Watertec Engineering Pty Ltd

Information Sheet

OZONE TREATMENT OF COMMERCIAL SWIMMING POOLS

Watertec Engineering Pty Ltd
Brisbane, Australia

ABSTRACT

Treating swimming pools with ozone, in conjunction with a maintenance disinfectant such as chlorine or bromine, is simple and effective. However, in practice, the overall chemistry is quite complex, as is the case with all swimming pool treatments. When ozone is used for swimming pools, three important benefits are provided. The ozone; carries out partial oxidation of organic contaminants, achieves effective disinfection and assists with flocculation to maintain optimum water clarity. When designed and operated correctly ozonation will achieve a water quality not obtainable using other pool treatments.

Several methods of applying ozone to swimming pools have been used, although to varying degrees of success. The most commonly used application methods will be discussed, detailing the limitations of each.

With specific reference to pool treatment, the limitations of application and chemistry of ozonation are often misunderstood. A clearer understanding of the basic chemistries involved together with limitations of different ozone generation techniques must be obtained before a valued judgement of the treatment process can be made.

To achieve the sought after benefits of ozone treatment, only ozone generated by corona discharge is suitable. Ozone generated by Ultraviolet radiation cannot provide sufficient residuals to perform simultaneous oxidation and disinfection.

INTRODUCTION

All swimming pool treatments commonly used today are effective, however with the great variation in pool design, hydraulics and use, some treatments have significant advantages over others. Over recent years the design criteria for commercial swimming pools have changed substantially with leisure activities taking the focus away from traditional lane swimming or training pools.

Many pool facilities have been upgraded to accommodate a larger cross section of patrons incorporating various fun pools, aquatic features etc. Also, many aquatic centres have incorporated other facilities such as gymnasiums, child minding, aqua-aerobics and non-water related ball games. As a result of these changes many pools are experiencing very high bather loads which obviously places great demand on the pool hydraulics, filtration and overall chemical treatment.

For swimming pools or aquatic facilities where heavy bather loads are anticipated, hydraulic designs have moved towards higher recirculation rates resulting in shorter pool turnover times. This is particularly the case with indoor heated pools with which the average turnover time may be as low as two hours. With this increased recirculation rate, additional effective filtration, and an ozone based treatment, the highest possible water quality achievable with current technology is provided. Due to the success of many aquatic centres using an ozone treatment, a definite benchmark has been set whereby pool patrons expect to use these facilities without the problems of strong pool hall odours or irritation to the eyes, nose and other mucous membranes. Also of significant importance is the clarity or general appearance of the pool water.

The most common treatments used for pool and spa waters are still chlorine or bromine. These halogen compounds are added until a specific free halogen residual is achieved. All oxidising pool disinfectants must perform two functions, one being to oxidise organic and some inorganic contaminants of the pool and two, to act as disinfectants. Chlorine is by far the most common halogen compound used in swimming pools, however for indoor heated pools, unpleasant chlorinous odours exist in the pool hall, chloro-organic by-products cause bather skin and eye irritation and volatile chemicals cause significant pool hall corrosion.

Looking at the main disinfectants, chlorine is an excellent oxidising chemical and an efficient disinfectant. However, chlorine reacts with nitrogen based compounds to form chloramines, which are very poor disinfectants. Bromine on the other hand, has weak oxidising capabilities although in both it's free and combined state has excellent disinfecting ability. Due to its lower oxidising capability, higher bromine residuals need to be maintained in the pool water. The molecular weight ratio between bromine as HOBr and chlorine as HOCl, is 97 to 52. It therefore becomes clear why a test kit multiplier is necessary when residuals are to be determined as bromine. Bromine turns the DPD test a little less than half as dark for a given quantitative residual.

As alternative oxidation chemicals where being sought, ozone became one of the obvious options. Ozone is the most powerful oxidant that is commercially available, however it is an unstable gas and must be generated and used at the point of application. Ozone is a far more effective oxidant and disinfectant than either chlorine or bromine. Its application and use in commercial swimming pools is therefore obvious. The main limitation of ozonation is that ozone is a toxic gas and therefore must not return to the pool in any significant quantity. Although ozone is used as a stand alone treatment for swimming pools, it is more commonly used in conjunction with a residual disinfectant such as chlorine or bromine.

PROPERTIES OF OZONE

Ozone is the triatomic state of oxygen which simply means that the ozone molecule contains three oxygen atoms, having the chemical symbol O_3. This is nothing more than another molecular form of oxygen, the chemical symbol for which is O_2. After oxidation, ozone primarily reverts back to oxygen and is therefore considered to be clean or environmentally friendly oxidant. The actual chemistry of ozonation is, of course, not as simplistic as this, however far less undesirable by-products are formed during ozonation than with other oxidants, such as chlorine.

