Would the Real -850 mV$_{CSE}$ Criterion Please Stand Up

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ABSTRACT

Some recent papers contain inaccurate information regarding the validity of the -850 mV$_{CSE}$ current applied criterion, the so-called on-potential criterion. To qualify as a corrosion control criterion the -850 mV$_{CSE}$ value must imply a sound engineering judgment of the corrosion rate. Only the -850 mV$_{CSE}$ polarized potential criterion does this, as supported theoretically and empirically through its development, where a corrosion rate of less than 1mpy (< 0.025mm/a) is generally accepted. There is no similar scientific backing for the -850 mV$_{CSE}$ on-potential criterion. Numerous comparative studies of these two criteria illustrate that the corrosion rate can not be judged on the basis of an on-potential criterion when the IR drop is ignored. Failure to correct the on-potential measurement, by removing the IR drop, leaves the public exposed to an unnecessary safety risk.

Key words: -850 mV$_{CSE}$ potential criterion, polarized potential, on-potential, IR drop, corrosion rate, cathodic protection criteria

BACKGROUND

Ever since the first publication of the NACE SP0169 standard in 1969, a clause has been included in this standard to caution users that voltage drops (IR drop), other than across the structure/electrolyte boundary, need to be considered for valid interpretation of the -850 mV$_{CSE}$ current applied criterion, often referred to as the on-potential criterion. Consideration is required because when the current is applied there are typically voltage drops

- in the earth between the reference electrode and the structure/electrolyte interface, and
- in the structure between the point of connection on the structure and the reference electrode location.

The resulting voltmeter potential difference measurement (Vm) therefore contains voltage drops that conceal the polarized potential (Ep) which indicates the level of corrosion control, as related by the following equation.

$$Vm = Ep + Ve \pm Vs \qquad (1)$$

Where:

Vm = potential difference between the point of connection to the structure and the reference electrode contacting the electrolyte
Ep = polarized potential across the structure/electrolyte interface
Ve = voltage drop in the earth between the structure/electrolyte interface and the reference electrode
Vs = voltage drop in the pipe between the point of structure connection and the reference electrode location

The IR drops are artifacts of the applied current or stray current and don't indicate the level of cathodic protection which resides only in the potential across the structure/electrolyte interface.

Consideration of these inherent voltage drops in the potential measurement has often meant ignoring their effect. A survey, conducted by the NACE T-10-1 criteria committee, during the revision of the RP0169-1983 standard, found that of 1166 responses, 813 (70%) did not consider IR drop. As a result, a -850 mV_{CSE} polarized potential criterion was inserted in the RP0169-1992 standard, which reflected the fundamental science and the empirical evidence from both laboratory and field trials. This was also an attempt to emphasize the importance of correcting for the earth and structure voltage drops in the interpretation of the on-potential criterion. Unfortunately, this created ambiguity in determining which criterion was correct and did little to dissuade operators from continuing to neglect the IR drop in the -850 mV_{CSE} on-potential criterion.

Attempts by the T-10-1, TG285, and TG360 criteria committees to clarify this ambiguity by inserting the words "correct for" or "account for" instead of "consideration" have been voted down by a segment of the pipeline industry in North America that prefers to continue to disregard the significance of the IR drop in the -850 mV_{CSE} on-potential criterion. Justification for neglecting the IR drops has been expressed in recent papers which contain misinformation about how the -850 mVCSE criterion was established in the first place.

Bash[1] claimed the effectiveness of the -850 mV_{CSE} is based on R.J. Kuhn's experience on protecting pipe-lines in New Orleans.[2] Kuhn stated in a 1933 paper that the potential criterion to stop corrosion was "probably in the neighborhood of -0.850 V" with respect to a copper-copper sulfate reference electrode. But his experience on cathodically protecting cast iron water mains and steel gas pipelines was in soils with a high water table, a very low resistivity, and on piping at shallow depths. Under these conditions the IR drop would be small, as calculated using the following equation.[3]

$$IR = 1.15\, \rho\, d\, I \log t/d \qquad (2)$$

Where:

ρ = soil resistivity in Ω-m
d = diameter of the pipe in m
I = pipe CP current density in A/m^2
t = depth of pipe in m
IR = voltage drop in V

For a soil resistivity of 500 Ω-cm, a pipe diameter of 0.2 m, a cathodic protection current density of 0.02 A/m^2, and a pipe depth of 0.9 m, the calculated IR drop is only 15 mV. It follows that in low resistivity environments an on-potential of -850 mV_{CSE} would be very close in magnitude to a -850 mV_{CSE} polarized

potential. The offshore pipeline standard[4] that applies to pipelines in sea water and saline mud, which are both low resistivity environments, stipulates a cathodic protection criterion of -850 mV_{CSE} with the current applied. This standard recognizes that in low resistivity environments the IR drop, included in a potential measurement, is typically small.

But land based pipelines are exposed to soil resistivities that are much higher than for brackish or sea water. Recalculating the voltage drop using equation 2 for a soil resistivity of 5000 Ω-cm, indicates an IR drop of 150 mV, which is a substantial error since at an on-potential of -850 mV_{CSE}, the actual polarized potential would be only -700 mV_{CSE}. Kuhn, after working on cathodic protection of an 840 mile (1352 km) Texas to Ohio pipeline, opined in 1950 that "on the extremely well coated pipe lines under discussion a potential of minus 1.000 volt to a copper sulfate electrode is usually striven for".[5]

