Peroxygen Compounds As Oxidizers For Swimming Pools & Spas

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Oxidation is an integral part of swimming pool and spa water treatment. It should not be confused with sanitation or considered a second job for chemical sanitizers. The functional roles of sanitizers and oxidizers are complementary, but distinctly different. Sanitizers are used to disinfect pool and spa water. Effective sanitation protects bathers against pathogenic organisms which can cause disease and infection. Oxidizers, on the other hand, are used to eliminate bather waste and other organic contaminants. Regular oxidation promotes maximum sanitizer efficiency and water clarity.

Adequate sanitation plus regular oxidation and proper water balance are the essential components of an effective, preventive water treatment program. The primary objectives of such a program are:

- To protect bathers against disease and infection caused by harmful microorganisms.
- To eliminate bather waste and other organic contaminants, thus improving the efficiency of chlorine, bromine and alternative sanitizers and producing maximum water clarity.
- To protect recirculation equipment and pool surfaces from the damaging effects of corrosive or scale–forming water.

Choice of Oxidizer

There are a variety of chlorine and chlorine–free oxidizers available for shock treating pool and spa water, including:

Chlorine	Chlorine–Free
Sodium hypochlorite	Hydrogen peroxide
Calcium hypochlorite	Sodium percarbonate
Lithium hypochlorite	Potassium monopersulfate
Sodium dichloroisocyanurate	Sodium persulfate (dipersulfate)
Chlorine gas	

While these products are all oxidizers, they have very different physical properties and react differently when added to pool and spa water. Since pools and spas are oxidized, or "shocked", for a variety of reasons, no single oxidizer will produce the best results in all situations. Therefore, the specific application, the type of pool, and the quality of the water should be carefully considered to determine which oxidizer will produce the desired results.

As a sanitizer, chlorine provides excellent protection against pathogenic organisms at relatively low doses in pools and spas. There are however, significant drawbacks to using chlorine at the higher doses which are commonly recommended for superchlorination and/or breakpoint chlorination. The primary drawbacks of superchlorination are: the formation of high chlorine residuals, which often require dechlorination before bathing can resume; and the formation of combined chlorine compounds, many of which produce strong, irritating odors and cause serious bather and operator discomfort.

The use of chlorine–free oxidizers for regular, preventive oxidation (shock treatment) is rapidly growing. Growth is being driven by pool owners and operators who want to simplify their water treatment programs, avoid the negative side–effects of superchlorination, and maintain superior overall water quality. The chlorine–free oxidizers which are commercially available to pool owners and operators consist of chemical compounds called peroxygens. Peroxygens are compounds that contain an oxygen–

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oxygen bond, –O–O– (also referred to as a peroxide bond), in their chemical structure, such as hydrogen peroxide, peroxycarbonates, peroxyborates, and peroxyacids.

Chlorine products commonly used for pool and spa water treatment can vary considerably in physical form. They can be liquid, solid, or gas. They are available as stabilized or unstabilized products, and in acidic or basic form. But once introduced into pool or spa water they all form the same reactive species, hypochlorous acid (HOCl) and/or hypochlorite ion (OCl^-). The peroxygen products listed above also vary, from liquid to solid, and from acidic to basic, but unlike chlorine products, they do not all form the same reactive species when added to pool and spa water.

There are four peroxygen products which are currently sold for pool and spa oxidation. They are 27% liquid hydrogen peroxide, sodium carbonate peroxyhydrate, potassium monopersulfate and sodium persulfate.

Peroxygens Compounds

The grouping of all peroxygen compounds into one family can be misleading because they do not all produce the same reactive chemicals when dissolved in water. Like chlorinated products, peroxygen compounds are oxidizers, but the similarities end there. Peroxygen compounds are evaluated on the basis of their oxidation potential, active oxygen content, and reactivity in a given application.

Oxidation potential, as measured by the standard electrode potential, is a relative comparison of the strength, or power, of a given oxidizer. It provides a means for predicting whether or not a reaction might occur. For example, if the standard electrode potentials of two half reactions are significantly different, then there is the potential for reaction to occur between them. Conversely, if the standard electrode potentials are very similar, the likelihood of a reaction proceeding is very low.