Ozone is an unstable gas having a pungent, characteristic odour. In the earth's stratosphere it is formed photochemically, but at ground levels is present in very low concentrations. At normal ambient temperatures ozone is a blue gas. This can be readily observed in the generation cells of corona discharge ozone generators.

The odour threshold for ozone is 0.01 ppm. Ozone will develop an unpleasant acrid smell and a faint blue colour at levels exceeding 5 ppm. Ozone is relatively stable in air with a half life of up to 36 minutes, at low concentrations. This half life changes significantly once ozone is introduced into water where many chemical reactions can occur.

The stability or depletion of ozone in an aqueous solution depends greatly on the water source and oxidisable contaminants it contains.

On a comparison of oxidation potential's of standard oxidants, ozone is 2.07 Volts as compared with chlorine at 1.36V and bromine at 1.09V (refer Table 1). For swimming pool treatment, when ozone is dissolved in water, it can react with water contaminants by either direct reaction as the O_3 molecule, or by indirect reaction by hydroxyl free radicals. In strongly acidic solutions, the direct reaction predominates, but above pH 7 the latter reaction predominates.

Table 1 - Oxidising Potentials of Various Reagents

Oxidising Reagent	**Oxidising Potential (V)**
Fluorine	3.06
Hydroxyl free radicals	2.80
Atomic oxygen	2.42
Ozone	2.07
Permanganate	1.67
Hypobromous acid	1.59
Chlorine dioxide	1.50
Hypochlorous acid	1.49
Chlorine	1.36
Oxygen	1.23
Bromine	1.09
Hypochlorite	0.94

As can be seen from **Table 1**, hydroxyl free radicals have an oxidation potential considerably above that of the ozone molecule itself. Therefore, the formation of these compounds assist with chemical oxidation, however with a very short half life (microseconds) they do not play a major part in achieving disinfection.

OZONE GENERATION

The use of ozone has grown rapidly and many ozonator designs have been produced. All generators vary to some degree, whether it be size, shape, cooling process, air preparation etc. However, there are still only two basic methods for ozone generation, being corona discharge (CD) and ultraviolet radiation (UV).

In practice, ozone is generated by passing an oxygen containing gas through either a high energy electrical field or a high energy radiation source, the former being corona discharge and the latter UV radiation. For swimming pool treatment, air is normally used as the feed gas for either type of generator. Only a portion of the oxygen is converted to ozone by these production techniques. With corona discharge an ozone concentration of up to 4.5% by weight is obtainable, however when generated by UV radiation a concentration of only 0.001 - 0.1% by weight is obtainable.

> **For swimming pool treatment the effectiveness of ozone as an oxidant and disinfectant is very dependant on the ozone concentration and dose**

application, therefore ozone generated by UV radiation will not achieve the same results as ozone generated by corona discharge.

Corona Discharge Generation

This style of generator is far more sophisticated than the UV radiation technique, however higher concentrations of ozone can be produced.

There are many generation cell designs, although the fundamental principle remains the same. **Figure 1** includes details of a typical corona discharge cell. For an air fed system, a clean dry air source is required. This oxygen containing gas is passed between the high voltage electrode and dielectric tube, in this case being glass. Dielectric materials can also include ceramics or specially formulated rubber compounds. In this case, cooling water surrounding the outside of the dielectric glass becomes the grounded high voltage connection. When a high voltage AC power source is connected across this air gap a corona discharge and therefore ozone generation occurs. The voltage at which corona discharge occurs varies according to the supply frequency and air gap.

Ozone generation by corona discharge is an exothermic physio-chemical reaction. Much of the energy used for ozone generation is lost in heat, therefore cooling efficiency is an important factor in generator design. As an example, generator designs that do not directly cool the dielectric can achieve internal dielectric temperatures of up to 190^{o}C. Direct cooling of the dielectric tubes greatly reduces the quantity of cooling water required. Also with this design, as the cooling water supply temperature increases, derating of the ozone output is less when compared to ozonators that do not directly cool the dielectric.

Typical voltages used in corona discharge generators vary between 7kV and 20kV. Generally speaking, as the voltage increases stress on the dielectric material also increases, therefore reducing reliability and service life of this component.

The amount of ozone generated is directly proportional to the energy applied to the generation cell. When the applied voltage exceeds the ionisation potential of the dielectric material, electrons travel across the discharge gap and collide with a portion of the oxygen molecules passing through the gap, resulting in the formation of ozone. In basic terms, the free electrons in the corona cause oxygen molecules to disassociate, which then reform as ozone. At the same time atomic oxygen and electrons react to form oxygen again. This is an exothermic reaction resulting in high temperatures. Without adequate cooling of the cell the temperatures can reach levels where ozone decomposition occurs. For this reason, poor generation cell cooling or high cooling water temperatures reduce the ozone production for a given energy input.

