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Towards a better understanding of Swimming Pool Chemistry and ORP

ORP as a Disinfection Parameter

Oxidation-Reduction Potential (ORP, redox) measurements are a very reliable indicator of the condition of the water, as they measure the relative oxidative properties that are immediately available. Research has shown that in chlorinated water, ORP values in excess of 720 millivolts (mV.) using a silver/silver chloride electrode should guarantee water that is in good microbiological condition.

Values in excess of 750 mV. can be achieved in good pools with excellent filtration and supplementary oxidation processes. However, the action of other chemicals, pH and temperature may affect ORP values.

When ORP is used as the sole water quality parameter in its own right, then verifying the sensor response using a 250 mV. (AS5250) and 475 mV. solution (AS5475) is essential to verify the accuracy of the sensor.

ORP measurements themselves do not guarantee the capacity of the system to disinfect or oxidise a minimum quantity of contaminants per litre of water, so regulatory authorities prescribe that minimum free disinfectant residuals need to be measured by other means.

Algae growth in pools presents a major problem to pool operators. Once established, algae are required which can be toxic to plants and stream life. Some algicides, particularly those containing metal ions or residual herbicides, have residual properties that last for many months and are harmful to the environment, even if discharged to sewer.

In a pool that is subject to regular use and is maintained in accordance with "best practice" regulations, algae problems should never occur. Regular superchlorination should be all that is required to oxidise algae spores. Thus the environment will not be subject to the problems associated with algicides. Indeed EPA policies require all unnecessary chemicals be avoided and that commercial pool operators undertake waste minimisation practices.

Most algicides actually increase the rate of chlorine consumption as metallic compounds and other complexes are oxidised by chlorine. The presence of metallic or other compounds may alter the oxidation profile of the pool water and can inhibit chloramine destruction and disinfection.

Algicidal compounds generated from ionising electrodes have no fundamental difference from residual metal-based algicides obtained from liquid or powder type products.

"Best Practice" Model

- ◆ Design disinfectant dosing systems for all pools to cope with a range of bather loadings.
- ◆ Use automatic monitoring and dosing of disinfectant and pH in all spa pools and other pools that are subject to inconsistent chlorine demand.
- ◆ Maintain disinfectant residuals at the lowest end of the regulatory scale, where possible. Pools with poor circulation rates or dosing systems may need to maintain higher residual levels to accommodate demand from the influx of pool users.
- ◆ Ensure that cyanuric acid is present in all outdoor pools to minimise chlorine loss to sunlight.
- ◆ Conduct superchlorination at least weekly to disinfect filters, control algae and oxidise bather pollution.
- ◆ Maintain a stable pH when using automatically controlled disinfectant dosing to avoid fluctuations in disinfectant levels.
- ◆ Dilution reduces bather pollution, disinfection by-products, excessive T.D.S. and cyanuric acid build-up.

Free and Combined Chlorine

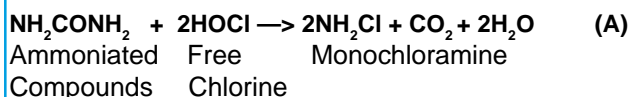
When chlorine in any form is introduced into pool or spa water, it forms free chlorine ($\text{HOCl} + \text{OCl}^-$), the ratio of HOCl to OCl^- formed depends on the actual pH. The HOCl is the more reactive molecule, and a much more efficient disinfectant than OCl^- , perhaps 100 times more. (The reason why good pH control is required.)

Free chlorine as HOCl 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.

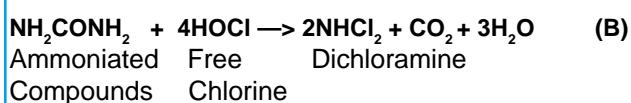
Most people in the pool and spa industry are, or should be, familiar with chloramines. However, the mechanisms of the actual formation and the destruction of chloramines generally are poorly understood in the pool industry.

