

# The Role of Dissolved Oxygen and ORP Measurements in Power Plant Chemistry

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## ABSTRACT

ORP (oxidation reduction or redox potential) and DO (dissolved oxygen) measurements can provide valuable information in makeup water treatment, cycle chemistry control and stator coolant. Taking the time to understand the principles of operation of these sensors is a worthwhile effort to help specify appropriate equipment and to obtain successful results with it. This discussion describes the various applications for DO and ORP measurements in power plants. It then provides detail on the significance of these measurements and operation of the sensors.

## INTRODUCTION

With the variety of cycle chemistry schemes now being used in power plants around the world, there is some ambiguity about the monitoring requirements and their significance. Here follows a brief review of cycle chemistry water treatment regimes identified by the Electric Power Research Institute and two key measurements used to monitor them: dissolved oxygen (DO) and oxidation reduction or redox potential (ORP). The use of ORP and dissolved oxygen measurements in makeup water treatment and dissolved oxygen in stator cooling are also covered. The techniques for making these measurements are described along with practical considerations in applying them.

## APPLICATIONS

Oxygen is a universal corrodent, but its effects on metals depend on a number of other variables in addition to its own concentration. For this reason, direct DO measurement is not always the most efficient way to control corrosion. In some applications ORP measurement can provide more useful information.

### ORP and Dissolved Oxygen in Cycle Chemistry

In the quest to minimize corrosion, various strategies have been used for boiler water treatment, and methods are still evolving. All-volatile treatment (AVT) using ammonia and hydrazine or similar combinations was developed primarily for once-through boilers that cannot tolerate dissolved solids. Other high-pressure boilers have also benefited

from this treatment. For feedwater treatment, this is subdivided into reducing all-volatile treatment, AVT(R), and oxidizing all-volatile treatment, AVT(O) [1].

AVT(R) is needed when there are copper alloys in the feedwater train. It uses deaeration and a reducing agent (hydrazine or other reducing amine) to lower DO content to low single digit  $\mu\text{g} \cdot \text{kg}^{-1}$  (ppb) concentrations to create the more protective, reduced, cuprous oxide layer. At these low levels, the measurement of DO operates with quite low signal-to-noise ratio and it is questionable whether a reducing agent feed rate controlled by DO concentration is effective. In fact, it can lead to excessive reducing agent feed, which is a waste in itself. More importantly, it can contribute to conditions that cause flow accelerated corrosion and can lead to catastrophic failure.

ORP measurement responds to both oxidizing and reducing conditions and is most sensitive in the transition range between the two. It can therefore respond to an excess of reducing agent where a DO measurement would likely be at or near zero with little response. Furthermore, ORP is a measure of the actual oxidizing/reducing environment inside the pipe and relates to corrosion more than oxygen measurement alone under these conditions. For these reasons, with AVT(R) ORP is the recommended measurement, usually measured at the deaerator inlet. ORP values near  $-300$  mV have been recommended though some plants operate successfully at levels less negative than that. [Figure 1](#) gives an example of the type of response expected of ORP. This curve may shift somewhat depending on pH, dissolved metals and electrode aging. Confirmation of the appropriate ORP value and treatment

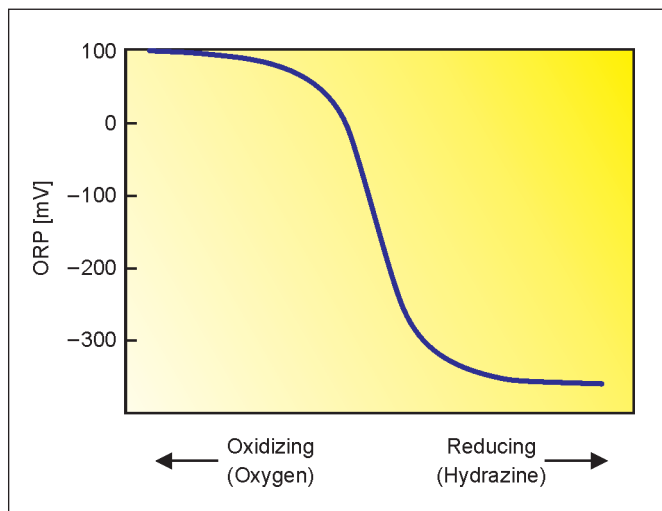


Figure 1:  
Example cycle chemistry ORP response.

level for a particular installation should be made by monitoring concentrations of iron and copper corrosion products released into the system.