The dielectric simply spreads the arcing potential over the entire surface of the high voltage electrode, eliminating individual heavy arcing. This enables a high current density and therefore efficient corona to be formed.

For swimming pool applications two basic types of CD generators would be utilised, low and medium frequency. Low frequency generators operate at 50 or 60 Hz frequency while medium frequency systems operate at between 100 and 1000 Hz. Each type of generator has its advantages and disadvantages, however for swimming pool applications either system, if designed correctly, is quite suitable.

UV Generated Ozone

This is a photochemical process and is far simpler and less expensive, from a capital equipment viewpoint, than corona discharge ozonators. Using this technique, air is passed over a UV lamp, from which a small portion of the oxygen is converted into ozone by high energy radiation. The main disadvantage of UV generated ozone is that only a very low concentration of O_3 is produced.

Low ozone concentrations produced by UV generation severely limit the practical uses of the technique.

For swimming pool treatment ozone generated by UV will <u>not</u> perform the same degree of treatment as CD generated ozone, due to the low quantity and concentration produced.

Most UV lamps used for disinfection purposes operate in the 254 nm range. As shown in Figure 2, at 254 nm ozone is in fact destroyed. For ozone production, a wave-length of 185 nm is normally used, although even under ideal conditions a maximum ozone concentration of only 0.1% is obtainable.

A UV lamp operating at 254 nm produces only trace quantities of ozone. (0.001%)

Using 185 nm lamps ozone production is optimised, however some of this ozone is photochemically decomposed by UV radiation to form hydroxyl free radicals. As discussed previously hydroxyl free radicals are very powerful oxidising agents which will perform chemical oxidation of dissolved organic material in swimming pool water. However, the concentrations available from UV generated ozone will be very low. Considering that the half life of these radicals is in the order of microseconds, they play no significant role in disinfection.

In commercial pools and spas with moderate to heavy bather loading UV generated ozone cannot produce sufficient residuals in the water to carry out effective oxidation of organic contaminants and achieve primary disinfection. Although the ozone is beneficial, most of the oxidation and disinfection is achieved by the residual disinfectant, normally being chlorine or bromine.

OZONATOR AIR PREPARATION

For efficient and reliable operation of CD ozone generators, air preparation is crucial. Either moisture or particular matter has a very detrimental effect on the generation cell electrodes and dielectric material. Moist air in the ozone generator will cause nitric acid to form which will decrease the ozone production and corrode the generation cell components. **Figure 3** shows the ozone generation production loss with increase in gas dew point temperature. For efficient ozone generation the final supply air must be filtered to remove particulate matter and any oil or hydrocarbons which may carry over from the air compressor.

For swimming pools, ozone generators are often installed in hot, humid plant rooms. Also many localities experience ambient conditions with both high temperature and high humidity which places additional requirements on air preparation systems. **Figure 1** details the air preparation typically used for corona discharge generators where less than ideal ambient conditions are experienced. Pressure fed systems are far more suitable for reliably supplying the necessary air quality for long term trouble free operation of an ozone generator.

The most appropriate air preparation steps are:

Air Compressor → Pre-filtration (5 μ) → Refrigerated cooler (2^oC PDP) →

Coalescing filter (0.01 μ) → Desiccant dryer ($^-70^oC$ PDP) → Dust Filter (5 μ) →
Flow control System → Flow Monitor → Ozone Generator

Air preparation is far less important to UV generated ozone than the corona discharge method. Although humidity affects the UV system by a loss of ozone production, nitric acid is not formed, as the case with CD systems.

SOLUBILITY OF OZONE

Ozone is only partially soluble in water, therefore the concentration of ozone in the generator gas stream becomes very important. According to Henry's Law, the efficiency of absorbing a specific gas into an aqueous phase is based on the partial pressure of that particular gas in the total gas flow. Therefore, the higher the concentration of ozone in the generator gas stream, the more complete will be the transfer of ozone into the water. **Table 2** shows the theoretical residuals of ozone that can be achieved in water, based on ozone gas concentrations and temperature.

Table 2 - Solubility of Ozone in Water

* Ozone generated by UV
** Ozone generated by Corona Discharge

Ozone Concentration % w/w	Ozone solubility in mg/l					
	at 5^{o}C	at 10^{o}C	at 15^{o}C	at 20^{o}C	at 25^{o}C	at 30^{o}C
0.001 *	0.007	0.007	0.006	0.005	0.004	0.003
0.1 *	0.74	0.65	0.55	0.42	0.35	0.27
1 **	7.39	6.50	5.60	4.29	3.53	2.70
1.5 **	11.09	9.75	8.40	6.43	5.29	4.04
2 **	14.79	13.00	11.19	8.57	7.05	5.39
3 **	22.18	19.50	16.79	12.86	10.58	8.09

As would be expected, the ozone solubility decreases with an increase in water temperature. Also, as a consequence of Henry's Law, the solubility of ozone increases with an increase in ozone concentration in the gas stream. In a practical swimming pool application, ozone and air are rapidly mixed together with high water flows, therefore an equilibrium condition is not actually achievable resulting in lower solubility levels than shown in **Table 2**. This being considered, UV generated ozone must be far less effective than that produced by CD.