Bash also contends that a -850 mV_{CSE} on-potential is valid because the corrosion potential of steel is not more negative than -800 mV_{CSE} and therefore there is a 50 mV IR drop buffer available in the -850 mV_{CSE} on-potential criterion. However, the polarization diagram for a corrosion cell shown in Figure 1 illustrates that, if the corrosion potential (Ecorr) is -800 mV_{CSE}, there is an IR drop error (x) in the corrosion potential measurement between the corrosion potential and the polarized potential of the anode (Ea,p).
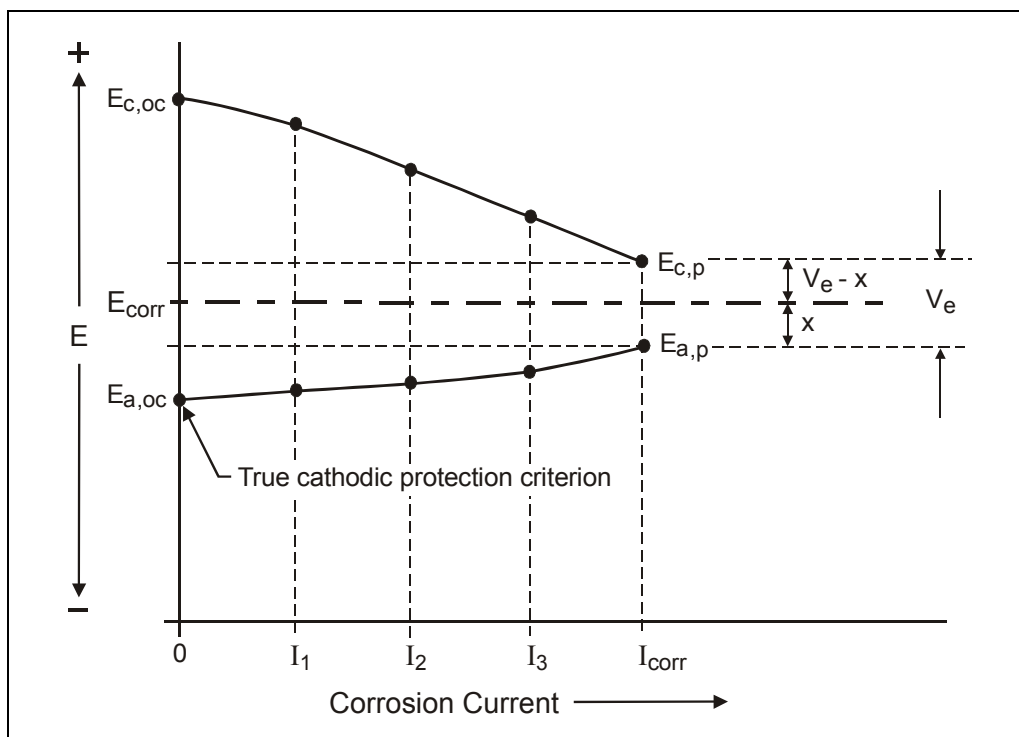

Figure 1: Corrosion Potential Indicated on a Polarization Diagram for a Corrosion Cell

Moreover, complete cathodic protection cannot be achieved according to the accepted Mears and Brown[6] definition of cathodic protection, unless the cathodes on a corroding structure are polarized to the potential of the most electronegative open circuit anode site (Ea,oc). Therefore, the open circuit potential of the anode (Ea,oc) is the true criterion for complete cathodic protection, which is more electronegative than the corrosion potential as well as the polarized potential of the anode (Ea,p). In practice, however, the true potential criterion cannot be determined, which then necessitates the need for an alternative potential criterion.

Trimble[7] supports the understanding that the early R.J. Kuhn experience was the basis for -850 mV_{CSE} on-potential criterion and, like Bash, seems unaware that Kuhn later expressed a preference for a -1000 mV_{CSE} on-potential criterion. He is also incorrect when he asserts that the -850 mV_{CSE} polarized potential criterion was somehow extracted from the Pourbaix diagram for steel based on the thermodynamic relationship between potential and pH.

THE ACTUAL DEVELOPMENT OF THE -850mV$_{CSE}$ CRITERION

The -850 mV$_{CSE}$ polarized potential was empirically determined and validated by Schwerdtfeger and McDorman[8] through laboratory testing at the National Bureau of Standards in the early 1950's. They measured the potential of steel electrodes in 20 air-free soils ranging in pH from 2.9 to 9.6 which produced the data plotted in Figure 2.
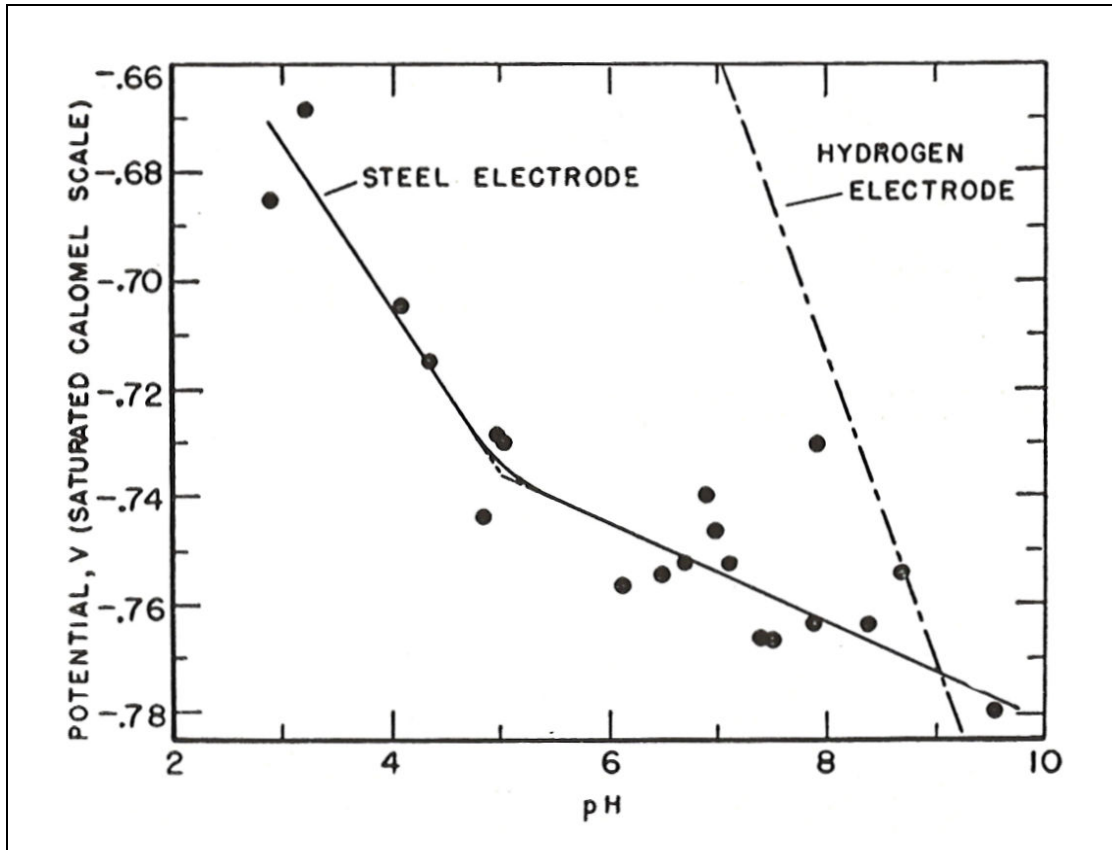

