

A Guide to Understanding Reference Electrode Readings

ROBERT M. PARK, *M.C. Miller Co., Inc., Sebastian, Florida*

Reference electrodes are essential to evaluate corrosion and cathodic protection on buried and submerged structures. This article discusses the nature of structure-to-electrolyte readings employing copper/copper sulfate (Cu/CuSO₄) electrodes (CSEs) and various other “acceptable” reference electrode types. A universal formula is presented that allows readings taken with non-CSE reference electrodes to be adjusted to the CSE potential.

As indicated in a number of NACE International standards, including SP0169-2007,¹ the critical decision as to whether or not a buried or submerged metallic structure is cathodically protected (polarized) to a sufficient degree is based on a measurement of the metal’s polarized potential, in its environment (soil, seawater, etc.), relative to the potential of a reference electrode. Consequently, no equipment item is of more fundamental importance to the cathodic protection (CP) industry than the reference electrode.

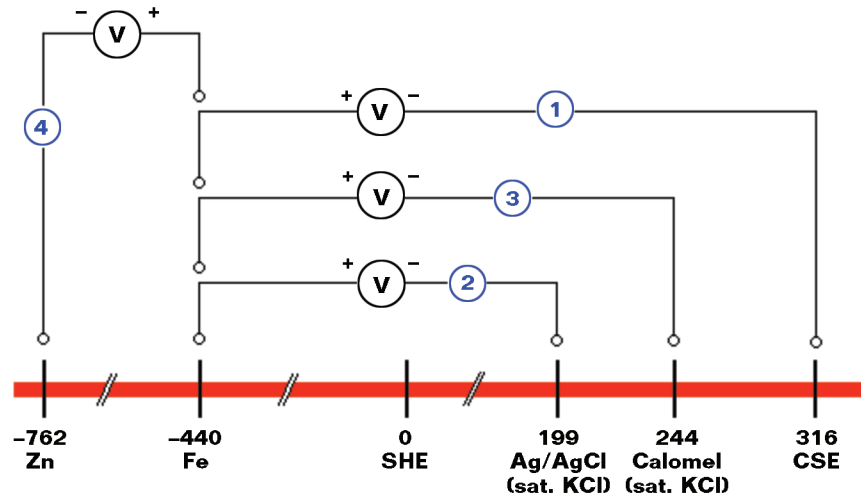
There are a number of different reference electrode types available, including those that are identified in SP0169-2007, that are acceptable alternatives to the copper/copper sulfate (Cu/CuSO₄) reference electrode (CSE). It is important for the corrosion engineer to appreciate the characteristics of the various electrode types and, in particular, how readings taken with different reference electrodes can be adjusted to the CSE potential.

The purpose of this article is not to discuss the relative merits of the various reference electrode types, but to provide a guide to the corrosion engineer regarding their application. A universal formula is provided that allows readings taken with alternative reference electrode types to be adjusted to the CSE potential.

Electrode Potentials

The starting point to understanding how different reference electrodes provide for different metallic structure-to-electrolyte readings is to examine electrode potential values. Just as different metals have different electrode potentials, also known as corrosion potentials or open-circuit potentials, different reference electrode types have different electrode potential values. And, even within a particular reference electrode family, the electrode potentials can have a significant range of values. Figure 1 presents

FIGURE 1



Electrode potential values (in mV at 25 °C), relative to the SHE potential, for the metal example under test (Fe), the CSE, two other reference electrode types, and a quasi-reference electrode (Zn). See Table 1 for the various expected voltmeter readings.

electrode potential values (in mV at 25 °C), relative to the standard hydrogen electrode (SHE) potential, for pure Fe,² pure Zn,³ and CSE.⁴ Also shown are the electrode potential values for the reference electrode types identified in SP0169-2007 as alternative reference electrode types to CSE, namely, the silver/silver chloride (Ag/AgCl [saturated KCl]) and calomel (saturated KCl) electrode types.⁵ The Zn electrode potential is indicated in Figure 1, since a Zn (metal) electrode is also used in the corrosion industry as a quasi-reference electrode. Finally, the Fe electrode potential is indicated in Figure 1 as an example of a metallic component that may be buried or submerged.

Low-carbon steel (CS), for example, having a clean and shiny surface, should have a similar electrode potential (corrosion potential) value (-440 mV relative to the SHE potential). As the surface of a metal, such as pure Fe or low-CS, begins to corrode freely, its electrode potential (corrosion potential) decreases (becomes less negative) relative to the SHE potential. Of course, the goal of CP is to minimize corrosion, so moving the electrode

potential (corrosion potential) to a more negative value (such as -540 mV vs. SHE, for the Fe example) would be the goal of a CP system.

Electrode "Potential Difference" Readings

When a high input impedance voltmeter is connected between two electrodes having different potentials in neu-

tral soils, a small current flows between the electrodes, causing the potential difference to translate to a voltage reading.