> **For effective ozone treatment of commercial or municipal swimming pools, CD generated ozone will provide a water quality that is not achievable with UV generated ozone.**

DIFFUSION OF OZONE IN WATER

Considering that relatively low concentrations of ozone gas are produced in the generator air stream, together with the limited solubility of ozone gas, the method of injection and mixing of these gases with the pool water is of great importance. For swimming pool treatment, the most common ozone injection and diffusion system is where the ozone is injected into the main recirculating pipeline, prior to or just after filtration. With this technique a separate pump supplies pool water at the required flow and pressure to operate a vacuum injector. The injector draws the air through the ozone generator, therefore the ozone generation cells and pipe work operate at a negative pressure. This provides the safest method of generation for pool applications, as should a pipe or equipment failure occur, no ozone gas can escape to the pool area or plant room. Should the ozonator utilise a pressure fed air preparation system, a specially designed vacuum regulating valve may be incorporated. When designed correctly, these injectors provide very efficient initial diffusion of ozone. The injected ozone would then be fed to a static mixing device installed in the main pool recirculating line. Considering that most pool systems generally operate at between 60 and 120 kPa pressure, this method of ozone diffusion is further enhanced. **Figure 4** details this ozone injection system.

For swimming pool treatment, ozone may also be injected into a sealed balance tank. (Refer **Figure 4**). For this diffusion system to be effective, the balance tank would need to have a contact chamber which is considerably deeper than the tank itself. For optimum ozone diffusion the contact tank should have a functional water depth of 4 - 5 metres which may be impractical for some installations.

There are advantages and disadvantages of each of these ozone injection techniques, detailed discussion of which is beyond the scope of this paper. However, the inline injection method has been commonly used and has shown to provide both efficient and reliable utilisation of the ozone gas.

When correctly designed, all of the above systems should achieve ozone diffusion efficiencies of up to 98%.

OZONE OFF-GAS

Ozone is an extremely oxidative and corrosive gas, which is harmful to humans above certain concentrations as shown in **Figure 5**. Ozone gas is heavier than air, therefore any undissolved ozone must be removed from the system and disposed of correctly. Also, ozone residuals should not be returned to the pool, particularly with indoor heated pools, as ozone gas could collect at the water surface and therefore be inhaled by swimmers. Ozone residuals should be removed by either activated carbon or by chemical reaction such as the use of the bromide ion.
The ozone is injected with a substantial quantity of air, which must be vented prior to water returning to the pool. Some operating problems have been encountered with the reliability of automatic air venting valves, however if the hydraulics and valving systems are designed correctly these components will function reliably and effectively. Even with high ozone diffusion efficiencies, municipal pool treatment systems may vent up to 20 g/h of ozone, which if not destroyed could present a potential health hazard. Various methods are available for destroying the ozone contained in this off gas, including granular activated carbon, catalytic destructors and thermal-catalytic destructors.

For the size of ozone generation equipment normally used on swimming pools, ozone destruction by granular activated carbon has proved to be the most cost effective method. This material is elemental carbon, which has been steam activated to provide a large internal surface area. Carbon is a strong reducing agent, therefore upon contacting ozone gas the carbon is oxidised to carbon monoxide and carbon dioxide, resulting in destruction of the ozone molecule. This reaction degrades or powderises the granular activated carbon, therefore it has a finite life. When designed correctly, the granular activated carbon would only need replacing on an annual basis.

Carbon ozone destruct systems are quite suitable for swimming pool applications due to the relatively low quantities of ozone involved. Also,

in such systems the frequency and cost of replacing the carbon media is not excessive.

Catalytic ozone destruction should not be used for swimming pool treatment, as halogen disinfectants such as chlorine or bromine cause fouling and accelerated deterioration of the catalysts.

CHEMISTRY OF OZONE IN SWIMMING POOL WATER

As previously discussed, the first and most important consideration of ozonation of swimming pools is efficiently dissolving sufficient ozone into the pool water to carry out the required oxidation and disinfection work. Ozone is able to provide a water quality not achievable with normal treatments such as chlorine or bromine, however adequate residuals of ozone must be maintained in the pool water.

The following ozone injection rates may be used as a guide for sizing of ozonation equipment. Ozone dose rates shown are based on the pool recirculation rate being ozonated, whether full stream or slip stream systems.

