Swimming Pool Chemistry

Those who own or maintain swimming pools know that frequent checks should be made on the water quality. One kind of pool "housekeeping" involves the removal of suspended particles such as leaves, dirt, and hair using skimmers and filters. A second kind deals with the much less visible buildup in the water of dissolved pollutants. Dissolved pollutants such as body wastes, algae, and disease-causing bacteria require chemical treatment.

Removing Bacteria

The chemical treatment of swimming pools involves the active disinfectant hypochlorous acid, HOCl. HOCl, a substance also used in drinking water purification and the final step of wastewater treatment, can be produced by the reaction of chlorine gas, Cl_2, with water:

$$Cl_2\,(g) + H_2O\,(l) \rightarrow HOCl\,(aq) + H^+\,(aq) + Cl^-\,(aq)$$

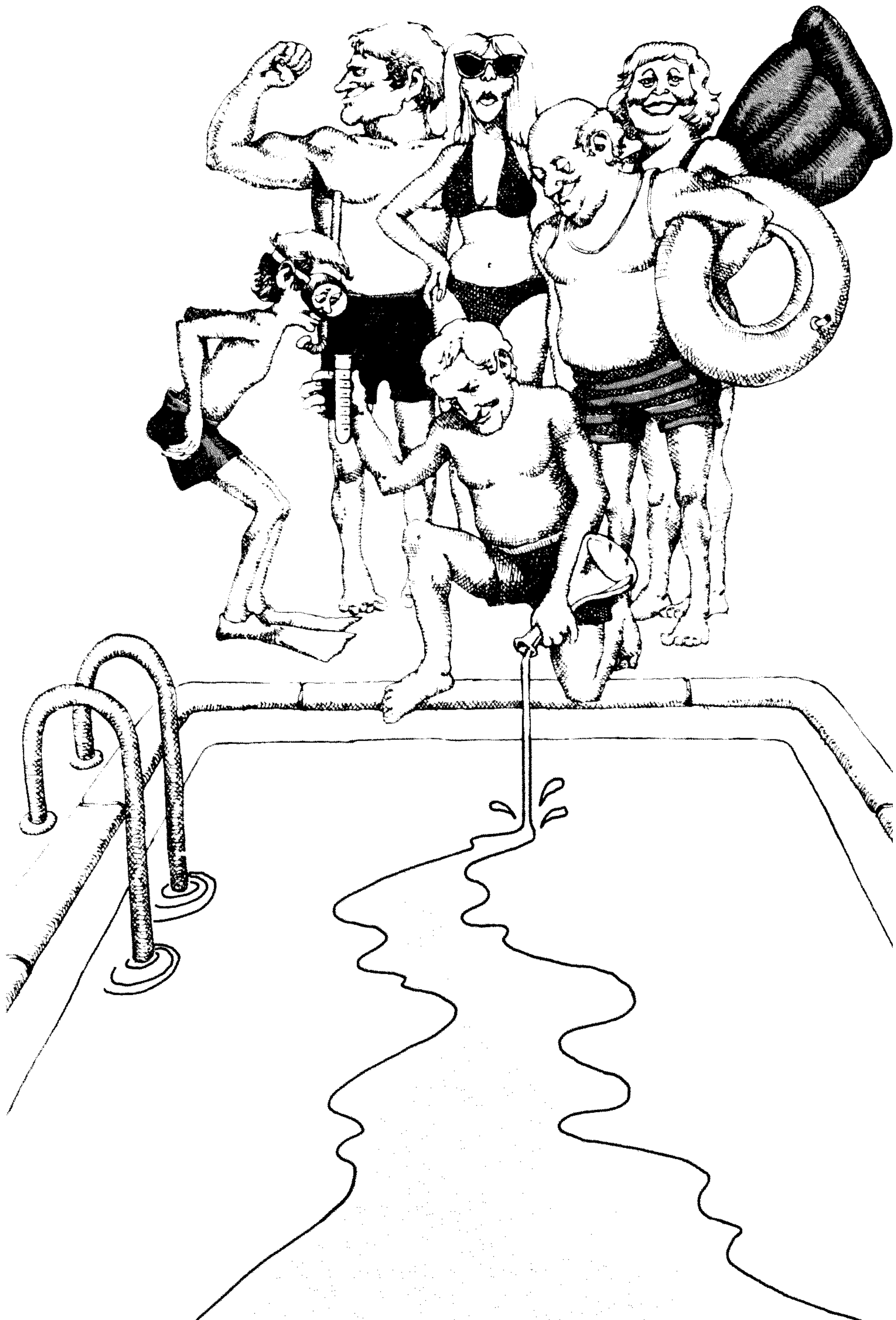
Because of the corrosive and toxic properties of chlorine gas, sophisticated equipment is needed to handle it. This makes it impractical for home swimming pool use. Therefore, chlorine-containing compounds that serve as a source of HOCl are used instead. Sodium hypochlorite, NaOCl, the active ingredient in household bleach, is a commonly used disinfectant because it reacts with water to produce HOCl:

