CLEAR WATERS AND A GREEN GAS: A HISTORY OF CHLORINE AS A SWIMMING POOL SANITIZER IN THE UNITED STATES

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In a piece in the *New York Times* in 2003, Garbarino wrote (1):

> To most people swimming pools conjure summer afternoons dedicated to carefree indulgences like lime daiquiris and a satisfying bad novel. Pools are pleasure ponds and symbols of suburban arcadia.

According to the US Bureau of the Census, swimming is the second most popular recreational activity next to walking in the United States, with more than 350 million persons participating each year. (2) Today in the United States some eight million families own a residential pool (3), and residential swimming pools are a $6.9 billion industry. (4)

Unlike a lake or a river, a pool has no source of fresh water or a means of flushing out the impurities. Some method of sanitizing the water is needed to make swimming safe and pleasurable. For almost a century, chlorinated compounds have provided it. Even for professional chemists, the chemistry of pool chlorination can be a mysterious art. Little or nothing has been written about the history of this process, and most pool owners have little understanding of its whys and wherefores.

Pools BC (Before Chlorine)

Although it is commonly believed that the ancient Romans invented the swimming pool or public baths, they were actually latecomers to the idea. The earliest known sacred baths date to about 3000 BCE in the Indus Valley. The Greeks built swimming pools near their gymnasiums about 500 BCE, and in ancient Israel public baths were available for ritual washing (5). The Romans built hundreds of bath complexes throughout their empire. The typical complex included swimming pools, warm baths, steam baths, and recreational facilities. With the fall of the Roman Empire the construction of swimming facilities declined in the west, although they remained popular in several eastern civilizations such as India, Turkey, Japan, and Ceylon (6).

The nineteenth-century British enjoyed public baths in India and Japan and brought the swimming pool back home to England. Elaborate swimming baths (as swimming pools were called in Great Britain) quickly spread throughout England and the European continent, especially at fashionable spas. In the 1860s, the local municipalities of Boston, Massachusetts started a program for salt-water bathing. By 1901, the city operated fourteen floating baths, ten public beaches, and two swimming pools. The number of Bostonians bathing nearly tripled between the years of 1897 and 1898, increasing from 657,275 to 1,920,368 (7). The first public swimming pool to open in the United States was in the town of Brookline, Massachusetts, in 1887 (6).

The Victorian era was a time when unprecedented advances in medicine, science, public infrastructure, and industrial technology raised the standard of living for millions of people. Yet, medical science was still unable to prevent outbreaks of diseases such as typhoid, cholera, and dysentery in both the United States and Europe. In the crowded cities of the nineteenth century large numbers of poor people living in tenements had no access to bathing facilities. Beginning in the 1890s, a hygienic reform movement grew in larger cities both in the United States and Europe, the goal being to promote health through cleanliness by providing the urban poor with public baths. Thus the American Association for the Promotion of Hygiene and Public Baths was founded in 1912 in New York City (8). A short time later Dr. Simon Baruch, one of the founders of the Association, persuaded New York City to open several public pools with showers and dressing rooms (8). By the summer of 1936, 80,000 people were using New York's public pools (9). During this era most cities had either built or were building bath facilities, and in time the organization focused less on promoting new facilities and more on serving as a forum for professional bath operators. Only later did the organization begin to promote the swimming pools and serve as a professional organization for pool operators (8). By the 1920s, there were several thousand pools in operation in the United States. About two thirds of them were operated by municipalities, YMCAs, schools, colleges, and Boys' Clubs, the rest being commercially operated (5). At the start of the 1930s, an estimated 42% of high schools in the United States had swimming pools (10).

