

Factors Affecting the Accuracy of Reference Electrodes

Frank J. Ansuini

Electrochemical Devices, Inc., PO Box 31, Albion, RI 02802

James R. Dimond

Dimondale Co., Inc., PO Box 838, Middlefield, OH 44062

This article discusses several factors that affect the reference potential established by silver/silver chloride and copper/copper sulfate reference electrodes. Data is presented on the effects of temperature, light, contaminants and solute concentration.

Reference Electrode Classifications

Element Types

In its most basic form, a reference electrode is simply a piece of metal immersed in a solution of one of its salts¹. In a thermodynamically stable reference, a known reversible chemical reaction occurs between the metal element and its environment. At equilibrium, the reaction rate in both directions is equal and the potential established follows the Nernst Equation². In theory, the only factors that affect the potential of a reference electrode are temperature, which has a linear effect, and solution concentration, which has a logarithmic effect.

There are two kinds of reference electrode elements in common use. The first is a metal in a solution containing dissolved ions of that metal. An example of this is the copper/copper sulfate (Cu/CuSO_4) electrode. The second is a metal coated with a salt of that metal and immersed in a solution of that salt. Both silver/silver chloride (Ag/AgCl) and calomel (mercury/mercury chloride) are electrodes of the second kind; their reference potential is established by the chloride ion concentration.

Electrolyte Types

Reference electrodes can also be classified by the form of the surrounding electrolyte. In dry electrodes, the element is immersed in the same electrolyte as the structure. The element is dry until it is placed in service; hence the name. The silver/silver chloride/seawater reference electrode is a well known dry reference³. Dry electrodes tend to be quite rugged and inexpensive. A disadvantage is that the reference potential they establish can change if the chemistry of the electrolyte changes. Also, the element of a dry electrode will be ruined if the electrolyte or the surrounding atmosphere during storage contains a contaminant for that type electrode.

The contamination problem is greatly minimized by using a wet electrode, in which the element is immersed in an electrolyte with a known salt concentration. This electrolyte should be renewed periodically. In use, the electrolyte will slowly leak into the environment through a porous plug. If a reverse flow condition occurs, the element may become contaminated. Commonly used wet references include silver/silver chloride and saturated calomel for laboratory use and portable copper/copper sulfate for field use.

Because wet electrodes require periodic electrolyte replenishment, they are not suitable for permanent

When measuring corrosion potential, a voltmeter is used to measure the potential (voltage) between the structure and a reference electrode placed in the same electrolyte. The entire circuit, structure plus reference, can be thought of as a single cell. Because a reference electrode comprises one half of this cell, it is commonly referred to as a "half cell". Measured potentials are actually the difference in potential between that of the reference and that of the structure. It is frequently assumed that the potential established by a reference electrode is absolutely invariant; therefore, any observed potential changes must be occurring on the structure. This is not always the case. The observed changes could also be caused by a change in the reference while the structure remains steady. To ensure accurate potential measurements, it is important to understand those factors that affect the potential established by a reference electrode.

installation. To overcome this limitation, references intended for permanent use have a gelling agent added to the electrolyte. Gelled references require no maintenance. However, they do have a fixed lifetime. Like wet electrodes, gelled electrodes are subject to dry out and contamination if they are not properly installed.

Reference Potential

The potential of a reference electrode is determined by the element metal and the active species concentration in the electrolyte. The form of the electrolyte, wet or gelled, has no effect on the reference potential. Figure 1 shows the potentials of commonly used reference electrodes. The potentials are shown relative to the Saturated Hydrogen Electrode (SHE) which has been defined as the zero point on the potential scale. Note that there are two positions for the Ag/AgCl electrode: 1) saturated, which refers to a saturated potassium chloride (KCl) electrolyte, and 2) seawater, which refers to a dry electrode immersed in seawater. The reference potentials of these two electrodes are about 40 mV apart. The laboratory Ag/AgCl electrode, not shown in Figure 1, uses a filling solution of 4 M KCl which is just under saturation. Its reference potential is about 7 mV positive to the saturated electrode.

