ORP: A Valuable Measure of Chemical Reactions

To many potential users of its measurement, ORP is a mysterious term. It has an obscure full name, "Oxidation-Reduction Potential," and an equally obscure alias, "Redox." Additionally, warnings about ORP measurement as being nonspecific and subject to variability with any slight change in chemical constituents add to the level of intimidation.

Despite this, ORP measurement has hundreds of successful applications. Typically, ORP sales are five percent of pH sales. More than 20,000 ORP control loops are purchased each year.

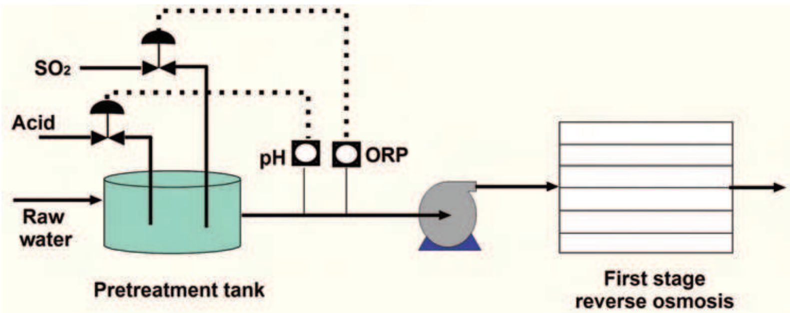

Figure 1. ORP for dechlorination of reverse osmosis feedwater.

The best way to simplify ORP in practice is to forget the long, technical discourses about it. The concept is best understood by examples coupled with some basic information.

Two General Axioms

Before briefly covering specific examples of ORP use, let us review two axioms that apply broadly:

1. ORP measurement is typically used to keep a slight excess of an oxidizing or reducing agent in solution. Oxidizers include: chlorine (Cl_2), ozone (O_3), and hydrogen peroxide (H_2O_2); reducers include: sulfur dioxide (SO_2), sodium sulfate (Na_2SO_3), and sodium hyposulfate ($NaHSO_3$).

2. In a majority of applications the process pH must be controlled separately for ORP to be successfully measured and controlled. There are exceptions - such as in disinfection (within reasonable pH levels) - but it's wise to assume that pH control is required for proper ORP measurement.

Example 1: Disinfection and ORP

One common application for ORP measurement is to control addition of an oxidizer to water to disinfect it. Common oxidants are chlorine, chlorine dioxide, sodium hypochlorite, ozone or bromine. Typical applications include swimming pools, drinking water, wastewater and cooling tower waters.

In these disinfection applications, the ORP measurements indicate trends related to the oxidant residual in the water system. ORP millivolt readings will increase from lower values (typically 100 to 150 mV) as the oxidant additions permeate throughout the water. The residual oxidant (its oxidizing potential) correlates well with the ORP mV reading. Using a continuous measurement of ORP, the residual oxidant can be controlled to a desirable level, ensuring disinfection.

Example 2: ORP for Control of Chlorine Removal Before R.O. Membrane

The cellulose acetate filter medium often found in reverse osmosis (R.O.) membranes requires pretreatment of the influent water to lower the pH. These types of membranes perform best between 5.5 and 6.0 pH, but normal feedwater is between 6.5 and 9.0 pH. Thin-film membranes, commonly used in semiconductor and other very clean water applications, may require pretreatment to the 7 to 8 pH range but also require removal of chlorine because its presence in treated feedwater (drinking water) can destroy such R.O. membranes.

A reducer such as sulfur dioxide or one of its salts (like sodium sulfite, sodium bisulfite, sodium metabisulfite or sodium thiosulfate) is used to dechlorinate the raw influent water, Fig. 1. If this water has low alkalinity (as is true of most municipal water with low conductivity, the sulfur dioxide and most of its salts will lower pH while reducing the chlorine.

Normal reducer feed rates can eliminate need for further pH control, while high feed rates may require that pH be raised back up with a different reagent. Sodium sulfite will increase pH, sometimes to the point where it may have to be lowered with a separate reagent.

Sulfur dioxide or one of its salts will lower the feedwater ORP. A typical ORP setpoint of 150-200 mV is used to assure that all chlorine has been reduced. Some plants feed to lower setpoints -- even into the negative mV range -- to assure that all chlorine compounds are scavenged. Generally though, overfeeding the reducer to these lower ORP levels is unnecessary and wasteful.

Example 3: ORP used in Chlorine Gas Scrubbers

ORP can control scrubbers that remove chlorine-based gases from industrial exhaust gas. A solution of NaOH showers down onto the scrubber media as the gas to be scrubbed rises upwards through it, as indicated in Fig. 2. The process produces sodium hypochlorite, salt (NaCl) and other oxidation compounds.

Scrubbers use weak or strong caustic solution, depending on the amount and types of chlorine gas compounds being "scrubbed." Light-duty scrubbers typically use a weak caustic solution, while heavy-duty scrubbers, such as found in pulp mills, use a strong solution. Many pulp mills have switched to "white liquor" instead of straight caustic. White liquor is a mixture of sodium hydroxide, NaOH, and sodium sulfide, Na_2S. These are manufactured at the mill and used for pulping the wood.

