Submersible Reference Electrodes Revisited

Robert M. Park, *M.C. Miller Co., Inc., Vero Beach, Florida*

This article examines the status of submersible reference electrodes and presents a new design concept for submersible copper/copper sulfate ($Cu/CuSO_4$) electrodes (CSE). In the new concept, the half-cell potential is independent of the salinity (chlorinity) of the electrolyte, the electrode is not subject to contamination, and structure-to-electrolyte voltages do not require correction to the CSE scale.

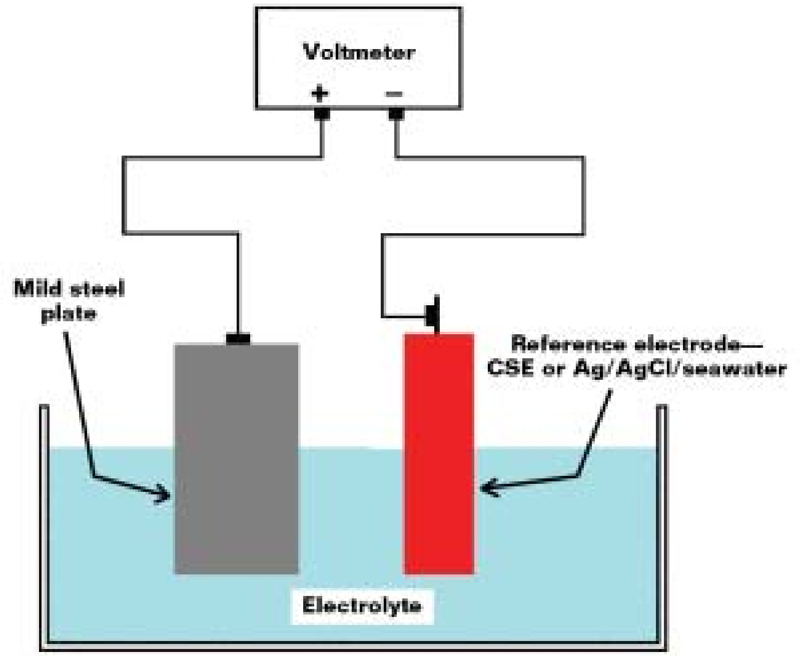
Although copper/saturated copper sulfate ($Cu/CuSO_4$) solution reference electrodes (CSEs) are the "industry standard" when it comes to measuring metallic structure-to-electrolyte voltages in the corrosion control field, such electrodes are deemed unsuitable for long-term immersion service (submersion applications).[1] This is because conventional CSEs have plugs (which make electrical contact with the electrolyte) that are porous. The porous nature of the plugs can lead to contamination of the $CuSO_4$ by chloride ions (in seawater or brackish water applications, for example), particularly when the solution in the electrode is not fully saturated, leading to changes in the half-cell potential of the electrode.[2] Contamination of the electrolyte by $CuSO_4$ solution leakage from the electrode might also occur.

As indicated in Reference 1, it is recommended that "dry" silver/silver chloride (Ag/AgCl)/seawater reference electrodes be used in submersion applications, rather than CSEs, since such electrodes do not employ porous plugs. Ag/AgCl/seawater reference electrodes have disadvantages of their own, however.

Silver/Silver Chloride Electrodes

First, Ag/AgCl/seawater electrodes couple directly with the electrolyte (seawater, brackish water, or fresh water, for example), since the electrolyte makes direct contact with the Ag/AgCl element when the electrode is immersed in the electrolyte. Direct coupling means that the half-cell potential of the electrode is a function of the nature of the electrolyte, rather than being independent of the electrolyte. For example, in seawater or brackish water applications, at a given temperature, the half-cell potential of the electrode is dependent on the salinity (or, more specifically, the chloride ion activity) of the electrolyte. Consequently, a knowl-

FIGURE 1



Experimental arrangement to measure the "native" potential of steel plate material with respect to both a Ag/AgCl/seawater reference electrode and a CSE in seawater and diluted seawater electrolytes (see Table 1). The CSE had a nonporous, ionically conducting plug.

TABLE 1

'Native' potential data from a mild steel test piece

Electrolyte Resistivity (Ω·cm)	Potential with Respect to a Ag/AgCl/Seawater Electrode (V)	Potential with Respect to a CSE (V)
20 (Florida Atlantic Coast Seawater)	–0.705	–0.771
200 (~7% seawater)	–0.760	–0.760
2,000 (<1% seawater)	–0.815	–0.748

Data measured with respect to both an Ag/AgCl/seawater reference electrode and a CSE in seawater and diluted seawater electrolytes using the arrangement shown in Figure 1. The CSE had a nonporous, ionically conducting plug.

edge of the chlorinity of the electrolyte is required in order to interpret metallic structure-to-electrolyte voltages recorded using Ag/AgCl/seawater reference electrodes. Peterson and Groover[3] have established a relationship between the resistivity of chloride ion-containing water and the chlorinity of the water (expressed as % seawater). These authors also provide a means to correct metallic structure-to-electrolyte voltages recorded using a Ag/AgCl/seawater reference electrode to the Cu/$CuSO_4$ scale using a nomogram, based on the measured value of the electrolyte resistivity. Using the nomogram and having to measure the electrolyte resistivity are inconveniences relative to a direct reading using a CSE, for example.