Table

Sterilization Methods used for High School Pools in the United States, 1930 (Ref. 10)

Method	Number of schools in the survey
Chlorine	20
Filter	9
Violet ray	4
Chlorinated lime	3
Gravel and chlorozene	1
Alum and sand	1
Chlorine bubble	1
Chloro-clock machine	1
Ozone	1
Vacuum	1

Jones' paper does not provide details of the processes listed and it may be supposed that his readers would not have needed them. The Chloro-clock machine was probably a simple granulated chlorine feeder fitted with a timer. It probably dispensed "chlorinated lime." The most popular choice "Chlorine" was probably a solution of sodium hypochlorite.

The numbers of home swimming pools also grew during the years between WWI and WWII, but they were only for the wealthy. In 1920, a 20 x 40 foot residential pool (called an "estate pool" for obvious reasons), complete with filter and recirculation system, cost $12,000 to $15,000 in the east and $8,000 or more on the west coast. In 1940 a technique introduced in California of applying concrete pneumatically revolutionized the residential pool market since it cut the construction cost by as much as three fourths (6).

Prior to the introduction of sterilization chlorine, bromine, ozone, or ultraviolet light, most swimming pools were filtered to keep them somewhat clean, and the water was changed frequently (5, 9). Many residential pools were built on sloping ground to facilitate drainage, and some were equipped with storage tanks to hold the replacement water. Because many impurities floated on the top of the water, almost all pools were fitted with "scum gutters" along the edges from which these could be drawn off (11, 12).

Industrial Production of Chlorine at the Dawn of the Twentieth Century

Bleaching powder had been produced in Europe throughout the 19th century for use in the textile and paper industries. The process used at the time consisted of generating chlorine from manganese oxide and HCl and then passing the gas through a solution of potash. In his multi-volume *American Chemical Industry*, Williams Haynes writes that a major impetus for the production of chlorine in the United States was the passage of a favorable tariff on bleaching powders, though he did not specify which particular tariff bill had the most influence on the industry. Favorable tariffs, general industrial growth, and inexpensive electricity created an environment in which domestic production of bleaching powder would rise from 10,979 short tons in 1899 to 155,190 short tons in 1914 (13).

Bleaching powder, calcium oxychloride ($CaOCl_2$), often erroneously called calcium hypochlorite [$Ca(OCl)_2 \cdot 4H_2O$] (13), was made by treating chlorine gas with lime. The chlorine was supplied as a byproduct of the electrolytic production of sodium hydroxide. Passing an electric current through a concentrated solution of sodium chloride liberates chlorine and hydrogen gases and leaves behind concentrated sodium hydroxide, commonly known as caustic soda. It was, and still is, used in a great variety of industrial processes including soap and glass manufacture. In 1895 the opening of the hydroelectric plant at Niagara Falls, New York, made inexpensive electricity available to any chemical manufacturer that chose to locate nearby. In 1906, The Roberts Chemical Company began supplying chlorine to the Electro Bleaching Gas Company, which was the country's first producer of liquid chlorine (13). The area quickly attracted additional electrochemical process plants, which by 1912 included Mathieson and the Hooker Electrochemical Company (14). Niagara Falls is still a major center of chlorine production. As recently as 2006, Olin Corp. expanded this plant by investing $6.5 million to double chlorine production. (15)

Anyone producing caustic soda needed to find a market for the chlorine byproduct. Each time there was an imbalance between the production of sodium hydroxide and the market for chlorine, chemists were set to work discovering new uses for the latter. The history of this search, as well as its economic and environmental consequences, is discussed in Thornton's book *Pandora's Poison, Chlorine, Health, and a New Environmental Strategy* (16). Outside the Niagara Falls area, the major chlorine producers were Michigan firms: Dow Chemical in Midland and the Pennsylvania Salt Manufacturing Company in Wyandotte (14).

The First World War dramatically increased the demand for all types of alkaline materials as well as for chlorine. Aside from military uses of chlorine for chemical warfare, it was in demand by the dyeing and bleaching industries. The loss of German supplies of chlorine forced European manufacturers to buy the material in the United States (17, 18). As more chemical production was dedicated to the Allied war effort, electrolytic chlorine producers found they could easily scale up production because their chief limiting factor was the supply of electricity. This gave them a huge competitive advantage over companies using other technologies such as the lime-soda method (19). The First World War also exerted another beneficial effect for the chlorine industry; namely the experience gained in the manufacture, handling, and shipping of chlorine-filled gas shells that would prove invaluable in peacetime.