For plants with all-ferrous feedwater trains AVT(O) has advantages. No reducing agent is used and the mildly oxidizing conditions promote the development of ferric oxide hydrate ( $\text{FeOOH}$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ) over the magnetite ( $\text{Fe}_3\text{O}_4$ ) layer. This combination creates the most durable surface and results in the least corrosion product transport. To accomplish this, the DO concentration is controlled only by deaeration. In this range, a DO measurement has better sensitivity and is useful to monitor the concentration present. ORP would have variable values near zero but without much significance [2].

The AVT(O) treatment may not provide adequate oxygen to passivate the entire feedwater train. Oxygenated treatment, OT, is the practice of feeding oxygen ahead of feedwater heaters to assure that the mildly oxidizing conditions are maintained and the  $\text{FeOOH}$  passivation covers the entire feedwater system. A DO measurement is definitely preferred with its greater sensitivity in the  $30\text{--}150\ \mu\text{g} \cdot \text{kg}^{-1}$  range. Under these conditions ORP would be on the upper plateau in the oxidizing region and would tend to stay there with little sensitivity to concentration changes.

From this review it is seen that ORP measurement is recommended for AVT(R) at the deaerator inlet while DO is recommended for all other measurements. In plants converting to oxygenated treatment, ORP measurement has also been of interest in tracking the transition from reducing to oxidizing conditions as it can take some time for the passivation to reach the ends of the system [3].

### ORP in Makeup Water Treatment

Makeup water and municipal water treatments usually include chlorination or treatment with another oxidizing

agent for disinfection of filters as well as downstream piping. However, any residual chlorine must be removed ahead of reverse osmosis membranes or deionization resins that would be damaged by oxidation. Addition of a bisulfite compound or flow through a carbon bed is used to remove chlorine by reducing it to chloride. To assure this removal, ORP measurement is commonly used due to its high sensitivity to the balance between oxidizing and reducing materials. It can warn if the bisulfite feed or carbon bed is not achieving the desired results.

An ORP titration curve for dechlorination shows the type of response that would be expected for treatment of an off-line grab sample, as shown in Figure 2. Chlorinated water in this example gives an ORP of over 700 mV on the left. As small amounts of reducing bisulfite solution are added, the ORP drops logarithmically. As the chlorine is all reacted and an excess of bisulfite accumulates, the response reaches a plateau near 350 mV to the right. It is important to establish the setpoint somewhat above the plateau to prevent wasting bisulfite or causing false alarms. The sensitivity of this measurement is apparent in the steep portion of the curve, which is the transition from oxidizing to reducing conditions. Continuous processes are controlled to operate near a single point on the curve.

It is important to recognize that this is only an example titration curve. The curve for a specific installation may be shifted significantly from these mV values, but the basic shape will be similar for any dechlorination reaction. On-line experience is necessary at startup to establish the particular mV operating range and setpoint for an installation.

The best practice for determining the setpoint for control is to use a colorimetric or other sensitive test for chlorine or bisulfite concentration as a reference. The ORP value nearest the inflection point at the time the desired concentration is reached is an appropriate setpoint value. Test kits for these measurements are readily available.

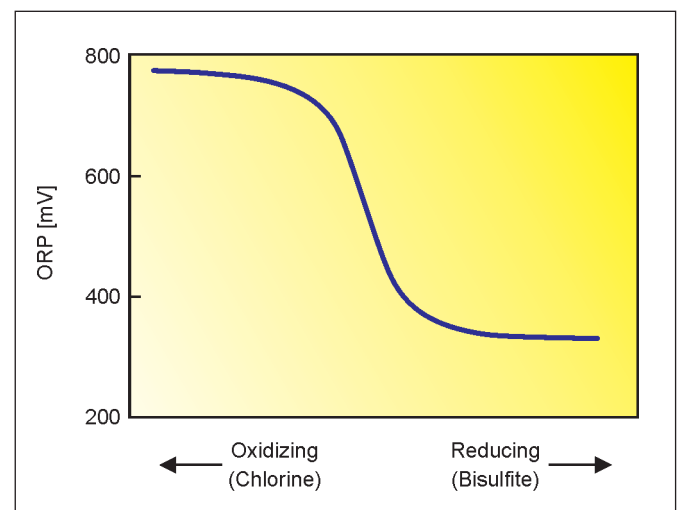


Figure 2:  
Example dechlorination ORP response.

