

Technical Bulletin 0014

Subject: How Internal Impedance of Meters Effects the Performance of Reference Electrodes

The internal impedance of a meter reading the value of a reference electrode has a great effect on the long term stability and life expectancy of the reference electrode.

When the meter impedance is too low, there are two general effects that will occur without fail.

First, is an error in the direct circuit measurement.

Second, is a polarization of the reference electrode.

The direct measurement error results in a reduction of that portion of the voltage difference between the structure and the reference electrode that appears across the meter. ***This is better understood by looking at Figure 1.***

From this equation, it can be seen that $V_m \approx (V_{se} - V_{ref})$ occurs only when R_m (meter impedance) is much larger than the sum of all of the other circuit resistances.

In most cases, the sum of all of the other resistances in the circuit is in the range of only a few hundreds to a few thousands of ohms.

Thus, a meter having a resistance of **20 megohms** or more will provide a measurement error of only a few percentage points, as shown by: $V_m = (V_{se} - V_{ref})$.

The second error that occurs is a polarization of the reference electrode. This happens when a **low impedance meter** (5 megohms or less) is used to measure the structure to electrolyte potential.

The **low impedance meter** allows current to flow in the measuring circuit which polarizes the reference electrode. Any current passing across a metal/electrolyte boundary will shift the potential across that boundary. **This effect is known as polarization.**

This effect continues as long as the current flows. After the current is interrupted, the potential will drift back to the equilibrium potential. For Copper-Copper Sulfate (Cu-CuSO₄) reference electrodes, the current required for a 10-millivolt

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shift is in the order of only a few microamps. This means that when you use a **low impedance meter** your measurements are always suspect and certainly not accurate.

Thus, the meter impedance required to assure that there is a limit to the amount of measurement current that the reference electrode is subjected to should be at least 10 megohms. A meter having an input impedance of **20 megohms** is a common standard for structure to electrolyte measurements when using a Copper-Copper Sulfate (Cu-CuSO₄) reference electrode.

Note: for both of these effects, "**Error in the Direct Circuit Measurement**" and "**Polarization of the Reference Electrode**", caused by using a **low impedance meter**, the reference electrode will return to a normal potential as long as the period of exposure to the **excessive current** is short.

The practice of permanently connecting the reference electrode to a rectifier meter, which is generally a **low impedance meter** or using an old analog meter connected to the reference electrode for extended periods, such as, leaving it connected while other work at the job site is being performed will certainly destroy the reference electrode. Many new rectifiers have a button that reads "Push to Read Potential" which returns to the "Off Position" when released (disconnects the reference electrode from the circuit).

Following this, the question is often asked, "**What exactly happens to a reference electrode when current is continuously passed through it?**"

The bottom line and final outcome is, the reference electrode will continually decrease in stability and eventually will stop working altogether, in other words it will be destroyed.

In an effort to clarify why this happens the following explanation is offered.

The stable potential of a reference electrode is due to a **reversible electrochemical reaction** which occurs on the surface of the sensing element. In the case of a Cu-CuSO₄ reference electrode, the reaction is this:



The potential of this reaction (the voltage of the electrons produced) is dependent, only on the purity of the copper element and the concentration of the copper ions in solution surrounding the copper element.

This concentration of the copper ions in solution, surrounding the copper element, in a Cu-CuSO₄ reference electrode is kept constant by having a saturated solution permanently present in the reference electrode. This is accomplished in the **Stelth[®] technology** by using a solid, but porous, block of copper sulfate that continually saturates the solution present in the pores.

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At a given temperature, the copper ion content of a saturated copper sulfate solution is constant.

Note: The variation of the solubility of copper sulfate with temperature is one of the reasons for the temperature dependence of the potential of a Cu-CuSO₄ reference electrode.

For example, the Cu-CuSO₄ reference electrode potential at 25°C (77°F) to protect steel in a working environments is -0.85 volts. For each degree centigrade above 25°C (77°F) a correction must be made of plus 0.9 millivolts. Therefore a measurement taken at a temperature of 28°C (82°F) you would add to it plus 2.7 millivolts. For more information on this phenomena see Technical Bulletin TB-0009.