Early Use of Chlorine in Water Disinfection

Credit for the first use of chlorine to disinfect potable water goes to the British scientist Sims Woodhead, who used "bleach solution" as a sterilizing agent during an 1897 typhoid outbreak in Maidstone, Kent. This temporary measure entailed introducing the solution at the distribution mains (20). The first regular use of chlorine for potable water treatment in the United States began at the Jersey City Boonton Reservoir in 1908 (21). In 1914 the US Department of the Treasury promulgated the first bacteriological standard for potable waters in the United States. The limit of 2 coliforms per 100 mL of water applied only to interstate water supply systems.

From the time when chlorination of potable water first began, there were alternative methods for water sanitation available, such as the use of ozone. This technology was first used in the Netherlands in 1893 (22). High start-up and equipment costs for systems like ozone disinfectant, when contrasted with an abundant supply of chlorine from caustic soda manufacture, meant that few alternative technologies could compete with the price and convenience of chlorine.

Destroying bacteria is only the first half of potable water purification the other critical element being a filtration system. Originally incorporated into waterworks as a means of removing sediments, color, and the organic materials causing odors, sand filtration was soon recognized by engineers as a useful means for removing harmful bacteria. The first modern city with a water supply purified by filtration was Paisley, Scotland, in 1804. It was built by Joseph Gibb to supply his bleachery with water. Although the city of Poughkeepsie, New York, had one of the first sand filtration systems in America in 1872, serious research in the United States did not began until 1887. By

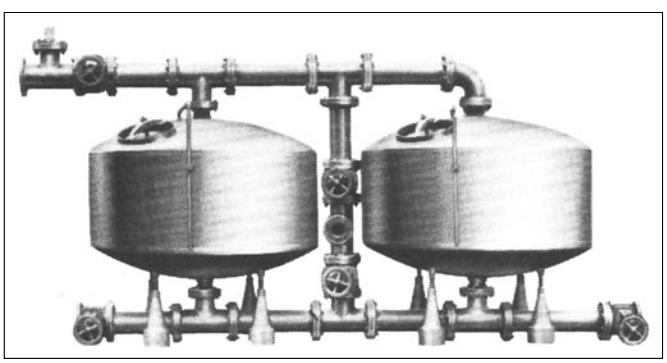

Figure 1. *These two sixty inch high flow-rate filtration tanks date to the late 1960's. They were designed to hold a single filter medium and could accommodate 46,800 gallons per hour. Courtesy Council for National Cooperation in Aquatics*

1899 a number of filtration units were operated throughout the United States (23), by which time it was estimated that filtration systems were used to supply potable water to 20,000,000 people in Great Britain and the European mainland (23).

Filtration technologies were of two types. Slow sand filters allowed water to percolate through a thick bed of sand at the rate of 1.5 to 2 million gallons per day per acre of filter bed. This method was inexpensive but required large filter beds. In the Rapid Sand Filtration technology a coagulating agent was first added to the water prior to filtration. This allowed the filtration to proceed an estimated fifty times faster than with the slow sand technology and the system required only about 2% of the filter bed area necessary for the slow sand (24, 25).

Into the Pool

By the early 1900s waterworks engineers had mastered the use of chlorine and filtration. Educators and health professionals appreciated the value of swimming for physical fitness. All of the elements of the modern swimming pool were in place. As near as the author can determine, the first attempt to sterilize a pool in the United States with chlorine was made at Brown University in Providence, Rhode Island. When Brown University's Colgate Hoyt Pool was opened on March 2, 1903, and filled with city water, the university quickly discovered that while "pure enough for drinking purposes," a large mass of the water exhibited a brown color. Once a mechanical filter had been installed, the 70,000-gallon pool could be filled in about 18 hours with filtered water (26). The 1911 chlorination experiment was reported in the *American Journal of Hygiene* and summarized in an item appearing in the *New York Times*.