Ozone/Chlorine Treatment

- Pools with a water temperature up to 28^{o}C - 0.8 to 1.0 mg/l O_3
- Pools with a water temperature above 28^{o}C - 1.0 to 1.2 mg/l O_3
- High use fun pools and spas - 1.0 to 1.2 mg/l O_3

Ozone/Bromide Ion Treatment

- Pools with a water temperature up to 28^{o}C - 1.0 to 1.6 mg/l O_3
- Pools with a water temperature above 28^{o}C - 1.2 to 1.6 mg/l O_3
- High use fun pools and spas - 1.2 to 1.6 mg/l O_3

The actual dose rate of ozone depends greatly on the effective turnover time of the pool and bather loading. This is especially the case with an ozone/bromine treatment as the ozone must achieve oxidation and produce the necessary bromine residuals.

If the dose rates of ozone, as shown above, are to be achieved, UV radiation as an ozone generating process is precluded. The German DIN standard 19 643 specifies that when ozone is employed for the treatment of public swimming pools, the ozone generator must produce a minimum ozone concentration of 18 g/m^3 of gas flow.

Effect of pH and Temperature

Both pH and temperature of the pool water have a significant effect on ozonation chemistry. Swimming pool and spa waters are often heated to approximately 30^{o}C temperature, at which the solubility of ozone generated by corona discharge is still quite adequate for oxidation and disinfection. As the pool water temperature increases the dissolved ozone decomposes to produce hydroxyl free radicals and molecular ozone. Reactions between water born contaminants and these compounds will be considerably faster than would be the case at lower temperatures, although this has no detrimental effect. However, considering the very short half life of hydroxyl free radicals, no significant disinfectant work is achieved. Therefore, to ensure that adequate ozone is available to carry out disinfection, higher ozone injection rates are required as the water temperature increases.

Swimming pools are normally operated within a pH range of 7.2 to 7.8, at which level both the ozone molecule and the hydroxyl free radicals will be present. This pH range has proved to be optimum for bather comfort and maintenance of correct water chemistry. Therefore, this pH range is quite suitable for an ozone treated pool.

Pool Water Contaminants

Both organic and inorganic contaminants are introduced to pool water, mainly by the human visitors. Organic contaminants include perspiration, urine, nasal secretions, body creams, ointments, etc. Inorganic contaminants include ammonia, chlorine, bromine, iron and manganese. There will also be microbiological contamination which includes bacteria, viruses, fungi, yeasts and cysts. The various chemical reactions involved in swimming pool treatment is a complex subject, particularly when ozonation is used in conjunction with a halogen residual disinfectant. An excellent account of the basic chemistries involved is provided by (Rice, 1991). However, the following key points are worth comment.

There are a few organic compounds which are rapidly and completely oxidised by ozone, however the majority of organic compounds are only partially oxidised in aqueous solutions. Most organic compounds, such as urea, creatinine, chloroisocyanurates and trihalometanes are only slightly reactive and therefore not destroyed by ozonation.

> **In swimming pool treatment, ozone only partially oxidises most organic compounds and relies on secondary chemical reactions and flocculation to remove many contaminants, such as ammonia.**

Ozonation of swimming pools provides optimum water clarity, due to micro flocculation. Although many non ozonated pools utilise a coagulant such as alum or polyaluminium chloride to assist with water clarification, ozonation greatly enhances the action of these chemicals. Ozone only partially oxidises many organic compounds present in pool water, making these materials more polar. In the presence of polyvalent cations, such as calcium or aluminium, an insoluble floc is produced which is removed by filtration.

Halogen Disinfectants

Either chlorine or bromine can be used in conjunction with ozonation. These disinfectants will ionise in water to form hypochlorous acid and hypochlorite ion with free chlorine and hypobromous acid and hypobromite ion with bromine. In both cases ozone will react with the ion, but not the acid forms. In the case of chlorine, hypochlorite ion is converted to chloride and chlorate, whereby with bromine the hypobromite is converted to bromide and bromate.

Both chlorine and bromine react with nitrogen based compounds, such as ammonia to produce chloramine or bromamine respectively. At pH ranges normally found in swimming pools, ozone has very little reaction with ammonia, however ozone will react quite rapidly with chloramines or bromamines. Therefore, during ozonation of swimming pools ammonia levels can be satisfactorily controlled by this secondary reaction.

Ammonia is controlled in swimming pools by secondary reactions with bromine or chlorine, not by direct oxidation by ozone.

Ozone/Chlorine

Within normal contact times between ozone injection and the treated water entering the pool, ozone residuals can not be removed by chemical reaction with chlorine products. Therefore, the ozone must be removed using granular activated carbon. Unfortunately this carbon also removes free chlorine that must then be re-established in the water entering the swimming pool.

With an ozonated pool, primary oxidation and disinfection is achieved before adding chlorine for residual maintenance. Therefore, little to no chlorine is consumed in chemical reactions. Only the required amount of chlorine to achieve the desired residual is needed.