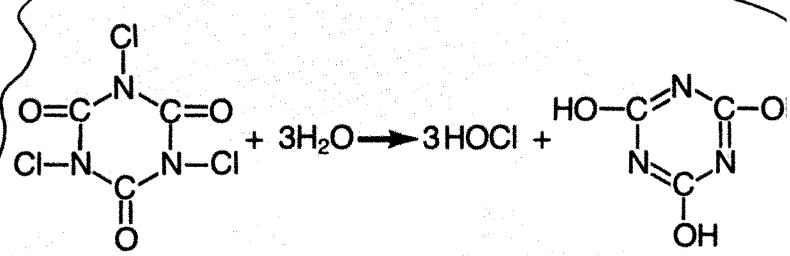
$$NaOCl\,(aq) + H_2O \rightarrow HOCl\,(aq) + Na^+\,(aq) + OH^-\,(aq)$$

Other examples of pool sanitizers are calcium hypochlorite, $Ca(OCl)_2$, which is marketed as HTH® and chlorinated isocyanurates, such as trichloroisocyanuric acid.

$$Ca(OCl)_2 + 2\,H_2O \rightarrow 2\,HOCl + Ca(OH)_2$$

HOCl is a small molecule that is deadly to bacteria. Because of its size





Trichloroisocyanuric acid + $3H_2O \rightarrow 3HOCl$ + Cyanuric acid and lack of charge, it can easily penetrate the cell wall of a bacterium. Once it is inside, both the chlorine and the oxygen from the hypochlorous acid molecule oxidize or "burn out" the interior of the bacterium by breaking down the bacterium's protein.

Maintaining Chemical Balance

The amount of HOCl available in a swimming pool depends on several factors. Immediately after treatment, there is plenty of HOCl in a pool. The level of HOCl decreases as it is used in destroying bacteria, algae, and other organic substances in the pool. Also, the amount of HOCl present in the water depends on the pH of the water in the pool.

To see how changes in pH affect the amount of HOCl available, we must understand that HOCl dissociates (breaks apart) to form hydrogen ion, H^+, and hypochlorite ion, OCl^-, in water:

$$HOCl\,(aq) \longrightarrow H^+\,(aq) + OCl^-\,(aq) \quad (1)$$

H^+ and OCl^- can also recombine to produce HOCl molecules:

$$H^+\,(aq) + OCl^-\,(aq) \longrightarrow HOCl\,(aq) \quad (2)$$

Because reaction 2 is just the reverse of reaction 1, and because both reactions are occurring at the same time, chemists usually write one equation to represent both processes.

$$HOCl\,(aq) \rightleftharpoons H^+\,(aq) + OCl^-$$

(Hypochlorous acid) (Hydrogen ion) (Hypochlorite ion)

When these two reactions occur at the same rate, we say that an equilibrium exists.

