White paper

# ABB Analytical – ORP/pH
# Chemical and mining

## ORP, like pH, a valuable measure of where a reaction stands

This document outlines six real-world ORP applications, in non-technical style, that will give the uninitiated reader a basic idea of the useful roles of ORP instrumentation

To many potential users of its measurement, ORP is an intimidating term. In the first place 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.

The best way to simplify ORP in practice is to forget the long, technical discourses about it. The concept is best understood by examples (see Sidebar "A Few ORP Basics" as background for these examples).

### 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 (Cl2), ozone (O3), and hydrogen peroxide (H2O2); reducers include: sulfur dioxide (SO2), sodium sulfate (Na2SO3), and sodium hyposulfate (NaHSO3).

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) and bleach making -- 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 in bleach making

Sodium hypochlorite (an oxidizing bleach) is made by mixing chlorine and sodium hydroxide (NaOH), which is also called caustic soda, or simply caustic. This is an easy ORP application to understand. Start with strong caustic and add chlorine until you get the right ratio of chlorine and caustic.

The chemical reaction is:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

Initial strength of the caustic will determine the overall concentration of bleach and its stability. The amount of chlorine will determine the pH and the bleaching effectiveness of the solution. By itself, caustic will produce low, negative ORP readings (in millivolts). Chlorine, being a very strong oxidizer, will create high ORP readings. The two are mixed to specific ratios that can be determined very effectively with an ORP controller.

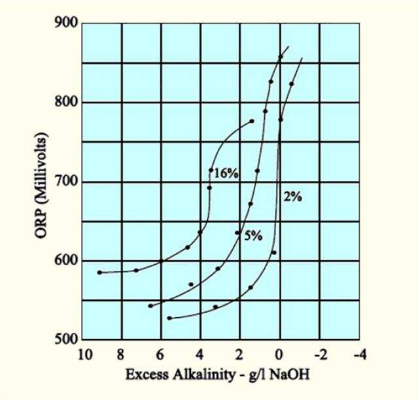


*Figure 1. ORP values of various concentrations of sodium hypochlorite solutions.*

Excess caustic is NaOH that has not been converted into bleach. High excess caustic will mean a high pH bleach solution and a corresponding low ORP. As the chlorine content increases, excess caustic decreases and the ORP reading increases. Chlorine can be added to such strength that the hypochlorous ion, HOCl, begins to appear (below pH 10). Continuing to add chlorine can actually turn the solution acidic with a very high ORP.

Sodium hypochlorite bleach can be made in many different strengths and ratios. Typical chlorine bleach bought in the laundry section of stores is weak and below 10.5 pH. Bleach used for disinfection is stronger, but typically contains even more chlorine; that is, it has a lower caustic to chlorine ratio. Industrial bleaching operations, such as in pulp and paper applications, typically run to higher caustic ratios.

Figure 1 graphically represents the relationship between ORP and bleach liquor composition, indicating the differences in various beginning caustic strengths.

ORP sensors are used instead of pH sensors because they offer more resolution and tighter control. Also, they last longer because pH sensors lose efficiency more quickly in the strong caustic solutions.

## Example 3: ORP used in chlorine gas scrubbers

Closely related to bleach making is the use of ORP to 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 Figure 2. The process produces sodium hypochlorite, salt (NaCl) and other oxidation compounds.

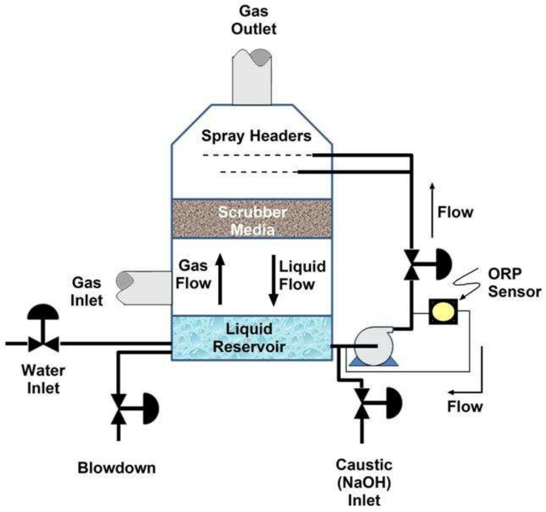


*Figure 2. Chlorine gas scrubber controlled by ORP.*

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.

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 follow:

- Small scrubber with weak caustic, -100 to +100 mV
- 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 more positive (less negative). If sulfides are present in the gases or scrubbing liquor, use of reference cells containing silver chloride are to be avoided.