The chemistry of chlorine in water is controlled by a very important factor: the ratio of free chlorine to 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, as outlined above), essentially all the

chlorine in the water is converted into compounds called monochloramines, such as NH_2Cl :



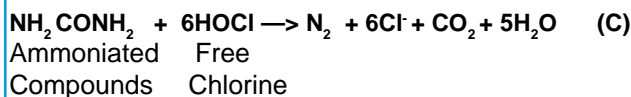
At a pH typical of swimming pools, this reaction takes place in a fraction of a second. Although chloramines have some bactericidal properties, their kill ratios for various microorganisms are much less than those of free chlorine. When the ratio of chlorine to nitrogen is progressively increased back 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 :



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

Finally, when more chlorine is added the chlorine to nitrogen ratio 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:



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.

Chloramine Removal

Chloramines are formed by a reaction between hypochlorous acid and nitrogen based products from bathers. Chloramines can be reduced by a number of processes. Superchlorination/shock dosing, ozonisation and dilution are three conventional methods of chloramine reduction. Continuous dilution is the best way to minimise the build-up of combined chlorine, particularly the stable organic-nitrogen complexes formed from nitrogen-based compounds present in sweat and urine. The continuous maintenance of a

free chlorine residual, which is at least 50 per cent (but preferably 75 per cent) of the total chlorine residual during normal pool operation, should control the accumulation of simple inorganic chloramines.

Superchlorination

Superchlorination is a pool industry term for a periodic maintenance procedure where the free chlorine residual is raised 2–4 times the normal operating level to prevent algae, remove colour and maintain clarity.

In most circumstances, superchlorination also assists in reducing combined chlorine. It also assists in keeping the pool water within bacteriological requirements during normal operation by periodically removing biofilms that can resist normal chlorine levels.

Superchlorination should be conducted when the pool is closed to bathers (for example, overnight). This will prevent the introduction of pollution that may hinder the superchlorination process.

Superchlorination must be carried out with the pH between 7.4 and 7.6. Under most circumstances superchlorination is achieved at chlorine levels around 6–8 ppm as Free Available Chlorine. (825 mV. ORP at pH 7.6) This level is usually sufficient to remove all the chloramine and will return to normal operating levels by the next morning.

It is generally recommended that superchlorination is conducted at weekly intervals. Some pools may require more frequent treatment, depending on their bather load and pollution profile. Chloramine concentrations may also be increased if the make-up water supply uses chloramines as its disinfectant.

Periodic superchlorination is recommended in these circumstances as the best method of removing inorganic chloramines. For pools using chlorinated isocyanurates as their regular disinfectant, superchlorination using these products may elevate cyanuric acid levels over time. Operators should consider using a hypochlorite for superchlorination purposes when cyanuric acid is at the preferred concentration.

Shock Dosing

Shock dosing is a term used to describe the process of superchlorination when it is specifically used to solve problems such as destroying algae blooms and treating colour and clarity problems. The chlorine dose level is usually higher than that used for superchlorination.

Shock dosing to 10–15 ppm as Free Available Chlorine (about 925–950 mV. ORP at pH 7.6) or around 5–7 times the normal free chlorine residual, may be used to help correct a serious problem.

Shock dosing immediately after refilling an empty pool from a town water supply that is heavily chloraminated will remove the chloramine present.

In this situation, the free chlorine should not be raised by more than ten times the combined chlorine residual, otherwise nitrogen trichloride will form.

◆ pH should be maintained between 7.4 and 7.6

when shock dosing, for the same reasons as for super-chlorination.

- ◆ Shock dosing good quality pool water will not change the water quality, and is simply a waste of chemical.
- ◆ More serious problems, such as persistent combined chlorine, can be solved by dilution through backwashing and by the introduction of fresh water.
- ◆ Consideration must always be given to the Regulations and bather comfort, as well as the levels of chemical in the water when the pool is open for use.
- ◆ If chlorine levels are too high to allow bathing even after allowing sufficient time for the process to work (for example, overnight), then dechlorination may be required prior to reopening the pool.