When the pH of the water in the pool is lowered, that is when more H^+ is added to the system, the extra H^+ reacts with some of the OCl^- already present to produce more HOCl. The concentration of HOCl available in the pool is increased and we say "the equilibrium is shifted to the left." If the pH is raised by adding a base, the extra hydroxide ion, OH^-, combines with some of the H^+ in the pool to produce water:

$$H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)$$

Some of the available HOCl in the pool then breaks apart to form more H^+ (to compensate for the H^+ that was used up by the OH^-) and more OCl^-. We say that the "equilibrium is shifted to the right."

Figure 1 shows how shifts in pH change the concentrations of OCl^- and HOCl.

Using the relative sizes of the symbols to show concentration, we can show the equilibrium at a pH of 7.5 as:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

If the pH drops below 7.5, the equilibrium shifts to the left because of the increase in H^+ concentration:

$$\mathbf{HOCl} \rightleftharpoons \mathbf{H^+} + OCl^-$$

If the pH rises, the equilibrium shifts to the right to try to replace the H^+ consumed by base:

$$HOCl \rightleftharpoons H^+ + \mathbf{OCl^-}$$

Figure 1

Effects of pH changes

pH	% of chlorine as OCl^-	% of chlorine as HOCl
6.0	3.5	96.5
6.5	10.0	90.0
7.0	27.5	72.5
7.5	50.0	50.0
8.0	78.5	21.5
8.5	90.0	10.0

The Ideal pH Level

The ideal equilibrium distribution is equal concentrations of HOCl and OCl^-. The table shows that a pH of 7.5 maintains this balance. If the pH is held in the range from 7.2 to 7.8, a suitable distribution of HOCl and OCl^- is provided. If the pH is lower than 7.2, the high concentration of HOCl is very irritating to the eyes of swimmers. Also, the growth of algae flourishes in this acid range. If the pH is higher than 7.8, too much of the disinfectant is present as OCl^-, which is decomposed rapidly by sunlight.

The pH is adjusted by adding acid or base to the pool water. If the pH is too high (if the pool water is too basic), hydrochloric (muriatic) acid, HCl, or sodium bisulfate, $NaHSO_4$, can be added to the water to react with this excess base. If the pH is too low (if the pool is too acidic), sodium carbonate, Na_2CO_3, added to the pool will react with the excess acid and bring the pH back up to an acceptable value.

Pool care involves both physical and chemical treatments. Although the tests used to determine the necessity of chemical treatment do not require an understanding of the chemistry involved, some knowledge of acid–base chemistry, pH, and equilibrium concepts provides the pool owner with the logic behind these chemical treatments. This knowledge also helps to ensure the safety of all who use the pool.

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SWIMMING

Mr. Smith handed his daughter a stack of books and a plastic box. "Christie, you have been begging for a swimming pool so here's the deal. The pool will be installed next week and I am appointing you our pool chemist for the summer. It's up to you to keep the water clean and safe."

Christie soon learned that pool chemistry is complicated. First, she needed to know the volume of the family's new swimming pool. The usual formula for volume is, of course, length x width x depth. However, because the bottom of the Smiths' pool slopes gradually from three feet to six feet, Christie needed to use the average depth of 4.5 feet in the formula.

The pool is 50 feet long by 20 feet wide. Christie looked up the conversion factor—one cubic foot of water equals 7.48 gallons, and calculated that the pool contains 33,660 gallons of water (4500 ft^3 x 7.48 gal/ft^3).

In chemistry class, Christie had used liters and molarity for volume and concentration. However, the pool literature that she read used gallons and ppm for these values. Parts per million (ppm) is often used instead of molarity when the concentration is very low. One pound of a chemical in one million pounds of water is one ppm. That's the same proportion as one penny in $10,000.

Swimming pools have filtration systems that remove debris and particles from the water. But sanitation of the pool water requires chemicals and frequent testing. The Smiths use "hard water" from their own well to fill the swimming pool. It is called "hard" because it contains ions that combine with soap and form a scum that makes it hard to wash with. The hard water is a factor that Christie had to consider when deciding which pool chemicals to use. Water with more than 100 ppm of calcium and magnesium ions is classified as hard water.