This is a critical adjustment that must be made when reading potentials on hot oil lines and tank bottoms that contain hot media where temperatures can range from 55°C (131°F) to 85°C (185°F).

If (conventional) current is passed from the copper element to the copper sulfate electrolyte, copper ions will be produced and the copper element will corrode and the copper content of the electrolyte will increase. This will eventually cause permanent damage to the reference electrode.

If (conventional) current flows from the copper sulfate electrolyte to the copper element, the copper ions in solution will plate out on the copper element. This will deplete the amount of copper in solution causing permanent damage to the reference electrode.

While reference electrodes can recover from short periods (a few minutes) of small current flow (milliamp) the continuous flow of even small currents can result in permanent damage to the reference electrode. It is therefore imperative to limit the current flow across the reference electrode. This is accomplished by using a high impedance voltmeter to measure structure to electrolyte potentials. A meter having a resistance of **20 megohms or more** is normally considered adequate, even if the structure to electrolyte potential is being measured continuously.

All of this leads to the following question, **"Why are my reference electrodes failing when used with a SCADA or remote monitoring system"?**

Most **SCADA** systems are not configured to accommodate the requirements for measuring reference electrodes. Their internal impedance is generally in the kilo ohm range and therefore they quickly kill any reference electrode they are connected to. A solution to this is to use a transducer, which has a minimum of **20 megohms** of impedance, that is connected between the output of the reference electrode and the input to the **SCADA** system. This will eliminate the problem and preserve the integrity of the reference electrodes measurements.

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An additional concern regarding some **SCADA** systems and "**Portable Dataloggers**" is when they are not taking a measurement and remain connected, the lead is channeled to ground therefore dumping all available current into the reference electrode. This of course destroys the reference electrode.

A similar problem exists with "**PC Based Remote Monitoring Systems**", especially those few that have withdrawn from the market place, either voluntary or through bankruptcy.

Most **PC Based systems** have two problems that contribute to reference electrode failures.

First, the recurring problem of internal impedance being high enough to preserve the health of the reference electrode.

Second, these systems chose to use a hardware architecture where each channel shares a common ground. The motivation to do this appears to be one of economics. The problem this architecture presents to reference electrodes is; when a single channel goes down it takes all of the other channels down with it allowing the system to dump all of the available current into the reference electrode destroying it in a matter of a few minutes.

Note: The PC Based **Comanche[®] remote monitoring & control system** uses, throughout the entire product line, a hardware architecture where each channel, from two to several thousand if required, is electrically isolated and employs an internal impedance of **20 megohms** specifically for reference electrode measurements.

Finally a question that is asked more than any other, "**Why do the measurements differ between the permanently installed reference electrode connected to the rectifier meter and the portable reference electrode when the rectifier is on but, are virtually the same measurement when the rectifier is turned off**"?

Several errors can occur when using a rectifier panel meter to read structure to electrolyte potentials.

The **first** being that the meter is connected to the structure through a current carrying conductor when the rectifier is on. The IR drop through the conductor will either add to or be subtracted from the actual structure to electrolyte potential difference. When the rectifier current is interrupted, this voltage drop will cease and this error will be eliminated. This is why the difference between the panel meter and the portable meter will be reduced when the current is interrupted.

A **second** problem when comparing readings taken with reference electrodes in different locations is IR drop through the electrolyte. It should be obvious that a reference electrode located buried 1 to 2 meters deep and close to the structure has less of an IR drop influence than a portable reference electrode 1 to 2 meters remote from the structure. This error will cease when the rectifier current is interrupted reducing the difference between the panel meter and portable meter.

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A **third** source of error in the panel meter readings is polarization of the reference electrode due to long term current flow through the reference electrode. This again, is a function of the low level of internal impedance in the panel meter. It will be more severe when a low resistance meter is being used continuously to measure the structure to electrolyte potential. This will result in a shift in the potential of the reference electrode, which will probably be several hundred millivolts.

