

Before we get into the guts of this lets clear up something right from the start and that is why Zodiac coined the term ACL (Active Chlorine Level). Well the short of it is that we thought it was more appropriate to use a term that consumers could relate to as opposed to the acronym ORP (Oxidation Reduction Potential) which doesn't really mean much to a consumer. For the purposes of this technical paper however, ORP will be used as it was written using the original terminology

The ABC's of ORP
Clearing up some of the mystery of Oxidation-Reduction Potential
By Robert W. Lowry and David Dickman
Extracted from *Service Industry News*

This is another in a continuing series of articles that *Service Industry News* is presenting on pool and spa sanitation, water balance and test methods. Although it is firmly based on sound, scientific study, it is not written as a scientific paper, but rather as a practical, understandable guide for pool and spa service technicians.

ORP stands for Oxidation-Reduction Potential. In practical terms, it is a measurement to oxidize contaminants. It's as simple as that.

Well, then, you might ask, if ORP is so simple that it can be reduced to an 11-word definition, why are you devoting an entire article to it, and why should it be important to me at all?

The answer to that is that right now, ORP is the only practical method we have to electronically monitor sanitizer effectiveness. Every true system of automatic chemical control depends on ORP to work.

If you've been in the pool and spa service industry for any length of time, you already know the routine involved in maintaining proper water chemistry. First you test the water, then you adjust it to recommended chemical levels.

That sounds simple, too. Of course, you could make automobile maintenance sound just as simple: Simply measure the car's performance; then adjust everything necessary to make it perform the way it should.

In the real world, we all know that chemical maintenance of pool and spa water is a fairly complicated balancing act. You must maintain sanitizer residual at a level sufficient to protect swimmers and bathers from the invasion of unwanted - and possibly harmful - plant and animal life. You must maintain the pH of the water at a level that assures the sanitizer works effectively and at the same time protects the pool shell and equipment from corrosion or scaling and the bathers from discomfort or irritation.

Along the way, you must make sure that all the other ingredients in this chemical mix - total alkalinity, water hardness, temperature, and total dissolved solids (TDS), to name four big ones - are also in balance or not out of the recommended range.

But of all the factors involved in chemical maintenance, the "frontline" troops are two: sanitizer residual and pH. By far, these are the chemical tests performed most often. By far, these are things that we are most concerned with.

ORP and pH sensors allow us to electronically monitor and control sanitizer residual and pH automatically. In a light usage residential pool, this might not be a primary concern. But in a public or semi-public pool or spa - one that is under constant observation by local health authorities - some form of dependable, accurate, automatic chemical control may well be a necessity.

"But," you might say, "I'm already in control. I've got a chemical feeder hooked up to the suction line, or a floater in the pool, or I've left chemicals behind with the owner to add between service calls. There should be plenty of sanitizer in the water by the time I return for my next call."

The key words are "dependable" and "accurate." The methods described above may get some sanitizer in the water, but will it be enough? Will it be too much? Will it get done at all?

A chemical feeder, hooked in-line with the circulation system, will dispense some chemicals whenever the system is running - whether they are needed or not. A floater will dispense some chemicals constantly - whether they are needed or not. Depending on a pool owner to take care of things between calls is - well - chancy at best and downright dangerous at worst.

Besides, chemical feeders and floaters only deal with sanitizer residual. There's still nothing there to control pH. pH, as we all know, is the thing that makes sanitizer work.

If you want true chemical control, you've got to have some method of monitoring both the sanitizer residual and the pH and using that information to chemically treat the water. That's where ORP enters the picture

So What Exactly Is ORP?

As we stated earlier, ORP stands for Oxidation-Reduction Potential. In some parts of the world, it is also known as Redox Potential. Sometimes, you'll see the words "oxidation" and "reduction" spelled without the hyphen connecting them. We chose the hyphen because the two chemical reactions are really "joined at the hip" - one cannot occur without the other also occurring.

When chemists first used the term in the late 18th Century, the word "oxidation" meant, "to combine with oxygen." Back then, it was a pretty radical concept. Until about 200 years ago, folks were really confused about the nature of matter. It took some pretty brave chemists to prove, for example, that fire did not involve the release of some unknown, mysterious substance, but rather occurred when oxygen combined rapidly with the stuff being burned.

We can see examples of oxidation all the time in our daily lives. They occur at different speeds. When we see a piece of iron rusting, or a slice of apple turning brown, we are looking at examples of relatively slow oxidation. When we look at a fire, we are witnessing an example of rapid oxidation. We now know that oxidation involves an exchange of electrons between two atoms. The atom that loses an electron in the process is said to be "oxidized." The one that gains an electron is said to be "reduced." In picking up that extra electron, it loses the electrical energy that makes it "hungry" for more electrons.

We also know that matter can be changed, but not destroyed. You can alter its structure, and can increase or decrease the amount of energy it contains - but you can't eliminate the basic building blocks that make things what they are.