Many pools use chlorine compounds to kill bacteria and viruses. The active chemical is HClO, hypochlorous acid, which passes through the cell wall and oxidizes or "burns up" the interior of the bacterium. Christie read that the concentration of HClO should be kept above 1.0 ppm. (Chemists usually write the formula for hypochlorous acid as HClO, but people in the swimming pool industry prefer to express it as HOCl.) Many factors affect this concentration and one of the most important of these is pH. In water HClO dissociates to a slight extent to form the hydrogen ion and the hypochlorite ion.

$$HClO \rightarrow H^+ + ClO^-$$

hypochlorous acid hydrogen ion + hypochlorite ion

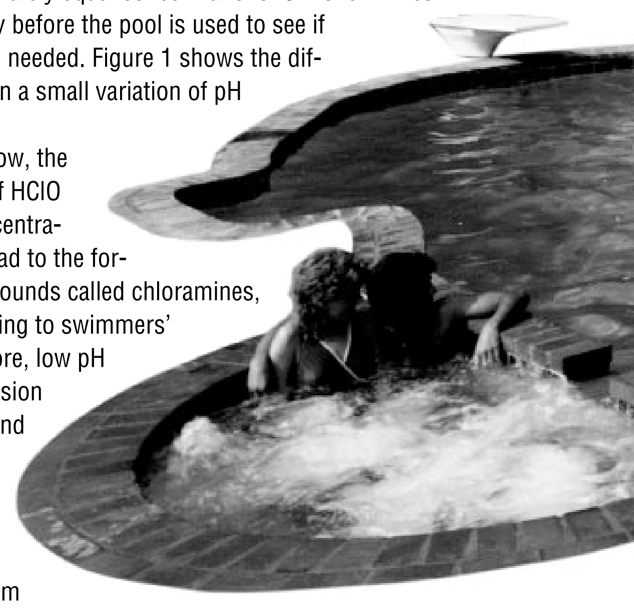
The opposite reaction

$$H^+ + ClO^- \rightarrow HClO$$

is also taking place. That is, there is an equilibrium in water involving HClO, H^+, and ClO^-, which we can depict by the equation

$$HClO \Longleftrightarrow H^+ + ClO^-$$

An acceptable pH range is 7.2 to 7.8, at which HClO and ClO^- are present in approximately equal concentrations. Christie will test for pH every day before the pool is used to see if adjustments are needed. Figure 1 shows the difference that even a small variation of pH can make.



If the pH is low, the concentration of HClO rises. High concentrations of HClO lead to the formation of compounds called chloramines, which are irritating to swimmers' eyes. Furthermore, low pH can cause corrosion of metal pipes and concrete surfaces. Christie can raise the pH of the pool by adding sodium carbonate. Her testing kit has a chart that gives the exact amount to add. This treatment raises the pH by removing some of the hydrogen ions from solution.

$$H^+ + Na_2CO_3 \rightarrow HCO_3^- + 2Na^+$$

hydrogen ion + sodium carbonate bicarbonate ion + sodium ions

A high pH is not good either because, under alkaline conditions, the ClO^- concentration is increased while the concentration of HClO is decreased, and the HClO is better at killing microbes. Also, mineral deposits will begin to form on the pipes and pumps. Christie will need to add an acid to lower the pH. One good choice is muriatic acid (diluted hydrochloric acid).

POOLS

by Roberta Baxter

$$HCl \rightarrow H^+ + Cl^-$$

hydrochloric acid   hydrogen ion + chloride ion

The additional hydrogen ion will combine with ClO^- to form the better oxidizer, HClO.

There are six basic chlorine chemicals used to sanitize home pools. Each has advantages and disadvantages, so Christie must study them all to make the decision of which to use. All six produce HClO when dissolved in water.

One of the compounds that is widely used is sodium hypochlorite—the active ingredient in household bleach. When sold for use in pools, it is twice as concentrated as laundry bleach. When it dissolves in water it forms hypochlorous acid.