The following is a relative ranking of chemical oxidizing agents which are commonly used for pool and spa water treatment:

Standard Electrode Potentials (volts)

–2.07	Ozone
–2.01	Sodium persulfate (dipersulfate)
–1.49	Chlorine
–1.44	Potassium monopersulfate
–1.07	Bromine
–0.87	Hydrogen peroxide

By comparing the oxidation potentials of these oxidizers, we can predict reactions that might, or might not occur. For example, the difference between chlorine (–1.49v) and hydrogen peroxide (–0.87v) is 0.62 volts, significant enough to conclude that there is potential for chlorine to oxidize hydrogen peroxide, and in fact, this is a very favorable reaction under pool and spa water conditions. By contrast, the difference between chlorine (–1.49v) and potassium monopersulfate (–1.44v) is only 0.05 volts, minimal enough to conclude that chlorine and potassium monopersulfate will probably not react with one another. Tests show that under pool and spa water conditions chlorine and potassium monopersulfate can, and do, co–exist. So, we can use this ranking system to compare the relative strengths of various oxidizers and also to predict the chemical compatibility of oxidizers which might be used together in water treatment systems. We must keep in mind, however, that oxidation potential alone does not provide sufficient information to determine how an oxidizer will perform in a given application.

Active oxygen content and reactivity are the other parameters used to compare oxygen–based oxidizers. Table 1 shows the active oxygen content and the general kind of reactivity expected from the four peroxygen compounds currently used for oxidation (shock treatment) of pool and spa water:

It is not enough to look at oxidation potential, or active oxygen content, or reactivity alone. All of these parameters must be considered in order to select the right oxidizer for a given application. For example if oxidation potential were the sole criteria, sodium persulfate (dipersulfate) would rank high, but

Peroxygen Compound	Active Oxygen (%)	Reactivity in Pools and Spas
Hydrogen peroxide (27% solution)	12.6	Oxidation/Reduction (Dechlorination)
Percarbonates (sodium carbonate peroxyhydrate)	13.0	Oxidation/Reduction (Dechlorination)
Monopersulfate (potassium monopersulfate)	4.5	Oxidation
Dipersulfate (sodium persulfate)	5.0	Low/No Reactivity

Table 1 – Active Oxygen Content and Reactivity

when we consider its low level of reactivity under pool and spa water conditions, the ranking drops considerably. If active oxygen content were the sole criteria, hydrogen peroxide and sodium percarbonate (sodium carbonate peroxyhydrate) would both be candidates. However, the fact that they are effective dechlorinating agents becomes a major barrier to their use in chlorine sanitized pools and spas.

Unwanted Dechlorination

In typical pool and spa applications, sodium sulfite, sodium bisulfite, and sodium thiosulfate are generally known as dechlorinating agents or chlorine neutralizers. These compounds are reducing agents. Reducing agents are the chemical opposites of oxidizing agents. Since oxidation and reduction always occur simultaneously, reactions that involve both oxidation and reduction are called redox reactions. Although hydrogen peroxide is generally considered an oxidizing agent, it has industrial application as a reducing agent as well, due in part to its moderate oxidation potential. Hydrogen peroxide is widely used to reduce free chlorine residuals in industrial wastewater streams and the same reaction can occur in swimming pool and spa water. Under slightly alkaline conditions (pH > 7), hydrogen peroxide reacts instantaneously with hypochlorite ion, according to the equation:

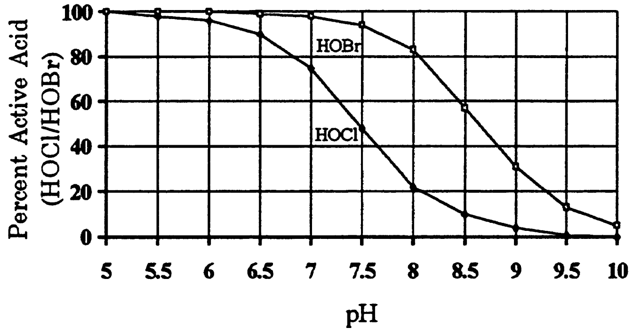
$$OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2 \qquad (1)$$

In this reaction the hypochlorite ion is reduced by hydrogen peroxide to a chloride ion, and hydrogen peroxide is oxidized to oxygen.

