PPM or ORP: Which Should Be Used?

Water treatment experts are becoming increasingly aware that water disinfection is dependent upon ORP and not the free residual chlorine ratio.

BY JACQUES M. STEININGER

Over the past few years, there has been an increasing recognition among water treatment specialists and health officials that the oxidation-reduction potential (ORP or Redox) can provide an effective measure of sanitizer activity in pool or spa water.

ORP technology has been recognized and incorporated into European and world water standards for several years. In 1972, the World Health Organization recognized in its Standards for Drinking Water (WHO 1972) that at an ORP level of 650 millivolts (mV), water is disinfected and viral inactivation is almost instantaneous.

In 1968, a laboratory study by Carlson, Hasselbarth and Mecke of the Water Hygiene Institute of the German Federal Health Office showed that the rate of killing of E. coli organisms in swimming pool water is dependent on ORP and not on the free residual chlorine level. As shown in Figure 1, the kill time is just a fraction of a second at a Redox level of 650 mV, but it increases rapidly to several hours at lower ORP values.

In Germany and other European countries where public health standards are very high, a minimum ORP level of 750 mV is required by DIN Standard 19643 (adopted in 1982) for public pools and DIN Standard 19644 for spas (December 1984).

In the U.S., many public pools and spas use ORP controllers for automatic chlorine control but this is disguised by the fact that the controller readouts usually are labeled in parts per million (ppm) of free chlorine instead of the more meaningful ORP mV. More recently, however, manufacturers of ozone generators and industry consultants have called for the use of ORP to monitor the effectiveness of disinfection in ozone/chlorine systems.

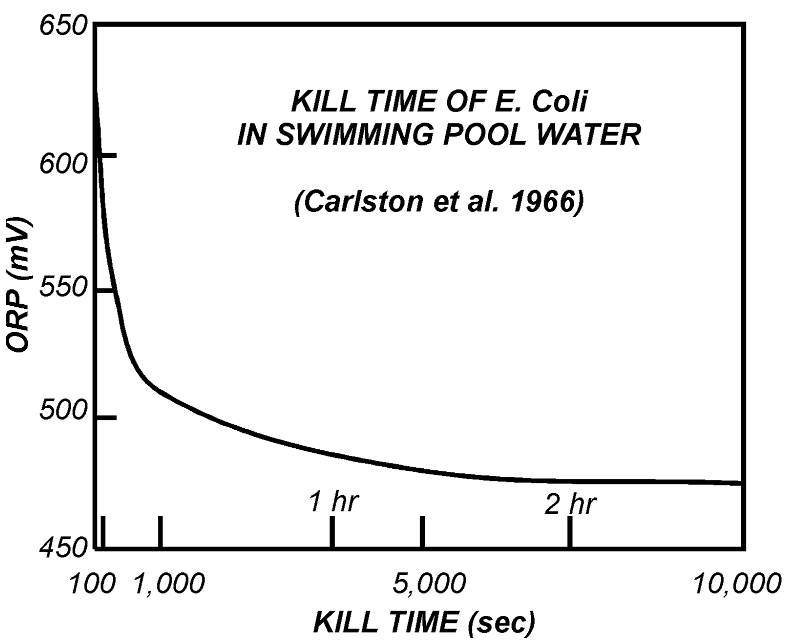

Figure 1 — Kill time of E. Coli as a function of ORP.

Oregon Study

This June, James C. Brown, a consultant formerly with the Oregon State Health Department, presented to the National Environmental Health Association Conference in Las Vegas the results of a remarkable field study on "Chemical and Microbiology Water Quality Constituents of 30 Public Spas" in metropolitan Portland, Ore.

Brown (et al.) found that: "Total and fecal coliform parameters proved to be unreliable indicators of bacteriological water quality (but) the oxidation reduction potential (ORP) was found to be a reliable indicator of bacteriological water quality. Waters having an ORP equal to or higher than 650 mV were well within accepted bacterial parameters."