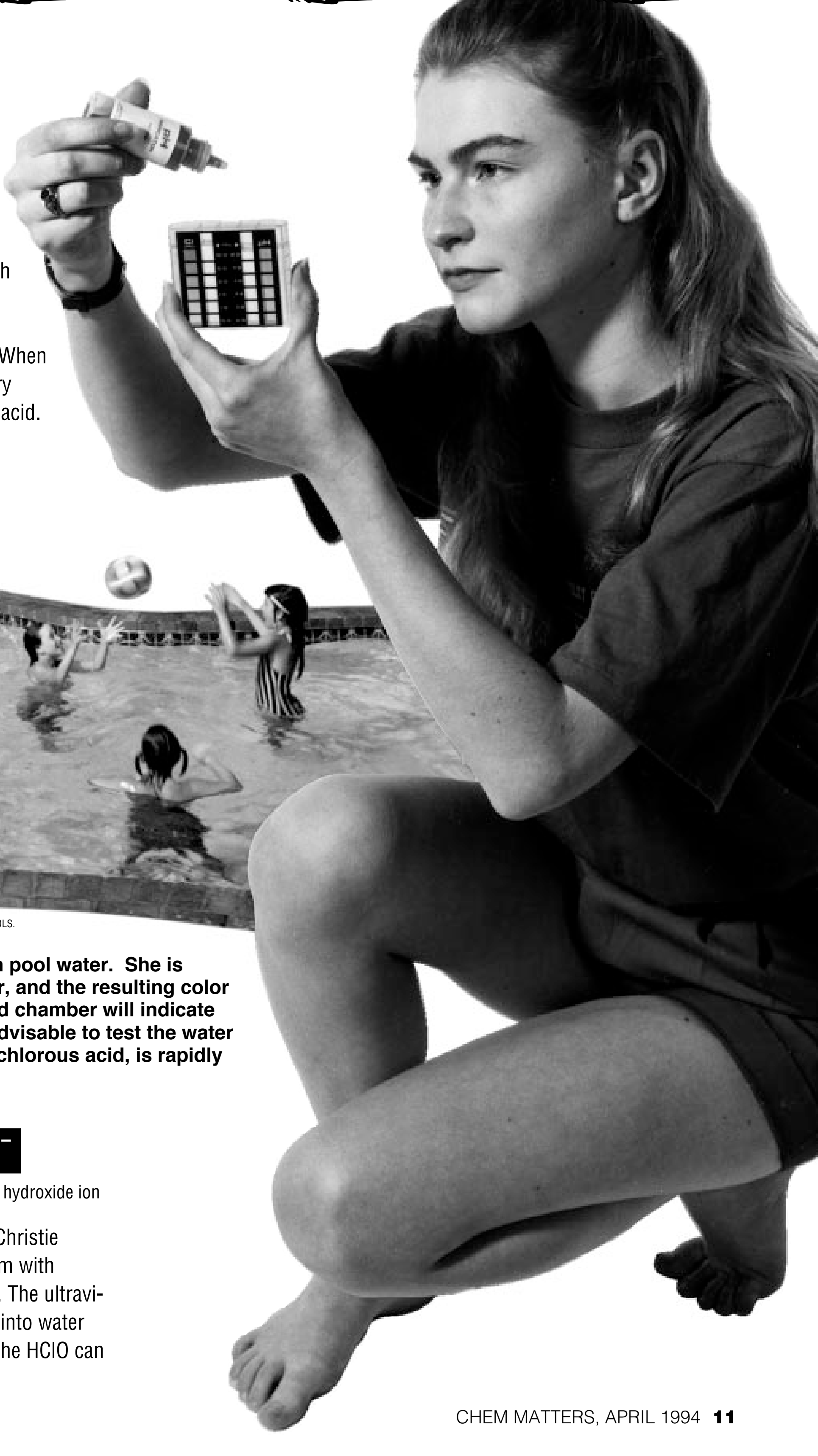


PHOTO OF CHRISTIE: AARON LEVIN.   PHOTO OF POOL COURTESY OF SYLVAN POOLS.

