

The ABC's of ORP

Clearing up the mystery of Oxidation-Reduction Potential

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Let's establish something from the start - ORP is not a word; it's a set of initials, like IBM or IRS or NFL. ORP stands for **Oxidation-Reduction Potential**. In practical terms, it is a measurement to oxidize contaminants. It's as simple as that. Well, you might ask, if ORP is so simple that it can be reduced to a one-sentence definition, why are you devoting an entire article to it, and why should it be important to me at all?

The answer 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 only two: sanitizer residual and pH. By far, these are the chemical tests performed most often, and, 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 may 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 an erosion 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 may get some sanitizer in the water, but will it be enough? Will it be too much? Will it get done at all?

An erosion 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, erosion 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 sanitizers work. If you want true chemical control, you must have some method of monitoring both the sanitizer residual and the pH, and using that information to chemically treat the water. And, that is where ORP enters the picture.

What Exactly Is ORP?

As stated, **ORP** stands for **Oxidation-Reduction Potential**. In some parts of the world, it is also known simply as **Redox Potential**. Sometimes, you will 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 material 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 blazing 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", since 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 you can increase or decrease the amount of energy it contains - but you cannot 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. However, 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 proper job – in other words, you keep "adding" in more oxidizers. 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 large results."*)

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 it is needed. 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 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 affect the measurement.

For practical purposes, oxidizing agents are the "*good guys*" in the water sanitation scenario – reducing agents are contaminants, and, therefore, they become the "*bad guys*."

If we had a body of water in which the concentration of oxidizers (**oxidants**) 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 an 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 oxidizers 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 the 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 affect 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.

Setting the Standard

Once the instruments and methods for measuring ORP were developed in the 1960's, researchers began working toward setting standards under which ORP measurements could be used as an accurate gauge of water quality.

In 1972, the World Health Organization (WHO) adopted an ORP standard for drinking water disinfection of 650 millivolts. That is, the WHO stated that when the oxidation-reduction potential in a body of water measures 650/1000 (about 2/3) of a volt, the sanitizer in the water is active enough to destroy harmful organisms almost instantaneously.

In Germany, which has about the strictest water quality standards in the world, an ORP level of 750 millivolts has been established as the minimum standard for public pools (1982) and spas (1984).

In its 1988 standards for commercial pools and spas, the National Spa & Pool Institute stated that ORP can be used as a *"supplemental measurement of proper sanitizer activity"* when chlorine or bromine are used as primary disinfectants. The recommended minimum reading under the NSPI standards is 650 millivolts, with no ideal and no maximum. The NSPI also stated that *"the use of ORP testing does not eliminate or supersede the need for testing the sanitizer level with standard kits."*

The above statement is not necessarily a matter of the NSPI being cautious about setting chemical

standards. The fact is that most health codes still specify that a measurable free available chlorine (FAC) residual - usually 1.0 ppm present in the water of public pools and spas, as measured with a DPD test kit.

Chemical Automation

ORP technology has received widespread application in this country as the basis of automated chemical control equipment. The reasoning is clear: *Only an ORP sensor can deliver the kind of feedback needed to control feeders for sanitizer and pH adjusting chemicals.* Unlike constant feed or timer controlled devices, ORP based chemical controllers can dispense chemicals as they are needed. Combined with a pH sensor, these controllers can be used to activate liquid feed pumps, gas chlorinators, and erosion type feeders for dry chemicals. They also can monitor pool water chemistry and record the reading on a chart. Further, electronic control assures that sanitizer and pH adjusting chemicals will be dispensed precisely as they are needed, eliminating the peaks and valleys in sanitizer residual and pH that often occur in pools and spas as bather load fluctuates.

Control equipment is generally installed with the ORP and pH probes placed in the pressure line, or water from the pressure line may be diverted to the probes. Probes are always installed prior to the point of chemical injection. This way, water passing over the sensors is representative of water in the pool, and the sensors are always ready to produce an accurate voltage.

When used with liquid chemical feed pumps, the signals from the pH and ORP probes determine when the controller activates chemical pumps. The pumps are turned on and off to achieve the set points (desired control levels).

When using a gas chlorinator, the controller activates a solenoid valve, which permits gas to be injected through a bypass line and into the recirculation line. A booster pump in the bypass line is often used to assure adequate dispersion of gas.

Erosion feeders (dispensing trichlor or calcium hypochlorite tablets or bromine sticks or tablets) can also be controlled by an ORP controller. The feeder is placed in a bypass line, which is opened or closed through the use of a solenoid valve.

In addition, ORP devices can be used to measure sanitizer effectiveness and to control ozone generators, chlorine generators, and ionizers (in combination with chlorine).

Oxygen Reduction Potential – ORP

Standard Reduction Potential (also known as **Redox Potential, Oxidation / Reduction Potential, or ORP**) is the tendency of a **chemical species** to acquire **electrons** and thereby be **reduced**. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced.