Figure 2: Relation between the Potential of Steel in Air Free Soils and the pH Values of the Soils

The hydrogen electrode line represents the potential of a hydrogen electrode relative to the pH and was considered to be the cathode potential in an air-free corrosion cell where steel is the anode. According to Holler[9] steel corrosion would be negligible at the point of intersection where the steel coupon potential equaled the hydrogen line potential because there would be no potential difference between the anode and cathode. This potential of -0.77 V to a saturated calomel electrode is approximately equivalent to a polarized potential of -850 mV$_{CSE}$. Schwerdtfeger and McDorman held numerous steel coupons at the intersecting point potential and used an instant-off potential method to monitor the potential. The corrosion was found to be negligible. They therefore concluded "Referenced to the copper-copper sulfate electrode, the protective potential is approximately -0.85 volt, which is in agreement with the practice for cathodic protection used by many engineers, in those cases where the measurements are free of IR drop external to the electrical boundary of the corrosion circuit".

The effectiveness of -850 mV$_{CSE}$ polarized potential criterion was later verified in the laboratory for both aerated and non-aerated soils by Barlo and Berry[10] in the early 1980's based on achieving a general corrosion rate of less than 1 mpy. These laboratory studies were succeeded by an American Gas Association sponsored 5 year criteria field testing program involving 14 sites spread over three different countries.[11] This study verified the effectiveness of the -850 mV$_{CSE}$ polarized potential criterion for controlling corrosion on steel coupons, installed adjacent to a 10 ft (3 m) length of bare 24 inch (60 cm) diameter pipe, based on a general corrosion rate of less than 1 mpy, as shown in Figure 3.
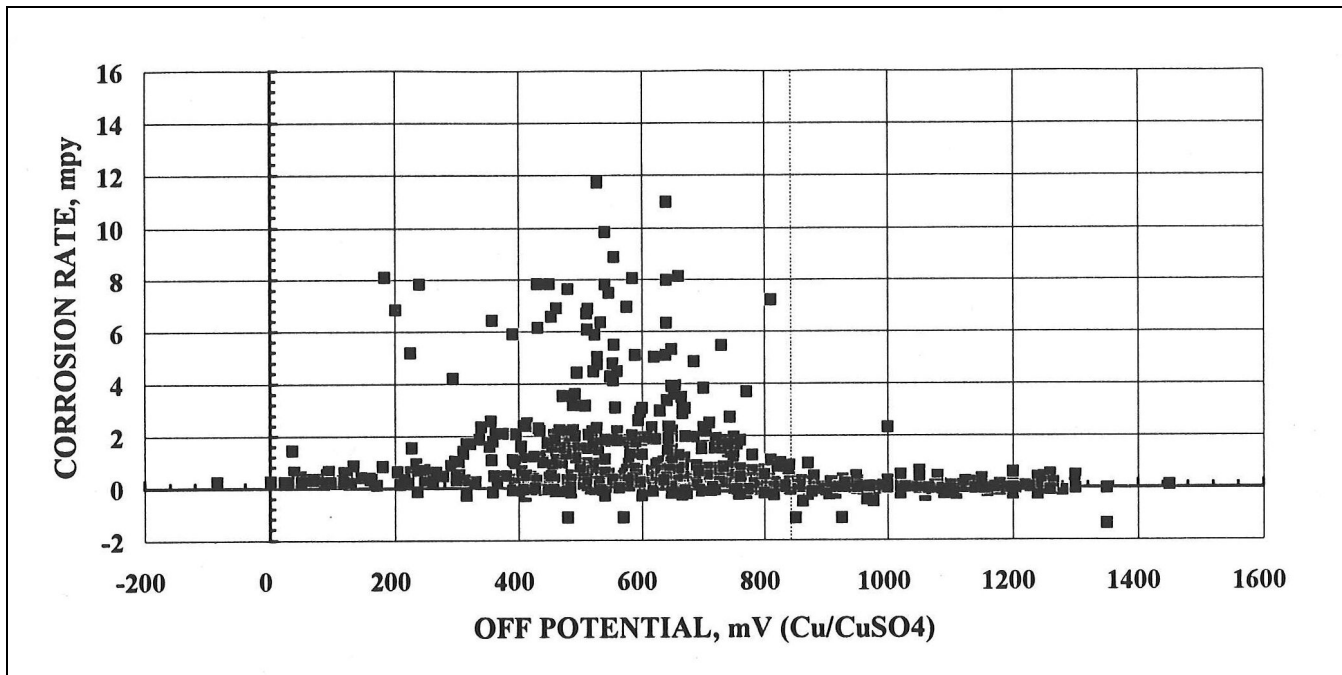
Figure 3: General Corrosion Rate of the Coupons at All of the Sites as Influenced by the Criteria and Related Parameters

In Europe, laboratory studies by Kirvian[12] in the early 1980's and by von Baeckmann et al[13] both confirmed that steel, if polarized to -850 mV$_{CSE}$ in various aqueous solutions, would have a corrosion rate much less than 1 mpy. The foregoing studies scientifically corroborate the understanding that the -850 mV$_{CSE}$ criterion should only be interpreted as a polarized potential (i.e. the potential across the steel/electrolyte interface).

The measurement of the -850 mV$_{CSE}$ criterion in the ISO international standard for onshore pipelines[14] is specified as an instant-off potential in keeping with the fundamental science that has proved the efficacy of this criterion.

There is no comparative theoretical or empirical data to support the -850 mV$_{CSE}$ on-potential criterion in the NACE SP0169-2007 standard, while ignoring the IR drop. The importance of considering the IR drop in the potential measurement with the current applied was stressed by Heverly[15] who was the chairman of the T-10-e committee that produced the original RP0169 standard. He stated that the reason for the on-potential criterion was "to include the voltage (IR) drop across the structure-electrolyte boundary, but not the voltage (IR) drop through the soil for a valid interpretation of the voltage measurement".