Christie has filled two chambers in this test kit with pool water. She is adding a solution of phenol red to the first chamber, and the resulting color change will indicate the pH. A reagent in the second chamber will indicate the chlorine concentration. In bright sunlight it is advisable to test the water several times a day because the disinfectant, hypochlorous acid, is rapidly decomposed by ultraviolet light.

$$NaClO + H_2O \rightarrow HClO + Na^+ + OH^-$$

sodium hypochlorite + water   hypochlorous acid + sodium ion + hydroxide ion

Pool bleach is fairly inexpensive and easy to use. But Christie learns that there are some disadvantages. One big problem with using bleach in a pool is that HClO is unstable in sunlight. The ultraviolet radiation in sunlight breaks the HClO molecule down into water and chloride ions. On a hot, bright day, 90% to 100% of the HClO can

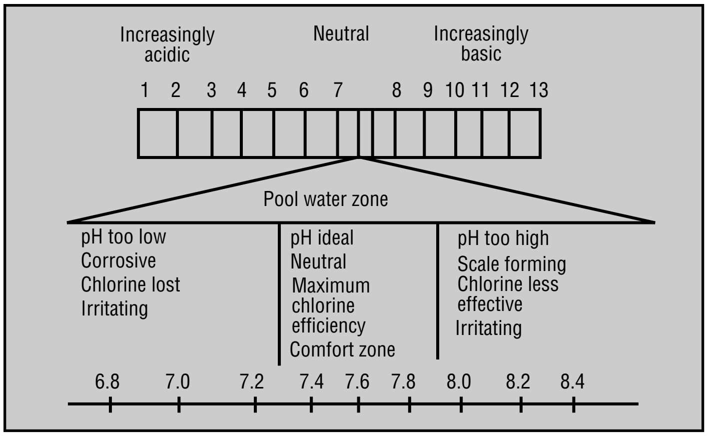


Figure 1. The chemical reactions that take place in swimming pools are highly affected by pH. For proper disinfecting, as well as swimmer comfort, pH must be maintained in the narrow range of 7.2 to 7.8.

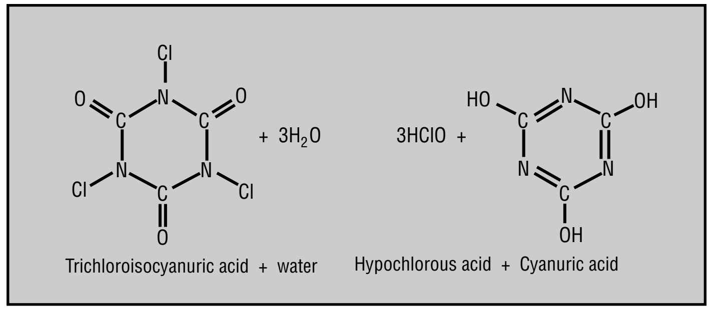


Figure 2. Trichloroisocyanuric acid is a good choice for outdoor pools because it is not decomposed by ultraviolet light. The first reaction product, HClO, disinfects the water; the second, cyanuric acid, absorbs UV and protects the UV-sensitive HClO.

be gone in minutes, leaving the pool without disinfecting power. This is one reason commercial pools are required to test the water every hour.

Another product, called powdered bleach, is calcium hypochlorite.

$$Ca(ClO)_2 + 2H_2O \rightarrow 2HClO + Ca^{2+} + 2OH^-$$

calcium hypochlorite + water   hypochlorous acid + calcium ion + hydroxide ion

Calcium hypochlorite is easier for Christie to handle. She can simply add the proper number of tablets to a basket in the filter system. Water that is flowing from the filter back to the pool flows through this basket where it dissolves the tablets. However, adding a calcium compound increases the water hardness, which can lead to mineral deposits.