Table 1 shows expected "native" Fe potentials in neutral soils as measured by the various reference electrodes illustrated in Figure 1. As indicated in the table, once the two electrode potentials involved in the measurement are known (the potential of the metal under test and

TABLE 1

Expected "native" Fe potential in neutral soil as measured by a variety of reference electrodes^(A)

Voltmeter Configuration (Figure 1)	Potentials of Electrodes Involved in Voltage Reading (at 25 °C)	ΔP (Expected Voltage Reading)	Expected Readings Adjusted to the CSE Potential
1	Fe [P = -440 mV] CSE [P = 316 mV]	-440 mV - 316 mV = -756 mV	N/A
2	Fe [P = -440 mV] Ag/AgCl (sat. KCl) [P = 199 mV]	-440 mV - 199 mV = -639 V	199 mV - 316 mV + reading = [199 - 316 + (-639)] mV = -756 mV
3	Fe [P = -440 mV] Calomel (sat. KCl) [P = 244 mV]	-440 mV - 244 mV = -684 mV	244 mV - 316 mV + reading = [244 - 316 + (-684)] mV = -756 mV
4	Fe [P = -440 mV] Zn [P = -762 mV]	-440 mV - (-762 mV) = 322 mV	-762 mV - 316 mV + reading = [-762 - 316 + 322] mV = -756 mV

^(A)Measurements are based on the voltmeter configurations indicated in Figure 1. Also shown are the expected readings adjusted to the CSE potential.

TABLE 2

Expected "native" Fe potential in neutral soil as measured by a number of Ag/AgCl reference electrodes having various molarities of KCl filling solution^(A)

Voltmeter Configuration (Figure 2)	Potentials of Electrodes Involved in Voltage Reading (at 25 °C)	ΔP (Expected Voltage Reading)	Expected Readings Adjusted to the CSE Potential
1	Fe IP = -440 mV CSE IP = 316 mV	-440 mV - 316 mV = -756 mV	N/A
2	Fe IP = -440 mV Ag/AgCl (sat. KCl) IP = 199 mV	-440 mV - 199 mV = -639 V	199 mV - 316 mV + reading = [199 - 316 + (-639)] mV = -756 mV
3	Fe IP = -440 mV Ag/AgCl (3.5 M KCl) IP = 205 mV	-440 mV - 205 mV = -645 mV	205 mV - 316 mV + reading = [205 - 316 + (-645)] mV = -756 mV
4	Fe IP = -440 mV Ag/AgCl (1.0 M KCl) IP = 222 mV	-440 mV - 222 mV = -662 mV	222 mV - 316 mV + reading = [-222 - 316 + (-662)] mV = -756 mV
5	Fe IP = -440 mV Ag/AgCl (0.5 M KCl) IP = 250 mV	-440 mV - 250 mV = -690 mV	250 mV - 316 mV + reading = [250 - 316 + (-690)] mV = -756 mV

^(A)Measurements are based on the voltmeter configurations indicated in Figure 2. Also shown are the expected readings adjusted to the CSE potential.

TABLE 3

Expected "native" Fe potential as measured by Ag/AgCl elements directly exposed to seawater and diluted-seawater electrolytes^(A)

Voltmeter Configuration (Figure 3)	Potentials of Electrodes Involved in Voltage Reading (at 25 °C)	ΔP (Expected Voltage Reading)	Expected Readings Adjusted to the CSE Potential
1	Fe IP = -440 mV CSE IP = 316 mV	-440 mV - 316 mV = -756 mV	N/A
2	Fe IP = -440 mV Ag/AgCl (seawater) IP = 250 mV	-440 mV - 250 mV = -690 V	250 mV - 316 mV + reading = [250 - 316 + (-690)] mV = -756 mV
3	Fe IP = -440 mV Ag/AgCl (<1% seawater) IP = 370 mV	-440 mV - 370 mV = -810 mV	370 mV - 316 mV + reading = [370 - 316 + (-810)] mV = -756 mV

^(A)Measurements are based on the voltmeter configurations indicated in Figure 3. Also shown are the expected readings adjusted to the CSE potential.

the potential of the reference electrode in use), expected readings can be determined. As the table illustrates, since the potentials of the various reference electrodes are different from each other, different Fe potentials are expected vs. the different reference electrodes.

All of the voltage reading values shown in Table 1 (and also in Tables 2 and 3) correspond to a particular voltmeter configuration—namely, the positive side

of the voltmeter connects to the metal under test, which is Fe in the example shown, and the negative side of the voltmeter connects to the reference electrode. For a given reference electrode in use, for example a CSE, the potential value of the metal under test will determine the voltage reading. As indicated in Table 1, a "native" Fe potential of -440 mV vs. SHE will yield a voltage reading of -756 mV vs. CSE. If, however, the Fe is polarized

by a CP system to, say, 100 mV above the native potential, the effective Fe potential will be -540 mV vs. SHE and the "instant-off" voltage reading will be -856 mV vs. CSE (-540 mV minus 316 mV).