### Dissolved Oxygen in Makeup Water Treatment

Dissolved oxygen is a concern in final makeup water before it goes into the storage tank and the condenser hotwell, where every effort is made to keep DO levels as low as possible. Deaeration is a critical stage in makeup water treatment to meet this requirement. To monitor the performance of the deaerator, DO measurement is essential. A rapid responding DO measurement can immediately flag any upset in deaerator operation before significant amounts of air are allowed to reach the hotwell.

### Dissolved Oxygen in Stator Cooling

Reliable and efficient power generation with water-cooled generator stators depends on that system's integrity. Proper cooling water monitoring and treatment can minimize copper corrosion and fouling with corrosion products. Deposits of copper oxides restrict and even plug the narrow flow channels of stator bars. The results can range from a mild increase in stator pressure drop to significant efficiency loss and, ultimately, to partial meltdown of the stator bars.

The corrosion rate of copper is strongly influenced by dissolved oxygen concentration, as well as pH and temperature. The relationships have been thoroughly studied and there is now an increasing appreciation for the need to monitor these critical parameters. In addition, conductivity must be maintained very low, usually in the area of  $< 3 \mu\text{S} \cdot \text{cm}^{-1}$ , to prevent electrical flash over as well as to reduce corrosion.

Dissolved oxygen influence is unusual in that either very low or very high concentrations will minimize corrosion, but mid-range concentrations are most detrimental as shown in Figure 3. This leads to two strategies for handling dissolved oxygen, usually defined by the generator manufacturer. It must be controlled to either  $< 20 \mu\text{g} \cdot \text{kg}^{-1}$  or  $> 2\,000 \mu\text{g} \cdot \text{kg}^{-1}$ . Concentrations between these levels promote rapid copper attack, and it is important that any excursions into this no-man's-land be very limited. Slightly elevated pH, between 8 and 9, also has great benefit and a small but growing number of plants are making pH adjustments to take advantage of this.

Continuous, reliable DO measurements are the key to assuring the right conditions are maintained. For generators using the low DO strategy, DO measurement can assure that air is not leaking into the system at the deionizer or other components of the circulating system and causing the DO level to rise into the high corrosion region. From the other direction, for generators using the high DO strategy, a DO measurement can make sure the hydrogen atmosphere within the generator core is not displacing oxygen in the coolant and lowering it into the corrosive mid-range [4].

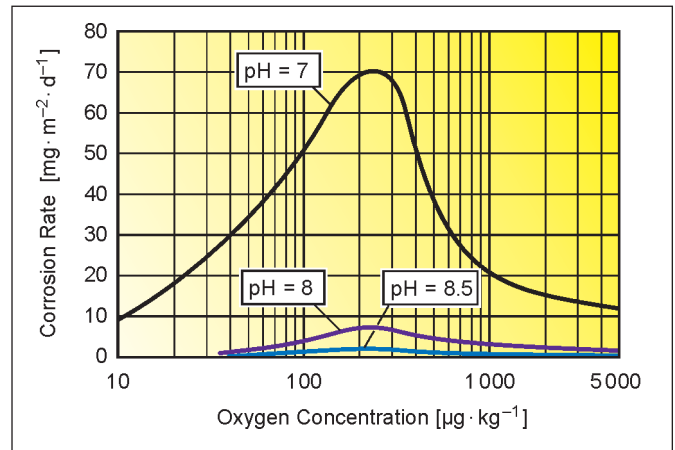


Figure 3:  
Copper corrosion rate as influenced by dissolved oxygen and pH.

Especially with the low DO strategy, a requirement of the DO instrumentation is that it must not be subject to interference from dissolved hydrogen. This interference is common among polarographic sensors. The hydrogen produces a negative response from the DO sensor, resulting in misleading low DO readings and a false sense of security. Fortunately, galvanic DO sensors are available that operate with low enough electrode potential that hydrogen does not react and accurate DO measurements can be made in its presence, as described later.