White liquor has a highly negative ORP (mV value) -- more so than straight sodium hydroxide. As a result, mills using white liquor control to a lower ORP.

Having a strong sulfide content, white liquor quickly destroys an ORP reference cell that contains silver chloride. Reference cells that avoid use of silver chloride are recommended for scrubber service or other applications involving sulfides.

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In a large scrubber, such as those in pulp mills, the ORP sensor should be installed in a bypass line, as shown. Large scrubbers often have high flow velocities and pulsing pressures. The bypass line protects the sensor from such severe operating conditions. On large scrubbers it is common to see both pH and ORP sensors, with pH used as a check on the ORP sensor.

In smaller scrubbers the ORP sensor can be placed directly in the main line after the reservoir (sump). Generally, it is not advised to place the sensor directly in the sump because of poor mixing and short circuiting of solutions in that location.

Typical ORP setpoints for scrubbers are as follows:

- Small scrubber with weak caustic, -100 to +100 mV

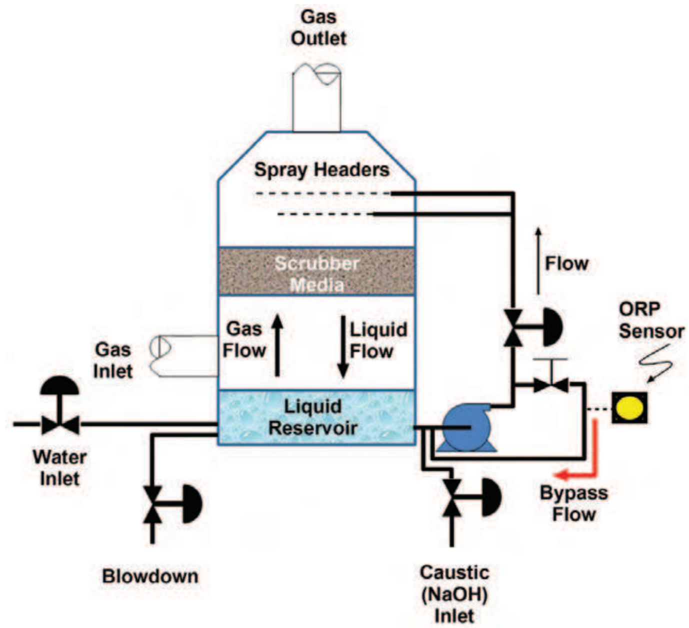

Figure 2. Chlorine gas scrubber controlled by ORP.

- Large scrubber with strong caustic, -100 to -200 mV
- Pulp mill scrubber with white liquor, -350 to -450 mV

Scrubbers for hydrogen sulfide, H_2S, and other gases operate similarly, though different reagents, such as sodium hypochlorite, are used and ORP setpoints tend to be less negative (more positive). If sulfides are present in the gases or scrubbing liquor, use of reference cells containing silver chloride are to be avoided.

Sidebar: A Few ORP and pH Basics

Like pH, ORP measurements are small voltages (millivolts) created by one or more chemicals, usually dissolved in water. In such aqueous solutions, a chemical like table salt (NaCl) breaks down (dissociates) into ions (e.g., Na+ and Cl-) that can interact with ions of other chemicals added into the solution. This is called a chemical reaction and is quite specific due to the ions involved. Measurements of both ORP and pH are broadly referred to as solution potential measurements. A simple example of neutralization helps to define terms used in this chemical reaction.

The following equation represents the chemical reaction for the process that involves interaction between an acid (such as hydrochloric acid HCl) and a base (sodium hydroxide NaOH) to form the products NaCl (salt) and water (HOH or H2O):

$$H^+ Cl^- + Na^+OH^- = Na^+Cl^- + H^+OH^- \text{ (water)}$$

This is a typical chemical reaction, with the acid and base being the two reactants in a neutralization process. A salt and water are the products when the reaction is completed. At that point, both the acid and base no longer exist; they neutralized each other.

The pH scale—Suppose a neutralization reaction starts with a solution that's all base, and acid is gradually added. At first the mixture would be highly basic, with few hydrogen ions in solution. The solution's pH, a measure of H+ ions present, would be near 14 on the pH scale, which ranges from 2 to 14. The fewer the hydrogen ions present, the higher the pH reading. As more acid is added and hydrogen ions increase, the pH readings would decrease, until, at pH 7, the neutral point would be reached.

If the original solution is pure acid to be neutralized it with a base such as NaOH, the initial pH for all acid would be 2 . As the base solution is added, the pH gradually rises to 7 when neutralization is reached. A sensor sensitive only to the solution potential created by the hydrogen H+ ions is used to measure the solution's pH.

All ions affect ORP - With ORP, the two main reactants are an oxidizing agent (oxidant) and a reducing agent (reductant). Ions of the two can interact in a manner analogous to that of an acid-base pair to a "neutral point." In contrast to pH measurement, ORP analyzers pick up voltages from all ions in solution. That includes the hydrogen ions specific to pH, which often makes it necessary to include both pH and ORP control in many applications.

For more information, please contact:

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