Universal Adjustment Formula

As the tables indicate, voltage readings taken vs. a non-CSE reference electrode can be adjusted to the CSE potential.

FIGURE 2

Equation (1) is a universal adjustment formula for the voltmeter configuration shown in Figure 1.

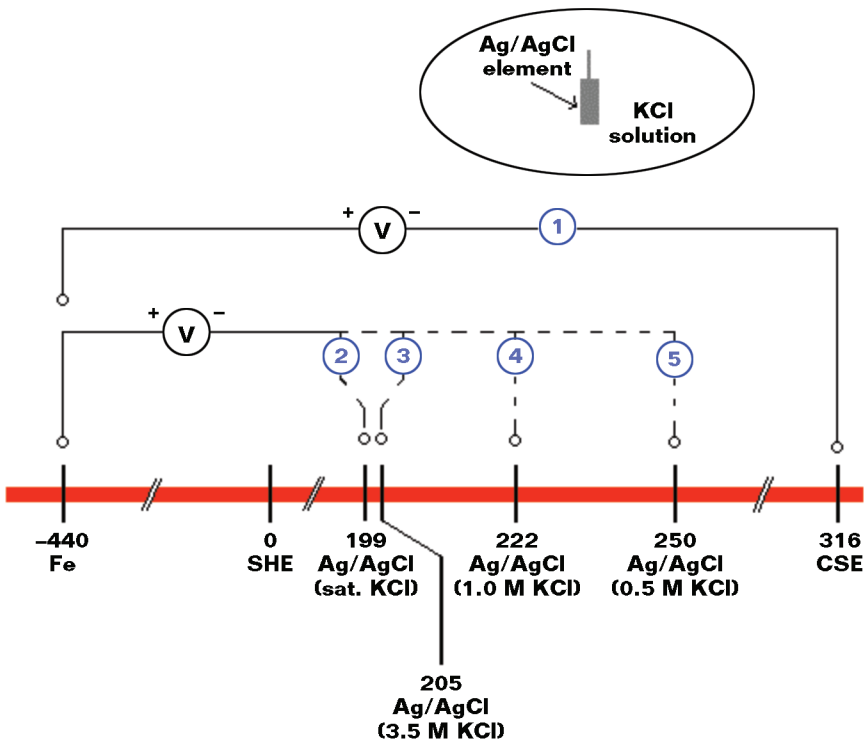
$$\text{Reading adjusted to CSE potential} = P(\text{RE}) - P(\text{CSE}) + (\text{reading vs. RE}) \quad (1)$$

where $P(\text{RE})$ is the electrode potential of the electrode in use (vs. SHE), $P(\text{CSE})$ is the electrode potential of a CSE (vs. SHE), and “reading vs. RE” is the voltage reading taken by the electrode in use. For example, if an “instant-off” voltage reading of 222 mV is recorded from a polarized Fe pipe using a Zn quasi-reference electrode, the voltage reading adjusted to the CSE potential is $-762 \text{ mV} - 316 \text{ mV} + 222 \text{ mV} = -856 \text{ mV}$, since $P(\text{Zn}) = -762 \text{ mV}$ and $P(\text{CSE}) = 316 \text{ mV}$ (Figure 1).

Ag/AgCl “Land-based” Reference Electrodes

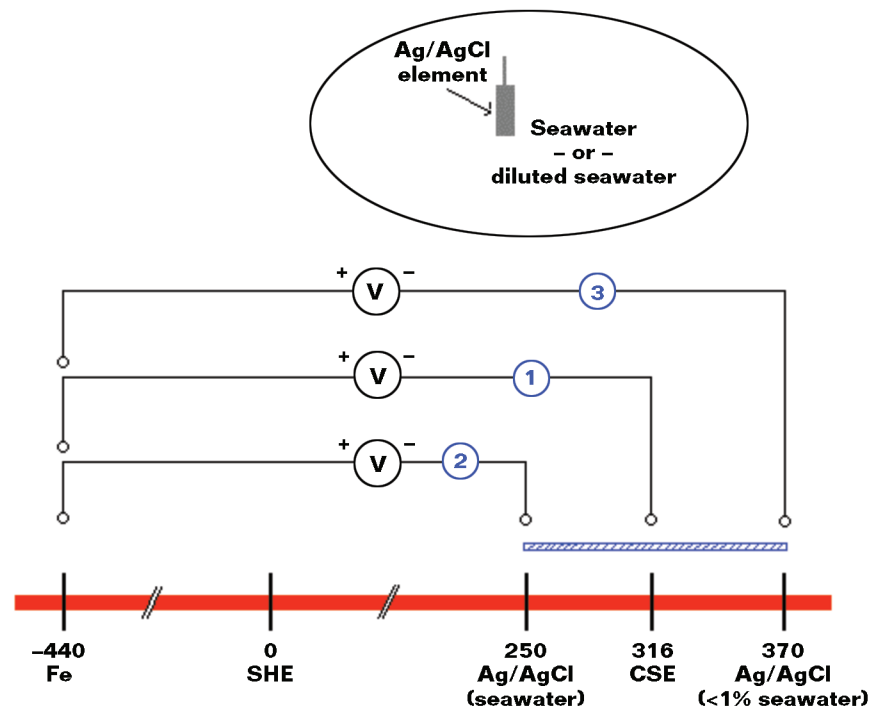
Ag/AgCl reference electrodes that are typically used in land-based applications (i.e., non-submersion applications) have a KCl filling solution to which the Ag/AgCl element makes intimate contact (Figure 2). The KCl solution can have a variety of molarities (concentrations) and the molarity of the KCl filling solution determines the electrode potential for a given KCl solution temperature. The maximum KCl concentration is 4.6 M at 25 °C, which represents the solubility limit of KCl in water (at 25 °C). This would be the “saturated” KCl concentration (at 25 °C).

