Dissolved Oxygen Measurement

Introduction

Dissolved oxygen is defined as the measure of water quality indicating free oxygen dissolved in water. The quantity of dissolved oxygen in water is typically expressed in parts per million (ppm) or milligrams per liter (mg/l). Since oxygen is soluble in water, the amount of dissolved oxygen in water is in the state of dynamic equilibrium. The solubility of the dissolved oxygen is proportional to the temperature and pressure of the water.

The most common application for dissolved oxygen measurement occurs in wastewater treatment. Biochemical breakdown of sewage is achieved by bacterial attack in the presence of oxygen. This process typically takes place in an aeration basin of a wastewater treatment plant, and is accomplished by aerating or bubbling air (or pure oxygen) through the wastewater. Maintaining the proper concentration of dissolved oxygen in the aeration basin is necessary to keep microorganisms alive and allow break down of organic waste. These microorganisms turn organic wastes into inorganic byproducts; specifically, carbon dioxide, water and sludge. When the measured dissolved oxygen decreases below a desired concentration, the plant control system automatically adds air to the aeration basin to provide life-sustaining oxygen for the microorganisms, and to facilitate thorough mixing of the organic waste. Without enough dissolved oxygen concentration, beneficial microorganisms will die while troublesome filamentous microbes proliferate, causing sludge settling problems. Conversely, aeration is the largest single operating expense, and oxygen levels greater than the required optimum concentrations are wasteful and inefficient.

Typical Membrane Sensor Design

Dissolved oxygen sensors for continuous process monitoring are usually a membrane-type design. Most membrane sensor designs use three basic elements:

- Electrodes - The electrodes provide the necessary reaction site for reduction of oxygen molecules and generation of electrons.
- Membrane - The gas permeable membrane is designed to keep the electrolyte around the electrodes, while allowing only dissolved oxygen to diffuse into the measurement cell.
- Electrolyte - The electrolyte facilitates dissolved oxygen migration and provides an electrical path to complete the current loop. It also removes metal oxides (a by-product of the reaction) from the electrodes so that their metal surfaces are clean to react. Electrolyte must be periodically replenished to insure that the electrodes remain clean.

The operational theory of a membrane sensor is that oxygen in the wastewater diffuses through the membrane into the electrolyte. The concentration of gases always tends to equalize on both sides of the membrane. When the concentration is not equal, gas molecules migrate to the membrane side that has a lower concentration. When the membrane is functioning, dissolved oxygen concentration in the electrolyte in the measurement cell approximately equals the dissolved oxygen concentration of the wastewater contacting the opposite side of the membrane. The diffusion process is extremely critical. The dissolved oxygen must be allowed to migrate freely through the membrane for the sensor to function properly.

Dissolved Oxygen Cell Chemistry

Most continuous measurement dissolved oxygen sensors in today's marketplace use galvanic (spontaneous voltage) or electrolytic (applied voltage) measuring cells. In either case, the system measures an electric current between two electrodes, which is proportional to the dissolved oxygen in the process.

■ Conventional Galvanic Measuring Cell

A conventional galvanic cell is illustrated in *Figure 1*. The oxygen content of the electrolyte is brought into equilibrium with that of the sample. The galvanic cell operates like a battery, two electrodes made of dissimilar metals are immersed in a filling solution. This causes an electrochemical reaction to take place when oxygen comes into contact with the electrodes. In this reaction, the cathode reduces the oxygen into hydroxide, thus releasing four electrons for each molecule of oxygen. These electrons cause a current to flow through the electrolyte, the magnitude of which is proportional to the oxygen concentration in the electrolyte. The most common electrode materials are gold, silver, copper or lead, and the most frequently used electrolyte is potassium hydroxide (KOH). The cathode must be a noble metal (silver or gold) for the cathode potential to reduce molecular oxygen when the cell circuit is closed. The anode should be a base metal (iron, lead, cadmium, copper, zinc or silver) with good stability and without any tendency toward passivation. The electrolyte is selected so that it will not dissolve the anode at a high rate when the cell is open.

Oxidation-reduction reactions for an iron anode and silver cathode are:

Reaction at cathode:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Reaction at anode:
$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$

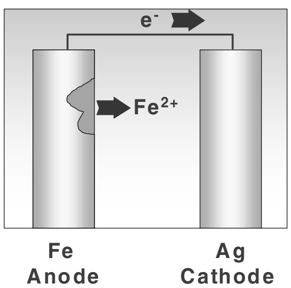

FIGURE 1 -- Conventional Galvanic Measuring Cell

The conventional galvanic measuring cell has some inherent disadvantages. It depends on the reduction of oxygen molecules to generate a measurement voltage, making it susceptible to contamination of the electrodes and electrolyte. If a contaminating material permeates the membrane, it will cause the cell potential to shift. This shift will be falsely interpreted as a change in dissolved oxygen concentration. Another problem occurs at low oxygen concentration levels. Since the output of a galvanic cell is linearly proportional to the amount of oxygen present, the potential for errors at low oxygen levels increases due to a low signal-to-noise ratio. Finally, the anode electrode will be consumed due to the electrochemical reaction necessary for the dissolved oxygen measurement.