Dechlorination by hydrogen peroxide is pH dependent. Free chlorine residual in water can exist as chlorine (Cl_2), hypochlorous acid (HOCl), or hypochlorite ion (OCl^-), depending upon pH. Cl_2 predominates at pH below 3, HOCl predominates at pH 3–7 and OCl^- predominates above pH 7.5. This can be shown by the following equation:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \xrightarrow{OH^-} OCl^- + H_2O \qquad (2)$$

Of primary concern in pool and spa water is what happens between pH 7 and 8. The dissociation curves below show the percentages of hypochlorous and hypobromous acid present as a function of pH. The chlorine curve clearly illustrates that the percentage of hypochlorous acid drops significantly as pH is increased from 7 to 8. This reduction is due to the conversion of HOCl to OCl^- as the pH increases. Since the pH of pool and spa water is generally maintained within the range of 7.2 to 7.8, hypochlorous acid and hypochlorite ion are always in equilibrium with each other. So, if hypochlorite ion is reduced by hydrogen peroxide, residual hypochlorous acid will be converted to hypochlorite ion in order to maintain an equilibrium concentration, and in the presence of sufficient hydrogen peroxide, free chlorine residuals will be depleted, according to equation (1) above.



Dissociation of Chlorine and Bromine % Active Acid vs. pH

Sodium carbonate peroxyhydrate, generally referred to as sodium percarbonate, dissolves readily in water to give a mildly alkaline solution of hydrogen peroxide and sodium carbonate. Sodium percarbonate is therefore a solid form of hydrogen peroxide and once added to swimming pool or spa water, the same dechlorination reaction will occur.

Active Oxygen

Active oxygen is represented in chemical equations by an oxygen atom enclosed in brackets, [O]. The following half reactions illustrate the concept of reactive active oxygen:

Ozone O_3	$\rightarrow$	O_2	+	[O]
Monopersulfate HSO_5^-	$\rightarrow$	HSO_4^-	+	[O]
Hydrogen peroxide H_2O_2	$\rightarrow$	H_2O	+	[O]

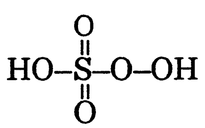
These compounds have an "extra" oxygen atom, or an active oxygen [O]. They are capable of accepting two electrons from a reducing agent and following the transfer of these electrons, we could say that the reducing agent (electron donor) has been oxidized by the active oxygen (electron acceptor).

The chemistry that occurs in pool and spa water is complex. Reaction conditions are extremely dilute, pH is neutral to slightly alkaline, and water temperatures are moderate. Under these conditions, hydrogen peroxide, sodium percarbonate, and potassium monopersulfate will all ionize to form reactive oxidizer species which yield active oxygen. Sodium persulfate, by contrast, has very limited reactivity in this environment.

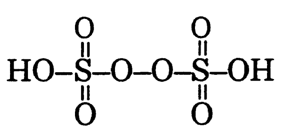
Persulfate Oxidizers

The persulfates used for oxidation of pool and spa waters are both peroxyacids. Beyond that similarity, they are very different compounds and under pool and spa water conditions (described above) they differ greatly in terms of reactivity. Potassium monopersulfate, simply referred to as monopersulfate, is the potassium salt of peroxymonosulfuric acid. Sodium persulfate, generally referred to as dipersulfate, is the sodium salt of peroxydisulfuric acid. The different chemical structures of monopersulfate and dipersulfate are illustrated below:

Monopersulfate
K^+ salt of H_2SO_5
Peroxymonosulfuric acid



Dipersulfate
Na^+, K^+, NH_4^+ salts of $H_2S_2O_8$
Peroxydisulfuric acid



Potassium monopersulfate dissolves quickly and ionizes readily over a wide pH range to form the reactive anion of peroxymonosulfuric acid, HSO_5^-. This anion has an oxidation potential similar to that of chlorine. It is a much stronger oxidizer than hydrogen peroxide or sodium percarbonate, and is compatible in solution with free available chlorine and bromine. Therefore, it will not react with chlorine or bromine residuals.