In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher reduction potential will have a

tendency to gain electrons from new species (i.e. oxidize them) and a solution with a lower reduction potential will have a tendency to lose electrons to new species (i.e. reduce them). Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution. Like pH, the reduction potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in much the same way that pH does not characterize the buffering capacity.

Reduction potential is measured in volts (V), millivolts (mV), or Eh ($1E_h = 1mV$). Because the true or absolute potentials are difficult to accurately measure, reduction potentials are defined relative to the **standard hydrogen electrode** (SHE) which is arbitrarily given a potential of 0.00 volts. **Standard reduction potential** (E^0), is measured under **standard conditions**: $25^{\circ}C$, a **1 M concentration** for each ion participating in the reaction, a **partial pressure** of 1 atm for each gas that is part of the reaction, and **metals** in their pure state. Historically, many countries, including the United States and Canada, used **standard oxidation potentials** rather than reduction potentials in their calculations. These are simply the negative of standard reduction potentials, so it is not a major problem in practice. However, because these can also be referred to as "*redox potentials*", the terms "*reduction potentials*" and "*oxidation potentials*" are preferred by the IUPAC. The two may be explicitly distinguished in symbols as E_r^0 and E_o^0 .

The relative **reactivities** of different **half-cells** can be compared to predict the direction of electron flow. A higher E^0 means there is a greater tendency for reduction to occur, while a lower one means there is a greater tendency for oxidation to occur.

Any system or environment that accepts electrons from a normal hydrogen electrode is a **half cell** that is defined as having a positive redox potential; any system donating electrons to the hydrogen electrode is defined as having a negative redox potential. E_h is measured in millivolts (mV). A high positive E_h indicates an environment that favors oxidation reaction such as free **oxygen**. A low negative E_h indicates a strong reducing environment, such as free metals.

Sometimes when **electrolysis** is carried out in an **aqueous solution**, water, rather than the solute, is oxidized or reduced. For example, if an aqueous solution of **NaCl** is electrolyzed, water may be reduced at the **cathode** to produce **$H_{2(g)}$** and **OH^-** ions, instead of Na^+ being reduced to **$Na_{(s)}$** , as occurs in the absence of water. It is the reduction potential of each species present that will determine which species will be oxidized or reduced.

Absolute reduction potentials can be determined if we find the actual potential between electrode and electrolyte for any one reaction. Surface polarization interferes with measurements, but various sources give an estimated potential for the standard hydrogen electrode of 4.4V to 4.6V (the electrolyte being positive.)

Many enzymatic reactions are oxidation-reduction reactions in which one compound is oxidized and another compound is reduced. The ability of an organism to carry out oxidation-reduction reactions depends on the oxidation-reduction state of the environment, or its reduction potential (E_h).

Strictly aerobic microorganisms can be active only at positive E_h values, whereas strict anaerobes can be active only at negative E_h values. Redox affects the solubility of nutrients, especially metal ions. Oxygen strongly affects redox potential.

Although measurement of the reduction potential in aqueous samples is relatively straightforward, many factors limit its interpretation, such as irreversible reactions, slow electrode kinetics, non-equilibrium, the presence of multiple redox couples, electrode poisoning, small exchange currents, and inert redox couples. Consequently, practical measurements seldom correlate with calculated values. Nevertheless, reduction potential measurement has proven useful as an analytical tool in monitoring changes in a system rather than determining their absolute value (e.g. process control and titrations).

Reduction potentials of aqueous solutions are determined by measuring the potential difference between an inert indicator electrode in contact with the solution and a stable reference electrode connected to the solution by a salt bridge. The indicator electrode acts as a platform for electron transfer to or from the reference half cell. It is typically platinum, although gold and graphite can be used. The reference half cell consists of a redox standard of known potential. The standard hydrogen electrode (SHE) is the reference from which all standard redox potentials are determined and has been assigned an arbitrary half cell potential of 0.0 mV. However, it is fragile and impractical for routine laboratory use. Therefore, Ag/AgCl and saturated calomel (SCE) reference electrodes are commonly used. The voltage relationships for several different reference electrodes at 25 °C can be interrelated as follows:

Reference electrode	Electrode potential with respect to SHE (mV)
Standard hydrogen electrode (SHE)	0
Saturated calomel electrode (SCE)	+ 245

Ag/AgCl, 1 M KCl	+ 236
Ag/AgCl, 4 M KCl	+ 200
Ag/AgCl, sat. KCl	+199

For example: If you had a reading of 100 mV using a saturated KCl Ag/AgCl reference and wanted to refer it back to an SHE you would add 199 mV to obtain 299 mV. Alternatively, if you took a reading in the same solution using an SCE, you would obtain 54 mV (subtract 245 mV from 299 mV).

Please review the following links:

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[Electrolytic cell](#)

[Electromotive force](#)

[Electrochemical potential](#)

[Table of standard electrode potentials](#)

[Oxygen radical absorbance capacity - **ORAC**](#)