When reporting corrosion potentials, it is important to describe the type reference electrode used to measure

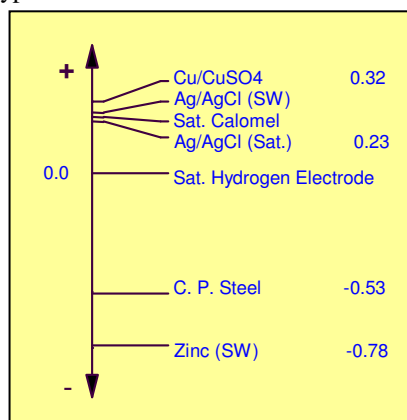


Figure 1
Relative potentials of common reference electrodes vs the saturated hydrogen electrode.

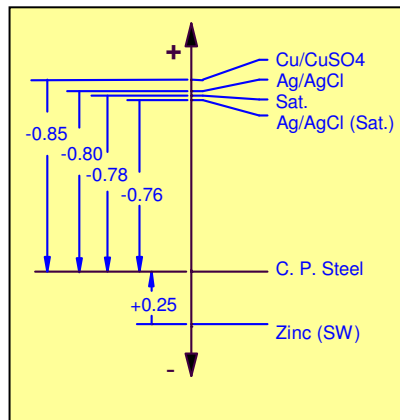


Figure 2
Potential of cathodically protected steel as measured by several common reference electrodes.

the potentials. While the potential of a structure may not change (Figure 2), the number used to describe that potential will depend upon the type of electrode used to measure it. The commonly used criteria of -0.85V for cathodically protected steel only refers to measurements made with a copper/copper sulfate electrode.

External Influences

Temperature, light, electrolyte concentration and contamination all affect the potential of a reference electrode. These effects are most likely to affect portable references which operate in a variety of environments. Permanent electrodes most often operate where there is no light and usually in a very narrow temperature. If they have been properly designed and installed, permanent electrodes are less likely to be influenced by changes in electrolyte concentration or contaminants. These points should be considered when a portable reference is used to calibrate an installed permanent reference: The observed variations may be due to a shift in the potential of the portable reference.

Temperature Effects

Temperature has both direct and indirect effects on reference potential. The direct effect is a linear variation of the reference potential with temperature. The indirect effect is that as temperature

increases, the quantity of salt which can be dissolved in a saturated solution will also increase. This increase in the salt concentration will affect potential. Only the linear variation will be seen in a non-saturated electrode such as a 4M or seawater Ag/AgCl electrode. Figure 3 shows the effect of temperature on the potential of an electrode in a fully saturated solution. These data include both the direct and indirect effects. The temperature coefficient for a saturated Cu/CuSO₄ electrode is about 0.5 mV/°F (0.9 mV/°C). Saturated Ag/AgCl electrodes have a much lower temperature coefficient: -0.07 mV/°F (-0.13 mV/°C).

These temperature coefficients are large enough to produce a significant error in potential measurements if they are left uncompensated. For example, the potential of a pipeline may be -865 mV when measured with a portable Cu/CuSO₄ electrode on a 90°F (26°C) day. If the same measurement were made on a 40°F (5°C) day, the temperature effect will cause a 25 mV shift in the reference potential so the pipeline would now measure -840 mV. The drift occasionally reported to occur on buried permanent electrodes is also likely due to temperature-caused drift of the portable electrode being used for calibration. When using a portable reference in the field, it is a good practice to record the ambient temperature and, if necessary, correct the readings.

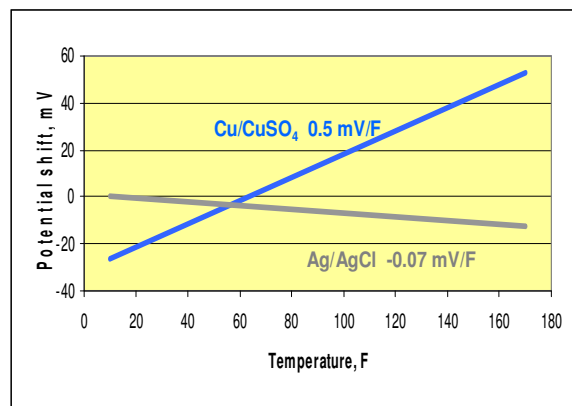


Figure 3
Effect of temperature on the reference potential of electrodes in a saturated electrolyte. Note: earlier versions had incorrectly stated the slope as -0.7 mV/°F.