## MEASUREMENTS

### ORP Significance

The correlation between the concentration of chlorine or other oxidizing or reducing material and ORP is not direct. ORP is proportional to the logarithm of the concentration ratio of all the oxidizing and reducing species in the sample as indicated in Eq. (1), which is a bit over-simplified. Oxidizing or reducing species may include minerals and dissolved oxygen, which can cause ORP response to shift significantly. pH and temperature can also have an effect. For these reasons there is no reliable conversion from ORP in mV to a concentration in  $\mu\text{g} \cdot \text{kg}^{-1}$  or  $\text{mg} \cdot \text{kg}^{-1}$ .

Nevertheless, in moving from an oxidizing to a reducing condition with extremely small ( $\mu\text{g} \cdot \text{kg}^{-1}$ ) concentration changes, the ORP typically drops several hundred mV. It is very sensitive in detecting the change and is therefore quite useful as a go/no-go alarm parameter. In alarm applications, the exact setpoint value is usually not critical. However, where ORP is used to control reagent feed, more precision is needed in establishing the control point. In this case, it is worthwhile to develop a titration curve to quantify the ORP response in the actual application.

$$\text{ORP} \propto \log \frac{[A_o] [B_o] [C_o] \dots}{[D_r] [E_r] [F_r] \dots} \quad (1)$$

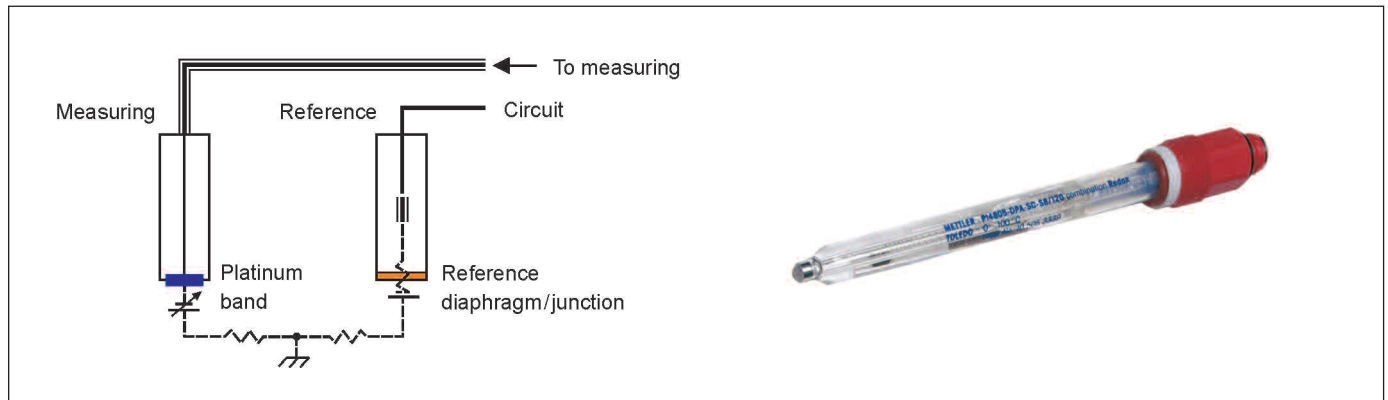


Figure 4:

ORP sensor schematic (showing separate measuring and reference electrode functions although both are usually incorporated into a single concentric probe as shown at right).

Oxidizing species:  $A_o$ ,  $B_o$ ,  $C_o$ ...

Reducing species:  $D_r$ ,  $E_r$ ,  $F_r$ ...

### ORP Instrumentation

ORP sensors and instrumentation are very similar to those for pH. However, the measuring electrode is an inert metal – usually platinum – instead of a pH-sensitive glass membrane. In oxidation-reduction or redox reactions, oxidation is the removal of electrons and reduction is the addition of electrons. The metal electrode develops the ORP mV signal, which is the solution's tendency to contribute or remove electrons at its surface, shown as a variable voltage battery in [Figure 4](#).

The reference electrode completes the measuring circuit and adds its own nearly constant potential. As with pH, the reference junction or diaphragm is a critical part of the measurement. In low conductivity samples the junction should maintain a flow of electrolyte through it to keep the resistance low and its own potential low and constant. The probe shown at the right uses a self-pressurized electrolyte gel to achieve this kind of performance without the need for a cumbersome electrolyte reservoir.

