ORP

A BETTER WAY TO ACCESS SWIMMING POOL WATER QUALITY

By V.Baratharaj

In India swimming pool water health is mostly measured in terms of residual chlorine. A 0.5-1.0 ppm residual chlorine (FRC) are standards everywhere depending whether ozone is being used as a disinfectant (for ozone, FRC is 0.5 ppm only). The concept followed is that, chlorine being an oxidizing agent will have a residual in the pool only when all the oxidizable materials (bacteria and organics) are removed from the pool water. Otherwise, it will still be consumed in the water. This concept, though theoretically correct, gives a very wrong indication on the health of the pool water. World standards are changing now, not only in the swimming pools but also in water treatment.

Free and Combined Chlorine

To know why, we need to look briefly into the actions of chlorine in water. When chlorine in any form is introduced into pool or spa water, it forms free chlorine (HOCl), which is an excellent bactericide C1 + H.O - HOCl +HCl.

Free chlorine, however, readily combines with organic waste materials that are present in the water (such as body perspiration, urine, cosmetics, hair sprays or other ammoniated compounds) to form combined chlorine compounds called chloramines, chlordanes, which are poor bactericides and have obnoxious properties. By now, everybody in the pool and spa industry is or should be familiar with chloramines. However, the mechanisms of formation and destruction of chloramines generally are poorly understood in the industry.

When the concentration of Nitrogen/ Ammonia compounds increases in the water, there is a high probability that the entire chlorine will get converted to mono-chloramines. At pH 7-8 the formation of mono-chloramines is within seconds. Mono-chloramines are very poor bactericides and their activity on micro organisms is more than 100 times lower than free residual chlorine. When we add more chlorine into the pool, these mono-chloramines get converted to di-chloramines which have even lower bactericidal actions. It is this di-chloramines that causes the typical chlorine smell, burning of eyes that swimmers often complain.

During break down chlorination (super chlorination) when more chlorine is added, these di-chloroamines and mono-chloramines get converted to non smelling nitrogen compounds. These super chlorination levels are about 10 times the FRC levels of normal pools.

MANY MNC PACKAGED WATER COMPANIES USE ORP TO CONTROL THE QUALITY OF THEIR WATER DURING TREATMENT. SO, WHY NOT IN SWIMMING POOLS?

Two Forms of Free Chlorine & pH of Water

The fact is that there are two forms of free chlorine:

- The molecular form, hypochlorous acid, HOCl, which is the fast-acting free chlorine, and
- The linic form, OCl^-, which is a slow-acting sanitizer. In fact HOCl is a weak acid.

The pH of the water controls the concentration of both forms of free chlorine in water.

The concentration of HOCl, the fast-acting sanitizer, decreases very rapidly with increasing pH in the range of interest for pools and spas (7 to 8).

- 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 HOCl and OCl^-.
- At a pH of 8.0, it is about 20 percent HOCl and 80 percent OCl^-.

Now, HOCl is 80 to 300 times more effective than OCl^-. So, when the pH of the water increases (as often in swimming pools) the effectiveness of chlorine comes down drastically. HOCL is 100 times more effective than OCL against cysts and 60-70 times more effective against E-Coli. So, you can imagine how much low the effectiveness of chlorine is at higher pH.

The DPD test kit (chlorotex color indicator) measures the residual total free chlorine readings, which combine both HOCl and OCl^-. That is why it can not be totally depended upon for pool water maintenance. DPD test kit and other free chlorine test kits do not differentiate between the two forms of free chlorine. Therefore, they cannot show the decrease in HOCl concentration when the pH is increased. This is absolutely no problem, if the pH remains where it should be - at 7.4 to 7.6. Therefore, controlling pH in chlorinated pools is the key to good maintenance.

