WHAT ARE POOL CHEMICALS AND HOW DO THEY PROTECT SWIMMERS?

Chlorine kills microbes in pools, but don't blame it for your green hair. By Celia Henry Arnaud/C&EN

The main article was adapted from "What Are Pool Chemicals, and How Do They Protect Swimmers?" The story first appeared in Chemical & Engineering News (C&EN) on Aug. 1, 2017.

eople love to complain about chlorine in pools—often as much as they enjoy plunging into the clean water. Chlorine-based compounds can dry out skin, turn eyes red, and produce the familiar and pungent pool smell.

On the other hand, thanks to chlorine, we can swim in water free of microbes, such as *Escherichia coli*, that can cause digestive troubles. In addition to disinfectants such as chlorine, pool operators also add chemicals to control other properties, including **pH** and **water hardness**.

'Free chlorine'

The chlorine (Cl) used to disinfect commercial pools is not added as chloride ions (Cl⁻) in solution. It's typically added as part of more complex molecules. These molecules include hypochlorite (CIO⁻) ions or disinfectants called isocyanurates, explains Thomas M. Lachocki, chief executive officer of the National Swimming Pool Foundation. When these compounds are added to water, they spontaneously form hypochlorous acid (HCIO), which is the disinfecting agent misleadingly called "free chlorine" in pool lingo.

Residential pool owners are most likely to use an isocyanurate known as trichlor $(C_3Cl_3N_3O_3)$ because it dissolves

oç₀ Water Words

» **pH** is a measure of how acidic or basic a solution is.

» Water hardness is determined by the amount of the dissolved minerals, calcium and magnesium, that it contains. slowly, has high chlorine content, and is easy to use, Lachocki says.

Getting the concentration of the disinfectant right is a balancing act. The concentration needs to be high enough that some disinfectant is always in the water. But it also needs to be low enough to be comfortable for swimmers. Adding a stabilizer helps protect the hypochlorous acid from breaking down in sunlight.

Complicating factors

Chlorinated compounds aren't the only options for first-line disinfectants. Bromine-containing compounds can also be used to kill pathogens, and are more commonly used in hot tubs because bromine-based disinfectants are more stable than chlorine compounds at warm temperatures.

Another limitation of chlorine is that



certain microbes that can cause intestinal infections are resistant to the disinfectant. For example, the microbial parasite *Cryptosporidium* has a protective coat that makes the microbe hard to destroy with chlorine.

To eliminate such pathogens, many pools now use ultraviolet (UV) radiation in their filtration systems. UV light disinfects water by penetrating organisms' cell walls and damaging their DNA. This treatment is particularly good for inactivating *Cryptosporidium*.

UV treatment, which is damaging to the skin, takes place in a chamber away from swimmers before water is released into a pool. But unlike chemical treatments that can work continuously even as people are swimming in pool water, UV light can't continue to disinfect water after it leaves the UV chamber. That means that microbes brought into the water by swimmers after the water is treated with UV light will stay alive if UV is the only disinfectant method used. Still, UV water treatment kills some harmful microbes, and it offers another benefit: It can reduce that potent "chlorine" smell associated with indoor pools. Swimmers are partly to blame for the stink. That odor is created when chlorine reacts with compounds, such as urea $(CO(NH_2)_2)$ in urine and sweat, to form trichloramine (NCl₃). In addition to causing pool smell, trichloramine and other by-products that result from pool chemistry might be linked to asthma in swimmers. Luckily, UV light can degrade these compounds. (Still, it's better not to pee in the pool! And yes, you should shower before getting in.)

Other than UV treatment and chlorine, additional substances are required to make sure pool water is safe for swimming. Pool disinfectants work optimally when the water pH is between 7.2 and 7.8. So pool operators add other compounds to maintain this pH range and push the equilibrium between hypochlorous acid (HCIO) and hypochlorite ions (CIO⁻) toward HCIO, Lachocki says (see *Why Pool pH Matters, p. 18*). Typical chemicals used to balance the pH include muriatic acid (also known as hydrochloric acid, or HCI), sodium bisulfate (NaHSO₄), carbon dioxide (CO₂) and sulfuric acid (H₂SO₄).

'Green' chemistry

Pool chemicals are big business. According to 2017 estimates by Pkdata, a market research firm that collects data on the swimming pool and spa industry, there were more than 8.5 million residential pools—inground and aboveground—in the U.S., not including Alaska and Hawaii. More than 719 billion liters (190 billion gallons) of water were treated to fill those pools. As a result, the market for chemicals used in treating all these pools was roughly \$2 billion.

Pool chemistry certainly produces a lot of



STRUCTURES AND POOL DIAGRAM: RS GRAPHX INC.





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IS IT OH TO PEE IN THE POOL?

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greenbacks, and sometimes even a green pool. When the diving pool at the 2016 Summer Olympics in Rio de Janeiro turned a shade of emerald, it was possibly because of algae growth or an excess of a copper-containing algicide. The actual culprit will never be known conclusively because Olympic officials drained and refilled the pool without running chemical tests.

On occasion, pool chemistry is also to blame for a bit of green hair. Urban myths would have you believe that chlorine causes unwelcome green highlights. But the change of hue is thanks to either copper-containing compounds added to the water to fight off algae, or copper found in the water that is used to fill the pool. Sometimes the copper even originates from corroded plumbing. The effect, regardless of what caused it, is like the green patina on the Statue of Liberty, except it's on your head.

Thankfully, if folks follow directions on pool chemical labels—which are regulated in the U.S. by the Environmental Protection Agency—these debacles can usually be avoided.

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During the 2016 Summer Olympics in Rio de Janeiro, a diving pool turned emerald green. Olympics organizers said there was no risk to athletes, but the cause of the color change was not determined.

WHY POOL PH MATTERS

When chlorine-based disinfectants are added to a pool, they react with the water to produce hydroxide ions (OH⁻) and the disinfectant hypochlorous acid (HClO).

Initially, there is plenty of HClO in the water. But over time, it gets used up as it destroys pathogenic bacteria. It also dissociates, or breaks apart, to form hydrogen ions, H^+ , and hypochlorite ions, OCl⁻. The reverse reaction also takes place. When the reactions occur at the same rate, they reach **equilibrium.**

$HClO(aq) \equiv H^{+}(aq) + OCl^{-}(aq)$

To maintain enough HClO in the water to keep the water clean, pool operators can adjust the water's pH so that the reaction will favor forming HClO.

You can apply **Le Châtelier's principle** to see how this works. Adding an acid would raise the H^+ concentration, lowering the pH. The extra H^+ ions from the acid would react with OCI⁻ to shift the reaction toward producing more HCIO.

But too much HClO irritates swimmers' eyes. To reduce the level of HClO when needed, a base can be added to react with the H^+ in the water, thus lowering the amount of these ions. Fewer H^+ ions would shift the reaction to produce more H^+ and less HClO.

In other words, the pool's pH must be just right.— and