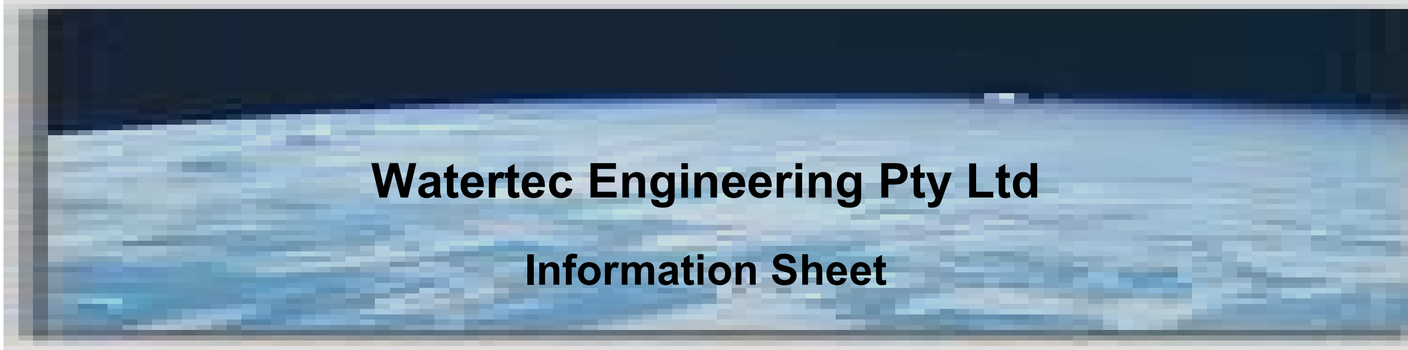

TECHNICAL DETAILS AND EXAMPLES OF OZONE USAGE

Ozone,O3, is an unstable gas as it is produced for commercial application, and has a pungent, characteristic odour. It is formed as a photochemical in the Earth's stratosphere, but exists at ground levels only in low concentrations. It is the most powerful oxidant used in swimming pool treatment and has the ability to destroy algae and bacteria, inactivate viruses, and to oxidise many organic and inorganic contaminants which are present in aqueous solutions. Thus ozonated water used for swimming pool water treatment purposes can be recycled without fear of having high concentrations of dissolved chemicals.

It should be kept in mind that swimming pool water treatment is unique because of the many types of contamination to which it is subject. Its visitors contribute a variety of pollutants which must be removed or destroyed (bacteria, viruses, urine, sweat, hair, cosmetics, etc.). Additionally, outdoor pools also are contaminated by bird droppings, dust, leaves, and atmospheric pollutants. Because of the large volumes of water contained in swimming pools, this water must be recycled.

NOTE: The proper treatment of swimming pool water poses a more complex water treatment problem than does the treatment of drinking water.

EARLY HISTORY OF OZONE TECHNOLOGY

Schonbein announced the discovery of ozone in 1840. He had observed a peculiar odour during electrolysis and sparking experiments. He also recognized that this was the same odour observed after a flash of lightning. He named this new substance ozone, derived form the Greek word, "ozein", meaning "to smell".

The earliest experiments on the use of ozone as a germicide were conducted in 1886 by de Meritens in France. In 1893, the first drinking water treatment plant utilizing ozone for disaffection was constructed and operated in Oudshoorn, in the Netherlands. Plants at Paderborn and Wiesbaden were constructed in 1902 and 1903 utilizing ozone for disaffection of drinking water. In 1907 the City of Nice, France began operation of a new water treatment plant incorporating ozone to deliver 22,500 cubic meters a day to the inhabitants of the city.

This Bon Voyage plant operated continuously until 1970, when it and two additional Nice plants built subsequent to 1910 were replaced with the new and modem Super Rimiez plant. There were at least 2,000 drinking water treatment plants in operation employing ozonization throughout the world, of which more than half of these were located in Europe.

The characteristic smell of ozone associated with lightning discharges has been known since antiquity, as has been shown by Mohr in citing four examples in Homer's Iliad and Odyssey. Homer called it "sulphur smell". Ozone was first described correctly in 1786 by van Marum. He found a characteristic smell when a breakdown of electrical sparks took place within a closed volume above water and he attributed this smell to the electrical matter. Schonbein can claim credit for the true discovery of ozone. In 1840, he isolated this gas and called it ozone (Greek, meaning "to smell").

