1175 Appleby Line
Burlington ON L7L 5H9
Phone: 905 335-4085
Fax: 905 335-1483
Customer Service: 877 281-7603
www.waterquality.net

Ozone and Salt Generators

Written By: Deborah Kon. B.Sc.
Laboratory Manager
UltraPure Water Quality Inc.

Introduction

Pool water sanitation becomes virtually automatic when Ozone is used with a salt generator. Ozone oxidizes the non-living waste from bathers in the pool water while the salt generator produces chlorine that acts as a disinfectant and provides a safety residual. The following paper discusses the operation of salt generators, the benefits of using Ozone and chlorine together, and the benefits of using Ozone with salt generators.

Salt Generators

Salt generators produce chlorine from a mixture of salt (sodium chloride, NaCl) and water (H_2O). Direct current is passed through a solution of salt and water to separate the components. This process is known as electrolysis. The following equation shows the initial steps in this process:

$$\textbf{(1)} \qquad 2\,NaCl_{(s)} + 2\,H_2O_{(l)} \rightarrow 2\,NaOH_{(aq)} + H_{2\,(g)} + Cl_{2\,(g)}$$

Products are sodium hydroxide (NaOH), hydrogen gas (H_2) and chlorine gas (Cl_2). Sodium hydroxide is a very strong base with a high pH close to 14. The hydrogen gas is vented off into the air.

Chlorine gas (Cl_2) reacts with water (H_2O) according to the following reaction:

$$\textbf{(2)} \qquad Cl_{2\,(g)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$$

Hypochlorous acid (HOCl) and hydrochloric acid or muriatic acid (HCl) are produced. The HOCl is the sanitizing form of chlorine. Hydrochloric acid is a very strong acid with a very low pH while the hypochlorus acid is a weaker acid with a near neutral pH.

There are two types of salt generators, brine system generators and in-line generators. Brine system generators use a brine solution held in a two chamber-holding tank. A porous diaphragm or a membrane separates the two chambers. A positive electrode or the anode, is found on one chamber and the negative electrode or the cathode, is on the other chamber. Electricity and sodium ions (Na^+) from the split salt molecule (NaCl) pass through the membrane. The chloride ions dissolved in the water (Cl^-_{aq}) from the split salt molecule cannot pass through the membrane. This prevents the chemicals produced at each electrode from coming into contact with each other. In the chamber connected to the positive electrode or the anode, the chloride ion loses electrons to produce chlorine gas. The following equation illustrates this process:

$$\textbf{Reaction at the Anode: } 2\,Cl^-_{(aq)} \rightarrow Cl_{2\,(g)} + 2\text{ electrons}$$

The chlorine gas (Cl_2) bubbles to the top of the chamber and is drawn off and introduced into the water. The chlorine gas then reacts with water according to preceding equation (2) to produce hypochlorous acid (HOCl) and hydrochloric acid or muriatic acid (HCl). In the chamber connected to the negative electrode or the cathode, the water molecule gains two electrons to produce hydrogen gas and the hydroxyl ion (OH^-). The following equation illustrates this process:

1175 Appleby Line
Burlington ON L7L 5H9
Phone: 905 335-4085
Fax: 905 335-1483
Customer Service: 877 281-7603
www.waterquality.net

Reaction at the Cathode: $2\ H_2O_{(l)} + 2\ \text{electrons} \rightarrow H_{2\ (g)} + 2\ OH^-_{(aq)}$

The sodium ions (Na^+) combine with the hydroxyl ion (OH^-) to produce sodium hydroxide (NaOH). Sodium hydroxide is a strong base with a very high pH. Brine systems are being less used today due to the problems with the disposal of very caustic sodium hydroxide that is produced.

In-line salt generators produce chlorine using the pool water with a low concentration (2000 – 3000 ppm) of salt. This means that the salt must be added directly to the pool water. Electrolysis of salt occurs in an electrolytic cell installed "in-line" in the recirculation system. The electrolytic cell contains layers of plates in pairs that are electrically charged. Each plate is made of titanium plated with platinum, iridium, or ruthenium. The plates have two identical sides that act as an anode/cathode pair. At each plate, the reactions shown above occur at the anode and the cathode.

The common occurrence with this type of a generator is the formation of scale or calcium carbonate ($CaCO_3$) and organic build up on the plates. This build up or fouling on the plates inhibits the electrolysis process. When this occurs, the plates need to be washed with a dilute solution of hydrochloric acid or muriatic acid, or the charge on the plates needs to be reversed to repel any build up that the opposite charge has attracted. In the presence of organic material, the scale still builds up on the plates even when the charge on the plates has been reversed.