The key data from this study has been computer-sorted and listed by decreasing ORP values in Table 1. The ORP values range from a high of 867 mV to a low of 296 mV, with an average of 643 mV. As noted by Brown, both the plate count and the pseudomonas count showed a high degree of correlation with the ORP level — the high counts being found systematically in the bottom half of the list, below the 650 mV mark.

The free chlorine level in the 30 spas included in the study varied from a low of 0.72 ppm to a high of 30 ppm, with an average of 3.8 ppm in spas without cyanurates and 6.7 ppm in spas using cyanurates. The pH varied from a low of 5.8 to a high of 8.2.

The cyanuric acid level varied from zero in the five spas using sodium or calcium hypochlorite to a high of 1,300 ppm in spas using cyanurates, with an average of 228 ppm in the cyanurated spas. This, of course, is well in excess of the maximum recommended values - 100 ppm, for instance, in California

San Diego Survey

These results unfortunately confirm those of a recent survey of commercial spas in San Diego, Calif., where more than 50 percent of the spas were found out of compliance with health department regulations.

In view of the wide variations in the levels of free chlorine, pH and cyanuric acid in the Oregon study, it is remarkable that the key indicator of bacteriological water quality was not ppm of free chlorine, as generally expected, but the ORP level, clearly confirming the earlier study of swimming pool waters in .Germany. In addition, both studies found the same minimum ORP level of 650 mV for safe water quality, whether cyanuric acid is used or not.

These results are expected to have a profound impact on water treatment procedures in this country, particularly in commercial spas but also in all public pools and spas. There is a need, therefore, for a new and comprehensive analysis of sanitizer chemistry in order to provide a better understanding of the reasons why ORP readings have been so successful in monitoring sanitizer performance.

Free and Combined Chlorine

When chlorine in any form is introduced into pool or spa water, it forms free chlorine (HOCl), which is an excellent bactericide:

Cl_2 + H_2O ---> HOCl + HCl (1)
Chlorine Water Free Chlorine Hydrochloric Acid

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, 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.

The chemistry of chlorine in water is controlled by a very important factor: the ratio of free chlorine divided by the concentration of nitrogen or ammonia radicals in the water. For proper water sanitation, this ratio should be as high as possible. Whenever it is allowed to fall below 5:1 by weight (either through chlorine loss or by introduction of waste products), essentially all the chlorine in the water is converted into compounds called **monochloramines**, such as $NHCl_2$:

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NH_2CONH_2 + 2 HOCl --->
Ammoniated Compounds Free Chlorine

2NH2Cl + CO_2 + H_2O (2)
Monochloramine

At a pH of seven to eight, this reaction takes place in a fraction of a second. Although chloramines have some bactericidal properties, their kill ratios for various micro-organisms are as much as 80 to 100 times lower than those of free chlorine, HOCl.

When the ratio of chlorine to nitrogen is progressively increased back above 5:1 by the addition of small amounts of chlorine, the monochloramines are transformed into other types of compounds called **dichloramines**, such as $NHCl_2$:

NH_2CONH_2 + 4 HOCl --->
Ammoniated Compounds Free Chlorine

2 $NHCL_2$ + CO_2 + 3 H_20 (3)
Dichloramine

Dichloramines are even worse than monochloramines. They are notorious for their bad smell (the so-called "chlorine odor") and for eye irritation. They are the source of most customer complaints about public pools and spas.

Finally, when more chlorine is added to the water and the ratio of chlorine to nitrogen is increased to 10:1, the mono- and dichloramines are almost completely destroyed and are converted back into inoffensive compounds, such as nitrogen compounds and chloride salts. This can be represented with some simplification by reactions of the type:

NH_2CONH_2 + 6 HOCl --->
Ammoniated Compounds Free Chlorine

N_2+ 6 C l+ CO_2 + 5 H_20 (4)

This last equation corresponds to what is generally known as "breakpoint chlorination." To prevent chloramine formation, a constant state of breakpoint chlorination is required. In other words, the free chlorine level must be at least 10 times the level of ammoniated compounds in the water at all times. This can be accomplished only with frequent testing of the water or, more easily and reliably, with automated equipment.