Second, again because of the direct coupling of the Ag/AgCl element to the electrolyte, coating of the element during the immersion process (by an oil film, for example) renders the electrode inoperable. Third, Ag/AgCl/seawater electrodes cannot be used in waters containing sulfide ions, since such exposure can permanently damage the Ag/AgCl element (silver sulfide [Ag_2S] is insoluble).

Consequently, conventional CSEs and Ag/AgCl/seawater reference electrodes are not ideal for submersion applications. The ideal scenario for a submersible reference electrode would be one in which the metallic structure-to-electrolyte readings would not require correction to the Cu/$CuSO_4$ scale and solution transfer into, or out of, the electrode would not be possible. The solution to this problem is to use a plug on a CSE that is nonporous (does not allow solution transfer), but is ionically conducting.

Experimental Procedures and Results

CSEs have been fabricated using a nonporous, ionically conducting plug material and metallic structure-to-electrolyte voltages have been recorded and compared to those recorded using a Ag/AgCl/seawater reference electrode. As indicated in Figure 1, the "metallic structure" in the experiment was a piece of mild steel and the "native" potential of the steel plate was measured in various seawater and diluted seawater electrolytes, with respect to both a Ag/AgCl/seawater electrode and a CSE having a nonporous, ionically conducting plug. The electrical resistance of the plug was measured to be ~10 kΩ. All voltages were recorded at an electrolyte temperature of 22°C using a high input impedance voltmeter. The data recorded using both electrode types are illustrated in Table 1.

With respect to the diagram shown in Figure 1, there are three contributions to the voltage as read by the voltmeter:

$$V = [\text{Metal Half-Cell Potential}] - [\text{Ref. Electrode Half-Cell Potential}] + IR \quad (1)$$

The "Metal Half-Cell Potential" term is typically a negative quantity (with respect to hydrogen) for anodic metals (like steel) and the "Reference Electrode Half-Cell Potential" term is a positive quantity (with respect to hydrogen) for both CSEs and Ag/AgCl/seawater electrodes. Consequently, the voltage data shown in Table 1 are negative quantities.

The IR term in Equation (1) represents the voltage dropped in the electrolyte itself. For a fixed geometry of experimental setup (i.e., fixed separation between the metal plate and reference electrode and fixed electrode [electrical] contact area), the primary variable contribution to the IR component is the resistivity of the electrolyte. If it assumed that the "Metal Half-Cell Potential" is essentially independent of the electrolyte resistivity, the measured voltage will be a function of both the "Reference Electrode Half-Cell Potential" and the "IR" components. As can be seen in Table 1, the voltage measured using the Ag/AgCl/seawater electrode shifts significantly in the negative direction as the electrolyte resistivity increases, while a smaller positive shift is indicated when using the CSE. These results can be explained as follows:

With respect to the CSE, the relatively small shift in the positive direction (23 mV for the electrolyte resistivity range examined) is due to an increase in the IR component with increasing electrolyte resistivity. In this case, the "Reference Electrode Half-Cell Potential" component is not a factor, since the half-cell potential of the CSE is independent of the electrolyte resistivity. On the other hand, when the Ag/AgCl/seawater electrode is used in the circuit, in addition to the same positive shift due to the IR change with increasing electrolyte resistivity (23 mV), a change in the "Reference Electrode Half-Cell Potential" causes an overall negative shift in the voltage (–110 mV). These data indicate that the "Reference Electrode Half-Cell Potential" component, in the case of the Ag/AgCl/seawater electrode, increases by 133 mV as the electrolyte resistivity is decreased over the range examined (–133 mV + 23 mV = –110 mV).

Conclusions

CSEs having a nonporous, ionically conducting plug are more suitable than Ag/AgCl/seawater electrodes for submersion applications, since their half-cell potential is independent of the salinity (chlorinity) of the electrolyte, they are not subject to contamination, and metallic structure-to-electrolyte voltages do not require correction to the Cu/CuSO$_4$ scale.

It should be noted, however, that the IR component impacts the structure-to-electrolyte voltage reading for any electrode type. A "native" potential reading should be taken in the actual in-service electrolyte (for example, seawater, brackish water, fresh water, etc.) with a given reference electrode and a given structure/electrode geometry to decide on the minimum structure-to-electrolyte voltage required for cathodic protection (as-read native potential plus 100 mV polarization, for example).

References

1 NACE Standard RP0176-2003, "Corrosion Control of Steel Fixed Offshore Structures Associated with Petroleum Production" (Houston, TX: NACE International).

2 S.J. Pawel, R.J. Lopez, E. Ondak, "Chemical and Environmental Influences on Copper/Copper Sulfate Reference Electrode Half-Cell Potential," MP 37, 5 (1998): p. 23-29.

3 M.H. Peterson, R.E. Groover, "Tests Indicate the Ag/AgCl Electrode Is Ideal Reference Cell in Sea Water," MP 11, 5 (1972): p. 19-22.

ROBERT M. PARK is currently director of research at the M. C. Miller Co., 3020 Aviation Blvd., Vero Beach, FL 32960. 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 refereed scientific journals and holds two U.S. patents. He is a four-year member of NACE. MP