The ORP instrument measures the combined potential and displays it directly in mV. There is generally no calibration of ORP measurement. Direct, absolute mV are the usual unit of measure. But because ORP instruments are typically pH instruments operating in a mV mode, calibration is generally available. However, this yields a relative mV reading which is not comparable to independent readings or data and is therefore discouraged.

ORP standard solutions are available primarily for verification of electrode response rather than for calibration. They tend to have fairly wide tolerances under process conditions. Recipes for standard solutions are also available to make up on site [5].

There is no temperature compensation with ORP instrumentation since each oxidation-reduction reaction has somewhat different temperature characteristics and most processes using ORP have fairly stable temperature. Maintenance of ORP sensors typically consists of wiping the platinum element with a clean cloth and/or cleaning in dilute hydrochloric acid to remove any accumulation of corrosion products, which tend to dampen its response.

### Dissolved Oxygen Instrumentation

Dissolved oxygen sensors are electrochemical devices that take advantage of the gas permeability of polymer membranes, which separate the heart of the sensor from the sample. This separation enables a sensor to provide a controlled environment for the electrodes and electrolyte while allowing oxygen to enter from the sample and react. It keeps the electrochemistry fairly well contained and clean.

There are two types of dissolved oxygen sensors in common use: polarographic and galvanic. Polarographic sensors require that a voltage be applied between electrodes to enable the reaction of oxygen to occur and produce a signal. Galvanic sensors are similar except that the selection of electrode metals and electrolyte produces adequate voltage for the reaction to occur without an applied potential. Polarographic sensors are characterized as highly accurate and fast responding but vulnerable to dissolved hydrogen interference. Some galvanic sensors have been designed with a very long service interval and immunity to hydrogen interference.

[Figure 5](#) is a schematic diagram of a polarographic DO sensor. The diffusion rate of oxygen through the membrane is proportional to the partial pressure of oxygen in the sample. Of course the membrane material and thickness also affect the diffusion rate, but they are fixed and those properties are accommodated in calibration.

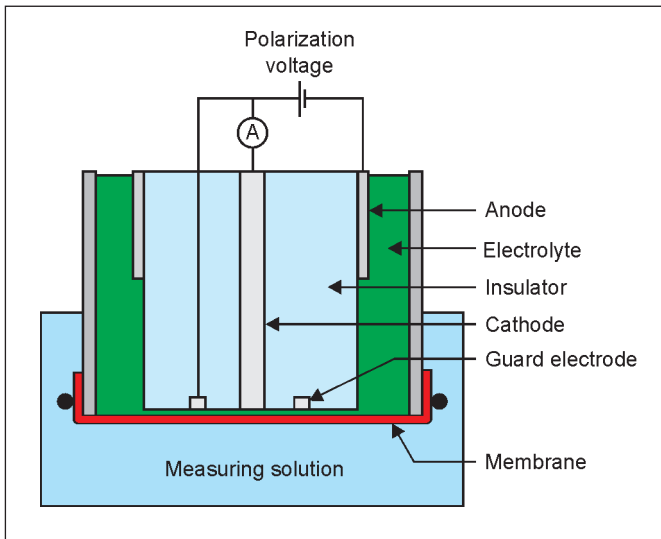


Figure 5:  
Polarographic dissolved oxygen sensor components.

The oxygen which permeates the membrane reacts at the cathode, producing a current in direct proportion to the quantity of oxygen that reaches it. This current is the measurement signal, which matches the oxygen partial pressure and the concentration of DO, at least at constant temperature.

To derive a DO concentration measurement from partial pressure with varying temperature, the signal must be compensated, based on the relationship of oxygen concentration in air-saturated water. That is, the DO concentration in water that a partial pressure represents is temperature dependent. The sensor's RTD (resistance temperature detector) signal is used by the instrument to temperature compensate the measurement. Further background on the use of these types of DO sensors is described in an ASTM standard test method [6].

The electrochemical reactions occurring within this probe take place in many stages, but the overall result is summarized in Eqs. (2)–(4), which occur when the sensor is energized by the measuring instrument with the appropriate polarization voltage and the probe is in the presence of oxygen.