Two Forms of Free Chlorine

Up to this point, we have assumed that the pH of the water remains low, (i.e. below 7.0). Now, the picture is further complicated by the fact that 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 <---> OCl- + H+ (5)
Hypochlorous Acid Hypochlorite Ion Hydrogen Ion

The equilibrium constant at 20°C is 3.3 x 10^{-8}. Figure 2 shows the familiar ionization curve for HOCl, representing the above reaction. Note that 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

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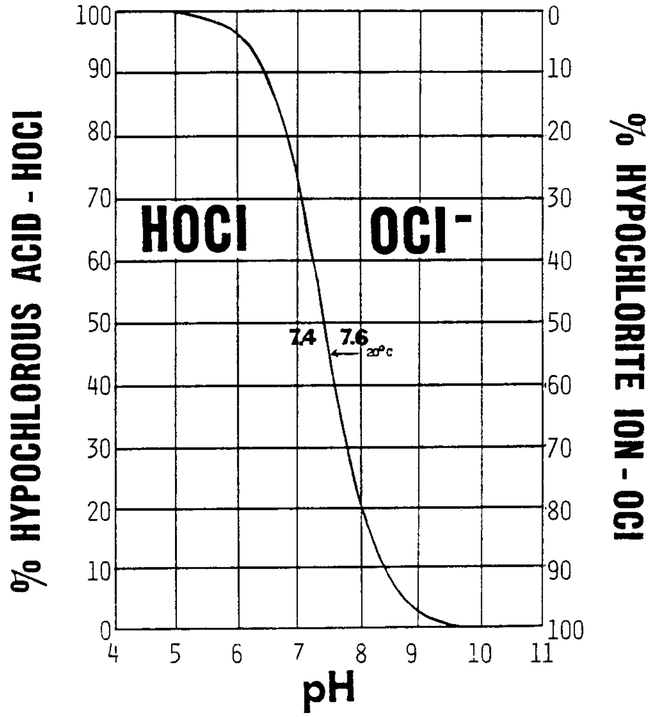

Figure 2 — Ionization curve of HOCl as a function of pH.

• 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. Therefore, they cannot show the decrease in HCOl concentration when the pH is increased. This is no problem if the pH remains where it should be - at 7.4 to 7.6. However, if the pH is allowed to rise - through the addition of an alkaline sanitizer, of alkaline make-up water or just body perspiration - the concentration of HCOl can decrease to almost zero even though the DPD test kit still shows the same level of free chlorine.

The increase in pH can take place very easily, especially if the water is chlorinated with one of the alkaline forms of chlorine — sodium hypochlorite (liquid bleach), NaOCl or, to a much lesser extent, calcium hypochlorite, Ca(OCl)2 — or if the total alkalinity levels are too low to adequately buffer the water against pH changes.

Remember, above a pH of 8, almost all the free chlorine is useless - and the DPD test kit does not show it

Free Chlorine and ORP

Fortunately, 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.

When an ORP sensor is placed in water containing a sanitizer - such as chlorine, bromine or ozone - which is also an oxidizer, 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. As shown by the Oregon spa study data in Table I, this potential can vary over a wide range, from a few hundred mV to 800 mV or more.

The *Handbook of Chlorination*, by Geo. Clifford White (Van Nostrand Reinhold Co., 1972) gives the half-cell oxidation-reduction potential Eo at 25°C for HCOl:

$$HCOl + H^+ + 2e \longrightarrow Cl + H_20 \qquad (6)$$
$$E_0 = 1.49V$$

If one assumes that Cl- is the reduced state for chlorine, the variation of ORP for HCOl is given by an expression of the form:

$$ORP = E_0 + 0.059/N*\log[(HOCl)/(Cl-) - E_h \qquad (7)$$

where N is the number of electrons e- and E„ is the potential of the reference electrode. The actual relationship for ORP is in fact more complex due to the need to consider the various oxidation and reduction states of chlorine. In general, though, one can see that ORP increases logarithmically with increasing HCOl concentration.