One of the most common chemicals for home pools is the one that Christie chooses for the Smiths' pool, trichloroisocyanuric acid or "trichlor." In contrast to sodium hypochlorite and calcium hypochlorite, trichlor is an organic compound. Whereas the inorganic compounds ionize very quickly in water to produce HClO, trichlor releases chlorine into the water gradually. Also, because trichlor is not decomposed by ultraviolet radiation, it acts as a reserve supply of HClO on sunny days. (see Figure 2).

A disadvantage of trichlor is that the other reaction product, cyanuric acid, eventually builds up in the water and Christie must test for cyanuric acid. When the concentration is too high, Christie can lower it by draining some of the pool water and replacing it with fresh water. It will probably be several months before she must do this.

Before using the pool each day, Christie tests the water to measure pH and free chlorine (HClO concentration). Less frequently she will run additional tests to measure cyanuric acid, total chlorine, calcium hardness, total mineral concentration (called total alkalinity), and total dissolved solids. She will not need the test for calcium if she is not using calcium hypochlorite.

After a lot of reading and a little practice with the test kit, Christie has adjusted all of the concentrations properly. But she also knows that each time her friends swim in the pool and each time the sun shines, the concentrations will change and she will have to add the necessary chemicals. Throughout the summer the water is clean and sparkling, and she hears her father remark to the neighbors that Christie has become a real pool chemist.

Hot line

If you are having difficulties bringing your pool water into chemical balance, you can call the pool hot line operated by Dr. Alison Osinski, who is an independent pool consultant and a member of the National Swimming Pool Foundation's Educational Advisory Committee. Osinski says that, unfortunately, the majority of back yard pools are not properly maintained.

To use the hot line you must be at least 18 years old; your phone bill will be charged $2.95 a minute. The number is 900/446-6075, extension 820.

It's a gas

For years, chlorine gas, Cl_2, was the disinfectant of choice at college swimming pools and other large pools that have a full-time operator. Due to its toxicity, Cl_2 is seldom used in commercial pools today. This gas was used in gas warfare in World War I. Sophisticated equipment is required to meter just the right amount of Cl_2 into the water.

$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^-$$

chlorine gas + water   hypochlorite + hydrochloric acid

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Testing Pool Water for OCl^- using Methyl Orange

Q1: What concentration of HClO (in ppm) is recommended in the article for effective control of bacteria and algae?
Q2: How many mole/L of HClO is this?
Materials

- Diluted commercial bleach solution – about 4% in the bottle, diluted to 1/50 initial concentration.
- Methyl orange solution ($C_{14}H_{14}N_3O_3SNa$ MM = 327.34g/mol) - 0.5g/L
- Dropper bottle of 1M HCl
- 2 plastic droppers
- 2 small test tubes
- Electronic balance to share with other groups

a. Find the concentration of the methyl orange solution (mol L^{-1})?
(Hint – Moles = mass/MM)

b. Draw up some dye solution into a plastic dropper, invert it and place it upside down in a small beaker on the balance. Weigh the dropper and dye, and record mass. **Mass of dropper and dye = ……….. g**

c. Add about <u>20 drops</u> of dye to a small beaker. Weigh the dropper and remaining dye and record the mass. **Mass of dropper and dye = ……..… g**

Therefore Mass of Methyl Orange solution used = ……………………….g

d. Add about 5 drops of 1M HCl to the dye solution –the colour changes.

e. Fill a clean plastic dropper with diluted bleach solution. Weigh the dropper and bleach solution, and record mass.
Mass of dropper and bleach = ……….. g

f. Slowly drop the bleach solution into the dye, mixing gently until a sharp colour change is seen. Reweigh the dropper and bleach solution, and record mass.
Mass of dropper and bleach = ……….. g

Therefore Mass of Bleach solution used = ……………………….g

Q3. From the masses of solutions used, calculate the concentration of chlorine in the bleach solution.
Assume 1 g of soln =1 mL of soln, and **1 HOCl reacts with 1 methyl orange.**

Q4. If you have time, test tap water in the same way to find the level of chlorine present.

Q5. Is the level of chlorination in (i) the bleach solution and (ii) tap water high enough for control of algae and bacteria?