In nature, ozone is produced by the influence of ultraviolet radiation on the oxygen of the Earth's stratosphere. It is supposed that two zones of relatively high ozone concentration surround the Earth. They are to be found at heights of25 to 55 km, and their estimated volume is approximately 3.5 thousand million tons. Werner von Siemens in about 1857 was successful in manufacturing a technically usable apparatus for ozone production, and by the turn of the century, the first ozone installations were applied to drinking water works. For example, the installation of an ozone producer at the water works of Petersburg, Russia was used for oxidation of organic materials (decolonizing) and for disinfecting.

REACTIONS OF OZONE IN AQUEOUS SOLUTONS

Since its installation in France for the disinfection of drinking water, ozone has evolved both as a disinfectant and as a chemical oxidant in water and waste water treatment.

1. ***Bacterial Disinfecting***....The French has pioneered the use of ozonization for bacterial disinfecting. O'Donovan points out that the usual dosage of ozone for drinking water treatment plants with ozone demand is 1.5 to 2 mg/L. When ozone-demanding materials (organic or inorganic) are present, however, these demands must be satisfied first. Thus, ozone dosages to achieve bacterial disinfecting can be much higher than the above range. When ozone is applied for disinfecting in French water treatment plants, however, it is usually applied under conditions which will also provide viral inactivation.

2. ***Viral Inactivation*** ....Pioneering work in this area also was conducted by French public health officials. Dr. Coin and his co-workers showed that when a dissolved ozone level of 0.4 mg/L was attained and then maintained for a minimum of 4 minutes, Poliomyelitis viruses, Types I, II, and III were at least 99.9% inactivated. This technique was adopted by the

City of Paris, France in the late 1960's as a standardised treatment whenever ozone was applied. Later, this technique was adopted throughout France as a required treatment whenever ozone is applied to drinking water for disinfecting/viral inactivation.

3. ***Algae Control***....During seasonal periods of climate changes and when the proper nutrient balances are present in water supplies, algae growths are promoted. Ozonization will disrupt the metabolic processes of many types of algae by oxidising their essential organic components.

USES OF OZONE IN SWIMMING POOLS

Bacteria Disinfecting, Viral Inactivation, Oxidation of Soluble Iron And Manganese, Decomplexing of Organically-Bound Manganese (oxidation), Color Removal (oxidation), Taste and Odor Removal (oxidation), Algae Removal (oxidation), Oxidation of Organics (Phenols, Detergents, Pesticides), Microflocculation of Dissolved Organics (oxidation), Oxidation of Inorganic (cyanides, sulfides, nitrites), Pretreatment for biological Processes(on sand, anthracite or GAC).

The rapid growth of swimming pools in Europe began after the end of World War II (1946) and has been growing ever since. As the industries in Europe grew, so did pollution, to the extent that it was and is a serious problem. The pollution affected the quality of water in the recreational areas (rivers, lakes and seaside's) to the point that it was necessary to construct both indoor AND outdoor swimming pools. Also, as the economy boomed and expanded, people became more affluent and overcrowded the existing resort areas, thus forcing the development of new areas requiring swimming pools.

Due to the rapid growth of swimming pools and the deteriorating environmental conditions, various governments started research into the procedures for the treatment of swimming pool water, thus developing specifications, rules and regulations governing the design, construction, water treatment for purification and disinfecting procedures.

The primary concern in the regulations for swimming pool water is to prevent the swimmers from becoming infected with bacteria and viruses in the water. Since European countries have not been tied to the use of chlorine for water purification as we are in the United States because of government regulations, they were able to study and develop new techniques. One of the differences in the European developments as compared to the United States concepts is that water treatment procedure for swimming pools is divided into two areas:

1) the water purification cycle which begins when the water leaves the pool and is completed just before the water is returned to the pool;

2) the disinfecting cycle which takes place just after the end of the purification cycle and before the water enters the pool.

The European concept of treating swimming pool water is that the water is purified and disinfected, not the swimmer. Every precaution is taken to prevent infection of the swimmer without affecting his health, well-being, comfort and aesthetic sense.

The primary concern in the United States is to reduce the total plate count to less than 100 and to totally eliminate the E. coli count without too much concern about such items as eye irritation, ear fungus, bad taste, unpleasant odor and the clearness of the water. Although the United States has rules and regulations concerning swimming pool water, the inspection and enforcement of these rules is poor to non-existent in most localities.