## Example 4: ORP in the treatment of metal wastes

ORP measurements are often used in the treatment of harmful metal wastes. A typical application is destruction by reduction of chrome waste from metal plating operations. The chromium is contained in a chromate ion, $Cr_2O_7^{-2}$. Here it is in the hexavalent form, $Cr^{+6}$ and is very toxic. It must be reduced to the trivalent form, $Cr^{+3}$ so that it can be precipitated out of the waste solution in a second reaction.

As shown in Figure 3, ORP controls $SO_2$ addition in the first stage of reducing hexavalent chromium. In this stage, pH must be controlled very rigidly because the hydrogen ion $H^+$ activity has a major effect on the ionic form of the reactants, so it affects the ORP values of all the reactants. The figure shows pH in the first stage (left) controlled between 2.0 and

2.5 pH (highly acidic). Even this 0.5 pH variance will affect the ORP reading (in the 250 to 300 mV range), so it is advised that control be even tighter.

The system controls pH by adding sulfuric acid, $H_2SO_4$. The reducing agent, sulfur dioxide gas, $SO_2$, is then added to the solution to an ORP reading around 280 mV. This reduces the hexavalent Cr to its trivalent form.

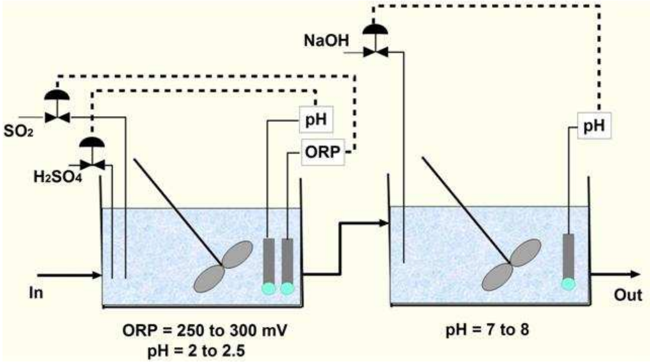


*Figure 3. Hexavalent chromium reduction is one ORP application where pH is critical.*

In the second stage (at right), sodium hydroxide, ammonium hydroxide or lime is added to precipitate out the trivalent chromium as chromium hydroxide sludge. Changing the reductant from sulfur dioxide to ferrous sulfate or similar reducer will require a change in the ORP setpoint, e.g., -550 mV for ferrous sulfate.

## Example 5: ORP in the Treatment of Cyanide Wastes

In the oxidation of cyanide wastes, ORP is used in both stages of this two-stage process, versus only the first stage in chrome waste treatment.

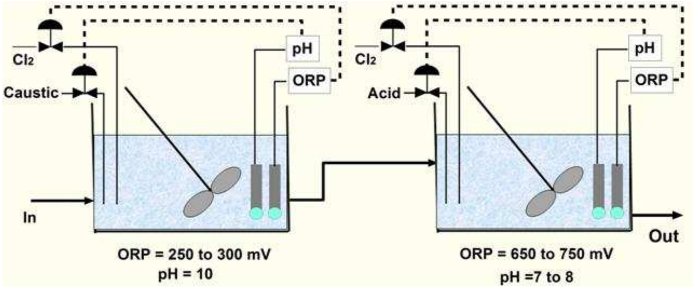


*Figure 4. ORP controls chlorine addition for cyanide destruction by oxidation. The second stage neutralizes the wastewater and adjusts pH*

Like the reduction of hexavalent chromium, the oxidation of cyanide requires rigorous pH control. In the first reaction tank, pH is raised to 10.0 with lime or sodium hydroxide (see Fig. 4). Below pH 10, cyanide turns into the toxic gas, hydrogen cyanide, HCN. So it becomes very critical to worker safety that this pH be preferably controlled slightly above 10. Chlorine is then added to turn the cyanide, $CN^-$, into cyanate ion, $CNO^-$. An excess of chlorine is used, with the typical ORP setpoint being +300 m , at which value addition of $Cl_2$ is stopped.

The second stage neutralizes the wastewater, promoting more oxidation and helping to meet limits on the discharge pH. Sulfuric acid typically reduces the pH to about 8.5, permitting more rapid oxidation. The second stage must not let pH levels fall below 7, however, or highly toxic hydrogen cyanide may result in the event of incomplete first-stage oxidation. The addition of chlorine under pH control completes the oxidation to sodium bicarbonate, NaHCO3 plus harmless nitrogen and sodium chloride. The ORP setpoint for the second stage ranges around 700 mV.