Some disadvantages of using an inline salt generator is the fouling of the plates discussed above and the expense of replacing the titanium alloy plates. Another disadvantage of using this system are problems that occur with water chemistry. As seen from equations (1) and (2), the salt generator produces NaOH, a strong base, HOCl, a weak acid, and HCl, a strong acid. The NaOH has a very high pH close to 14. HOCl has a near neutral pH of 5 – 7, and HCl has a very low pH of 1. Based on the reaction balance or stoichiometry, two parts of NaOH are produced for every one part of HOCl and one part of HCl that are produced. As the salt generator runs, the pH of the water keeps increasing and becomes more and more basic. The climbing pH has a definite effect on the efficiency of chlorine. The sanitizing form of chlorine, HOCl, is most efficient around pH 7.2 – 7.6. As the pH climbs above 7.6, the hypochlorite ion (OCl^-) becomes more prominent in the water. The hypochlorite ion is less efficient at sanitizing than the hypochlorous acid. To correct this climbing pH, acid must be added to the pool water. If the acid is added incorrectly, it can burn-out the alkalinity which leads to pH bounce and more problems in maintaining the pool water chemistry.

Ozone and Chlorine

Whether one uses a floater, erosion feeder or a salt generator as the source of chlorine, the objective is always the formation of the sanitizing HOCl in the pool water. Tremendous benefits are achieved when Ozone is used in conjunction with chlorine. Ozone and chlorine work well together, each fulfilling a unique and complementary role in pool water sanitation.

Water sanitation involves three parts; **biocidal action or disinfection, oxidation** and a **safety residual.** Biocidal action or disinfection is the killing of viruses, bacteria, and algae, on contact. Oxidation is the breakdown or altering of non-living bather wastes such as organics (greases and oils) found in suntan lotions, body oils, and nitrogen containing compounds or amines found in perspiration and urine. Residual is amount of free available biocide in the water to ensure that disinfection is fulfilled. The typically recommended free available chlorine (FAC) residual is 1.0 – 3.0 ppm.

UltraPure Water Quality Inc.

1175 Appleby Line
Burlington ON L7L 5H9
Phone: 905 335-4085
Fax: 905 335-1483
Customer Service: 877 281-7603
www.waterquality.net

If chlorine is used on its own in outdoor residential swimming pools without other supplemental products, approximately 15% of chlorine is used up for the biocidal action or disinfection, 70% of the chlorine is used up for partial oxidation, 5% of chlorine is used to maintain a safety residual, and 10% of chlorine is reduced by UV light from the sun.

There is no doubt that chlorine is an excellent disinfectant but is a weaker oxidizing agent than Ozone. Oxidation is the removal of electrons from the bonds holding the molecules together. This removal of electrons breaks down or chemically alters the compound. Both, Ozone and chlorine are electron deficient and have a high oxidizing potential. This means that they oxidize other compounds by removing or sharing electrons. The strength of an oxidizing agent is determined by the agent's electro negativity or the ability to pull electrons away from other compounds.

Ozone and chlorine differ in the speed and strength with which they oxidize other compounds. At pool residual levels (up to 5.0 ppm), chlorine shares electrons with and becomes incorporated into the compound, thus chemically altering it. In this fashion, chlorine combines with organic and amine compounds in the water. These compounds include components of body oils, sun tan lotions, cosmetics, dead algae, dead bacteria, perspiration, and urine. Large amounts of chlorine are consumed in forming these new "chlorinated" compounds. Chlorine is therefore no longer available to function as a biocide and residual. The altered chlorinated organic compounds (combines) form scum lines, greases that clog filters, and layers with calcium carbonate ($CaCO_3$) that result in the formation of soft scale.

At operating residual levels, chlorine also combines with nitrogen containing compounds or amines. The killing form of chlorine, HOCl, reacts with ammonia and nitrogen compounds to form chloramines. The following reaction shows how chlorine combines with ammonia to form chloramines:

Formation of Chloramines:

3 HOCl +	**NH_3** →	**NCl_3** + **3 H_2O**
Hypochlorous Acid	**Ammonia**	**Trichloramine, a chloramine**

Chloramines are less effective biocides than HOCl and the hypochlorite ion (OCl^-) by a factor of 10 or more. In addition, chloramines are responsible for the "chlorine" odour and eye and skin irritations associated with chlorinated water. The formation of chloramines consumes considerable amounts of the free available chlorine. Consequently, more chlorine needs to be added to establish a sufficient free chlorine residual in the water, a process known as "superchlorination" or "shocking". Chloramines can only be removed by shocking.

Since Ozone is a more powerful oxidizing reagent than chlorine, Ozone will react with organic and nitrogen containing compounds faster than chlorine will. Ozone does not combine with these compounds; instead it causes the organics to break apart. The smaller molecules are more water soluble, and some can even gas-off. Amine/nitrogen compounds are altered so that they no longer combine with chlorine. Ozone stops the build-up of chlorinated organic and chloramine compounds and does not form combines.

To summarize, chlorine's biocidal and residual properties are excellent, and in the pool water, chlorine is the primary biocide and the free available residual. Ozone is the primary oxidizer. Through this role, Ozone increases chlorine's effectiveness as a biocide and residual, while using less chorine. Ozone provides a continual effective high-level non-chlorine shock. Without Ozone, the homeowner will end up using a lot more chlorine to keep a free available residual. Superchlorination or "shocking" compounds, as well as other expensive specialty chemicals are required to treat problems caused by combining properties of chlorine.

UltraPure™
Water Quality Inc.