Generally, European swimming pool water treatment procedures include: rough filtering, flocculating, pressure sand filters, ozonization in the contact chamber, and activated carbon (to remove free ozone). The United States system of swimming pool water treatment includes: rough filter, pressure sand filter, pH control and the injection of chlorine immediately prior to the re-entry of the treated water into the pool.

OZONE VS CHLORINE

Ozone possesses many advantages over chlorine in the processing of swimming pool water. Basically, ozone is used as a purification agent and chlorine is used for disinfecting. Actually, ozone can be used both as a flocculating agent and as a disinfectant in addition to its function as a purification agent. The pool water is flocculated to remove various colloidal material and substances that create turbidity, as well as bacteria and virus. The water passes through sand filters to remove the precipitate before being osculated. By removing the colloidal matter and the cause of turbidity, the ozone is given a better chance of doing a fine job.
Some of the advantages and disadvantages of ozone and chlorine used for swimming pool water purification:

1. Chlorine is highly toxic, and is a poisonous gas.

2. Ozone is rated as toxic at the 1.0 mg/llevel by the United States EP A, and no one has ever been known to have died as a result of inhaling it. Ozone has a very pungent odor, noticeable at the 0.01 mg/llevel, and is highly irritating at elevated levels.

3. Chlorine is often stored in high pressure containers on the premises and can be dangerous. A broken chlorine line causes serious problems.

4. Ozone is generated on the premises (not stored).

5. Chlorine, when mixed with urine and perspiration, will form chloramines that cause eye irritation and are toxic to aquatic life.

6. The cost of chlorine is constantly increasing and has become quite expensive. Ozone, on the contrary, is becoming less expensive due to the increase in efficiency and lower energy consumption. The overall cost of using ozone instead of chlorine will be less costly to the pool owner.

7. Ozone is the most active oxidising agent that can be used with safety. It is sometimes called "activated oxygen".

8. Tests have proven that ozone is trom 600 to 3000 times more active in the destruction of bacteria and viruses than chlorine in the same concentration. Escherichia coliform (E.coli) is killed within 5 seconds by ozone at a concentration of 1 mg/l, whereas 15,000 seconds for the same results using chlorine at the same concentration.

9. Ozone is an excellent deodorising agent for many substances, such as organic putrefaction, hydrogen sulphide, urine, smoke, cooking, paint, etc.

10. Ozone is effective against mustiness, mildew, fungus and can be used to eliminate the "locker room" odour in dressing rooms.

11. Ozone is used in therapeutic pools and baths for the treatment of skin infection and burns.

12. Due to the flocculating process and the ozonization process, the water in an osculated pool is very clear. A sky blue colour is imparted in the pool water.

13. Osculated pools do not have the "bath tub ring" that is caused by skin oils, grease, ointments, hair dressing and cosmetics used by the swimmers.

14. Chlorine is more effective against algae growth. Outdoor pools using ozone have a problem with algae bloom under high temperature conditions that can be eliminated by chlorine "shock treatment" of 5 to 10 mg/l, when needed.

15. Chlorine needs pH control (7.0 to 7.4 pH) for reliable results. Ozone does not require pH control., although your pool's surfaces and equipment will still benefit from proper pH. Research has been conducted regarding the eye irritation caused by the chlordanes that are formed in a swimming pool using chlorine. The tests were conducted on the eyes of rabbits (being nearly the same size as the human eye) using high purity water with free chlorine and high purity water using bound chlorine (chloramines formed from chlorine and urine or perspiration mixing). The eyes showed signs of irritation when using the free chlorine solution at 20 mg/l of chlorine and a very little increase in irritation as the level of chlorine

was increased. When the bound chlorine solution was used, eye irritation showed up at 4 mg/l and the irritation increased when the bound chlorine was increased to 5 mg/l and continued to increase as the bound chlorine level was increased. These tests proved that eye irritation is caused by the chloramines and not free chlorine. Bound chlorines (chloramines) cause unpleasant odours and are toxic to aquatic life. The Environmental Protection Agency plans to eliminate the discharge of effluents containing any chloramines.

APPLICATION OF OZONE TO POOL WATER

In a swimming pool using ozone for the purification of the water, the following steps are to be followed:

THE ELIMINATION PHASE:

1. The water, upon leaving the pool, goes into a collection basin where make-up water and chemicals are added.

2. The water goes through a rough filter to remove large floating matter and to protect the pump.

3. A flocculate is added to remove turbid matter and colloidal material (skin, scale, algae, skin oil, soap, nasal drip, cosmetics, bacteria and viruses).