## Example 6: ORP for control of chlorine removal before reverse osmosis 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.

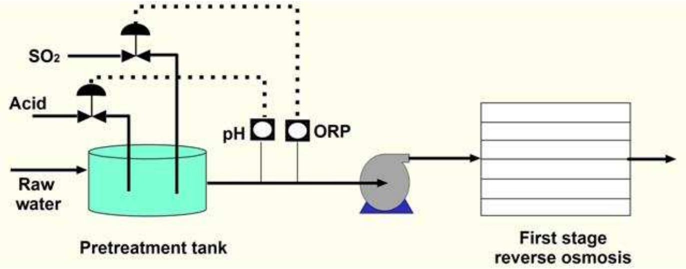


*Figure 5. ORP for dechlorination of reverse osmosis feedwater.*

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. 5. If this water has low alkalinity (as is true of most municipal water with low conductivity, < 150FS), 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.

## 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 common 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 and we will use a simple example of neutralization to define more terms used in this chemical reaction. Here's the chemical equation for the process that involves interaction between an acid (hydrochloric, HCl) and a base (sodium hydroxide, NaOH) to form the products NaCl and water (HOH, H2O):

H+ Cl- + Na+OH- = Na+Cl- + H+OH- ( 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

If neutralization starts with all base and acid is gradually added, at first, the mixture would be highly basic, with few hydrogen ions in solution. Then, the solution's pH, a measure of H+ ions present, would be 14 on a scale with a range of 2 to 14. As more acid is add, the pH would decrease, until, at pH 7, the neutral point would be reached.

If we start with all acid and want to neutralize it with a base, like NaOH, pH for all acid would be 2. As the base solution is added, the pH gradually rises to 7 when enough base is added to neutralize all acid. A sensor sensitive only to the solution potential created by the H+ ions is used to measure pH.

## All ions affect ORP

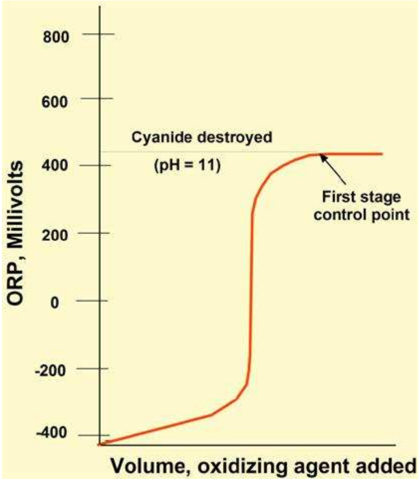
With ORP, the two main reactants are an oxidizing agent (oxidant) and a reducing agent (reductant). Ions of the two can interact in a manner analogous to that of an acid-base pair to a "neutral point." Here, however, only the ions' negatively-charge electrons are involved. For example, a hexavalent chromium, Cr +6 ion that is highly toxic is reduced to the harmless trivalent (Cr +3) form by gaining three electrons for the reducing agent. See Example No. 4.

For the cyanide destruction example of Example No. 5, the figure below shows a typical curve of ORP millivolts vs. volume of added oxidizing agent. Note that the ORP mV reading for complete cyanide oxidation can be the setpoint for an ORP controller.

In contrast to pH measurement, ORP analyzers pick up voltages from all ions in solution. That includes pH ions, which is why you see pH control included in some of the article examples.

## ORP instrumentation

Details of equipment for ORP measurement and control are beyond the scope of this article. For those familiar with equipment for pH instrumentation, the methods used are very similar. The sensors both have an electrode assembly with two half cells -- a measuring electrode and a reference electrode. Immersed in a solution, this assembly acts like a voltaic cell to produce a small voltage. The same types of amplifiers and other accessory equipment can be adapted for ORP and pH measurement and control. ORP instruments read out in millivolts that can be positive or negative, depending on the reactants involved.



*Typical curve showing how an ORP controller can be set to assure total destruction of cyanide via oxidation by chlorine, discussed in Example 5. Note the characteristic S curve for such reactions, indicating how quickly ORP decreases for inadequate additions of chlorine.*

*Source: Lipták, Béla G., Instrument Engineer's Handbook, Vol. I, p. 1512, CRC Press, Boca Raton, FL, 2003.*

WP_N_ORP_Chemical_Mining_5-27-10

## Contact:

**ABB Instrumentation**
125 East County Line Road
Warminster, PA 18974 USA
Tel: +1 215 674 6000
Fax: +1 215 674 7183
www.abb.com/measurement

Power and productivity
for a better world™