OCl has a much lower ORP value than HCOl, consistent with its much lower activity as a sanitizer:

$$OCl + H_2O + 2e \longrightarrow Cl + OH \qquad (8)$$
$$E_0 = 0.90V$$

The expression for the ORP of the hypochlorite ion OCl- is similar to that of HCOl in Equation 7, but since Eo is lower, the ORP values are much lower than those of HCOl. As a result, when HCOl is present, it tends to “mask” the ORP of OCl-. The same effect applies to chloramines, too. This is why the ORP sensor is said to read only the fast-acting free chlorine, HCOl.

ORP and pH

The variations of the ORP of free chlorine with pH are shown in Figure 3. The experimental curves were determined at the Uniloc Co. in Irvine, Calif, in the early 1970s. Close analysis of the apparently complex set of curves shows that they simply reflect the effect of HCOl ionization (Equation 5) on the expression for ORP (Equation 7).

This is illustrated in Figure 4, a previously unpublished combination of data from Figures 2 and 3. The

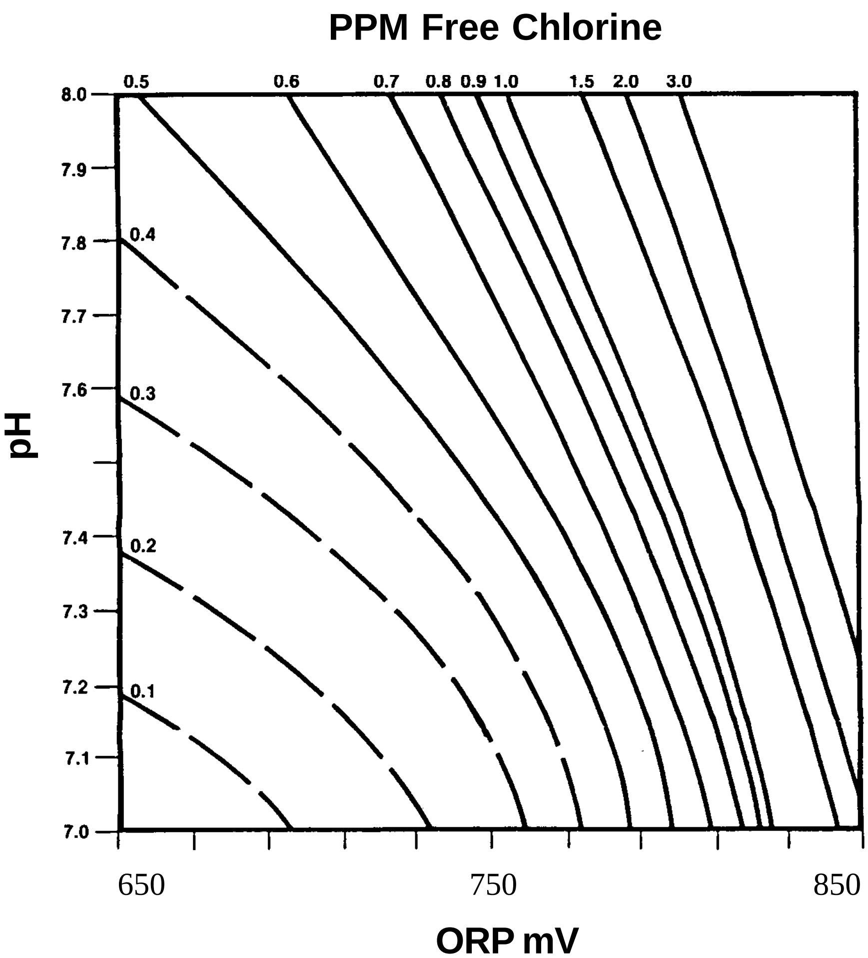

Figure 3 — Variation of ORP for Free Chlorine as a function of pH.

solid lines show the variation of ORP readings (from Figure 3) in the pH range of 7 to 8 for total free chlorine levels of 0.3, 0.5, 1.0 and 3.0 ppm, respectively. As the pH increases between 7 and 8, the ORP sensor shows a marked decrease in value for all chlorine levels.