Sodium persulfate dissolves quickly in water to form peroxydisulfuric acid anion, but unlike monopersulfate, it has limited reactivity under swimming pool and spa water conditions. It will hydrolyze to form reactive peroxymonosulfuric acid, but only under very acidic conditions. Solutions of peroxydisulfuric acid decompose very slowly under swimming pool and spa water conditions according to the following equation:

$$2S_2O_8^{2-} + 2H_2O \rightarrow 4HSO_4^- + O_2 \qquad (3)$$

Some reactivity may be observed as a result of the formation of an unstable free radical intermediate, particularly in outdoor pools where UV light can accelerate the decomposition reaction. But for the most part, the oxidative power of dipersulfate can not be fully realized under pool and spa water conditions. In order to utilize dipersulfate as an effective oxidizing agent, temperatures must be elevated to 120 degrees F (~50°C), or above, or a metal ion catalyst must be added.

Comparison of Peroxygen Compounds for Pool & Spa Oxidation

Hydrogen peroxide is not recommended for use with chlorine sanitizers because of its efficient dechlorinating capabilities. The same is true for bromine sanitizers, however the debrominating reaction is expected to be much slower.

Hydrogen peroxide is sold as a 27% solution. It is used as an oxidizer in conjunction with polymeric biguanide sanitizers. The weaker oxidative power of hydrogen peroxide, as compared to chlorine and persulfate products, is partially offset by a combination of higher active oxygen content and higher recommended doses (approximately 30 ppm/shock treatment). But most important is peroxide's unique compatibility with biguanide polymer chemistry, which makes it the oxidizer of choice for these chlorine–free sanitizer systems.

Sodium carbonate peroxyhydrate (sodium percarbonate) is an addition compound of hydrogen peroxide and sodium carbonate. It releases hydrogen peroxide when added to water and will have the same reactivity in pool and spa water as liquid peroxide solutions. The key difference is that sodium percarbonate is a granular solid, and since it contains sodium carbonate, it will add some alkalinity to the water.

Sodium percarbonate is currently being sold as a general purpose non–chlorine shocking agent and it is indiscriminately being used in chlorinated swimming pools. While there may be some application for this product in pool and spa water treatment, it is not recommended for use with chlorine sanitizers because of its efficient dechlorinating capabilities.

Potassium monopersulfate (peroxymonosulfate) is a peroxyacid. It is a granular free–flowing powder with strong oxidative power and high versatility in pool and spa water treatment applications. It is compatible with chlorine, bromine and most alternative sanitizers. Monopersulfate readily oxidizes bromide ion to bromine. Once formed, the bromine reacts with water to form hypobromous acid, which is the active sanitizer that is present (in a bromine system) at the normal pH of pool and spa water. Monopersulfate will also oxidize chloride ion to chlorine, although not as readily. This reaction can become a factor in pools that are laden with high chloride ion content or if a heavy dose of monopersulfate is applied. Like chlorine, monopersulfate is not recommended for use with polymeric biguanide because it will oxidize and destroy the biguanide polymer.

Sodium persulfate (peroxydisulfate, or dipersulfate) is a peroxyacid. While the oxidative power of sodium persulfate is nearly equivalent to that of ozone, it can not be fully utilized under pool and spa water conditions. The major use of sodium persulfate is as a source of free radicals to initiate polymerization reactions for the chemical production of a variety of polymeric compounds. Heavy metal ions and sulfites are added to accelerate the rate of radical generation. The pH of a pool or a spa is essentially neutral, and operating temperatures are moderate. The concentration of pool contaminants is normally very low, and thus there is little impetus for sodium persulfate to react under these conditions. The addition of a few ppm copper does not appear to initiate or accelerate the reactivity of dipersulfate. As a result, sodium persulfate has very low reactivity in pool and spa water, particularly in indoor pools where concentrations of sodium persulfate can build up significantly. Dipersulfate does not react with bromide ion, and in spite of its oxidative power does not oxidize polymeric biguanide.

Conclusion

Regular oxidation is an essential component of preventive water treatment chemistry. Peroxygen compounds can provide powerful oxidation without the drawbacks associated with heavy chlorine doses. However, peroxygen compounds vary widely in their properties and their effects in swimming pool and spa environments. It is necessary to select the right peroxygen compound to accomplish the intended objective.

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