



Understanding ORP Systems

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Oxidation Reduction Potential (ORP) is a useful online process measurement that is often misunderstood and, as a result, is under-utilized. ORP is related to the concentration of oxidizers or reducers in a solution, and their activity or strength. It provides an indication of the solution's ability to oxidize or reduce another material. Because oxidizers and reducers are relatively unstable in solution, the only ones normally present in a system are those that have been added for a specific purpose.

Typically, oxidizers and reducers are added for such operations as water disinfection, bleaching, cyanide destruction, chrome reduction and metal etching. Commonly used oxidizers include chlorine, bromine, ozone, sodium hypochlorite and hydrogen peroxide, while sodium

bisulfite (also known as sodium metabisulfite) and sulfur dioxide are well-known reductants.

These chemicals have the ability to oxidize (accept electrons) or reduce (donate electrons). When present in a solution, the presence of an oxidizer will raise the ORP value, while a reducer's presence will lower the ORP value. The greater the concentration of an oxidizer or reducer in the solution, the faster will be the rate of reaction.

The actual ORP value of a solution depends on both the concentration and activity of the oxidizer present. The table on p. 3 provides a comparison of commonly used oxidants and their oxidation potentials relative to that of chlorine. It shows that ozone, for example, is one-and-one-half times as active an oxidizer as is chlorine. Thus, on a per molecule basis, one needs less ozone than chlorine to achieve the same ORP value.

What it is

For most purposes, water is generally considered "neutral" with regards to its ORP value. Actually, water is a very weak oxidizer, a result of oxygen dissolved in nearly all water samples. (Oxygen itself is a very weak oxidizer.)

Consider the reaction between water and a mold steel, where corrosion (oxidation of the steel) will occur. Here, water has an ORP value of between 200 and 300 mV, a range that is considered the "zero" point. The addition of oxidizing chemicals increases this value to greater than 300 mV, while the addition of reducing chemicals suppresses it to less than 200 mV.

The ORP value of the solution quantifies the true ability or potential that the solution has to oxidize or to reduce. In most applications, this property is more important than the absolute concentration of the oxidizer or reducer in the solution.

Optimize reactions by measuring oxidation — reduction potential



FIGURE 1. Besides ORP controllers such as this one can measure pH, 4-20 and 0-20 mA, and 0- to 5- and 0- to 10-V d.c. They come equipped with relays for alarms and on-off control, and various analog outputs

In water disinfection applications, the ORP value of the solution is more meaningful than are ppm (parts-per-million) measurements of residual (free) or total chlorine. This is because the equilibrium between two forms of the chlorine in the water shifts with changing pH.

The molecular form of free chlorine in water is HOCl, or hypochlorous acid, a strong, fast-acting

oxidizer. As the pH increases, the HOCl converts to its ionic form, OCl^- (the hypochlorite ion), a weaker, slower acting oxidizer.

As a result, the pH of a solution containing a given concentration of chlorine by itself would not be an indicator of this effect. Further, if the chlorine is combined with an amine or with a stabilizer, the "total" chlorine concentration is affected. The mixture does not provide oxidizing capability, however.

When using ORP for process control, it is important to realize that it is the presence of the oxidizer or reducer that is being monitored, and not the chemical it is reacting with. This is extremely important to remember in such processes as cyanide destruction or chrome reduction.

The ORP value of a process solution will generally relate to a rate of oxidation or reduction. Although many reactions, such as disinfection, can occur almost immediately, others, such as cyanide oxidation, require significant retention time to

ensure nearly complete destruction.

Complete control of cyanide oxidation requires control of the ORP (i.e., the concentration of chlorine), retention time in the system (flowrate, if the process is continuous), and the amount of cyanide loading (ppm). If the loading of the process increases significantly, or the retention time decreases, then increasing the ORP value will enable a faster rate of destruction, and the process will thus continue to operate in compliance.

Of course, continuous operation of any process at a higher ORP setpoint will result in the use of greater amounts of oxidizer. Figure 1 shows a typical device for automatically monitoring and controlling such a process, to ensure that it stays within prescribed constraints.