For comparison, the dissociation curve of HOCI (from Figure 2) is superimposed on Figure 4 as a broken line. It shows that the decrease of the ORP reading with increasing pH closely parallels the decrease in concentration of HOCI. This comparison of the curves for ORP and HOCI is a key factor in understanding the meaning of ORP measurements. It explains why the ORP sensor can be used very effectively to monitor HOCI in the water. This is true not only when the pH varies but also when a cyanuric stabilizer is used, as evidenced by the results of the Oregon study.

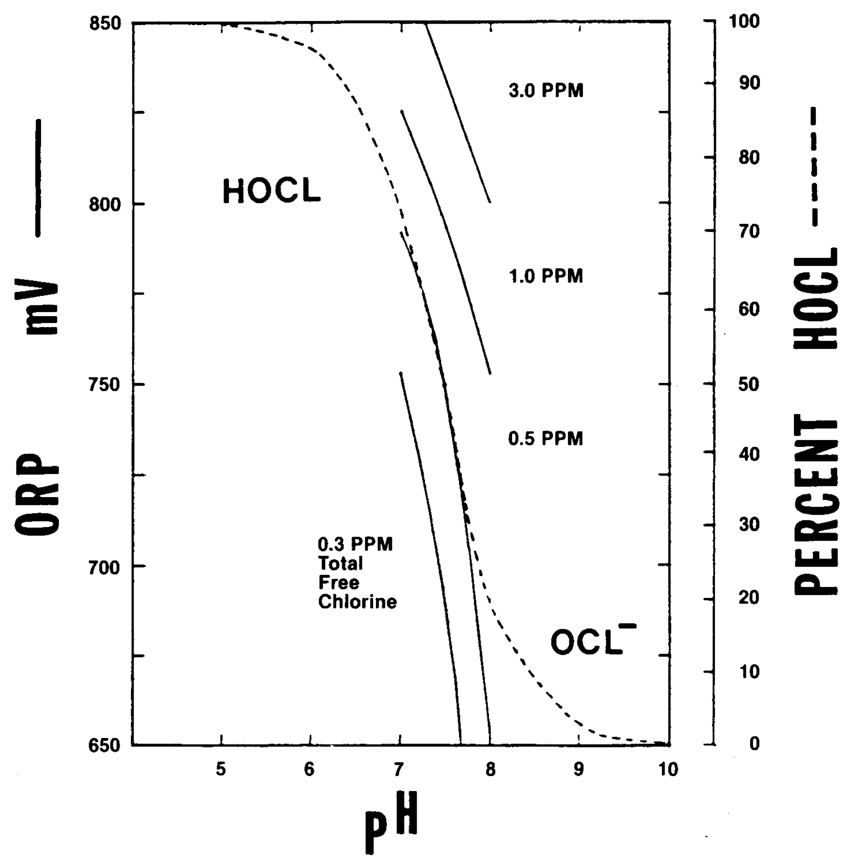

Figure 4 — Comparison of ORP and HOCI variations as a function of pH.

ORP and Cyanuric Stabilizers

Introduced in 1956, cyanuric acid and other stabilizers are now widely used in pools and spas, but unfortunately often without regard to their limitations. The key advantage of stabilizers is that they react with chlorine to form compounds that - unlike free chlorine - are not destroyed by the UV rays in sunlight. Field tests on outdoor pools in the St. Louis, Mo. area showed that, without stabilizers, chlorine residuals would be 90 percent destroyed in two to three hours on sunny days. With 25 to 50 ppm of cyanuric acid in the water, only 10 to 15 percent were destroyed during the same period of time.

The chemistry of chlorocyanurates is somewhat similar to the formation of chloramines. If cyanuric acid is represented by H(CYA), the following reversible reaction takes place:

H(CYA) + HOCI <---> Cl(CYA) + H_20 (9)
Cyanuric Acid — Free Chlorine — Chlorocyanurate

The difference with chloramine formation is that the equilibrium constant for the reaction in Equation 9 is much higher (about 10^{-4} instead of 10^{-10}). This means that the chlorocyanurates are much more unstable than chloramines and can readily dissociate to recreate HOCI when it is needed. The reverse reaction of Equation 9 takes place automatically as HOCI is used up in the water. The chlorocyanurate therefore constitutes a reservoir - or a bank - of free active chlorine protected from the destructive effects of UV rays.