The most common method of determining what the potential is across a steel/electrolyte boundary is by measuring the instant-off potential (Ep) immediately after interrupting the current, which is in keeping with the definition of the polarized potential as expressed in equation (3).

$$Ep = Ecorr + \Delta Ep \tag{3}$$

Where:

Ep = polarized potential; Ecorr = corrosion potential; ΔEp = amount of cathodic polarization

All the research involving the -850 mV$_{CSE}$ polarized potential criterion was conducted using a current interruption technique. Regrettably, on distribution pipelines with direct connected anodes, the cathodic protection current can not be easily interrupted to obtain a polarized potential. Nevertheless there are

other methods available to determine the IR drop, although generally not adopted by the gas distribution utilities. Furthermore, distribution pipeline utilities are continuing to use direct connected anodes on new piping without installing facilities such as, coupons, to determine the IR drop. Without determining the pipe/electrolyte potential free of IR drop, the corrosion rate cannot be estimated, which obscures the effectiveness of an on-potential criterion.

WHAT IS A CRITERION?

According to the Oxford dictionary[16] a criterion is "a principle or standard that a thing is judged by". For cathodically protected pipelines the 'thing' that is being judged is the corrosion rate in order to determine the level of corrosion control and to prevent pipeline failures due to external corrosion. Although the active corrosion rate can sometimes be estimated from successive in-line inspection (ILI) runs, this technique cannot be applied to most distribution piping. Electrical resistance probes (ERP) are the only method, other than direct examination, of estimating the actual corrosion rate on gas distribution piping with direct connected galvanic anodes. Therefore, the indirect measurement of the pipe potential relative to a potential criterion is the principle method of judging whether or not there is satisfactory corrosion control. The measurement of the polarized potential is the only potential that reflects the level of corrosion control because the polarized potential is thermodynamically related to the pH at the pipe/soil interface. It is the development of an alkaline pH by the application of cathodic protection current that reduces the corrosion rate as shown in Figure 4.[17]
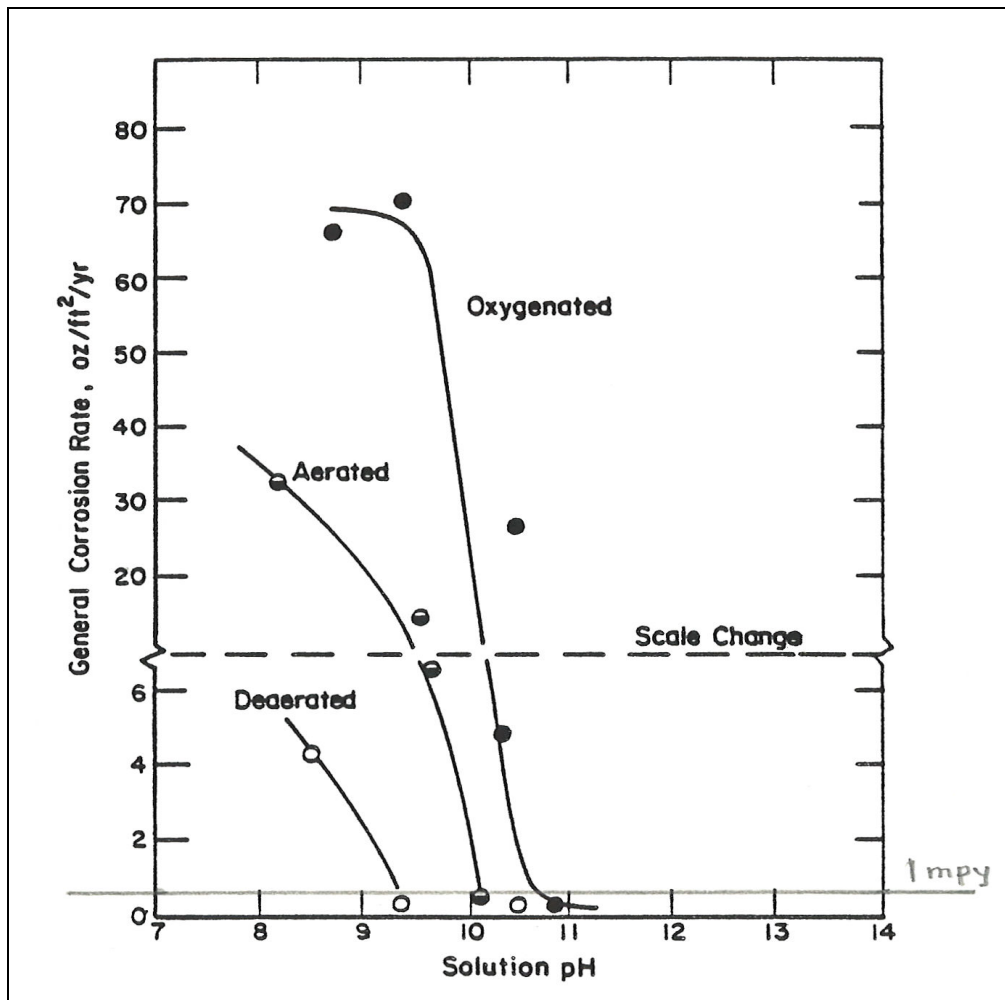

Figure 4: General Corrosion Rate of Bare Steel in a Simulated Groundwater
at the Free-Corrosion Potential as Influenced by pH and Oxygen Level

The corrosion rate of steel drops dramatically with a pH increase in the 9-11 range, depending on the aeration of the electrolyte. Soil electrolytes adjacent to the steel surface are generally poorly aerated after the cathodic protection has been applied for a period of time. The potential at the steel/electrolyte interface (Ep) is related to the pH according to the following relationship.

$$Ep = -316 \text{ mV}_{CSE} + (-59 \text{ mV} \times pH) \tag{4}$$

Therefore, the calculated potential across the structure/electrolyte interface for pH 9 and pH 10 is -847 mV$_{CSE}$ and -906 mV$_{CSE}$ respectively. Considering that the pH developed at the steel/electrolyte is a fundamental corrosion control criterion, then the instant-off potential (polarized potential) is a direct indication of the pH whereas the on-potential is not.

HOW DO THE TWO -850 mV$_{CSE}$ CRITERIA COMPARE IN CORROSION CONTROL PERFORMANCE?

Companies, who claim that they are utilizing the -850 mV$_{CSE}$ current-applied criterion, are often using more negative on-potential criterion values, such as -900 mV$_{CSE}$, -950 mV$_{CSE}$, or even -1000 mV$_{CSE}$, thereby incorporating an allowance for some IR drop in the measurement. But even this procedure may not provide a level of protection equivalent to the -850 mV$_{CSE}$ polarized potential criterion, as revealed in a study conducted by Brian Holtsbaum[18] and as illustrated in Figure 5.