4. The water passes through the sand filter for the removal of precipitate from the flocculating process.

THE REACTION PHASE:

1. Ozone is injected into the water in the contact chamber to remove urine, amino, acids, bacteria and viruses. The osculated water is held in the retention tank from 1 to 2 minutes to complete the ozone reaction.

2. The water is passed through the activated carbon filter to remove the free ozone and to polish the water. In some installations, excess ozone is removed by a cascade (water fall).

3. The fresh water is added in the collection basin. The ozone injection rate will vary from 0.5 to 1.4 mg/l, depending upon the need, but the ozone level in the contactor chamber shall be 0.4 mg/l.

Since ozone has many advantages over chlorine in the purification of swimming pool water, it should be used extensively for this purpose because:

1. The ozone water purification system for swimming pools is superior to the chlorine system because the swimmer has better protection against infection, the water quality is higher and the water is cleaner.

2. By the use of strainers - flocculating - filtration ozonization - activated carbon - disinfecting system, it is possible to treat the water to such an extent that the swimming pool will be a truly safe and healthy place for swimmers.

3. By using an ozonization system, the chlordane's and eye irritation are eliminated.

4. Ozone will eliminate or greatly reduce the growth of fungus.

5. The cleaning and maintenance of a swimming pool is reduced by using ozone; Therefore; the cost of operation should be reduced.

6. Due to the rapidly increasing cost of chlorine, ozone should not be more costly than chlorine to use. In some cases it should be less.

7. Since ozone is generated at the site, it is safer to use than either chlorine gas or pellets.

8. Ozone is effective in treating skin infections in either the conventional pool or a therapeutic pool.

9. Existing pools can be converted from using chlorine to ozone for the treatment of the water.

Depending upon the point of injection, one speaks of precondition or of post-ozonation. When the ozone is introduced before the filters, it acts principally as an oxidant; it causes the formation of a more or less large quantity of flocs which one can then separate from the water. The purification of water also can be improved by a biological filtration. In this case the objective of ozonization is doubled: oxygenation of the water on the one hand, and improving the biodegradability of organic materials on the other. In the filters, besides the classical degradation's, nitrification also occurs, which is at least a partial solution to the problem of ammonia. When ozone is introduced after filtration, it contributes to the disinfecting of the water. In this case a free dissolved residual of 0.4 mg/L of ozone must be maintained during a minimum time of 1 minute.

PROBLEMS IN POOL WATER TREATMENT

In contrast to natural, biological self-cleaning of surface waters, an artificially constructed swimming pool lacks various symbiotic micro-organisms. When pathogenic organisms from humans are put into a natural symbiotic state of, say, a lake, they certainly do not encounter ideal conditions for living. They will undergo competition for nutrients with organisms far better suited to their particular environment; they will not be able to multiply suitably due to the prevailing low temperatures; they will encounter the inhibiting metabolic products of other organisms; and are usually no longer present in numbers which could cause infection, due to the high degree of dilution. In comparison to the vanishing small significance of pollutants introduced by bathers in large swimming lakes, pollution of artificially constructed swimming pools results primarily from bathers. Upon entering a pool, each bather is likely to carry not only 300 to 400 million bacteria but also 0.5g of organic materials in the form of small skin particles, skin fat, sweat, sputum, urine, cosmetics, etc. Because of the fact that the introduced microorganisms, mostly bacteria and fungi, but also protozoa and viruses as well, stem directly form the bathers (originating from body surfaces, nasal-throat passages, urinary and intestinal tracts), there will be a relatively high proportion of disease-causing organisms present, which will present an acute hygienic problem. Additionally, the amount of available nutrients and the relatively high temperatures (28-30oC) favour a corresponding increase in the propagation rate of these microorganisms and therefore encourage the tanks. It is therefore indispensable to guarantee a hygienically unobjectionable quality of swimming pool waters by proper design and operation of the water treatment plant.

Only a very small amount of the influence contaminating material can be portion through direct screening in the filter unit. The principal portion of the organic substances, are present in colloidal form or in completely soluble form. The material existing in colloidal form in the influence water can be filtered after prior treatment with a flocculating agent (aluminium - or iron-containing salts). Completely soluble organic compounds, e.g., nitrogen compounds, cannot be removed by this mode of treatment; they can be eliminated, however, to a high degree by oxidation reactions or by adsorption. Removal of a substantial amount of organic substances signifies not only a micro-organisms, but also a lowering of the time necessary for killing of germs during disinfecting.

