November 1993

WATER
Engineering & Management

Technology Trends for Water/Wastewater Industry Leaders

Understanding ORP's Role in the Disinfection Process

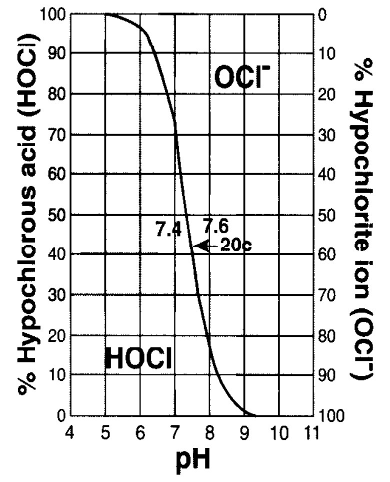
by Lori L. McPherson

The measurement of oxidation reduction potential (ORP) is a useful on-line process control tool often misunderstood and underutilized. ORP is an indicator of the ability of a solution to oxidize and is related to the concentration of oxidizers and their activity or strength.

In water disinfection applications, the ORP value of the solution has been proven to be more meaningful than the concentration of residual (free) or total chlorine. This is a result of the equilibrium between two forms of chlorine in water that shifts with changing pH. Also, chlorine may combine with amines or stabilizers to form compounds which contribute to total chlorine, but are not effective as disinfectants.

Water itself is a very weak oxidizer, thanks to the dissolved oxygen that is nearly always present. Oxygen is in fact a weak oxidizer. Consider the reaction between water and a mild steel. Corrosion (oxidation) of the steel occurs. Water has an ORP value of between 200 and 300 mV. This range is considered the "zero" point, where the addition of oxidizing chemicals will result in values greater than 300 mV. The ORP of the solution quantifies the ability or potential of the solution to oxidize or reduce.

ORP became a world standard in 1968 when a German Federal Health Office Laboratory first proved that the killing rate of *E. coli* bacteria was dependent on ORP and not on free residual chlorine. In 1972, the standard for drinking water Issued by the World Health Organization recognized that an ORP value of 650 mV provided instantaneous disinfection of viral bacteria. DIN standards set a minimum ORP level of 750 mV for pools in 1982 and spas in 1984.



Chlorine in Water

When chlorine is added to water it forms hypochlorous acid (HOCl), a strong, fast-acting oxidizer. As pH increases, the HOCl disassociates to its ionic form, OCl^- (the hypochlorite ion), which is weaker and slower acting (Fig 1). Consequently, as the pH of a chlorine-containing solution increases, the oxidizing capability decreases and is reflected directly in the ORP reading. Monitoring free chlorine concentration by itself would not indicate this. Also, chlorine which has combined with other compounds, e.g. amines, contributes to "total" chlorine, but provides little oxidizing capability. If the process objective is to oxidize, ORP gives a true measurement of the solution's ability to do so.

To maintain free chlorine in its most active form, solution pH should be maintained between 7.4 and 7.6. If it rises to 8.0, 80 percent of the free chlorine will change to the hypochlorous ion form. This is 80 to 300 times less effective as an oxidizer, depending on the specific bacteria involved. We can see that a free chlorine measurement alone cannot guarantee disinfection. ORP provides a single measurement of the total oxidation capability, regardless of the pH, the concentration of chlorine and the form in which the chlorine exists. An ORP level of 650 mV provides instantaneous *E. coli* destruction regardless of whether it is a result of 0.3 ppm free chlorine at 7.6 pH, or 0.4 ppm free chlorine at 7.8 pH.

The effect of pH on chlorine concentration and ORP is magnified when the oxidizer used is sodium hypochlorite (NaOCl). This common liquid form of chlorine normally comes in a very high pH solution of 13 to 13.5. When added to a neutral water solution, it raises pH rapidly. The logarithmic nature of pH causes changes near pH 7.0 (neutral) to occur very quickly, then slow by a factor of 10 for each unit change. With the HOCl/OCl^- equilibrium relationship affecting the oxidation reaction, initial additions of sodium hypochlorite to water may, in fact, cause decreasing oxidation capability unless acid is used to counteract the alkalinity. For this reason, pH control is very important when disinfecting with sodium hypochlorite.

The data in Tables 1 and 2 show the affect of the alkalinity of sodium hypochlorite on the pH and ORP values of a solution. Table 1 represents values when a 12 percent solution of NaOCl is added to water. Note how quickly the pH changes with the initial additions of NaOCl. As the pH rises, the ORP decreases as the inactive OCl^- is formed.

Reprinted from WATER/Engineering & Management, NOVEMBER 1993

Table 2 is derived from a two percent solution of NaOCl, where sulfuric acid is added to counteract the alkalinity and drop the pH value. Although the concentration of free chlorine has not changed, the oxidation potential of the solution increases significantly.