Cathode:



Anode:



Net:



From this it can be seen that there is a direct linear relationship between the current signal and oxygen that gets

reduced, coupled with the anode getting oxidized to silver chloride. The maintenance interval for this type of sensor can be upwards of 6 months, depending on the concentration of DO that is measured. The measuring instrument provides the carefully controlled polarizing potential. When the probe is not polarized, there is no consumption of the anode, giving it a long shelf life.

Most DO sensors have rapid upscale response, which is a useful factor in responding to air leaks or other upsets. Rapid downscale response of a DO sensor is harder to achieve but is important in order to resume monitoring after air calibration or to provide quick response to process changes. A key to producing rapid downscale response is the designed-in guard ring electrode shown in Figure 5. It is a ring around the cathode that is also polarized so it can reduce oxygen at its surface, the same as in Eq. (2). However, its signal is not measured. Instead, it serves only to help eliminate oxygen from the bulk electrolyte before it diffuses to the cathode and thereby eliminates response from this "carry-over" oxygen. Response is limited to oxygen permeating the membrane directly in front of the cathode. With this feature, a downscale response time of 98 % in 90 s is routinely achieved.

The ability to measure accurately at low sample flowrates requires a flow chamber design that directs the sample flow as a jet, directly at the membrane. See the right side of Figure 6. This assures that the flow against the membrane is turbulent and there will not be a boundary layer of sample against the membrane that gets depleted of oxygen as the oxygen permeates the membrane and is consumed. Operating with sample flowrates down to  $50 \text{ mL} \cdot \text{min}^{-1}$  without compromising accuracy can save a substantial amount of pure water on a continuous flow basis.

The incorporation of these features into a sensor results in a fast-responding, accurate sensor requiring only infrequent service. Service consists of dropping in a low-cost pre-mounted membrane cartridge and replacing electrolyte. Figure 6, left view, illustrates the probe components.

The probe is based on a robust steam-sterilizable biotech design. The design has been well proven in process use for many years. The instrumentation complements the sensor design with stable amplification, accurate temperature compensation, convenient calibration with atmospheric pressure correction plus digital and multiple analog outputs.

### Galvanic DO Sensors

As noted previously, galvanic DO sensors are recommended where hydrogen is present in the sample or where a very long service interval is advantageous. Galvanic sensors function very similarly to polarographic sensors but use different electrode and membrane materials, different electrolyte composition, no guard ring electrode and no