Ozone/Bromide Ion

The concept of oxidising bromide ions to bromine which in turn primarily reduce back to the bromide ion again is quite simple and effective. When ozone is used to oxidise bromide ion to bromine, three important treatment benefits are provided. The ozone; carries out partial oxidation of organic contaminants, assists with flocculation and produces the bromine residual from the bromide salt. When designed and operated correctly this is a very effective and economical treatment, however the actual ozone dose needed is dependant on more factors than an ozone/chlorine process. Enough ozone must be injected to produce sufficient bromine to maintain minimum residuals throughout the pool system. This ozone dose could be significantly higher than an equivalent pool using chlorine as the residual disinfectant.

To obtain the benefit from an ozone/ bromine treatment the ozonator must be adequately sized to produce the necessary quantity of bromine for residual maintenance. Slipstream ozonation will <u>not</u> provide the same degree of water quality as full stream ozonation, when used to oxidise bromide ion.
UV generated ozone can not produce sufficient quantities of ozone for oxidation, disinfection and production of bromine from the bromide salt.

With the bromide ion process, sodium bromide is added to the pool water so that an excess residual of bromide ions is provided, 20 and 40 mg/l as Br^- being adequate. With this bromide excess, no ozone can remain as free ozone, as it must react with the bromide ion to form bromine. Therefore, no activated carbon deozonation stage is required with this pool treatment. **Figure 6** details a simplistic reaction cycle for this treatment technique for swimming pools. The injected ozone carries out oxidation, disinfection and production of bromine. This bromine residual then reacts with pool water pollutants and microorganisms to primarily form bromide ions again. Therefore a recycling system occurs, greatly improving treatment economics.

DISINFECTION

Microbiological contaminants, including bacteria, viruses, fungi etc, can all be destroyed by ozone, although different conditions are necessary for each species. The extent of deactivation or destruction of microorganisms is related to the contact time and concentration of ozone in the water.

Bacteria are the most rapidly destroyed species of microorganisms while cysts are the most resistant to all disinfectants, because of their protective shells. Extensive research has been carried out on the disinfecting ability and reactions of ozone, mainly associated with drinking water treatment, which is closely aligned to swimming pool disinfection.

With an ozone/chlorine treatment an ozone residual of approximately 0.4 mg/l is maintained for a contact period of two minutes. This has proved to be quite adequate for effective disinfection. There are many informative papers detailing the reaction of ozone with microbiological contaminants, such as (Rice 1991).

When ozone is used in conjunction with bromide ion in swimming pools, the half life of ozone is reported to be 5.6 seconds. (Haag and Hoigne 1983). Therefore, no measurable ozone residual will be remaining after 30 seconds contact. With this treatment, disinfection is achieved jointly by bromine and ozone, as the ozone is in contact with the water contaminants for a considerably shorter time and at a lower average residual when compared to an ozone/chlorine system.

An ozone/bromine treatment will not provide the same degree of oxidation as an ozone/chlorine system.

Although each treatment method will provide similar and excellent water quality, with an ozone/chlorine treatment, the ozone residual is in contact with the water for a longer time, at a higher residual.

GRANULAR ACTIVATED CARBON

As discussed earlier, when ozone is used in conjunction with chlorine granular activated carbon (GAC) must be used to prevent ozone returning to the pool. GAC used for deozonation of pool water is basically the same material as used for ozone off-gas destruction. When GAC destroys ozone in the gas phase, it is degraded in the process. In contrast, with deozonation in the aqueous phase the activated carbon acts as a catalyst, reducing the ozone to oxygen.

The capability of a specific activated carbon to deozonate water is normally expressed in terms of the halving value. The halving value represents the depth or contact time of the carbon layer required to reduce the original ozone concentration by 50%. The halving value for a given carbon will depend on several factors, the main one being the internal surface area. For carbon to be effective for pool water deozonation the surface area should be between 800 and 1200 m^2/g. On this basis effective deozonation will be achieved with a contact time of 90 seconds.

Due to the catalytic reaction for deozonation the actual carbon itself is not destroyed, therefore the GAC in theory could have an indefinite life. However, in reality the carbon's effectiveness is eventually reduced due to physical fouling by organic compounds in the normal adsorption process. Also some carbon is physically lost due to abrasion and carryover during normal backwash.

The actual life of the activated carbon, in swimming pools, depends on several factors such as; the pool location, bather loading, pool use, contaminant loading, whether used in single or dual stage applications etc. As a general guide, the carbon life expectancy would be between 3 and 5 years for single stage ozonation and 5 to 10 years for dual stage ozonation.

G.A.C. will gradually deteriorate, resulting in a slow increase in ozone residual breakthrough. The carbon will not simply stop deozonating and allow ozone residuals to pass through.