Chlorine Demand

The quantity of chlorine needed in a water treatment process to provide a residual for disinfection depends upon how much bacteria and other organic wastes are present in the water. Ammoniated compounds combine with chlorine to form monochloramines. The addition of further chlorine converts these to dichloramines, which are responsible for the chlorine odor and eye irritation common in public pools. With the addition of still more chlorine, dichloramines can be destroyed by conversion to nitrogen and carbon dioxide. This is the point referred to as breakpoint chlorination. A ratio of 10:1 of chlorine to ammoniated compounds is required to achieve *breakpoint chlorination.*

Automatic control of this process with an electronic ORP controller (for instance the George Fischer, Inc.'s SIGNET Intelek-Pro 9040 ORP Controller) can provide immediate breakpoint chlorination of the ammoniated products, as well as destruction of the bacteria. ORP control maintains the oxidizing capability of the solution at the necessary reaction level. As a continuous monitoring and control process, it immediately senses when this capability has been diminished and replaces the chlorine that was used.

Other Oxidizers

Other common disinfection oxidizers include sodium hypochlorite, bromine and ozone. By definition, an oxidizer is a chemical that has the ability to accept electrons. In solution an oxidizer will raise the ORP value. The greater the oxidizer concentration, the faster will be the rate of reaction.

The actual ORP depends on both the concentration and the activity of the oxidizer. Table 3 lists commonly used oxidants and their oxidation potential relative to chlorine. One can see that ozone is one-and-a-half times as active as chlorine, and in the disinfection process less ozone on a per-molecule basis is required to achieve a certain ORP value. It is the ORP, not the oxidizer concentration, that reflects oxidation rate.

ORP Measurement Systems

Measuring ORP is similar to measuring pH. Platinum is sensitive to electron activity in the same manner as pH-sensitive glass is sensitive to the presence of (activity) the hydrogen ion. In a typical ORP sensor, the electrode is nearly identical to the pH electrode, with the platinum surface (usually a platinum rod or band) serving as the measuring half of the electrode, and a silver/silver chloride reference wire in a potassium chloride (KCl) reference electrolyte serving as the reference half (Fig 2). Several manufacturers offer ORP sensors.

Table 1

Water Solution of NaOCl

% NaOCl	ORP Value	pH Value
Water only	210	6.80
0.3	715	8.90
0.5	690	8.90
1.0	655	10.06
1.5	630	10.56
2.0	599	11.18
3.0	570	11.69

Table 2

pH Adjustments to 2% NaOCl Solution

ORP Value	pH Value
611	10.97
721	9.24
815	8.02
864	7.00
929	6.03

Table 3

Water Solution of NaOCl

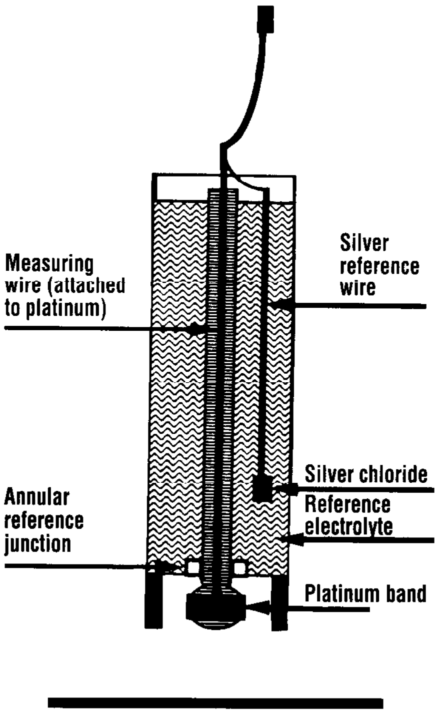
Oxidant	Oxidation Potential (in volts)	Oxidation Potential (relative to chlorine)
Fluorine	3.05	2.25
Ozone	2.07	1.52
Hydrogen peroxide	1.78	1.30
Potassium permanganate	1.68	1.25
Chlorine dioxide	1.57	1.15
Chlorine	1.36	1.00
Bromine	1.07	.79

The electrode can be looked on as a battery where voltage flows from the measuring side to the reference side. The reference electrolyte completes the circuit by providing an electrical connection back to the solution being measured. For this reason, the reference junction must remain clean and free flowing.

Care of the ORP electrode also mimics that of pH instrumentation. For instance, the electrode must remain in the solution at all times, and the system will require routine cleaning and calibration to compensate for electrode degradation. It is likely that the electrode will require replacement every one to two years, depending on the application.

Cleaning the ORP electrode is best done with a five percent hydrochloric acid solution. This solution is most effective for solubilizing hard-water deposits that may occur 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 2.
Cross section of ORP electrode



Calibration should be a regular maintenance task. A monthly frequency is typical in many disinfection situations. Calibration is best accomplished in freshly made solutions of quinhydrone saturated into pH 4.0 and 7.0 buffer solutions. Quinhydrone is a weak reducing agent whose activity changes with pH. By adding it to solutions of known pH, standard ORP solutions of 87 mV (7.0 pH) and 264 mV (4.0 pH) can be produced. These solutions are used to monitor the offset (standard) and space (slope) of the electrode as it degrades over time. Quinhydrone should be stored cool, and fresh solutions employed for each calibration.

In summary, ORP measurement historically has taken a back seat to determination of residual chlorine, or of ozone. But recent work suggests that ORP should be considered as the primary indication of oxidation (or disinfection) capability. On-line ORP control can provide the insurance that bacteria or ammoniated compounds present in water being treated for human consumption will be rapidly destroyed.

About the Author:

Lori L. McPherson, B.S., M.S. is analytical systems product manager with George Fischer, Inc., Tustin, California.

Reprinted from WATER/Engineering & Management, NOVEMBER 1993