Light Effects

Copper salts and silver salts are both photo-sensitive so it should not be surprising that light has an effect on the reference potential. To measure this effect, special electrodes were made up in which two elements shared the same electrolyte. One element was kept permanently in the dark by a double baffle while the other was exposed directly to ambient light. The magnitude of the light effect on Ag/AgCl electrodes was usually less than a millivolt and so it could be safely ignored. Cu/CuSO₄ electrodes, however, showed a high degree of light sensitivity. At high noon on the summer solstice, a copper element in direct sunlight measured -52 mV vs a second element kept in total darkness. In open shade, the value was closer to -10 mV while interior fluorescent lights caused a -2 mV shift. When the element was removed to a dark location and then re-exposed the following day, potential shifts of a similar magnitude were again observed. However, when the element was left in the sun for several hours, it apparently became desensitized and subsequent photo-errors seldom exceeded -10 mV.

Housings of commercial portable electrodes are usually transparent red or yellow with a clear stripe to check the liquid level. When the direct illumination was through the red portion, no photo-error was observed but if the illumination was through the clear portion, then values similar to those above were measured. To get consistent readings with a portable reference, the photo-error must be eliminated. The simplest way would be to place a strip of tape over the clear window. Permanent electrodes do not have this problem since they are usually installed in dark locations and have opaque housings.

Electrolyte Concentration Effects

The reference potential will vary with the logarithm of the concentration of active species in the cell electrolyte. This will cause variations in potential readings when using dry electrodes in an

electrolyte in which the composition changes, such as Ag/AgCl/Seawater references in a tidal estuary. The electrolyte of wet and gelled references

simultaneously. The actual potential of the electrode then becomes a composite of all the potentials established by the various reactions. Very often, the effect

is permanent if the compound formed between the element metal and the contaminant is more stable than the compound formed as part of the reference electrode's intended reaction. Chlorides are the contaminant most likely to cause a problem with a Cu/CuSO₄ reference. The effect, (Figure 5), is to shift the reference potential in the negative direction. Other halides (iodides, bromides) and sulfides will have a similarly deleterious effect

on both Cu/CuSO₄ and Ag/AgCl electrodes. Sulfides in the atmosphere will even affect dry Ag/AgCl references in storage if proper precautions are not taken to protect them.

Design Life of Permanent (Gel) Cells

The useful life of a dry or wet reference electrode can be indefinite if it is properly maintained. A gel electrode, on the other hand, has a fixed life expectancy. In both wet and gel electrodes, a composition difference exists across the membrane separating the element's electrolyte from the environment. This difference acts as a driving force for diffusion, which is both outward for the active species and inward for contaminants. As diffusion changes the composition of the electrolyte, the reference potential changes. In a gel electrode, this change is permanent since the electrolyte cannot be renewed. Methods used to extend the life of a permanent reference electrode, therefore, must focus on extending the time before the effects of diffusion reach the element electrolyte interface where the reference potential is established.

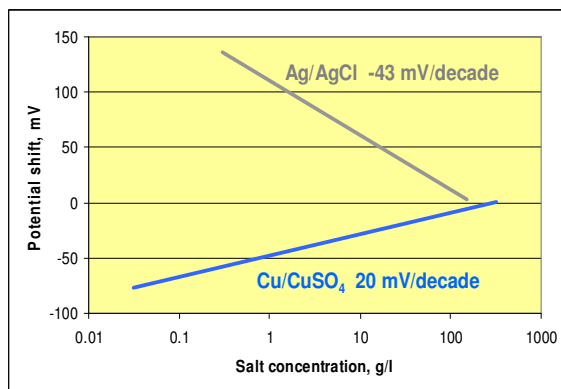


Figure 4

Effect of electrolyte concentration on the reference potential of Cu/CuSO₄ and Ag/AgCl reference electrodes.

has a constant composition which eliminates this source of uncertainty. The concentration coefficient for Cu/CuSO₄ electrodes is about 20 mV/decade in the negative direction (Figure 4). This means that for each order of magnitude drop in the concentration of CuSO₄ in the electrolyte, the reference potential will shift 20 mV in the negative direction. For Ag/AgCl references, the concentration coefficient is about 43 mV/decade in the positive direction.