Chemicals like chlorine, bromine, and ozone are all oxidizers. It is their ability to oxidize - to "steal" electrons from other substances - that makes them good water sanitizers, because in altering the chemical makeup of unwanted plants and animals, they kill them. Then they "burn up" the remains, leaving a few harmless chemicals as the by-product.

Of course, in the process of oxidizing, all of these oxidizers are reduced - so they lose their ability to further oxidize things. They may combine with other substances in the water, or their electrical charge may simply be "used up." To make sure that the chemical process continues to the very end, you must have a high enough concentration of oxidizer in the water to do the whole job.

But how much is "enough?" That's where the term potential comes into play.

"Potential" is a word that refers to ability rather than action. We hear it all the time in sports. ("That rookie has a lot of potential - he hasn't done anything yet, but we know that he has the ability to produce.")

Potential energy is energy that is stored and ready to be put to work. It's not actually working, but we know that the energy is there if and when we need it. Another word for potential might be pressure. Blow up a balloon, and there is air pressure inside. As long as we keep the end tightly

closed, the pressure remains as potential energy. Release the end, and the air inside rushes out, changing from potential (possible) energy to kinetic (in motion) energy.

In electrical terms, potential energy is measured in volts. Actual energy (current flow) is measured in amps. When you put a voltmeter across the leads of a battery, the reading you get is the difference in electrical pressure - the potential - between the two poles. This pressure represents the excess electrons present at one pole of the battery (caused, incidentally, by a chemical reaction within the battery) ready to flow to the opposite pole.

When we use the term potential in describing ORP, we are actually talking about electrical potential or voltage. We are reading the very tiny voltage generated when a metal is placed in water in the presence of oxidizing and reducing agents. These voltages give us an indication of the ability of the oxidizers in the water to keep it free from contaminants.

How Do You Measure ORP?

An ORP probe is really a millivolt meter, measuring the voltage across a circuit formed by a reference electrode constructed of silver wire (in effect, the negative pole of the circuit), and a measuring electrode constructed of a platinum band (the positive pole), with the pool water in between.

The reference electrode, usually made of silver, is surrounded by salt (electrolyte) solution that produces another tiny voltage. But the voltage produced by the reference electrode is constant and stable, so it forms a reference against which the voltage generated by the platinum measuring electrode and the oxidizers in the water may be compared.

The difference in voltage between the two electrodes is what is actually measured by the meter. Modern ORP electrodes are almost always combination electrodes, that is both electrodes are housed in one body - so it appears that it is just one "probe."

Incidentally, the meter circuitry itself must have very high impedance (resistance) in order to measure the very tiny voltages generated by the circuit.

What Does an ORP Meter Tell US?

Now that you know the basis of how an ORP meter works, let's take a look at how changes in the oxidizer level in the water will effect the measurement.

For practical purposes, oxidizing agents are the "good guys" in the water sanitation picture, reducing agents are contaminants and therefore are the "bad guys."

If we had a body of water in which the concentration of oxidizers (or oxidants as chemists are apt to say) exactly equaled the concentration of reducers (reductants), then the amount of potential generated at the measuring electrode would be exactly zero. As you might guess, the water would be in pretty sad shape, because if any additional contaminants were introduced into the water, there would be no oxidizer to handle it.

As we add oxidizer to the water, it "steals" electrons from the surface of the platinum measuring electrode. To make things a little more confusing, we need to point out that electrons are negatively charged particles. When we remove these negatively charged things from this electrode, the electrode becomes more and more positively charged. As we continue to add oxidizer to the water, the electrode generates a higher and higher positive voltage

How pH Affects ORP

Service professionals are already well aware that sanitizer effectiveness can vary rather significantly with changes in pH - particularly in regards to chlorine, which is by far the most commonly used chemical for water sanitation.

You will recall from previous articles about chlorine that the killing form of chlorine is hypochlorous acid (chemical formula HOCl), which, not coincidentally, is a powerful oxidizer. You

will also remember that the percentage of hypochlorous acid is present in pool and spa water depends directly on the pH.

For example, at a pH of 6.0, 96.5 percent of the Free Available Chlorine in the water is in the form of HOCl, while at a pH of 8.5, only 10 percent is in this active killing form.

Testing the water with OTO can tell you the concentration of chlorine, but it cannot tell you how much of the chlorine is combined into organic compounds or how much is in the form of hypochlorous acid. Changing the pH of the water will not affect the result of an OTO test.

A DPD test can tell you how much of the chlorine is combined and how much is free and available, but it cannot tell you what percentage is in the form of hypochlorous acid. To determine this, you must take a pH test and calculate the results. Altering the pH will not effect the results of a DPD test.

Although ORP does not specifically tell you the chlorine concentration in parts per million, it does indicate the effectiveness of the chlorine as an oxidizer. An ORP reading will vary as pH fluctuates. As the pH goes up, the millivolt reading on an ORP meter will go down, indicating that the sanitizer is not as effective. Bringing the pH down or adding more sanitizer will raise the millivolt reading.

That is why most ORP instruments also incorporate an electronic pH meter - which measures the difference in electrical potential between the pool water and a sample of known pH that is contained in the probe in a small glass bulb.