As indicated in Figure 2, the Ag/AgCl electrode potential vs. SHE varies significantly with KCl filling solution molarity in the range of 4.6 M (saturated) to 0.5 M. Consequently, as indicated in Table 2, expected “native” Fe potentials in neutral soils measured vs. Ag/AgCl (KCl filling solution) reference electrodes are significantly dependent on the specified KCl molarity. As above, readings can be adjusted to the CSE potential. For ex-



Electrode potential values (in mV at 25 °C), relative to the SHE potential, for the metal example under test (Fe), the CSE, and a number of Ag/AgCl electrodes having various molarities of KCl filling solution. See Table 2 for the various expected voltmeter readings.

FIGURE 3



Electrode potential values (in mV at 25 °C), relative to the SHE potential, for the metal example under test (Fe), the CSE and Ag/AgCl elements directly exposed to seawater, and diluted-seawater electrolytes. See Table 3 for the various expected voltmeter readings.

ample, if an “instant-off” voltage reading of -745 mV is recorded from a polarized Fe pipe using an Ag/AgCl (3.5 M KCl) reference electrode, the voltage reading adjusted to the CSE potential is $205\text{ mV} - 316\text{ mV} + (-745\text{ mV}) = -856\text{ mV}$, since $P(\text{Ag/AgCl [3.5 M KCl]}) = 205\text{ mV}$, and $P(\text{CSE}) = 316\text{ mV}$ (Figure 2).

Ag/AgCl “Seawater” Reference Electrodes

Ag/AgCl reference electrodes that are typically used in submersion applications do not have a KCl filling solution, but rather, the Ag/AgCl element makes direct contact to the electrolyte itself, which is typically seawater (Figure 3). In this scenario, the electrode’s potential is a function of the salinity of the electrolyte at a

given electrolyte temperature.⁶ As shown in Figure 3, a significant range of electrode potentials vs. SHE is indicated for electrolytes ranging from natural seawater to highly diluted seawater. In turn, as indicated in Table 3, expected “native” Fe potential readings recorded using Ag/AgCl (seawater) reference electrodes exhibit a range of values. As above, readings can be adjusted to the CSE potential. For example, if an “instant-off” voltage reading of -790 mV is recorded from a polarized (submerged in natural seawater) Fe pipe using an Ag/AgCl element (seawater) reference electrode, the voltage reading adjusted to the CSE potential is $250\text{ mV} - 316\text{ mV} + (-790\text{ mV}) = -856\text{ mV}$, since $P(\text{Ag/AgCl [seawater]}) = 250\text{ mV}$, and $P(\text{CSE}) = 316\text{ mV}$ (Figure 3).

Conclusions

As illustrated in this article, for a given structure material, a structure-to-electrolyte reading is significantly dependent on the nature of the reference electrode used in the measurement, and, of primary significance is the electrode potential of the reference electrode in use. Should a reading require adjustment to the CSE potential, the universal adjustment formula presented in this article can be employed, assuming that an appropriate electrode potential can be identified, vs. the SHE potential, for the reference electrode in use.

References

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ROBERT M. PARK is currently director of research at the M. C. Miller Co., 11640 U.S. Highway 1, Sebastian, FL 32958. Previously, he spent six years as a research scientist with the 3M Co. and 10 years as a professor of materials science and engineering at the University of Florida. He holds B.Sc. and Ph.D. degrees in electronics and electrical engineering from the University of Glasgow, Scotland. He has published more than 70 papers in referenced scientific journals and holds two U.S. patents. He is a six-year member of NACE International. *MP*