Contamination Effects

Contamination of the electrolyte will alter the reference potential of an electrode because competing chemical reactions, each with their own characteristic potential are occurring

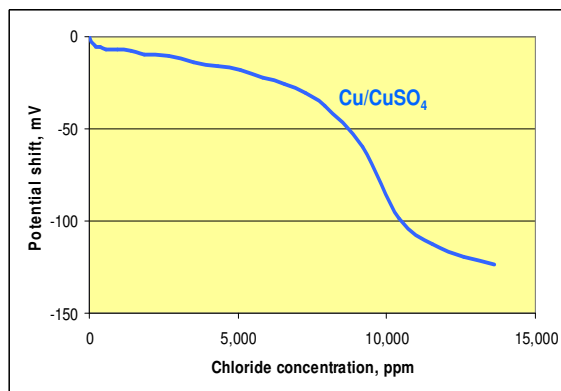


Figure 5

Effect of chloride contamination on the reference potential of Cu/CuSO₄ reference electrodes.

Three broad factors affect the service life of a permanent reference electrode: the environment in which it operates; the chemical make-up of the gel; and the physical design of the electrode itself. Environmental effects include both temperature and concentration difference across the membrane. Increasing either one will reduce service life by increasing diffusion rate. Permanent electrodes use a saturated salt solution as the basis for the electrolyte gel. The chemical make-up of the gel can be modified to provide a reserve of salt to make up for that which is lost by diffusion. Both the amount and distribution of this reserve affects electrode life. There are limits, however, to the amount of excess that can be added to the gel before its properties are affected.

Two design details of an electrode have a significant effect on service life: membrane type and electrolyte path length. The nature of the membrane controls the quantity of salt which diffuses through it. Reducing this quantity can extend the service life but it also will increase internal cell resistance. Clearly, there are limits to the extent to which this technique can be used for life extension since a high internal resistance will cause measurement errors. Electrolyte path length is also important because diffusion is a time dependent phenomenon. Increasing the internal electrolyte path length, that is the

distance from the element to the membrane, increases the time for the effects of diffusion to reach the element/gel interface where the reference potential is established. This factor is particularly significant when using gels with low ionic mobility. When the electrolyte next to the element becomes diluted, the reference potential will shift thereby ending the useful life of the electrode.

Another very important design criterion for a permanent reference electrode is that it be engineered specifically for its intended service. There are a wide variety of applications for permanent reference electrodes. For each application, it is necessary to consider such factors as size limitations, ambient temperature range, operating pressure and installation procedures. If these requirements are ignored, service life will be drastically shortened.⁴

Conclusions

- Accurate readings with portable references require that the ambient temperature be recorded and a temperature correction be applied.
- Light striking the element of a portable Cu/CuSO₄ reference through the clear-view window can induce significant photo-errors. This window should be covered with tape.
- Portable reference electrodes should be cleaned and the electrolyte be

replaced on a regular basis in order for them to maintain their accuracy.

- Dry electrodes should only be used in electrolytes known to have a consistent composition and which contain nothing that can adversely react with the element metal.
- Permanently installed references are usually not affected by photo-errors and their ambient temperature range is much narrower (not including concrete bridge deck applications). For this reason, they are more accurate than a portable reference.

References

1. J. Morgan, Cathodic Protection, 2nd ed., (Houston, TX: NACE, 1987).
2. D. G. Ives & G. J. Janz, Reference Electrodes, Theory and Practice, (New York, NY: Academic Press, 1961).
3. M. H. Peterson & R. E. Groover, MP 11, 5 (1972): p.19.
4. F. J. Ansuini, J. R. Dimond, "Long-term Stability Testing of Reference Electrodes for Reinforced Concrete," CORROSION/94, paper no. 295, (Houston, TX: NACE, 1994).

More information is available in CORROSION/94 paper no. 323, presented in Baltimore, Maryland.

Note: This is an exact reprint of the 1994 MP article. It has been reset and color added when it was converted to electronic format.