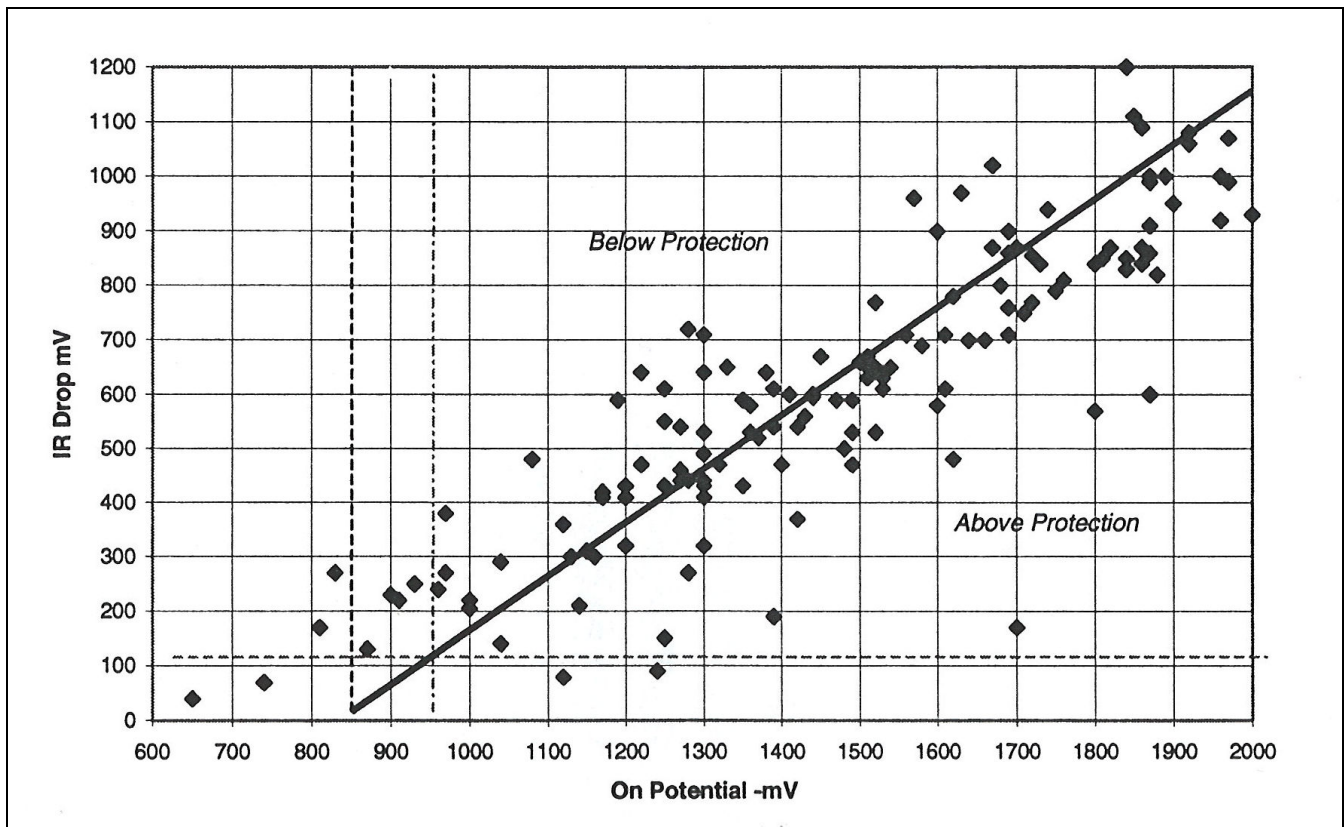**Figure 5: IR Drop versus On-Potentials to Illustrate a Dangerous Use of a Constant IR Drop Factor of 100 mV in a -950 mV$_{CSE}$ On-Potential Criterion**

About 45% of the measured on-potentials that were more electronegative than -950 mV$_{CSE}$ were actually less negative than the -850 mV$_{CSE}$ polarized potential criterion and therefore the piping might be inadequately protected at those locations. Also, it should be noted that the overwhelming majority of on-potential measurements contained more than 100 mV of IR drop.

Unlike for the -850 mV$_{CSE}$ polarized potential criterion, there have never been any published studies, where the current-applied potential was held at -850 mV$_{CSE}$ for coated pipe in order to determine what would be an expected corrosion rate. Clearly, a -850 mV$_{CSE}$ current applied criterion could in practice be effective in controlling the corrosion rate to less than 1 mpy in some specific environments such as very low resistivity soil where the amount of polarization contained in the current-applied potential is equal to or greater than 100 mV and, also where the natural corrosion rate is very small (e.g. very high resistivity soil).

Without knowing how much polarization has been obtained, the resulting corrosion rate is unknown, which makes it difficult to determine the corrosion control effectiveness. Therefore, when using the current applied criterion other measures, such as, ILI, corrosion rate probes, or cathodic protection coupons, must be employed to evaluate the corrosion control efficacy. These additional techniques increase the cost of operating the cathodic protection system in terms of maintenance, materials, and monitoring, and hence are seldom utilized, especially on distribution piping. Disappointingly, this leaves the external corrosion failure rate as the only indicator of the degree of corrosion control.

