AQUARIUS TECHNOLOGIES PTY LTD
WATER QUALITY CONTROL

Unit 1, 23 Richland Avenue
Coopers Plains Q 4108
PO Box 71 Coopers Plains Q 4108

T: +617 3274 4750
F: +617 3274 4736
W: www.aquariustech.com.au

Quality Endorsed Company ISO 9001 Lic 5403

More About ORP

Oxidation-Reduction Potential (ORP) is the potential (Voltage) at which oxidation occurs at the anode (positive) and reduction occurs at the cathode (negative) of an electrochemical cell. In simple terms, from a microbial perspective, an oxidizing chemical pulls electrons away from the cell membrane, causing it to become destabilized and leaky. Destroying the integrity of the cell membrane leads to rapid death.

1. Free and Combined Chlorine

When chlorine in any form is introduced into a water system, it forms free chlorine (HOCl), which is an excellent bactericide: $Cl_2 + H_2O \longrightarrow HOCl + HCl$

However, readily combines with organic waste materials that are present in the water to form combined chlorine compounds, which are poor bactericides and have obnoxious properties.

2. Two Forms of Free Chlorine

There are two forms of free chlorine: The molecular form, hypochlorous acid, HOCl, which is the fast-acting free chlorine, and the ionic form, OCl^-, which is a slow-acting sanitizer. HOCl is a weak acid. As the pH increases, it dissociates to produce the hypochlorite ion and a hydrogen ion:

$$HOCl \longleftrightarrow OCl^- + H^+$$

The concentration of HOCl, the fast-acting sanitizer, decreases very rapidly with increasing pH in the range of interest for cooling water systems:

- At a pH of 7.0, about 75 percent of the free chlorine is HOCl
- At a pH of 7.5, it is about 50/50 HCOl and OCl^-.
- At a pH of 8.0, it is about 20 percent HCOl and 80 percent OCl.

HCOl is 80 to 300 times more effective than OCl^-. For instance, it is more than 100 times more effective than OCl^- against cysts and 60 to 70 times more effective against E. coli. The activity of OCl^- as a sanitizer therefore can be compared to that of chloramines, (i.e. much below that of HCOl).

For good bacteriological quality, it is therefore essential to maintain a proper HCOl level in the water at all times. Total free chlorine readings, which combine both HCOl and OCl^-, cannot be depended upon for proper water maintenance. Unfortunately, the DPD test kit and other free chlorine test kits do not differentiate between the two forms of free chlorine.

3. Free Chlorine and ORP

There is another way of testing the water that is both simple and reliable. It is called ORP.

ORP or Redox refers to the oxidation/reduction potential - a measure of the oxidizing properties of the sanitizer in water - which is determined by a sensor with a noble metal electrode, usually platinum, and a standard Ag/AgCl reference electrode.

Unit 1, 23 Richland Avenue
Coopers Plains Q 4108
PO Box 71 Coopers Plains Q 4108

T: +617 3274 4750
F: +617 3274 4736
W: www.aquariustech.com.au

When an ORP sensor is placed in water containing a sanitizer – such as chlorine, bromine or ozone - it acts like a small battery and creates a small but measurable electric potential. The value of this potential varies with the type of sanitizer and its concentration.

4. ORP and pH

As the pH increases between 7 and 8, the ORP sensor shows a marked decrease in value for all chlorine levels. The decrease of the ORP reading with increasing pH closely parallels the decrease in concentration of HOCI. The comparison of the curves ORP and HOCI curves shows that ORP sensor can be used very effectively to monitor HOCI in the water. This is true even when the pH varies.

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 water and a sample of known pH that is contained in the probe in a small glass bulb.

5. ORP Controllers

Chemical controllers used in water treatment industry normally use an ORP sensor to monitor the sanitizer level as well as a pH sensor to monitor the pH. The controller automatically turns appropriate chemical feeders on and off, as required to maintain the proper sanitizer (and pH levels if required). Very close control can be maintained, typically within 0.1 ppm of the chlorine setpoint and 0.1 pH units. This results in good water quality and elimination of unpleasant products, as well as in savings in chemicals and labor.

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 cooling tower, and the sensors are always ready to produce an accurate voltage. When using a bromine canister, the controller activates a solenoid valve, which permits water to flow through the bromine tablets and to the tower water.

6. Benefits of ORP Systems

Oxidation-Reduction Potential (ORP) offers many advantages to “real time” monitoring and recording of water disinfection potential, a critical water quality parameter. Improvements in probe design and continuous data logging has been a largely automated activity.
Evaluation of process control by fluctuating water quality, Temperature pH … are easier with the graphic outputs of ORP controllers. Probes have been integrated to audible, visual and remote alarm systems to notify the operator of out-of-range operation.

Unit 1, 23 Richland Avenue
Coopers Plains Q 4108
PO Box 71 Coopers Plains Q 4108

T: +617 3274 4750
F: +617 3274 4736
W: www.aquariustech.com.au

A primary advantage is that using ORP for water system monitoring provides the operator with a rapid and single-value assessment of the disinfection potential of water. Researches have shown that at an ORP value of 650 to 700 mV, spoilage bacteria and bacteria such as *E.coli* and *Salmonella* are killed within a few seconds. Spoilage yeast and the more sensitive types of spore-forming fungi are also killed at this level after a contact time of a few minutes or less. Unfortunately, resistant spore-forming decay pathogens and human parasites, such as *Cryptosporidium*, are highly tolerant of chlorine, bromine, iodine and other weak oxidizers or metabolic poisons used for water disinfection. If hazard analysis identifies the potential for the presence of these parasites, a combination of ORP and Non-Oxidizing biocide system would be necessary.

A practical benefit in water treatment systems is that the measured ORP values accurately define the antimicrobial potential of the water for free-floating microbes. More conventional systems of measuring parts per million (ppm) with titration kits or paper test strips can give the same information but these must be combined with a measurement of water pH and reference to a table of Hypochlorous acid (HOCl) availability. The water pH becomes an essential variable since the color-based test kits and paper strips detect Hypochlorous acid and hypochlorite ion equally. Recent researches in water systems have shown that, ORP limits can be relied on to determine microbial kill potential across a broad range of water quality.

ORP technology has received widespread application as the basis of automated chemical control equipment. Only an ORP sensor can measure the sanitizer effectiveness and deliver the kind of feedback needed to control pumps or feeders for sanitizer. 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).

Unlike constant feed or timer controlled devices, ORP based chemical controllers can dispense chemicals as they are needed. These controllers can be used to activate liquid feed pumps and erosion type feeders for dry chemicals. They also can monitor water chemistry and record the reading on a chart.

Clearly, this type of chemical automation can result in significant savings for cooling tower owners because chemicals are only dispensed when they are needed. Further, electronic control assures that sanitizers will be dispensed precisely as they are needed, eliminating the peaks and valleys in sanitizer residual that often occur in water systems.