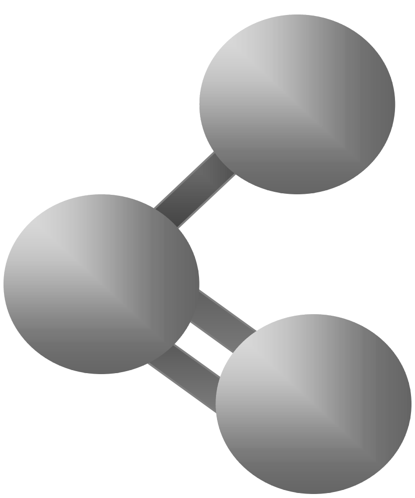
1175 Appleby Line
Burlington ON L7L 5H9
Phone: 905 335-4085
Fax: 905 335-1483
Customer Service: 877 281-7603
www.waterquality.net

Salt Generators and Ozone

Since Ozone performs most of the oxidation work in the pool water as a continual non-chlorine “shock”, Ozone can increase the capacity of a salt generator. Near the plates of the salt generator, where chlorine is generated, the concentration of chlorine is high, 20 – 40 ppm. This concentration is high enough to ‘break point Chlorinate’, ‘shock out’ or oxidize bather waste. Without Ozone, up to 80% of the sanitizing HOCl would be immediately used up and would never get out into the pool. When an Ozone generator is installed in front of the pump, water that has already been oxidized by Ozone is sent to the salt generator plates. The Ozone has ‘oxidized-out’ the organic and nitrogen compounds before they can reach the salt generator. At this point, approximately 80% of the HOCl can enter the pool water and perform its disinfection function and can create a safety residual. In practice, this allows the chlorine generator to have 2-3 times the capacity to disinfect and produce a residual. This allows the salt generator to be run half the time only, or it can be turned down to at least half ‘speed’. This means extra capacity for chlorine production when the pool water is under a heavy load. The fact that Ozone allows the salt generator to be run half the time or allows it to be turned down to half ‘speed’ has other advantages as well. For example, the salt generator plate-life is increased and fouling of the plates is decreased. The expensive titanium alloy plates can last twice as long, 5 – 6 years compared to 2 – 3 years if Ozone was not used and the salt generator was run longer and/or at full ‘speed’.
Another major advantage is that pool water chemistry is evened out. As previously mentioned, rising pH of the pool water can cause water chemistry problems. With Ozone allowing the salt generator to be run less or turned down significantly, the pH climb is greatly slowed and the pool water chemistry is greatly stabilized.

Conclusion

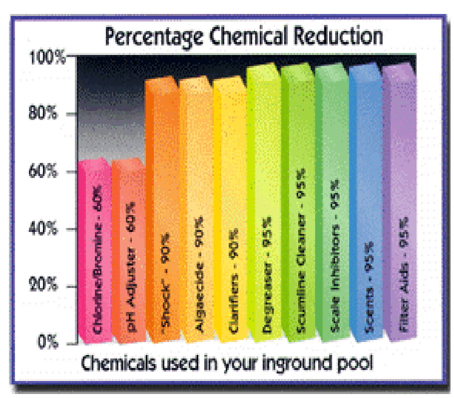
The combination of Ozone and a salt generator produces the best water quality as automatically as currently possible. The pool water is sanitized while the pump is running. Ozone performs the oxidation function to remove non-living bather waste, while most of the chlorine produced by the salt generator provides the disinfectant or biocide to kill algae, bacteria and viruses and a measurable, safety-backup residual. Pool maintenance involves controlling pH, and achieving proper levels of free available chlorine (FAC) and adding salt as needed. The combination of Ozone and a salt generator improves the quality of the pool water thereby providing a better bathing experience allows for easier maintenance of the pool water and allows the usage of fewer chemicals.



OZONE (O_3)

<u>**Results Achieved when Using Ozone**</u>

- **The Least Work**
- **The Cleanest Water**
- **The Fewest Chemicals**



1175 Appleby Line
Burlington ON L7L 5H9
Phone: 905 335-4085
Fax: 905 335-1483
Customer Service: 877 281-7603
www.waterquality.net

Glossary (taken from "Chemistry Principles & Practice", by Reger, Goode, Mercer)

Anode

The electrode in a cell at which oxidation occurs. This electrode is positively charged. At this electrode, electrons are removed.

Cathode

The electrode in a cell at which reduction occurs. This electrode is negatively charged. At this electrode, electrons are gained.

Electrode

A metal or other electrical conductor that connects an electrochemical cell to the external circuit.

Electrolysis

An otherwise nonspontaneous oxidation-reduction reaction that is caused by the passage of an electric current.

Oxidation

The loss of electrons by an element, compound, or ion.

Oxidation-reduction (redox) reaction

A reaction in which electrons are transferred from one species to another.

Oxidizing agent

The reactant that is reduced in a redox reaction. This reactant gains electrons.

Reduction

The gain of electrons by an element, compound, or ion.

Stoichiometry

Quantitative relationships involving substances and their reactions. Balancing chemical reactions, balancing reactants and products of chemical reactions.