Mark Mateer[19] has probably produced the most comprehensive comparative study involving the two -850 mV$_{CSE}$ criteria, based on cumulative corrosion failures over a 50 year time period on a very large gas transmission system with thousands of miles of piping. The results, shown in Figure 6, indicate a significant reduction in failures when the -850 mV$_{CSE}$ instant-off criterion was adopted, after about 16 years of operation using the -850 mV$_{CSE}$ on-potential criterion.
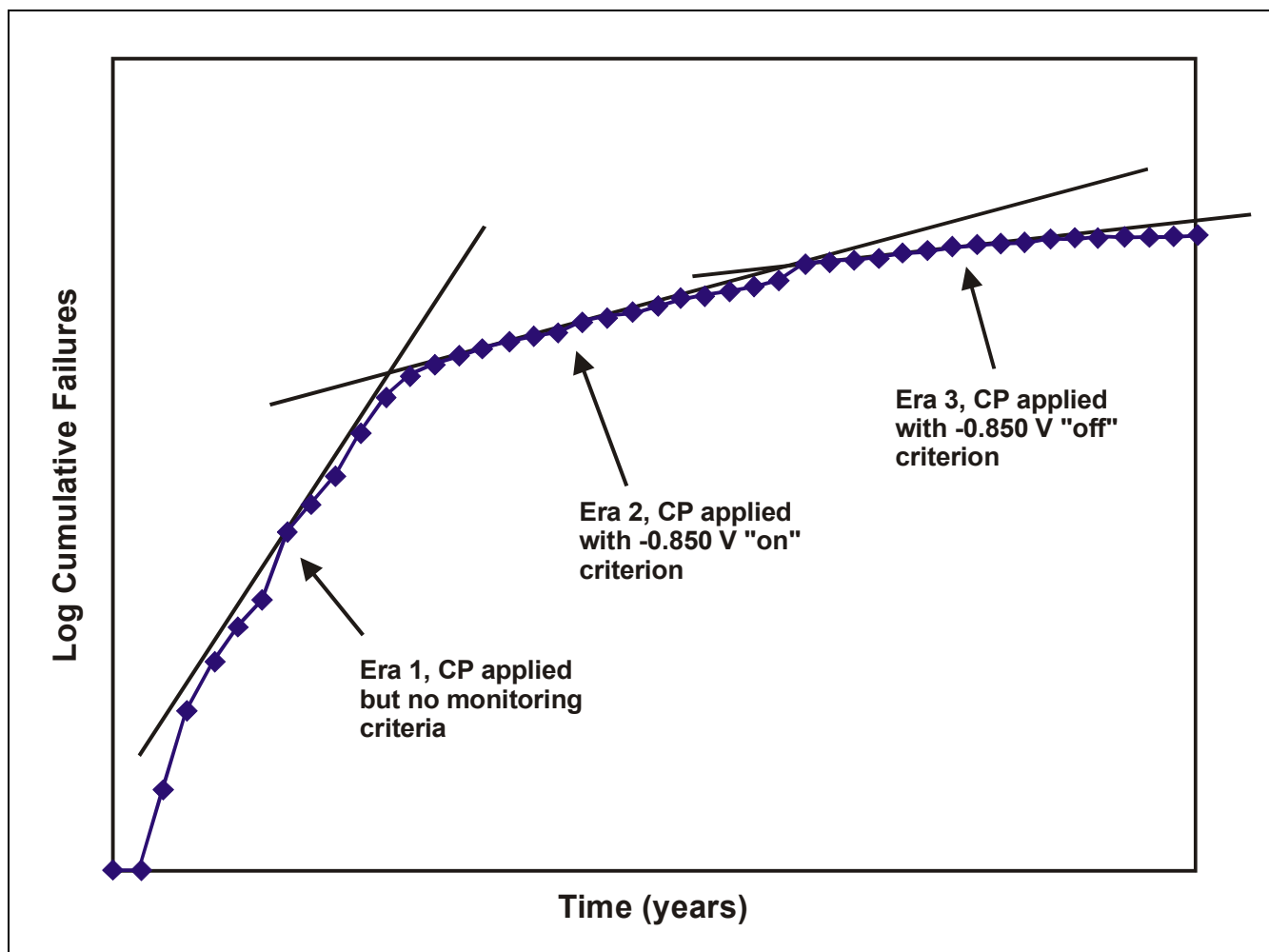

Figure 6: External Corrosion Failure Probability Plot for "Test Structure"

His analysis of the data concluded that "The benefit of the "off" or polarized potential criterion was a fivefold decrease in the number of failures". This result would likely be typical if the -850 mV$_{CSE}$ polarized potential criterion was applied to gas distribution piping, which historically experience more corrosion failures than transmission piping and, where the -850 mV$_{CSE}$ current-applied criterion has been used for many years. It is interesting to note that the last few years of data for the -850 mV$_{CSE}$ polarized potential criterion resulted in a negligible increase in corrosion failures, which in part was attributed to the adoption of an ILI program.

Another investigation into the effectiveness of the -850 mV$_{CSE}$ on-potential criterion was carried out by Dewey Millar at Columbia Gas Transmission Corporation in the late 1980s. Dewey, who was a member of the NACE T-10-1 criteria committee and initially a proponent of the -850 mV$_{CSE}$ on-potential criterion, reviewed his company's leak records over a 10 year period. From this data he produced a frequency distribution graph based on different ranges of on-potential, as shown in Figure 7, which exhibits a disturbing lack of correlation between the corrosion failure frequency and the on-potential.

It is alarming that 46% of the 144 corrosion failures occurred at on-potentials equal to or more electronegative than -850 mV$_{CSE}$ and that 11% of the corrosion failures were at on-potentials equal to or more negative than -1500 mV$_{CSE}$. Accordingly, it would be difficult to make a case for effective corrosion control for any particular on-potential value in this analysis.
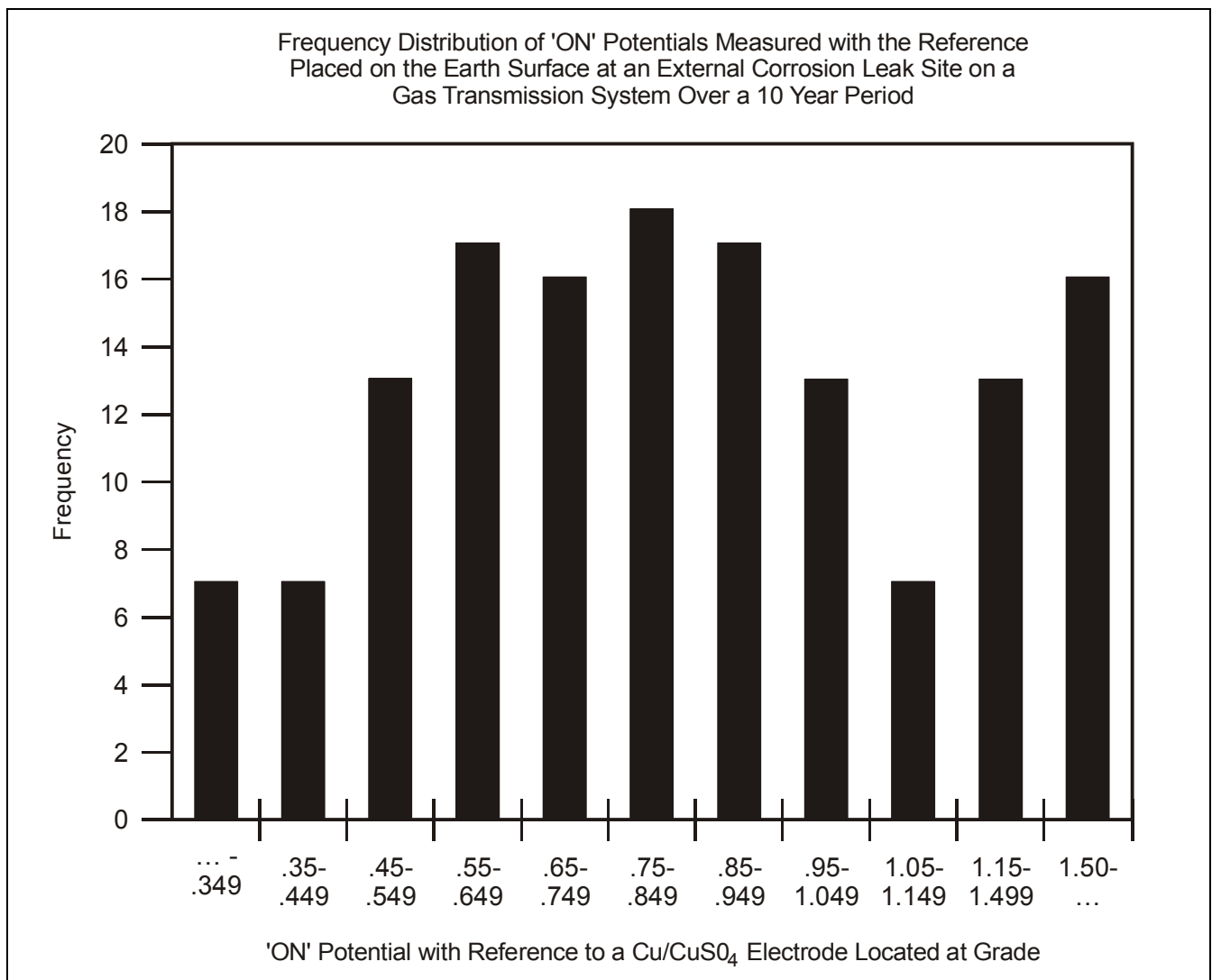