Field studies have shown that the bactericidal properties of chlorine in pool water are not affected by the presence of normal concentrations of cyanuric acid (up to 100 ppm). However, it is recommended to use higher levels of chlorine residuals in stabilized water, (i.e. two or three times the "normal" values).

The data of the Oregon study shows that the presence of cyanuric acid reduces the ORP reading of the sensor. We understand now that this is because it reduces the concentration of HOCI in the water.

Cyanuric stabilization is used in two ways:

- By dissolving cyanuric acid into the water until a level of 25 to 30 ppm is reached. This is the method used with chlorine gas, sodium hypochlorite or calcium hypochlorite in outdoor pools.
- By using cyanurated chlorine compounds - either trichloroisocyanurate tablets (trichlor) or sodium dichloroisocyanurate powder or granules (dichlor).

The data of the Oregon study in Table I shows that the presence of cyanuric acid reduces the ORP reading of the sensor. We understand now that this is because it reduces the concentration of HOCI in the water. It is therefore very important not to exceed the maximum recommended concentration in the water (normally 100 ppm). If that concentration is exceeded, all or part of the water must be dumped and replaced with fresh water.

Commercial Spas Study, Portland, Oregon

Sample#	ORP mV	Total Cl	Free Cl	pH	Cyanuric Acid	Plate Count	Pseudo-monas
7	867	25.00	21.00	6.77	275	0	0
6	805	5.10	3.92	5.78	15	0	0
13	795	34.00	30.00	7.13	200	0	0
3	787	10.00	8.54	6.83	0	0	0
30	769	9.00	6.35	6.21	185	4	0
14	754	17.00	13.60	7.28	240	0	0
27	741	3.95	2.41	7.19	0	6	0
23	736	2.90	2.50	7.49	250	0	0
16	732	6.62	4.38	7.42	150	0	0
12	696	7.50	5.62	7.61	390	1	0
17	695	23.00	18.40	7.47	550	0	0
15	686	30.00	25.00	7.47	200	0	0
26	681	4.40	3.75	7.30	95	2	0
2	668	6.62	4.92	7.90	0	0	0
22	653	3.50	2.30	7.81	175	0	0
28	634	3.80	2.35	6.97	130	13	0
8	633	8.94	7.34	7.49	720	0	0
9	623	3.84	2.28	7.83	150	12	2
5	618	3.08	1.20	7.06	225	170	12,400
21	605	3.84	2.34	7.23	0	0	0
25	595	3.75	2.23	7.56	200	30	23
10	590	1.93	0.78	7.84	200	310	2,400
18	564	1.87	0.83	7.87	0	150	94
29	554	3.54	1.88	7.39	185	15	0
24	551	2.62	1.31	7.48	130	69	13
20	537	4.00	2.41	6.95	1,300	140	1,600
19	509	2.98	1.14	7.89	235	4,600	920
11	480	1.98	0.67	8.25	95	15,000	2,400
4	412	1.43	0.72	8.25	57	2,200	540
1	296	1.59	1.20	7.79	150	640	1,600
Average	**643**	**7.93**	**6.05**	**7.38**	**217**		

Analysis of Oregon Study Data

In view of the above analysis of ORP, it is useful at this stage to take a new look at Table I, the data of the Oregon study.

It is now evident that the ORP value reflects the effects of at least three separate factors - free chlorine level, pH and cyanuric acid concentration. High ORP values result from a combination of high ppm levels, low pH values and low cyanuric levels. The data shows that high pH values and high cyanuric levels can lead to low ORP levels, even though the ppm of free chlorine is above the minimum recommended value.

The Oregon study confirms that good water bacteriological quality can be maintained in the presence of cyanuric acid, if the proper ORP level is maintained.

In other words, a low ORP value (defined by Brown as below 650 mV) should be used as an alarm signal to alert the pool or spa operator or the health department inspector that one or more of these three factors - ppm, pH or stabilizer - or their combination - has resulted in unsanitary water conditions.