ORP measurement systems

The measurement of ORP is very similar to that of pH. Platinum is sensitive to the activity level of the electrons in the same manner as pH-sensitive glass is sensitive to the

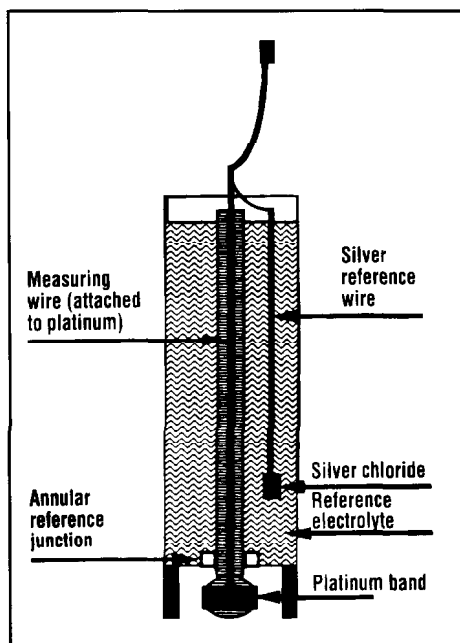


FIGURE 2. ORP and pH electrodes have quite similar constructions.

presence (activity) of the hydrogen ion. The ORP electrode is nearly identical to a pH electrode, having a platinum surface (generally either a platinum rod or band) for the measuring half of the electrode, and a silver-silver chloride reference wire in a potassium chloride reference electrolyte for the reference half (Figure 2). In practice, there are many other configurations that can be used as well for measuring ORP.

The electrode can be considered a battery, where voltage flows from the measurement side to the reference side of the electrode. The function of the reference electrolyte is to complete the circuit to the solution being measured. For this reason, it is important that the reference junction remain clean and free-flowing.

Maintenance of an ORP electrode is similar to that for a pH electrode: The electrode should stay in solution at all times; the system requires routine cleaning and calibration to compensate for electrode degradation; and, the electrode will have to be replaced on a regular basis (every 1-2 years, depending on the application).

Cleaning an ORP electrode is generally best done with a 5% hydrochloric acid solution. This solution is most effective for solubilizing the various hard-water deposits that may form in the reference junction. It is important to keep the reference junction free-flowing, to enable the reference electrolyte to carry the reference voltage back to the solution.

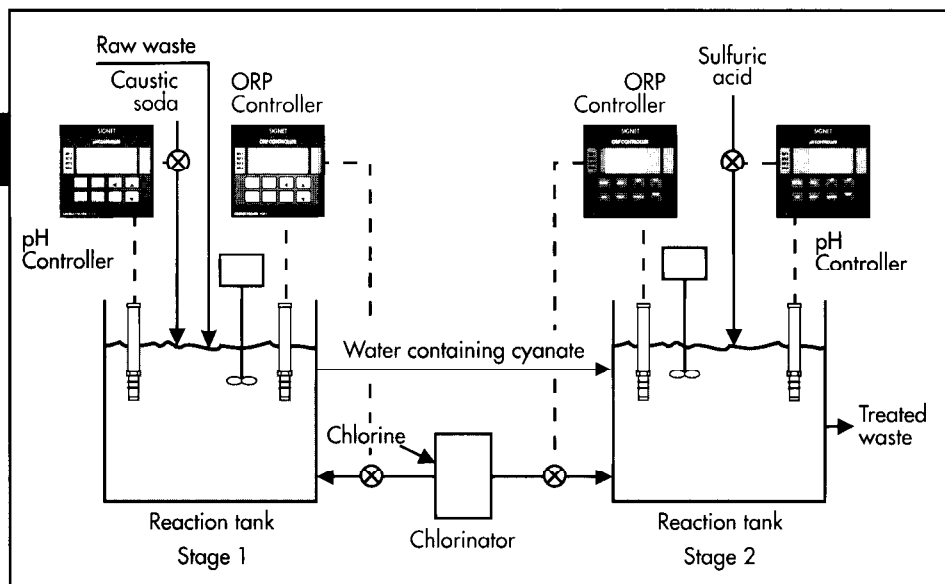


FIGURE 3. A typical control system for two-stage cyanide oxidation includes instruments for both ORP and pH measurement.

COMPARISON OF COMMONLY USED OXIDANTS

| Oxidant | Oxidation potential (volts) | Oxidation potential (relative to chlorine) |
|------------------------|-----------------------------|--|
| Fluorine | 3.05 | 2.25 |
| Ozone | 2.07 | 1.52 |
| Hydrogen peroxide | 1.78 | 1.30 |
| Potassium permanganate | 1.68 | 1.25 |
| Chlorine dioxide | 1.57 | 1.15 |
| Chlorine | 1.36 | 1.00 |
| Bromine | 1.07 | .79 |

Calibration should be performed on a regular basis, with the frequency dependent upon the cleanliness of the application and the desired accuracy of the system. Once per month is an average calibration frequency for most processes. Calibration is best accomplished in freshly made saturated solutions of quinhydrone (a dry, light-sensitive powder) in buffer solutions of pH 4.0 and 7.0.