Figure 7: Frequency Distribution of External Corrosion Leak Failures versus a Range of On-potentials Measured On-Grade at Site

An interim report[20] on the AGA criteria field study compared the relative effectiveness of the two -850 mV_{CSE} criteria based on the range of potentials required to control the general corrosion rate to less than 1 mpy. The corrosion rate was determined by weighing coupons extracted annually from the various test sites. All the potentials were measured with respect to a saturated copper-copper sulfate reference electrode placed in a soil tube positioned directly above the coupon where the coupon was installed about 1 foot (0.3 m) from a 10 foot (3 m) length of bare steel pipe. This meant that some of the IR drop was eliminated in the on-potential measurement and, because of the proximity of the reference to the bare pipe, the on-potential measurement was less than would be the case had the reference been placed at grade.

The instant-off potential measurement was made, not by disconnecting the coupon, but by interrupting the cathodic protection current supplied to both the pipe and the coupons. The corrosion control effectiveness of the instant-off potential is shown in Figure 8 for 11 of the test sites for which data was available.
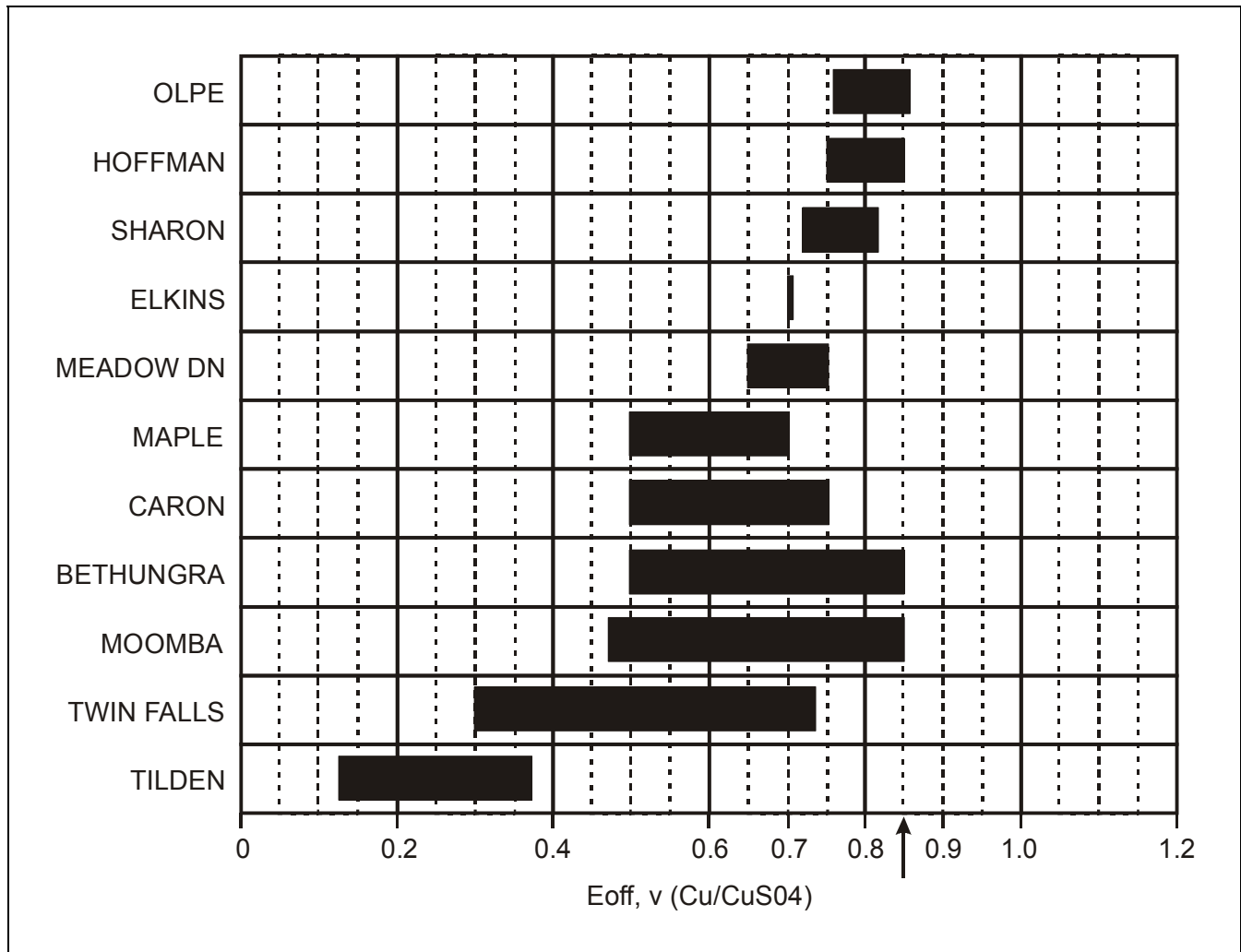