Why Does the pH Increases in Pool Water

pH of the pool water will increase due to:

- Use of alkaline chlorine compounds like NaOCL (liquid bleach) and solid bleach
- Make up water addition
- Body oil, sweat, etc from swimmers

Oxidation-Reduction Potential (ORP)

ORP stands for oxidation reduction potential. Ideal ORP obeys the Nernst equation:

$$E_{eq} = E^{\circ}_{ox/Red} + \left(\frac{RT}{nF}\right) .\ln \left(\frac{[Ox]}{[Red]}\right)$$

Where [Ox] is the active concentration of an oxidized species, say ferric ion, Fe^{3+} and [Re] is the active concentration of the reduced form of that species say ferrous ion Fe^{2+}. The pair provides a redox couple.

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.

Like pH, ORP represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in the same way pH does not characterize the buffering capacity.

When an ORP sensor is placed in water containing a sanitizer - such as chlorine or ozone which is also an oxidizer, it acts like a small battery and creates a small but measureable electric potential. The value of this potential varies with the type of sanitizer and its concentration. Each disinfectant has different ORP value. The higher the ORP value, the greater is the disinfectant property. Here are some ORP values of most commonly used disinfectant agents (measured in volts or milli-volts).

Fluorine	+ 3.060 V
OH free Radicals	+ 2.800 V
Ozone	+ 2.07V
Hydrogen Peroxide	+ 1.776V
Permanganate	+ 1.679V
Hypochlorus Acid	+ 1.482V
Hypobromous Acid	+ 1.331V
Hypochlorite Ion	+ 0.810V
Hypobromite Ion	+ 0.761V

Table 1

OCl has a much lower ORP value than HOCl, consistent with its much lower activity as a sanitizer when the pH of the water is above 8.0 (0.9 V).

ORP and Cyanuric Acid Stabilizers

Cyanuric acid stabilizers are often used as a substitute to liquid bleach. This is because the cyanuric acids will combine with cholrine to form compounds that are not destroyed readily by the UV rays of the sunlight. The amount of cyanuric acid in the pool water should not exceed 100 ppm and should ideally be between 25-50 ppm only. This is because at higher levels, the bacteriological effects of chlorine are drastically reduced. It is suggested that FRC in pools using cyanuric acid as stabilizers must be 3 times more than the normal FRC in pools.

The presence of cyanuric acid reduces the ORP reading of the sensor. This is because it reduces the concentration of HOCl in the water. It is, therefore, every important not to exceed the maximum recommended concentration in the water (normally 100 ppm).

ORP and Ozone

The ORP value, as seen from the table, is very high ozone is another strong oxidizer.

$$O_1 = 2\,H + 2e - O_2 + H_2O$$
$$E_0 = 2.07V$$

Ozone also can be monitored with ORP sensors. Because of its short lifetime and lack of residual value, we need to maintain a residual disinfectant level in the pool. In addition, it may also be required for safety reasons to reduce the ozone level in the water with activated charcoal before returning it to the filtered water into the pool.

ORP and Residual Ozone

Lots of studies have been conducted in trying to correlate the ORP levels to residual disinfectant levels. Separate studies have been made in circulating waters (like cooling towers and swimming pools) and in pure water (potable water). In swimming pools, ORP levels of 500 mV would be a reasonably good levels to achieve. Achieving higher levels of 600-650 mV will depend totally on the quality of water, bather load and control of pH.

Ozone Generators with Inbuilt ORP Display and Probes

Today, ozone generators come with an in-built ORP digital display and good reliable ORP sensors. The sensors are normally located after ozonation and connected to the digital display. Care should be taken that while installing an ORP probe on line, we ensure that the location does not permit turbulence of water. This may cause false reading of the ORP levels. The probe must ideally be platinum tipped and screw type so that it is easily removable and cleaned. When the ORP is very low, the pool maintenance guy can check the pH, the residual chlorine levels as well as the check on the performance of the ozone system.

Today, many water treatment systems have adopted this ORP system only because they are more reliable and reasonably accurate. Many MNC packaged water companies use ORP to control the quality of their water during treatment. So, why not in swimming pools?

About the Author

V. Baratharaj is the CMD of Ozone Technologies & Systems India Private Limited. With more than 25 years experience in ozone technology, he is an invited guest speaker in many water and wastewater seminars. He is also a guest lecturer in few leading universities in South India. An environmentalist by himself, he loves to impart ozone applications technical knowledge to others in industry.

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