

ORP Measurement in Pure Water

Application Note AN-0118

ORP (Oxidation-Reduction or redox Potential) measurement is used to indicate the presence of oxidizing or reducing conditions in water. In pure water treatment, ORP is most commonly used to assure removal of chlorine or other oxidizing agent ahead of membranes or deionization resins that could be damaged by oxidation. It can warn if the bisulfite feed or carbon bed is not properly removing the chlorine. ORP is also used in other process and wastewater applications, including monitoring reducing conditions in power plant cycle chemistry, covered later in this document.

| | Oxidizing Agents | Reducing Agents |
|--------------------------|---|--|
| Example chemicals | Chlorine, hypochlorite, peroxide, ozone, permanganate | Bisulfites, activated carbon, hydrazine |
| Typical reaction | $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ | $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$ |
| Electrochemical response | accepts electrons, raises ORP | donates electrons, lowers ORP |

ORP Significance

The correlation between the concentration of chlorine or other oxidizing or reducing material and ORP varies. ORP is logarithmically related to concentration, however, the variables of pH, temperature and other oxidizing or reducing materials in the water can cause ORP response to shift significantly. For this reason there is no reliable conversion from ORP in millivolts to concentration in parts per million or billion.

In moving from an oxidizing to a reducing condition with extremely small (parts per billion) concentration changes, the ORP typically drops several hundred millivolts. It is very sensitive in detecting the change and is therefore quite useful as a go/no-go alarm parameter. In alarm applications, the exact setpoint value is usually not critical. However, where ORP is used to control reagents feed, more precision is needed in establishing the control point. A titration curve illustrates ORP response and the considerations in establishing a setpoint.

Dechlorination

An ORP titration curve of dechlorination shows the type of response that would be expected for treatment of an off-line grab sample. Chlorinated water in this example gives an ORP of over 700 mV on the left. As small amounts of reducing bisulfite solution are added, the ORP drops in a very non-linear fashion. As the chlorine is all reacted and an excess of bisulfite accumulates, the response reaches a plateau near 350 mV to the right. It is important to establish the setpoint somewhat above the plateau to prevent wasting bisulfite or causing false alarms. The sensitivity of this measurement is apparent from the steep portion of the curve which is the transition from oxidizing to reducing conditions. Continuous processes are controlled to operate near a single point on such a curve.

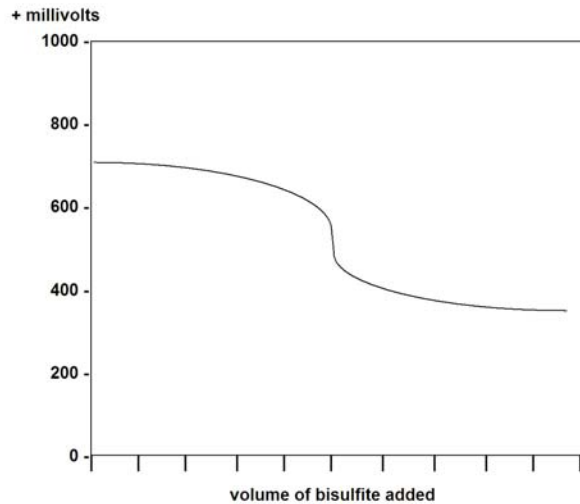


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NOTE: This is only an example titration curve. The curve for a specific installation may be shifted significantly from these millivolt values but the basic shape will be similar for the dechlorination reaction. On-line experience is necessary at startup to establish the particular millivolt operating range and setpoint for an application

The best practice to determine a setpoint for control is to use a colorimetric or other sensitive test for chlorine or bisulfite concentration as a reference. The ORP existing at the time the desired concentration is reached is an appropriate setpoint value. Test kits for these materials are readily available.

Typical ORP Titration Curve for Dechlorination



Power Plant Reducing Cycle Chemistry

Power plants that include copper alloy feedwater components must control dissolved oxygen to very low concentrations to minimize corrosion. This is usually accomplished with the use of a reducing agent or oxygen scavenger such as hydrazine or a reducing amine. While dissolved oxygen measurement is sometimes used to monitor this, it has been found that ORP is more closely related to the actual conditions that affect the passive layer of metal oxides in the feedwater train. In addition, ORP is sensitive to excess feed of reducing agent that can lead to flow accelerated corrosion.

In reducing cycle chemistry control, it has been found that the feed of reducing agent can be based on ORP. The measured ORP for reducing conditions typically goes to -100 to -350 mV, depending on the particular plant and other cycle chemistry parameters. The setpoint should be determined based on long-term operation where iron and copper corrosion product concentrations are minimized. Too high ORP can allow oxidation conditions to affect the copper; too low ORP can contribute to slow accelerated corrosion of iron piping.

If an ORP titration curve could be developed for a power plant with ORP vs. hydrazine feed, it would have a shape similar to the previous figure for dechlorination but would be shifted downward 500 to 600 mV.

ORP Instrumentation

ORP sensors and instrumentation are very similar to pH. However, the measuring electrode is an inert metal--platinum or gold. The metal electrode merely picks up the ORP millivolt signal -- the solution's tendency to contribute or remove electrons from its surface. The reference electrode completes the circuit and adds in its own (nearly constant) potential. The instrument measures the combined potential and displays it directly in millivolts.

There is generally no calibration of ORP sensors. Direct, absolute millivolts are the usual unit of measure. (Because ORP instruments are typically pH instruments operating in a millivolt mode, calibration is possible which yields a relative millivolt reading. ORP standard solutions are available but they have fairly wide tolerances under process conditions. ORP standards are used primarily for verification of electrode response rather than calibration.)

There is no temperature compensation with ORP instrumentation as each oxidation-reduction reaction has somewhat different temperature characteristics and most processes using ORP have fairly stable temperature.

Other Applications

ORP has excellent sensitivity in low concentrations (ppb ranges) where it is desired to remove an oxidizing or reducing material. At higher concentrations, such as to establish a residual chlorine concentration of several parts per million, the sensitivity for the particular application should be examined by actual titrations of samples under various operating conditions. In some cases, a residual chlorine analyzer may provide better sensitivity.

Plating Wastewater treatment uses ORP to control treatment of plating rin waters containing chromium or cyanide. Chromium must be reduced under acidic conditions (usually with bisulfite) to the form that can be precipitated and removed when the pH is raised again. Cyanide must be oxidized (usually with chlorine) under alkaline conditions to produce harmless bicarbonate and nitrogen. For further information on these processes contact Mettler-Toledo Thornton application support.

Further Reading

1. ASTM Test Method D1498, ASTM, Conshohocken, PA.
2. Gray and Marshall, "ORP Measurement in Water and Wastewater," *Ultrapure Water Journal*, Sept/Oct 1993.
3. Liptak, ed, *Instrument Engineers' Handbook--Process Control*, Chilton, Chapter 8.15, 1985.
4. Shinsky, *pH and plon Control in Process and Waste Streams*, Wiley 1973.
5. Dooley, MacDonald, Syrett, "ORP - the Real Story for Fossil Plants," *PowerPlant Chemistry*, Jan 2003.

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