Unraveling the Mystery

HERE'S WHY IT'S IMPORTANT TO UNDERSTAND OXIDATION-REDUCTION POTENTIAL — AND WHY AN ORP METER CAN BE A POTENT ITEM IN AN OPERATOR'S TOOLKIT

By Mark Spencer

Everyone in the water and wastewater industry knows and measures pH. Conductivity is a concept we all readily grasp. Dissolved oxygen and free chlorine are actual chemicals, so we understand them.

But oxidation reduction potential (ORP or redox) is another matter. For most, it's a mystery, and that's a shame because ORP can be used in more applications than any other measurement. Furthermore, the analyzers that measure it are inexpensive and simple. The more you know, the more you will want to use them.

WHAT ORP MEANS

ORP is mysterious to most because it doesn't measure anything in particular. It is an aggregate measurement of all the chemicals in the water that either give up electrons (oxidize) or steal electrons (reduce). Chemistry is the study of what happens when molecules or atoms of one kind take electrons from molecules or atoms of another kind.

We say a chemical that is oxidized by another is a reducing agent, and a chemical that is reduced by another is an oxidizing agent (or oxidant). Sort out this nomenclature and you're halfway to understanding ORP.

The other convention we use when describing ORP is that chemicals that oxidize have positive ORP values while those that reduce have negative values. Knowing this, we can define what an ORP value is.

> To make sure the processes are optimized, all we need to do is measure and control the ORP. That's why the ORP sensor is one of the most powerful tools in the water quality instrumentation toolbox.

To do so, we must understand the most fundamental law of oxidation-reduction reactions: It takes two to tango. You can't have one chemical that oxidizes unless there is another that reduces and can take up the liberated electrons. For instance, iron in a vacuum will stay iron. But add oxygen and the iron gives up electrons to oxygen, and the two them combine to form iron oxide (rust).

The chemicals that disinfect or break down matter, such as oxygen, ozone, chlorine, hypochlorite or potassium permanganate, are oxidants and grab electrons. But they can't do anything unless they find a partner to give them electrons. In water treatment, that partner is always organic matter: ammonia, bacteria, dead leaves and anything else that needs breaking down.

ORP is the sum of all the possible oxidation and reduction reactions that can take place in the water. But they don't take place until there is balance between oxidation and reduction. A hypochlorite solution has a positive ORP that stays positive until it comes across some organic matter.

Once we understand that oxidation-reduction reactions constitute an exchange of electrons between the oxidizing chemicals and the reducing chemicals, we can see that they work just like batteries. Just as batteries are characterized by a voltage, so are oxidation-reduction reactions. That's why ORP is measured millivolts (mV).

HOW AN ORP SENSOR WORKS

Now we can look at how an ORP probe works. If we examine at the glass electrode of an ORP sensor, we see a platinum band that wraps around the glass and connects to the interior of the probe. Platinum is a great catalyst: it speeds up reactions. (The catalytic converter in a car contains a strip of platinum that accelerates the conversion of toxic carbon monoxide to carbon dioxide.)

On the platinum surface, redox reactions can proceed rapidly, but we need a partner to balance the flow of electrons. Every giver needs a taker. That's where the reference electrode comes in.

Decades ago, the reference electrode was a hydrogen electrode in which hydrogen gas broke down into positive hydrogen ions and electrons, or vice versa. That's why ORP reactions are generally referenced to the standard hydrogen electrode (SHE).

But carting hydrogen gas around is cumbersome, so we now use a silver wire in a potassium chloride (KCl) solution. Some of the silver dissolves in the KCl solution as positive silver ions. This is nothing more than an off-the-shelf pH electrode — that's why ORP probes and pH probes have identical reference electrodes. They differ only in the process electrode.

When the process electrode (the one with the platinum band that sticks in the water) is in a solution that has a positive ORP (likes to oxidize), the silver wire in the reference electrode balances out the chemistry by dissolving silver atoms to form silver ions and electrons. The electrons flow to the process electrode to satisfy the oxidizing agent's appetite for electrons, and we measure the voltage as a positive ORP value.

When the probe is in a reducing environment — say, a solution of hydrogen sulfide — the opposite happens. The positively charged silver ions in the KCl solution grab electrons from the process electrode, turn back into neutral silver atoms, and plate onto the silver wire. Because the current flow is now reversed, we measure a negative voltage.

A word of caution: While platinum makes reactions speed up, some redox reactions are slow no matter what. Put an ORP sensor in calibration solution and it will give a reading in 30 seconds. Put it in tap water and it takes up to 20 minutes. This is because the reactions involving iron compounds in the calibration solution are fast, but the reactions of residual chlorine and other minor constituents in tap water are slow.

WHY ORP MATTERS

The ORP probe is a "bottom line" instrument: It doesn't care what's in the water. It simply measures the redox potential of everything in the water. Whether it's ozone, chlorine, sodium metabisulfite or dissolved oxygen, it doesn't care. We only care that whatever is in the water can do the job, whether breaking down contaminants, turning nitrates into nitrogen, or any other chemical reactions that occur in a treatment facility.

To make sure the processes are optimized, all we need to do is measure and control the ORP. That's why the ORP sensor is one of the most powerful tools in the water quality instrumentation toolbox.

Let's end by citing the most common uses of ORP analyzers. Oxidation reactions are behind two of the most common reactions in wastewater processing.

In wastewater, one variety of bacteria includes little chemical factories that oxidize (nitrify) ammonia to nitrite. Another variety further oxidizes the nitrite to nitrate. Then, in a reversal of bacterial philanthropy, another set of bacteria that is deprived of oxygen reduce (denitrify) the nitrate to nitrogen gas, which floats off into the atmosphere.

The usual course of action is to measure dissolved oxygen (DO) — keeping it high enough during the nitrification stages and low during the anoxic (denitrification) stage. This is the role of the aerator, which ensures that the water has enough DO — about 4 to 8 ppm, or at least 50 percent saturation. Normally a DO sensor does the job, but an ORP sensor can measure the actual aerobic chemistry and do it for less money.

In water treatment, disinfection in the form of chlorine or hypochlorite works by breaking down bacterial cell walls. Regardless of the form of chlorine going into the water, it is hypochlorous acid — HOCl — that kills the bacteria. We are all familiar with chlorine analyzers used to dose the right amount of chlorine and keep the free chlorine concentration in the right range. An ORP analyzer gives us the bottom line, which is the oxidation potential that does the work of disinfection.

THE OTHER SIDE

So far, we've discussed oxidation reactions in a wastewater plant, but reduction reactions also play a role. Denitrification reduces nitrate to nitrogen gas — bacteria do this work in low-oxygen conditions. The reducing environment is characterized by a negative ORP value. It is much easier to measure this value with an ORP analyzer than to measure very low oxygen with a dissolved oxygen analyzer.

The reduction of phosphate is similar to the reduction of ammonia by bacteria. One set of microbes do their work in a very low oxygen environment and another set do it an oxygen-rich one. ORP to the rescue.

I'm not suggesting that a water treatment plant throw out its chlorine analyzer, or that a wastewater plant dispose of its DO analyzer. But I am suggesting that, for a modest investment, arming these facilities with ORP analyzers can ensure that their chemical processes are doing exactly what they are supposed to.

If you would like to learn more about ORP measurements, you can download a more comprehensive paper at www.WaterAnalytics.net/Resources.

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