If polarization has occurred for long periods, the potential of the reference electrode may return **only very slowly** to its normal potential, if at all when relieved of the burden of the **excessive current**.

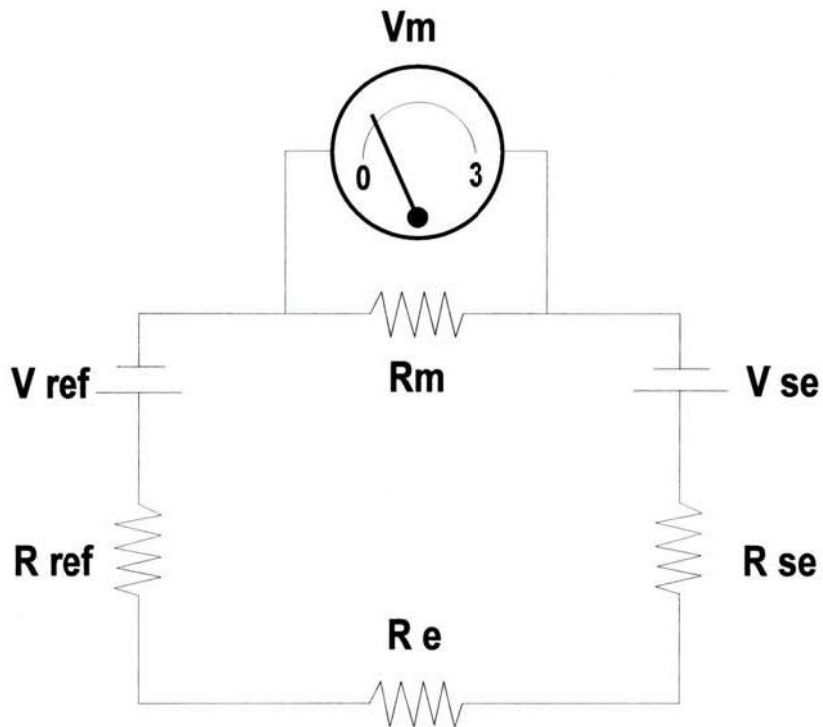
Using a low resistance meter to continuously measure structure to electrolyte potentials will result in **immediate errors** due to polarization of the reference electrode and, if continued for long periods (several months) will eventually destroy the reference electrode.

To correct this condition, a high impedance meter of at least **20 megohms** must be used, or the measurement must be made periodically for a very short period with the circuit being interrupted for most of the time.

A final note should be directed towards "**Auto Potential Rectifiers**". We have found several rectifier manufactures in various countries produce rectifiers that utilize the reference electrode to automatically adjust the rectifier output without concern for maintaining a minimum of **20 megohms** of impedance in the reference electrode feedback sensing circuit.

When you requisition a rectifier you should insist that this minimum level of **20 megohm** resistance be supplied not only for "**Auto Potential Rectifiers**" but also, in the meters measuring reference electrodes in any rectifier. After all this is the 21st Century and the Corrosion Industry has to be in the vanguard of technology not saddled with 1900s tools.

Equivalent Structure to Electrolyte Potential Measuring Circuit



R_m = Meter Impedance
V_m = Meter Voltage Reading
V_{ref} = Potential of Reference Electrode
R_{ref} = Total Resistance of Reference Electrode
V_{se} = Structure to Electrolyte Potential
R_{se} = Total Resistance of Structure to Electrolyte
R_e = Resistance of Electrolyte

It can be seen that the potential that is read across the meter (V_m) is a function of the other resistances in the circuit as well as the potential difference between the reference electrode and the structure.

$$V_m = V_{se} - V_{ref} \left(\frac{R_m}{R_m + R_{ref} + R_{se} + R_e} \right)$$

$$V_m \approx V_{se} - V_{ref} \text{ when } R_m \gg R_{ref} + R_{se} + R_e$$

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