Dechlorination

Dechlorination can be achieved by adding sodium thiosulphate to the pool water if chlorine levels are above the regulatory limits. This will enable the operator to reduce chlorine levels and allow bathing.

Situations that require dechlorination should be avoided. When using sodium thiosulphate, it is important to fully dissolve the crystals before adding them to the pool, as inadequate dissolution may prevent satisfactory chlorine neutralisation.

Overdosing may result in a higher residual of sodium thiosulphate than required and this may prevent adequate free chlorine levels being achieved.

Approximately 10 gms of sodium thiosulphate per 10,000 litres (10 m³) of pool water is required to lower chlorine levels by 1.0 ppm.

Cyanuric Acid

Cyanuric acid is a granular compound which, when dissolved in pool water, shields a percentage of chlorine from sunlight, thereby significantly reducing chlorine loss. It is an essential ingredient in outdoor pools, but has little if any benefit for indoor pools.

A slightly higher level of disinfection residual should be maintained within the pool water body because some studies have suggested that the speed of disinfection is slower when cyanuric acid is present.

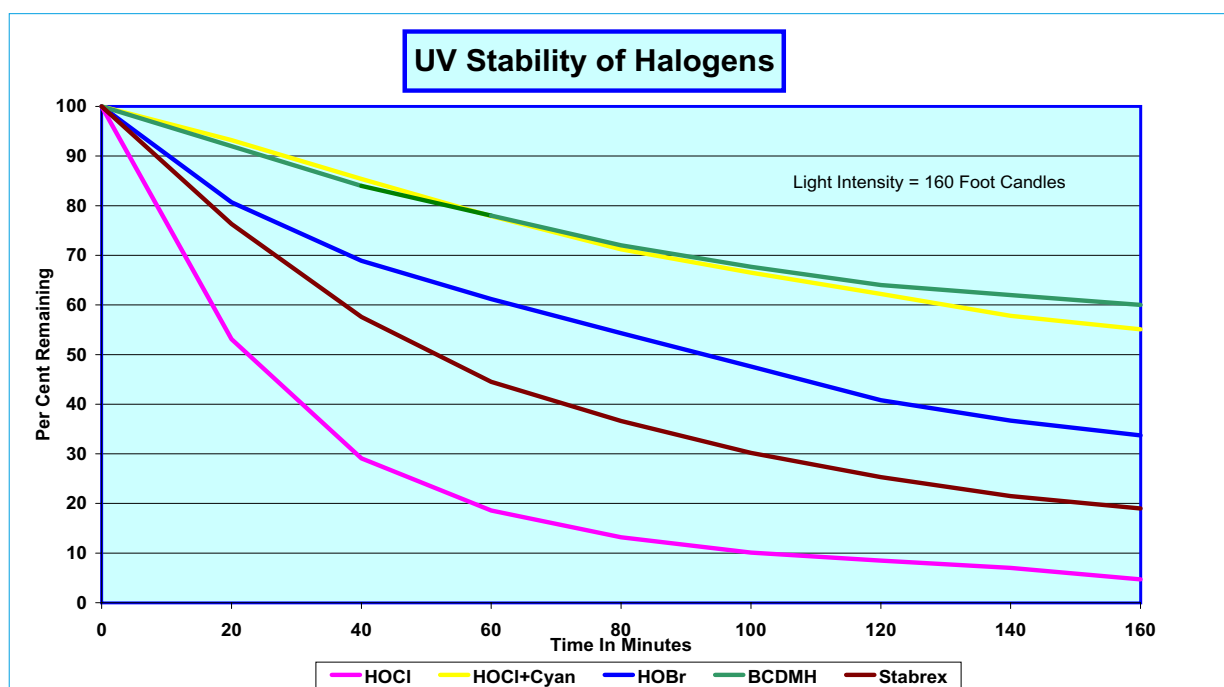
Oxidation is also impaired by the use of cyanuric acid as the oxidation-reduction potential is reduced, 40 ppm of cyanuric acid will reduce ORP from 725 mV. to about 700 mV. for the same Free Available Chlorine reading. It is the ORP value that is the measure of disinfection power. Cyanuric acid works by "locking" up some of the HOCl which is the effective disinfectant.

