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Pool Tip #47: Breakpoint Chlorination

Chlorine is also used to shock or superchlorinate pool water in order to remove unwanted organic compounds from the water, destroy impurities and dissolved waste products and algae, and break apart the chemical bond that holds chlorine and ammonia and nitrogen together. The point at which this chemical bond is broken is called "breakpoint". Breakpoint chlorination eliminates chloramines and other reductants which cause an increased chlorine demand.

In order to achieve breakpoint, a quantity of 7.6 molecules of free chlorine are used to break apart each molecule of combined chlorine. Several chemical reactions take place. Chlorine reacts with ammonia (NH_3) to form monochloramines (NH_2Cl). Free chlorine reacts with monochloramines to form dichloramines ($NHCL_2$). Free chlorine reacts with dichloramines to form trichloramines or nitrogen trichloride (NCl_3) and nitrates before the breakpoint is achieved. Nitrogen trichloride forms when the HOCl to nitrogen molecular weight ratio is 12 to 1, and oily, insoluble colloidal particles will appear, cloud the water, migrate toward the water surface, and may be released into the ambient air, further contaminating the natatorium environment.

Reaching the breakpoint is an all-or-nothing reaction. If breakpoint is not reached, the problem will be worse. When the chemical bond with ammonia is broken, free chlorine, nitrogen, water and inorganic chloride (salt) remain.

Superchlorination of pool water should be done periodically, as needed, when the level of chloramines present in the water is greater than 0.2 ppm. Products used for superchlorination include chlorine in any form, however, stabilized chlorine products, or isocyanurates (trichlor or dichlor), should not be used for superchlorination since excess cyanuric acid would be added to the water solution concurrently.

Before attempting breakpoint chlorination, lower the pH to 7.2 to 7.4 to increase the percentage of hypochlorous acid which forms, and make sure the water is chemically balanced. Shocking a pool with unbalanced water, particularly with a high (basic) pH or high total alkalinity, will result in the formation of a white carbonate precipitate which will cloud the water. However, some operators prefer to raise the pH when using acidic chlorine products like elemental gas chlorine for superchlorination since more offensive forms of chloramines develop rapidly at a very low pH.

To calculate breakpoint in order to superchlorinate, use a DPD (N,N-diethyl-p-phenelynediamine) or FAS (ferrous ammonium sulfate) test kit to find both the free and total available chlorine levels. Subtract the free available chlorine (FAC) from the total available chlorine (TAC) to find the combined available chlorine (CAC) level. Multiply the CAC by the factor 10, although only 7.6 is actually needed, to find the dose of chlorine you must introduce into the pool in order to reach the breakpoint. Ten is used as a factor because most pool operators are not sure of the precise amount of water in their pools, or of the exact percentage of available chlorine in the chlorine compound being used. We use ten as a factor to err on the side of caution and so that enough chlorine is left over after breakpoint has been achieved to satisfy the chlorine demand and leave an adequate residual.

Determine the number of gallons of pool water to be treated and the percentage of available chlorine in the product that will be used to superchlorinate the pool. Calculate the amount of chlorine needed by weight, or refer to a standard chart or a chart provided by the chlorine manufacturer.

Amount of available chlorine necessary to raise the chlorine level 1 ppm per 10,000 gallons of pool water		
Amount	% Available Chlorine	Chlorine Product
1.5 cups	10%	sodium hypochlorite
1.3 cups	12%	sodium hypochlorite
1 cup	15%	sodium hypochlorite
2.25 oz	60%	sodium dichloro-s-triazinetrione
2 oz	65%	calcium hypochlorite
1.5 oz	85%	trichloro-s-triazinetrione
1.3 oz	100%	elemental gas chlorine

For example: If free available chlorine is 1.0 ppm and total available chlorine is 1.5 ppm, the difference (combined available chlorine) is 0.5 ppm. Multiply 0.5 by 10 to determine that 5 ppm of chlorine must be added to the water in order to reach breakpoint. You know that the pool in question contains 25,000 gallons of water, and you plan to superchlorinate using 10% available sodium hypochlorite. By following the chart and inserting the appropriate numbers into the formula, you can determine that 1 gallon of 12% sodium hypochlorite must be added to a 25,000 gallon pool, to eliminate 0.5 ppm of combined chlorine.

(1.5 cups) (1 ppm) (10,000 gallons)
(1.3 cups) (5 ppm) (2.5) = 16.25 cups ÷ 16 = 1 gallon

Some health department regulations may prohibit swimmers from using the pool when chlorine concentrations are elevated. It is best to superchlorinate in the evening or during hours the pool is not in operation to avoid respiratory irritation to users from off gassing during the superchlorination process, and to allow chlorine levels to drop back to normal levels. How fast breakpoint is reached depends on several factors, including: pH, pool water temperature, the ratio of free available chlorine to combined chlorine, and the concentration of ammonia/nitrogen and organic nitrogen compounds which place a demand on the chlorine. If the chemical reaction takes place and breakpoint is reached, the large amounts of chlorine added to the water will be used up in the process. Free chlorine will return to normal operating levels, and the combined chlorines will be eliminated.