



KAREN RIGSBY is a technical services senior specialist with BioLab Inc. in Lawrenceville, Ga. She holds a B.S. in chemistry from Georgia Tech, and has been with BioLab for 10 years.

Supply and Demand

Understanding the interactions between hypochlorous acid and contaminants is critical in dealing with chlorine demand problems

Chlorine demand can be defined as the inability to maintain a chlorine residual. An almost infinite number of substances can contribute to demand. These include bacteria, algae, ammonia, urine, sweat, health and beauty products, bather waste, and animal waste. Such contaminants can enter the water in a number of different ways — through source water, rain water, bathers, animals, fertilizers, plants/leaves and industrial pollution. Thus, determining the cause of chlorine demand in a particular pool can sometimes seem like an insurmountable task.

Hypochlorous acid, or free available chlorine, can be a great tool in tackling chlorine demand problems. That's because hypochlorous acid reacts easily with many different types of materials. By looking at the chemical structure of some contaminants, one can predict whether there will be an interaction with hypochlorous acid — which will determine whether that particular contaminant contributes to demand.

All atoms have what is referred to as a preferred "oxidation state," or "oxidation number." This is simply a number that is assigned to a particular atom based on its chemical properties. For example, the preferred oxidation number for chlorine is -1. The preferred oxidation number for nitrogen and phosphorous is +5. Atoms in an oxidation state that is not preferred are very reactive, while atoms in their preferred oxidation state are stable and are much less reactive. It is not important to know how the oxidation numbers are determined, but knowing what they are is very helpful.

In hypochlorous acid (HOCl), chlorine actually has an oxidation number of +1, which is not preferred. Because chlorine is constantly trying to reach its preferred state of -1, hypochlorous acid is very reactive. This is why it's such a great oxidizer. When hypochlorous acid oxidizes other materials, the chlorine atom ends up where it wants to be, at -1.

In the ammonia (NH₃) molecule, the nitrogen atom has an oxidation number of -3. As mentioned earlier, it prefers +5. This makes it very reactive as well. Because the chlorine in hypochlorous acid needs a decrease in oxidation number (from +1 to -1), and the nitrogen in ammonia needs an increase in oxidation number (from -3 to +5), these chemicals are

perfect to react with one another.

Ammonia is removed from pool water through the application of chlorinating products, and hypochlorous acid is used up during this process. A similar process happens with bather waste contaminants such as urea and creatinine. However, the oxidation process is much longer for these compounds because they are more complex.

Just as some compounds readily react with hypochlorous acid, some compounds do not tend to react with it. For example, the nitrogen in nitrate (NO₃⁻) already is where it wants to be at +5. The same is true for the phosphorous atom in phosphate (PO₄⁻³). In the orthophosphate molecule, the phosphorous atom also is where it wants to be at +5.

POSITIVES AND NEGATIVES

Here's a look at some common recreational water contaminants and their reactivity to hypochlorous acid based on their oxidation numbers. Remember, HOCl has an oxidation number of +1 and chlorine has an oxidation number of -1.

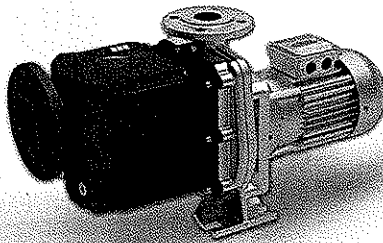
	Oxidation Number	Type of Change Needed	Reaction with HOCl?
Nitrogen in Ammonia (NH ₃)	-3	Increase in oxidation number	Yes
Nitrogen in Nitrite (NO ₂ ⁻)	+3	Increase in oxidation number	Yes
Nitrogen in Nitrate (NO ₃ ⁻)	+5	None	No
Phosphorous in Phosphate (PO ₄ ⁻³)	+5	None	No

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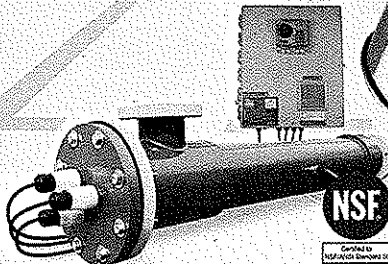
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This makes them quite stable and unlikely to react with hypochlorous acid. If material does not react with hypochlorous acid, then it does not contribute to chlorine demand. If phosphate or nitrate reacted with chlorine, then these compounds would be removed when shocking the pool, but this does not occur.

Unfortunately, there is no easy cure for many chlorine demand situations. In most cases, there are still only two options.

The first is to apply the appropriate amount of chlorinating product; the second is to replace some of the water with fresh water that has no chlorine demand.

In situations where the chlorine demand is accompanied by very cloudy water, a flocculant treatment may reduce the demand by physically removing some of the contaminants from the water. Keep in mind that a floc treatment or water replacement does not completely cure the demand — it only lessens it. It will be necessary to re-test and apply the newly recommended amount of chlorinating product.

Treating chlorine demand can seem overwhelming, especially if the demand is large. During treatment it is important to recognize that there are two categories of contaminants being treated. The first is "fast reacting," which includes small molecules such as ammonia. The second type is "slow reacting," which includes the larger molecules such as amino acids and proteins. Typically more complex than the smaller molecules, they require more time to oxidize. These larger, slower-reacting contaminants are usually the result of swimmer waste such as sweat or urine, and can take up to 36 hours to completely oxidize. Chlorine demand is likely caused by a combination of different types of contaminants, so treatment time and difficulty can vary.

Of course, the best course of action is always prevention. Doing routine oxidation as well as application of a maintenance algacide will help keep water clear and free from contaminants that can contribute to chlorine demand.

It's also important to know when additional oxidation is needed. This includes heavy bather loads, rain, warmer-than-normal temperatures and any time there is suspected contamination of the pool water. Designing a maintenance program specific to the characteristics of each facility will help prevent problems before they begin. ■