The deozonated water may be monitored using an ORP controller which can be set up to raise an alarm and stop the ozonator should a preset ozone residual pass through the GAC.

With correct selection, the GAC will have very similar hydraulic and filtering characteristics to filter sand. Therefore, additional filtering capacity is provided.

SINGLE STAGE OZONATION

With single stage ozonation, ozone contact, deozonation and filtration are carried out in a single vessel. The main process difference with this system over dual stage ozonation is that the ozone is dosed prior to filtration. The basic design criteria remains the same for either system, requiring two minutes contact for ozone then ninety seconds contact for deozonation. **Figure 7** details the layout of a typical single stage ozonation installation.

There are some obvious advantages and disadvantages of single stage system over the dual stage. Advantages of this system include;

- The capital cost is lower due to only one vessel being required. Also piping and installation costs are lower.

- The single stage system can more easily be retrofitted to an existing pool.

As would be expected there are some disadvantages with single stage ozonation that should be taken into consideration when considering its implementation.

- The ozone is injected prior to filtration, which presents a higher organic loading and therefore consumption of ozone.

- The GAC acts as a prefilter, therefore the carbon will exhaust more quickly than with a dual stage system. Frequency of backwashing will be higher than with a post-filter deozonation vessel, therefore physical carbon loss due to bed expansion and particle abrasion will be higher, resulting in a shorter carbon life.

- The deozonation stage cannot be by-passed. Therefore, if the ozonator is off line, additional chlorine will be required to replenish residuals lost in the carbon bed.

DUAL STAGE OZONATION

The term dual stage ozonation simply means that ozone injection, ozone contact and deozonation is carried out in a separate vessel, after filtration. **Figure 8** details a typical layout for dual ozone treatment systems.
With dual stage ozonation most of the filterable organic and particulate material will have already been removed by sand filtration. Therefore the GAC acts as a polishing filter, primarily to remove particulate organic contaminants resulting from the microflocculation action of the ozone. Due to the lighter organic contaminant loading of the GAC filter, the frequency of backwash is greatly reduced. Some additional benefits of a dual stage ozonation system, over a single stage, include;

- Additional filtration is provided with the deozonation media, therefore higher pool loadings can be accommodated with improved water clarity recovery times.

- Should the ozonation equipment be off-line for any reason, the carbon filter can be easily by-passed so that a normal chlorine residual can be economically maintained.

The obvious disadvantage of a dual stage treatment is the higher capital and installation costs.

SLIPSTREAM OZONATION

Used correctly slipstream ozonation can be very effective and provide far superior water quality to single treatment such as chlorine or bromine. The maximum benefit is only achieved with slipstream ozonation when used in conjunction with chlorine. As discussed previously, to obtain the desired benefits from an ozone/ bromine process all of the bromine must be produced from the ozone dosed, otherwise inadequate oxidation will be achieved. However, it is worth noting that any ozone additions will be of benefit to the overall pool treatment.

With slipstream ozonation approximately 20 to 30% of the pool water is diverted to a separate stream which is then ozonated under the same basic design criteria as a full ozonation system. The treatment steps for the bypass should be;

> ozone injection → 2 minutes contact → 1.5 minutes deozonation (GAC) → return to main filtration line. Chlorine would then be added to compensate for the residual lost by the GAC.

The effectiveness of slipstream ozonation will mainly depend on the hydraulic design of the pool and bather or contaminant loadings. For example, a deep diving pool which will normally have light bather loadings relative to water volume can be effectively treated with slipstream ozonation. However, only full stream ozonation should be considered in a heavily loaded municipal swimming pool.

OZONATOR AUTOMATION

The success of any swimming pool treatment is reliable automation, which results in stable and consistent chemical residuals. Many pools suffer from significant variations in chemical residuals due to automation systems that are not designed or set up correctly.

When ozone is used in conjunction with chlorine or bromine, the primary ozonator control must maintain a specific oxidation reduction potential (ORP) in the ozone contact tank. This represents inline correction that requires more control logic than simply feeding the ORP analyser signal direct to the ozonator output regulation system. This method of chemical control is commonly used in the water and wastewater industry where corrective dosing is required in a flowing pipeline. Very accurate and stable ozone residuals may be maintained with the use of a PID controller. PID stands for; Proportional, Integral and Derivative. PID controllers look at parameters such as, the rate of ORP increase with a relative ozonator output increase, the decay of ORP when the injection ceases, the delay between ozone injection and sample response and the rate of ORP increase when maximum ozonator output is applied. The control algorithm programmed into these controllers looks at all of these parameters then provides the necessary output signal to the ozonator, to maintain the desired ORP of the water in the ozone contact tank. **Figures 7 and 8** further detail this basic automation technique.