OZONE DOSAGE

The average design dose for ozonization of the recycled sub-stream of water abstracted for purification from public swimming pools can be considered as 1.38 mg 03/m3 ranging between 1.07 to 1.7 mg 03/m3 recycled sub-stream.

Principles and functions of a typical ozone generator for swimming pools:

Because of the relatively small loads in private pools as compared to public pools, the ozone equipment can be much smaller and simpler in design than those used in commercial and municipal swimming pools; and far less ozone needs to be produced.

The main features of a typical swimming pool ozone generator are:

1. Works together with the normal filter system and without affecting its performance.

2. Nothing complicated, few moving parts only.

3. Economical to purchase as well as in operation. Cost of unit to be amortized by savings of maintenance products.

4. Compact design, easy to install into existing or new filter system.

5. Reliable, fully automatic, proper functioning to be checked at a glance.

6. Absolutely safe for swimmers, that is to say, the maximum permissible ozone concentration a) in the pool water (0.01 mg/l) and b) in the air above the pool water (0.1 ppm) prescribed by some European authorities, not to be reached, let alone surpassed.

7. Unlike other disinfecting systems, nothing to refill, replace or regulate and virtually no regular maintenance need.

8. Adaptable to any well designed pool. The ozone generator is simply connected into the filter-to-pool return line right after the filter and, if possible, after the heater. Thus all the water flowing through the filter also passes through the ozonization system.

FREQENTLY ASKED QUESTIONS

1) The toxic questions: All that counts is to avoid too much ozone getting into the lungs of swimmers and bystanders. What "too much" means is very well known, namely anything above 0.1 ppm during eight hours, according to authorities on either side of the Atlantic. A typical ozone generator for pools will never be able to reach this concentration in the air, not even if all the ozone gas produced escapes directly into the air instead of being injected into the water first.

2) The residual question: If the pool is used strictly as private, i.e., family members only, no residual chlorine at all is needed in addition to ozonization. If used as a semi-public pool, a small chlorine dose of + 0.1 MPG can be applied as a residual.

3) What ozone cannot do: It cannot go into the pool and brush walls and floor, that is to say, it is not an automatic pool sweeper. It cannot do what an overdose of chlorine might do, compensate for any defect in the filtering system like insufficient turnover, bad water circulation through the pool, inefficient filter, inoperative skimmer, etc.

4) Useful side-effects: There is first of all the dissolved oxygen, of which saturation is soon reached and maintained all the time. As is known, the point of saturation varies with the temperature, for example at 190C (660F) = 9 mg 02/L, at 260C (790F) = 8 mg 02/L at 350C (950F) = 7 mg 02/L. Dissolved oxygen performs a certain self purification. Then, due to the permanent aeration of the water, very fine air bubbles are present throughout the entire water mass of the pool. These bubbles stick to suspended particles and lift them to the water surface where the skimmer sucks them away. It is therefore possible to stir up dirt from the floor and have it raised all the way up to the water surface, thus less vacuuming is needed.

5) Not so desirable side-effect? Natural rubber is not good in oxygenated water, for such material may swell and certainly will become slimy and slippery, which is sometimes mistaken for algae. Certain liners may also become slippery after a few weeks and need to be brushed off or shock-treated with chlorine.

6) The oxidation ashes and foam: As said before, any oxidizable matter will be "burned-up" in fact, some sort of wet combustion takes place and ashes will be created. These ashes are quite fine and there must be a good filter to retain them. If not, the water gets more and more turbid after a week or so. And unfortunately some of these ashes are greenish or brownish in color and are then mistaken for growing algae. Some of these ashes may go to the walls and after some time pile up in some quiet comer or at the seam of the liner, but the water remains crystal clear. These ashes can easily be brushed off like dust, or better still, by an automatic pool sweeper. As long as there is something to oxidize in the water, some foam will appear in the skimmer. This is a sure sign that the ozone is working properly. When there is no foam the water if practically free of any contaminants.

7) The corrosion question: To combat the corrosive properties of ozone gas, the necessary precautions have been taken by using proper material for the ozone. Once the water is ozone, i.e., when leaving the mixing tank, there is no danger of corrosion n the piping, filter tank and pump housing. On the contrary, dissolved oxygen, together with a minimum of hardness (always present) form bicarbonate, which precipitates to the walls and makes a very fine protective film. This film is similar to what occurs with certain additives used in industrial water treatment as corrosion inhibitors.

<u>However paradoxical as it may sound, "ozone prevents corrosion."</u>