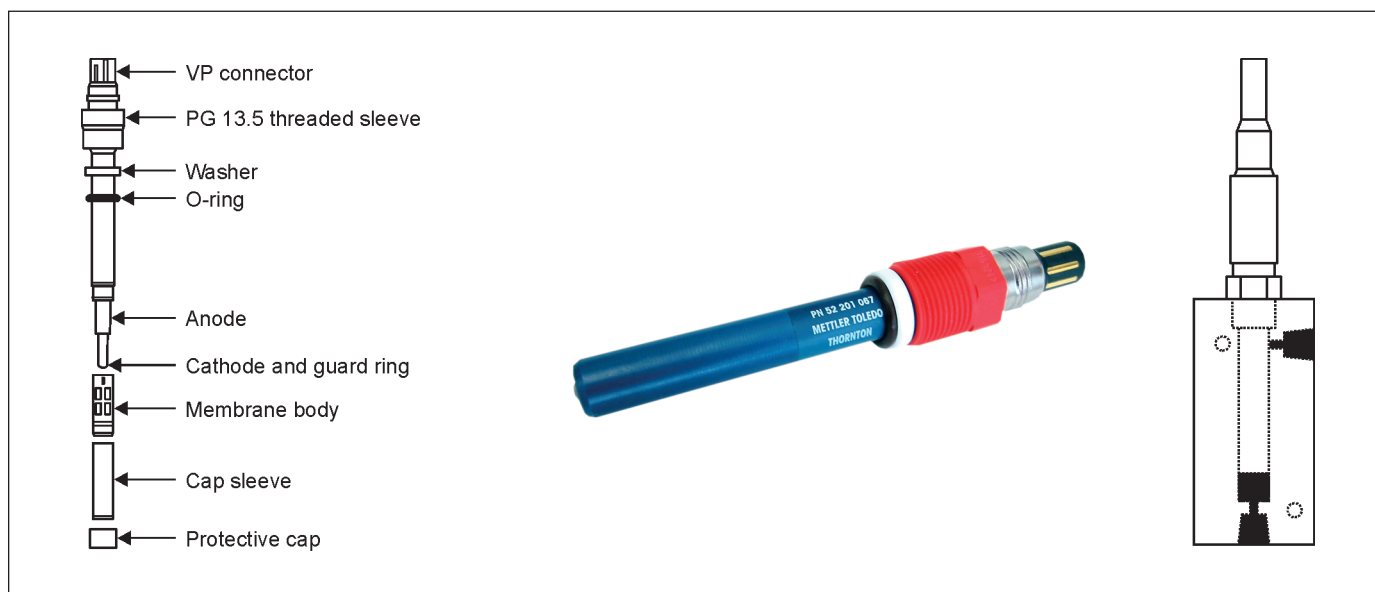


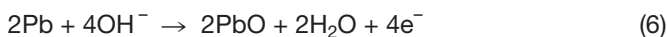
Figure 6:  
Polarographic dissolved oxygen sensor: components, photo, flow housing.

applied voltage. The reactions occurring in a galvanic sensor design are given in Eqs. (5)–(7).

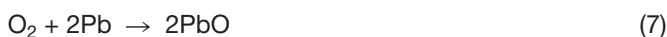
Cathode:



Anode:



Net:



From this it can be seen that there is no consumption of electrolyte. Only the lead anode is oxidized. With a large, active anode surface area a vastly extended operating life can be obtained. With this limitation out of the way, the maintenance interval for this type of sensor is often upwards of 3 years. Its immunity to hydrogen interference and use of non-Teflon membrane material make it quite applicable for nuclear power and stator cooling applications.

### DO Measurement Interferences

Probably the most common problem with  $\mu\text{g} \cdot \text{kg}^{-1}$  (ppb) level DO measurement is air leaks into the sample. Although the sample is usually under positive pressure, air may still leak through any thin water film at a loose fitting or may be pulled into the sample by the Venturi effect at a fitting and contaminate a low  $\mu\text{g} \cdot \text{kg}^{-1}$  (ppb) sample. It always causes a high, flow-sensitive reading. Rotameters, some valves and fittings are particularly prone to air leakage.

A similar problem can occur if using a section of polymer tubing sample line since it is gas permeable. The ubiquitous laboratory vinyl tubing is *not* recommended for DO samples. A study has shown that polyvinylidene difluoride (PVDF) has a much lower permeability, with Nylon and polypropylene also considerably better than vinyl [7]. Stainless steel or other non-permeable material is preferred but if a flexible connection is needed, the tubing should be of one of the low-permeability materials, have a thick wall, and be as short as possible in order to minimize oxygen ingress.

Interference from either leaks or permeation through the sample line can be diagnosed by increasing the sample flowrate. If there is no oxygen intrusion, the reading should remain nearly constant. If the DO reading decreases, a leak or permeation is occurring since the higher flowrate dilutes the oxygen ingress. If there is an *increase* in the reading, then the original flowrate was too low or the probe requires cleaning. Accumulation of corrosion products on the membrane surface will cause lower than actual, flow-sensitive readings. Cleaning with a soft cloth and/or dilute hydrochloric acid is needed.

Under some conditions, oxygen-consuming bacteria can grow on DO sensor membranes or inside polymer sample lines. This will affect the readings of any type of sensor by lowering the actual concentration at the surface of the membrane, which, in turn, causes low readings. Here also, an increase in flowrate would cause an increase in DO reading. Chemical sterilization with very dilute hydrochloric acid or very dilute hypochlorite bleach can eliminate the bacteria.

Dissolved hydrogen interferes with most polarographic DO sensors. Hydrogen is often present in power plant stator

cooling or nuclear reactor samples. This can suppress the measurement or even result in negative readings. For these samples a galvanic sensor which is not sensitive to hydrogen is strongly recommended.

## CONCLUSION

ORP and DO measurements can provide valuable information in makeup water treatment, cycle chemistry control and stator coolant, but it is necessary to apply them wisely. Taking the time to understand the principles of operation of these sensors is a worthwhile effort to help specify appropriate equipment and to obtain successful results with it.

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