ORP and Bromine

When dissolved in water in the presence of a strong oxidizer, such as chlorine or monopotassium persulfate, bromine forms hypobromous acid (HOBr) and the hypobromite ion (OBr). The respective oxidation-reduction reactions are similar to those of chlorine but with lower E_0 values:

$HOBr + H^+ + 2e^- \rightarrow Br^- + H_20$ (10)
$E_0 = 1.33V$
$OBr + H_20 + 2e^- \rightarrow Br^- + 2 OH^-$ (11)
$E_0 = 0.70V$

The same ORP sensor can be used for either chlorine or bromine, but there are several key differences:

• Because of the lower E_0 values, the recommended bromine levels are about twice the amount for chlorine, (i.e. between 3 and 6 ppm for spas).

• Bromamines are reputed to be effective sanitizers and to have no unpleasant odors.

• Hypobromous acid (HOBr) dissociates into hypobromite ions, OBr^- - just like chlorine - but this takes place at a higher pH level, (i.e. above the normal pH range used in pools and spas). At a pH of 8, there is about 83 percent of HOBr. Even at a pH of 9, the ionization ratio is still about 33 percent compared to 4 percent for chlorine. The “pH shift” for bromine compared to chlorine is about one full pH unit. In addition, bromine solutions are nearly neutral in pH, so that they do not affect the pH of the water nearly as much as most chlorine compounds.

• There is no stabilizer for bromine, but it is reputed to be more stable than chlorine in the presence of sunlight (65 percent loss in two hours).

ORP and Ozone

Ozone is another strong oxidizer used in pool and spa water sanitation. Its ORP value is very high:

$0_3 \rightarrow 2H^+ + 2e^- + 0_2 + H_20$ (12)
$E_0 = 2.07V$

Ozone also can be monitored with ORP sensors. Because of its short lifetime and lack of residual value, health departments require the maintenance of a chlorine or bromine residual if ozone is used on public pools or spas. In addition, it also may be required for safety reasons to reduce the ozone level in the water with activated charcoal before returning it to the pool.

Ozone is very effective in destroying bacteria and bad odors and gives the water a “polished” look. It is also very good in oxidizing oil and grease, especially in spas and hot tubs and in filters, but it is mostly ineffective in the prevention of algae growth.

Ozone is commonly used in Europe prior to chlorination or bromination. This allows the operator to reduce the chlorine or bromine levels in the water while maintaining high ORP values and good water clarity.

ORP Controllers

Chemical controllers used in the pool and spa 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. 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 chloramines and other unpleasant products, as well as in savings in chemicals and labor.

As mentioned earlier, most U.S.-built ORP controllers have readouts labeled in ppm free chlorine. The more recent controllers show the variation of fast-acting free chlorine associated with variations in pH. Older controllers use a correction based on the curves shown in Figure 3 to mask this effect and display only total free chlorine. This correction, however, is not applicable if there is any cyanuric acid or chlorine-based cyanurate in the water.

For certain applications, such as smaller pools and spas, it is also possible to use an ORP-only controller, that is, without pH control. This is normally limited to the use of neutral-type sanitizers such as a “dichloro” chlorine (sodium dichloro-S-triazinetrione) solution or bromine ”dihalo” (bromo-chloro-dimethylhydantoin) sticks. Generally, ORP controllers without pH control should not be used with alkaline sanitizers such as sodium hypochlorite or calcium hypochlorite. If the pH remains fairly constant, these inexpensive controllers provide a very cost-effective solution to the problem of chemical control in small commercial installations.

ORP Standard Recommendation

In view of the European experience, plus the results of the Oregon study and the new scientific understanding of ORP, it is recommended that pool and spa professionals and health department officials agree on a new standard for water quality in commercial or public pools and spas based on a clearly defined minimum ORP level.

It is further recommended that the minimum ORP level be set at least 650 mV or at 750 mV.

The ORP standard should apply to all sanitizers - including all forms of chlorine, stabilized and nonstabilized, and bromine - as well as to systems using ozone or other sterilization methods.

Dr. Steininger is president of Santa Barbara Control Systems, Santa Barbara, Calif., the manufacturer of the Chemtrol line of chemical automation equipment for pools and spas.