Monitoring ORP leads to successful treatment

ORP and REDOX are terms which confuse many users. Here is an article that takes some of the mystique out of these terms and the measurement itself, and helps the reader to form a basic understanding of how the sensor works and why it can be useful.

Mike Ross

- *Cutaway view of a fitting used in ORP measurement.*

Oxidation reduction potential (ORP), also known as redox, is the measurement of a solution's oxidising and reducing activity. The ORP process can be compared to stock-market activity: Whenever one material is oxidised, another material is reduced (for someone to purchase a share, another person must sell that share).

Fire is an example of rapid oxidation and reduction. The carbon from a hydrocarbon combines with oxygen from the air to make CO_2 while hydrogen from the hydrocarbon combines with oxygen to make H_2O. The carbon and hydrogen have been oxidised while the oxygen has been reduced.

Rust is a slower example of an oxidation/reduction reaction. Oxygen combines with iron to form iron oxides. In this process, the iron is oxidised and, once again, the oxygen has been reduced.

Fire and rust illustrate the basic characteristics of oxidation/reduction processes; namely, that materials involved undergo chemical changes. More pertinent to water treatment is the oxidation/reduction potential of chlorine reacting with bacteria or algae.

Bacteria and algae essentially are hydrocarbons, and chlorine is a powerful oxidising reagent. Even though it can't really be seen, chlorine destroys bacteria and algae by literally burning their carbon and hydrocarbon into CO_2 and H_2O. When all of the oxidising and reducing materials have reacted, an equilibrium is reached and there is usually a surplus. It is this surplus material that creates the oxidation or reduction potential of a solution.

Measuring ORP

ORP can be measured by colorimetric or potentiometric means. Colorimetric techniques take advantage of the fact that certain chemicals can change their colour as for example; the amount of chlorine in water changes and has a yellow colour depending on concentration. Colorimetric kits are inexpensive but subject to errors from the colour of the water and the subjective comparison by the interpreter. They are not well-suited for monitoring or control applications.

The principle of potentiometric operation is that whenever a metal is exposed to varying concentrations of chemicals, a millivolt level (mV) electrical potential is generated. The millivolts generated are a function of the type of metal used, the type and concentration of the chemicals in solution and the solution's temperature. By selecting a particular metal, a correlation to the chemical type and concentration can be made and useful information obtained.

In actual practice, a noble metal (a pure, elemental metal) is always used in ORP electrodes because it will not enter into unwanted chemical reactions that can lead to measurement errors. The use of a noble metal is important because the ORP value is a function of both the solution's chemicals and the type of metal in contact with that solution (even different noble metals can give different readings in the same solution).

Platinum is normally the metal of choice; however, gold and other noble metals such as silver can also be used.

The ORP potential generated at the platinum electrode varies as the chemicals in the solution change. This signal is compared to that of a reference electrode (one so constructed that its potential remains constant even when the chemicals in the solution change). The most commonly used reference electrode is a silver or silver chloride (Ag/AgCl) type.

Unlike the pH electrode which responds only to hydrogen ion activity, an ORP electrode responds to chemical reaction activity in which material is converted from one oxidised state to another through electron transfer. There are many similarities between pH and ORP measurements as shown below.

- Both are examples of electrochemical measurements
- Both are forms of batteries and have limited lives
- Both require a special high impedance mV input circuit
- Both use the same Ag/AgCl reference electrode design
- pH electrodes are designed to respond to hydrogen ion activity, while ORP electrodes respond to all ions that have oxidising or reducing activities
- pH measuring electrodes are constructed of hydrogen ion sensitive glass. ORP electrodes are constructed of a noble metal
- pH measuring electrodes can be made to automatically compensate for temperature changes, but the effect of temperature on ORP is variable

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Why Measure?

Many industries can benefit from the use of ORP measurements, including waste water treatment applications and the pulp and paper industry. From a water treatment perspective, use of ORP for controlling water disinfections or the growth of algae with chlorine, chlorine dioxide, bromine and ozone in applications such as cooling towers, swimming pools, potable water supplies and a multitude of other sterile water applications is of prime interest. Other oxidisers include fluorine and hydrogen peroxide. It is also a cost effective method of controlling chromate reduction or cyanide destructions in wastewater treatment applications.

The pH measuring electrodes are constructed of hydrogen ion sensitive glass while ORP electrodes are constructed of a noble metal.

On a practical note, ORP electrodes typically reach a saturation point where they begin to indicate a negligible change as the concentrations get higher. As an example, they are not typically effective at chlorine levels over 2.5ppm. With chlorine dioxide, they are effective up to about 0.6ppm.

The ORP measurement is commonly made using a pH meter with a mV scale. The ORP electrode is simply connected in place of the pH electrode and the meter is used in the mV mode. The mV signal generated by the electrode is representative of, for example, the free chlorine in solution. This ORP potential is temperature-dependent; however, temperature compensation is normally not used because the compensation would vary for each different oxidation/reduction reaction occurring, and it is likely that several reactions are taking place at the same time.

Another factor to consider when making ORP measurements is that they can be pH-dependent (remember that pH is a measure of hydrogen ions). For example, chlorine exists in solution as hypochlorous acid (OCl^-). Depending on the pH, this hypochlorous acid will shift its equilibrium to provide more or less free chlorine (this accounts for chlorine reacting more strongly at low pH values — as pH is lowered, more free chlorine is generated).

Even though the concentration of chlorine remains constant, its oxidising power is pH dependent. To obtain accurate residual chlorine information, the pH must either be constant or adjusted.

ORP measurement is slow when compared to a pH measurement. Whereas a pH electrode will respond in seconds, a new or cleaned ORP electrode can take several hours to initially equilibrate or re-equilibrate to a sample. Once equilibrated, an electrode's response time is measured in minutes, not seconds.

ORP measurements can be defined as a measurement of oxidant demand relative to whatever ORP value needed to accomplish a particular disinfection goal. Actual ORP levels required for bacteriological control will vary with use of different oxidisers and makeup waters. Both concentration and activity of the oxidiser will affect the ORP levels. In addition, water

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chemistry-which may inhibit an oxidiser's performance-can affect the ORP levels and affect the choice of oxidising agents.

For example, cyanuric acid is used in swimming pools to minimise the loss of chlorine. The cyanuric acid reacts with the hypochlorous acid to bind it in a form that reduces the free available chlorine. This chemical binding has the net effect of lowering the concentration of chlorine detected by the ORP electrode.

Verifying Electrode Operation

Calibration is not normally required. In fact many ORP meters may not have calibration adjustments. However, measurement error can occur due to contamination or coatings on the electrode. Even though the meter cannot be adjusted, calibration verification can be helpful.

To verify the operation of an ORP electrode, quinhydrone is added to pH buffers 4.0 and 7.0. When added to these buffers, two known, stable ORP solutions will be created. A 7.0 buffer with quinhydrone will produce a solution which will generate 90mV with a platinum ORP electrode. A 4.0 buffer with quinhydrone will produce a solution of 265mV. Other solutions such as Zobel and Lights solution may also be used.

If the electrode responds correctly in the samples, no further steps are required. If the values are incorrect, clean the electrodes measuring surface and reference junction with 5% hydrochloric acid. Scratches to the metal surface should be avoided. However, if acid treatment is not effective, very lightly abrade the metal measuring surface with a 600-grit wet silicon carbide sandpaper using a circular polishing motion. After such abrasive cleaning the electrode may require several hours of soaking in a quinhydrone solution before providing stable readings.

If these cleaning procedures do not restore the electrode's calibration, the electrode will need to be replaced. **AW**

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