**Figure 8: Range of Instant-off Potentials Required to
Control the Corrosion Rate to Less than 1 mpy**

Of the 11 sites reported, the -850 mV_{CSE} instant-off potential was completely effective and for the Olpe site it was almost completely effective. These results are in sharp contrast to results for the on-potential measurements as shown in Figure 9.[21] The on-potential ranges in this figure have been adjusted for the 103 mV average IR drop difference between the reference on-grade and the reference in the soil tube.[22] The -850 mV_{CSE} on-potential was only effective in 3 of 11 sites (27%) when the on-potentials were adjusted to represent the reference on grade. Therefore, it failed to control the corrosion rate to less than 1 mpy at 73% of the test sites.
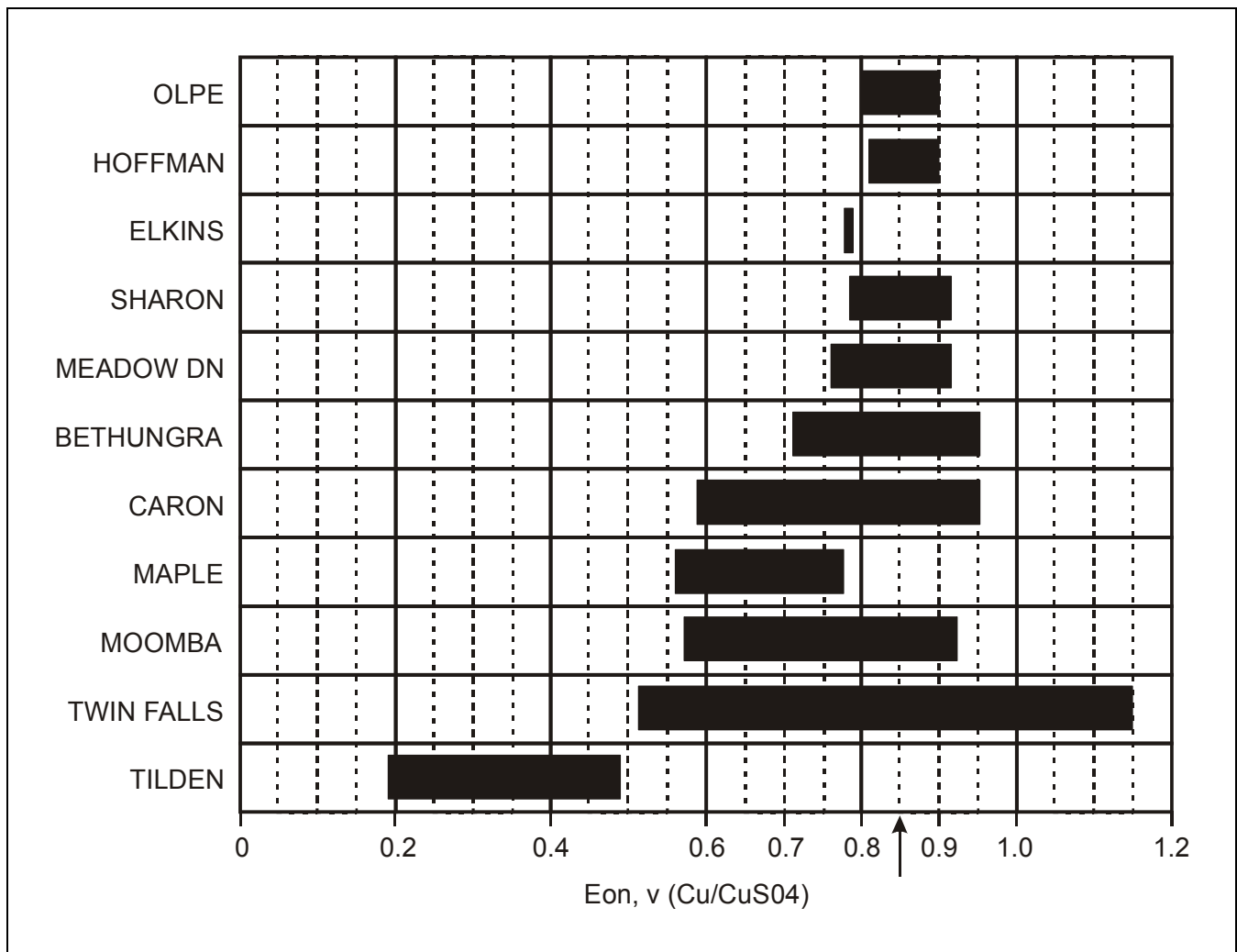
Figure 9: Range of On-potentials Required to Control the Corrosion Rate to less than 1mpy.

SUMMARY

Some recent papers about the development of the -850 mV_{CSE} criterion contain inaccurate information which overstates the validity of the on-potential criterion.

Both theoretical considerations and results of laboratory and field research investigations indicate that establishing a -850 mV_{CSE} polarized potential will reduce the corrosion rate under normal soil conditions to less than 1 mpy.

There is no theoretical or empirical evidence in the literature to support the corrosion control effectiveness of the -850mV_{CSE} on-potential criterion in terms of corrosion rate.

Comparative empirical data indicates that the -850 mV_{CSE} on-potential criterion is decidedly less effective than the -850 mV_{CSE} polarized potential criterion.

To persist in using the -850 mV_{CSE} on-potential criterion when the expected corrosion rate is unknown, when the original intent to remove the IR drop in the measurement except across the structure/electrolyte boundary is ignored, and to wait for external corrosion failures to judge the corrosion control performance, exposes the public to an unnecessary safety risk and is certainly not sound engineering practice.

If the NACE SP0169 standard continues to include the -850 mV$_{CSE}$ current applied criterion and provides loop-holes were the IR drop can continue to be ignored, then it means that "NACE did not adopt a standard in conformity with the best and most current technology available, and serious liability can result if such technology is not incorporated into a standard or if inappropriate factors are involved".[23]

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