Quinhydrone is a weak reducing agent whose activity changes with pH. By placing the quinhydrone in known pH solutions, one can produce standard ORP solutions of 87 mV (7.0 pH), and 264 mV (4.0 pH). These two solutions are used to

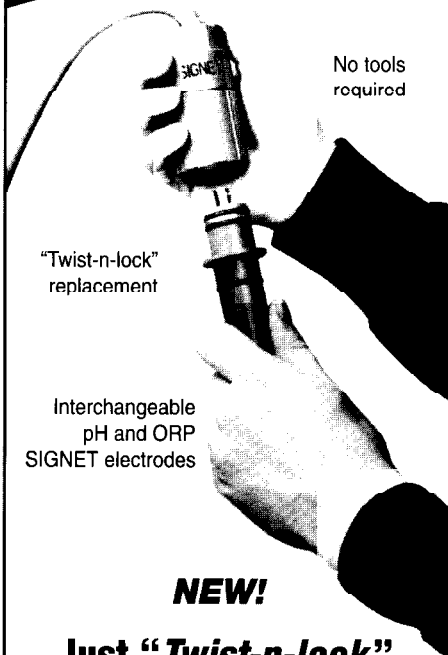
monitor the offset (standard) and span (slope) of the electrodes as they degrade over time. The quinhydrone should be stored in a cool, dark place, and fresh solutions should be made up prior to any calibrations that may be done.

Some typical applications

The common ORP applications include water disinfection, cyanide destruction, chrome reduction, metal etching, H₂S destruction, and dechlorination. Some examples of the reactions follow:

- **Cyanide oxidation** — Here, cyanide is converted to cyanate in the first stage of the process (Figure 3). In the second stage, the cyanate is further converted to carbonate and

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nitrogen. The equations for these reactions are as follows (oxidizer is chlorine gas):

Stage 1:

1. $\text{NaCN} + \text{Cl}_2 \rightarrow \text{CNCl} + \text{NaCl}$
2. $\text{CNCl} + 2\text{NaOH} \rightarrow \text{NaCNO} + \text{NaCl} + \text{H}_2\text{O}$

Stage 2:

1. $2\text{NaCNO} + 4\text{NaOH} + 3\text{Cl}_2 \rightarrow 2\text{CO}_2 + \text{N}_2 + 6\text{NaCl} + 2\text{H}_2\text{O}$
2. $\text{CO}_2 + \text{NaOH} \rightarrow \text{NaHCO}_3$
3. $2\text{NaCN} + 5\text{Cl}_2 + 10\text{NaHCO}_3 \rightarrow 2\text{NaHCO}_3 + \text{N}_2 + 10\text{NaCl} + 4\text{H}_2\text{O} + 10\text{CO}_2$

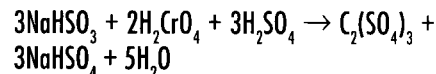
In stage one, the cyanide converts from an ionic charge of -1 to an ionic charge of +1, a loss of two electrons. Likewise, the chlorine is reduced, with the two chlorine ions each accepting one electron, for a total transfer of two electrons.

In stage two, two cyanate molecules (with a CN^{+1} ion charge) convert to two carbon dioxide molecules, each with a carbon charge of +4, and one nitrogen molecule with a zero charge. This equals an electron change of +6 (+3 for each carbon ion). These six electrons are accepted by the three chlorine molecules as they convert to six Cl ions.

The cyanide oxidation process is hazardous for many reasons. For one, users must be trained to take precautions when handling chlorine gas. In addition, if the pH control of the first stage does not allow a sufficient supply of sodium hydroxide, the toxic intermediary, cyanogen chloride (CNCl), will be released.

• **Chrome reduction** — In chrome reduction, hexavalent chrome, with a +6 charge, is converted to the trivalent form, which carries a +3 charge. It is clear from the nomenclature that the chrome is accepting free electrons. Likewise, the sulfite ion contains a sulfur ion with a +6

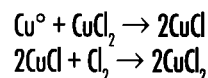
charge. It is oxidized to the sulfate ion, where the sulfur ion has a +8 charge. The balanced reaction with sodium bisulfite and a total transfer of six electrons is as follows:



The importance of reducing the hexavalent chrome is twofold. First, the trivalent form of the chrome is less toxic than the hexavalent form. Second, it is quite easy to precipitate the trivalent chrome as chrome hydroxide, in a standard metal-hydroxide precipitation process.

• **Metal etching** In such processes, metal is removed, or oxidized, by conversion from its zero-charge metallic state to its charged ionic form. One example of this is copper etching, which is done extensively in the printed-circuit industry. In this case, metal Cu^0 is converted to Cu^{+2} . A dual oxidation-reduction reaction occurs with the liquid etchant, cupric chloride (CuCl_2), and the intermediary, cuprous chloride (CuCl).

In the first step, copper metal is oxidized to its +1 charged state by the cupric chloride. The +1 cuprous chloride is then oxidized to cupric chloride by chlorine gas. The complete process produces additional etchant, instead of a diluted byproduct. The reactions are as follows:



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About the author

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