- Clark Polarographic Measuring Cell

A Clark polarographic cell is illustrated in *Figure 2*. The dissolved oxygen in the sample diffuses through the membrane and into the electrolyte solution, typically an aqueous potassium chloride (KCL) solution. When a constant polarizing voltage is applied across the gold and silver electrodes, oxygen will be reduced at the cathode. The resulting current flow is directly proportional to the dissolved oxygen content of the electrolyte.

Oxidation-reduction reactions for the Clark cell are:

Reaction at cathode:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Reaction at anode:
$$4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$$

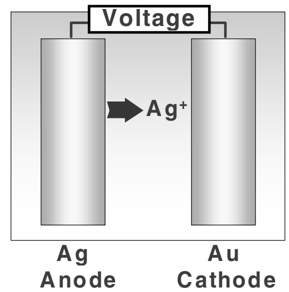

FIGURE 2 -- Clark Polarographic Measuring Cell

The Clark polarographic measuring cell addresses some of the problems associated with a conventional galvanic cell. The polarographic cell requires a polarization voltage to be applied to the electrodes. As long as this voltage is maintained at a constant level, the cell will not be as susceptible to contamination of the electrodes and electrolyte as a galvanic cell. If a contaminating material does permeate the membrane, the cell potential will not shift. A polarographic cell measures the current flow that results from reduction of the oxygen molecules in the cell. Since this current flow is linearly proportional to the amount of oxygen present, potential for errors at low oxygen levels is reduced. Finally, the anode electrode will not be consumed by the electrochemical reaction.

- Ross Polarographic Measuring Cell

Another variation of the conventional polarographic cell is the Ross polarographic cell, shown in *Figure 3*. The reaction cell, which consists of a working electrode (cathode) and a counter electrode (anode), is isolated from the process solution by an oxygen permeable membrane. Like the other measurement cells (galvanic and polarographic), oxygen penetrates the membrane and is reduced at the cathode. Unlike the other measurement cells that consume oxygen without replacing it, the electrochemical reaction of a Ross cell causes the anode to generate an amount of oxygen equal to the amount consumed by the cathode. Measurement current flow is generated by this steady-state diffusion of oxygen from the anode to the cathode. This reaction continues until equilibrium exists across the boundary between the membrane and its surroundings. When the concentration of oxygen in the process changes, oxygen will pass into or out of the sensor until equilibrium is re-established. The new steady-state diffusion rate will result in a new current proportional to the oxygen concentration.

Oxidation-reduction reactions for a Ross Cell are:

Reaction at anode:
$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$

Reaction at cathode:
$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$

Net reaction = Zero (Balanced)

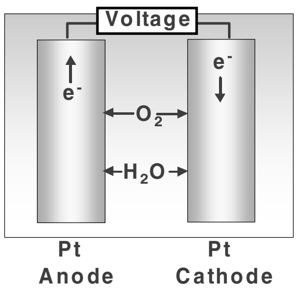

FIGURE 3 -- Ross Polarographic Measuring Cell

By operating at equilibrium, the Ross Cell helps minimize sensor maintenance and extends electrolyte life. The other measurement cells consume oxygen at the cathode without replacing it. When their membrane becomes coated, the oxygen consumed at the cathode will exceed the rate of diffusion through the membrane. This will cause the sensor output to trend toward zero. This cannot happen with a Ross cell because it is producing oxygen at the same rate as it is being consumed. Thus, the Ross cell is not affected by a reduction in the diffusion rate of oxygen through the membrane. Since measurement accuracy is not affected by partial membrane fouling, the sensor will provide accurate readings as long as the membrane is not completely fouled. Measurement at equilibrium also eliminates electrolyte depletion and anode electrode consumption.

Summary

There are many different dissolved oxygen sensor technologies, each with its own advantages and disadvantages. One sensor technology will not fit all applications. Consider the important factors (accuracy, reliability, price, maintenance, etc.) when selecting the correct technology for your application.

A basic galvanic cell depends on the reduction of oxygen molecules to generate a measurement voltage, making it susceptible to contamination of the electrodes and electrolyte. Another problem with the galvanic cell is the consumption of the anode electrode due to the electrochemical reaction necessary for the dissolved oxygen measurement.

The conventional Clark polarographic cell addresses some of the problems associated with a galvanic cell. This measurement technique uses a polarization voltage that is applied to the electrodes. As long as this voltage is maintained at a constant level, the cell will not be as susceptible to contamination of the electrodes and electrolyte as a galvanic cell. Another advantage of the polarographic cell is that the anode electrode consumption is negligible.

The Ross polarographic cell eliminates even more of the typical measurement problems because it operates at equilibrium, which minimizes sensor maintenance and extends membrane cartridge life. The accuracy of the measurement is not affected by partial membrane fouling, so the sensor provides accurate readings as long as it is not completely fouled. Measurement at equilibrium also eliminates electrolyte depletion and electrode oxidation formation which would normally consume the electrodes.

Finally, the unique non-membrane (Züllig) galvanic design dissolved oxygen sensor is quite different from membrane sensor types. The sensor does not rely on diffusion through a membrane to complete the dissolved oxygen measurement. Electrolyte and membrane are eliminated and electrodes are kept clean with a rotating diamond grindstone. This design enables the dissolved oxygen system to maintain its calibration over a longer time period and significantly reduces the frequency of cleaning. This sensor is designed for trouble-free operation in harsh wastewater treatment environments, making it ideal for applications where heavy concentrations of grease or oil exist.