At least 25 ppm of cyanuric acid is needed for it to work efficiently but there is no advantage increasing levels above 50 ppm except to allow for a drop-off in levels, due to backwashing and water losses on the pool deck.

Disinfectants that contain isocyanurate continue to add cyanuric acid through the swimming season, so there is no need to top up cyanuric acid levels. High levels of cyanuric acid may contribute to water cloudiness and are controlled by dilution with fresh make-up water. In these pools a start up dose of 25 ppm is recommended after refilling.

Cyanuric acid is extremely difficult to dissolve, and the gradual addition of cyanurate to bring up the level may be the easiest method for some operators.

The graph below highlights the loss of chlorine to UV light as approx. 80 % in 60 minutes, versus chlorine with cyanuric acid which only shows a 20% loss over the same period and thus use of cyanuric offers considerable savings in chlorine, in pools exposed to sunlight.



Summary

The chemistry of swimming pools is much more complicated than what is first envisaged. The bather load not only introduces bacteria which consume chlorine but also a host of ammoniacal products such as sweat, urine, skin particles, suntan lotions, and cosmetics which react with chlorine to form the nasty chloramines.

Chlorine is attacked and degraded by UV light from sunlight. Its disinfection ability is effected by pH, and the professional test kits for free and combined chlorine leave a lot to be desired in terms of accuracy.

The ORP sensor really is the measure of disinfection ability, a pool maintaining in excess of 725 mV. will be in very good microbiological condition.

If the ORP level falls below about 675 mV. and your test kit is saying that you have 2.0 ppm or more of free chlorine, verify the operation of both the ORP probe and the electronics by using both the 275 mV. and 475 mV. verifications solutions as per the procedure outlined in the Poolpac Operating Instructions, then check out for the following:

Is the pH value in the correct range 7.2 - 7.6 ?

Has the bather load been high over the past few days ?

Does the pool get a regular superchlorination on a once per week basis, ?

Do I have an electrochlorinator as my chlorine source ? and is the salt level up to about 0.5%? or as recommended by the manufacturer ?

If an outdoor swimming pool, is the cyanurate between 30 - 45 ppm ?

The ORP sensor, as well as being a very valuable measure of disinfection ability, is also a good indicator of water chemistry in that ORP levels below 675 mV. indicate:

(a) disinfection capability is not that good and

(b) the pool chemistry needs attention and correction to return the disinfection capability up to the correct level.

The graph below shows how millivolt readings are

reduced when Free Chlorine is converted to chloramines, with the greater the reduction in millivolts due to greater amounts of chloramines.

For example, if the ORP mV. levels have dropped down to around 500 mV. and the test kit says you have 1.5 - 2.0 ppm chlorine, in fact you very likely have a chloramine problem and superchlorination needs to be carried as soon as possible. Only when ORP is returned up to 700 + millivolts can disinfection be considered adequate.

Recommended Further Reading

ACT Dept. of Health & Community Care -

A Code of Practice to minimise the Public Health Risks from Swimming/Spa Pools - Part A General Guidelines

Pool Operators' Handbook. -

Victorian Government Publishing Service 2000.

NSW Dept. of Health -

Public Swimming Pool & Spa Pool Guidelines

QLD Dept. of Health -

Swimming & Spa Pools Water Quality and Operational Guidelines

QLD Asset Management AM-02 -

School Swimming Pools Guidelines for Operators

World Health Organization -

Guidelines for Safe Recreational Water Environments Volume 2 - Swimming Pools, Spas and similar recreational water environments - Final Draft.

Author

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