For chlorine control a separate analyser would monitor the ORP of the water returning to the filters, prior to ozonation. The chlorine dosing pump output would be regulated by this second controller, utilising a proportional control to minimise residual oscillations. This chlorine control is no different to any normal chlorine treated pool.

With an ozone/bromine treatment the ozonator automation becomes more difficult, in that it must also compensate for bromine consumption across the pool. The method of ozonator automation for this treatment would depend on the hydraulic design and bather loading of the pool. With light to moderate bather loadings a simple reactive automation system will be quite satisfactory. As detailed in **Figure 9** this simplified control method uses an ORP monitor to measure the bromine residual of the pool exit or soiled water prior to ozone injection. This instrument would normally be set up to provide a 4 - 20 mA signal to a PID controller, or similar proportional control system, to regulate the output of the ozonator. With long pool turnover times the use of PID control instrumentation becomes more difficult due to the time delay between chemical injection and sample measurement. To make this system work effectively the output regulation of the ozonator must have a very slow response time. A supplementary bromination system should always be provided to maintain the necessary bromine residuals during periods that the ozonator is out of service or being maintained. Using a supplementary backup chemical such as sodium hypochlorite, the bromine residual can be automatically maintained. For the supplementary chemical, the dosing pump control would be set up so that the chemical additions would not occur until the bromine residual dropped to a minimum figure say 1mg/l. This would indicate that the ozonator has insufficient capacity to generate the required quantity of bromine. A proportional pump control would be most suitable to ensure that over dosing and residual oscillations do not occur. With this proportional control system, the supplementary chemical additions would increase as the ORP reduced from this lower set point.

For pools where significant variations in oxidant demands occur, a simple reactive automation system is not ideal. Controlling a specific ORP or bromine residual returning to the pool is quite simple, as previously described. In this instance accurate bromine control may be achieved using a compound loop control system, which utilises a programmable dual input PID controller to automate the ozonator. With this system the inline correction becomes the primary bromine control, whereby a specific residual is maintained returning to the pool. In the compound loop technique the ORP of the water exiting the pool is measured and a 4 - 20 mA signal fed as the second input to this PID controller. This second input automatically adjusts the ozonator output by manipulation of the primary control system. Although more complex in actual operation, a simple way of looking at this control technique is that the primary bromine control system is set up so that the ORP of the water returning to the pool is maintained at say 780 mV. The ORP of the water exiting the pool will be set to maintain approximately 670mV, representing an approximate bromine residual of 2 mg/l as Br_2. Should the ORP of the pool exit water drop below this figure, the secondary control circuit will automatically regulate the output of the PID controller as though it was increasing or decreasing the primary circuit control set point. This has the overall effect of accurately altering the bromine residual entering the pool. **Figure 10** further details this control method.

CONCLUSIONS

Pools treated with ozone in conjunction with chlorine or bromine provides a quality of water not achievable with single treatment disinfectants.

When used by people with a strong working knowledge of its strengths and weaknesses, ozone will achieve a reliable, safe, high quality pool treatment, however when misapplied ozone can also be very dangerous.

Although ozone is ozone, when generated by corona discharge its suitability as a swimming pool treatment is very different to ozone generated by UV radiation. UV generated ozone can only produce low concentrations of ozone gas (0.1 % max). In contrast, corona discharge generators produce ozone at up to 4.5% by weight.

For effective oxidation and disinfection of pool water an ozone injection rate of between 0.8 and 1.6 mg/l based on flow is necessary. In a commercial or municipal swimming pool, this is not achievable using UV generated ozone.

When used for swimming pool treatment, ozone initially performs its primary oxidation work prior to disinfection. In addition, ozone acts as a microflocculant that effectively lowers organic contamination and provides improved water clarity.

The primary goal of ozonation of swimming pool water is to lower or remove chlorinous odours in the pool hall, provide aesthetically pleasing water, reduce pool hall corrosion and reduce or eliminate bather irritation. When designed and operated correctly, either an ozone/chlorine or ozone/bromine treatment system will effectively satisfy these goals.

An ozone/chlorine system, when designed to the German DIN standard 19 643, will provide the highest quality pool water achievable with current technology. With this process an ozone residual of approximately 0.4 to 0.5 mg/l is in contact with the pool water for two minutes, prior to deozonation.

An ozone/bromide ion process will achieve similar results to the ozone/chlorine system, however ozone is in contact with the pool water for a considerably less time, therefore an equivalent degree of oxidation is not possible. The main advantage of an ozone/bromide treatment is that no deozonation stage is necessary and the bromine primarily reduces to bromide ions which inturn are reoxidised to bromine by the ozone. Therefore, this is usually a very economical treatment from an operating point of view, with lower initial capital costs.

Ozonator automation is very important in maintaining correct and reliable water quality and chemical residuals. An ozone/bromine treatment requires different automation techniques to an ozone chlorine process, as the ozone must perform the extra duty of residual maintenance.

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