one study[20] has indicated that as the polarized potential increases so does the AC current density due to the increase in hydroxyl ion concentration at the holiday. Under such circumstances the 100mV cathodic polarization criterion could have a significant advantage over the –850mV$_{cse}$ polarized potential criterion in terms of mitigating AC corrosion.

SUMMARY

The 100mv cathodic polarization criterion appears applicable to non-mill-scaled steel surfaces operating at temperatures below 30°C, in non-sulfate reducing bacteria conditions, for AC induced current densities less than 20A/m^2, at soil moisture content greater than 5% by weight of dry soil, and in conditions that will not promote high pH stress corrosion cracking. This criterion may not be valid on mixed metal structures depending on the relative surface area of the most cathodic metal and its cathodic polarization characteristics.

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