Figure 2. *Colgate Hoyt Pool, courtesy John Hay Library, Brown University*

The experiment was performed by John Wymond Miller Bunker, a member of the class of 1909. Bunker graduated with honors in biology and then went on to earn a M.S. in 1911 and a Ph.D. in 1912. He subsequently held positions as instructor in sanitary biology at Harvard University and director of the biological division of Digestive Ferments Co. in Detroit. Bunker was appointed Assistant Professor of Physiology & Biochemistry at MIT in 1921 and made Professor in 1928, where he remained until his retirement in 1952 (26). Although the Brown University pool had never been the site of a serious infection, some ear-aches and minor nasal infections had been reported by members of the swim team. Prior to the initial chlorination experiments, when the pool water was still, Bunker measured bacterial counts of 300 to 500 bacteria per cc (incubated on agar at 37°C for 24 hours). When the deep end of the pool was stirred up by use, the counts rose as high as 1000 (27). Bunker's first application was "hyperchlorite of lime" (sic) to 2 liters of pool water at a concentration of 1 ppm. The results were spectacular. Bacteria counts went from 700 to 0 in only 15 minutes. The experiments were duplicated with an application at 0.5 ppm. The full-scale application came next (27). The powdered compound was placed in a cheesecloth bag, was dragged over the pool until the material was distributed, the final concentration of chlorine being 0.5 ppm. Surface bacteria counts fell from 500 to 30 in only 15 minutes, to 10 in 30 minutes, and "complete sterility" after an hour (27). According to the *Times* report, the pool remained sterile for four days. (The *Times* report did not indicate whether anyone was swimming in it during those four days, but it does not seem likely.) (28). The news item went on to report that there was "no odor and no perceptible taste." The report concluded by saying "hypochlorite (sic) of lime is an effective sterilizer of swimming pools (28)." (Hyperchlorite of lime and hypochlorite of lime are actually the same material.)

About the same time as the Brown University experiment the *Lancet* was publishing papers related to the bacterial contamination of swimming baths and means to sterilize them, including chlorination (29, 30). A decade later the *Lancet* reported that chlorine levels of 0.5 to 1.0 ppm were sufficient for this purpose (31).

By 1923 seven states had passed regulations for the control of swimming pool sterilization (32). The technology of pool chlorination was still not fully developed, however. During the 1920s pools still had to be drained periodically and the entire volume of water replaced (33).

During the 1920s there were no pumps or filter devices designed for use with residential pools. Contractors usually adapted pumps from the marine industry and filters from either the chemical or dry cleaning industries. The first specialty pool supply company was founded in 1925 by John Mudge, a former chemical engineer. In 1929 Mudge also founded the first pool maintenance company, Chemtech, in California. One of Mudge's equipment inventors, Dave Cavanah, was the first head of Chemtech (33).

A survey of high school pools in 1930 revealed that most used "Chlorine" or "chlorine in one of its forms" for sterilization. The results of the survey are listed in Table I (10). The pool manager of the 1930s not only had to contend with the issues of chlorine levels, alkalinity, and water clarity, but the state of swimwear. In 1937, the pioneering women's physical education promoter, Mabel Lee, offered a number of suggestions. Because wool bathing suits tended to shed lint that clogged filters and the fabric dyes came off in the water, a standardized "ugly, gray-cotton uniform" was preferred for collegiate swimming. Lee wrote that in the 1930s treated wools and less soluble dyes made suits available in "Gay colors, pleasing styles, and materials that hold their shape". Even so, she recommended that the school purchase swim suits for students so that no one would enter the pool with an older or poor quality suit that would shed lint and leak dye (34).

Figure 3. WPA Poster titled "Swim for health in safe and pure pools," Library of Congress.

The Common Methods of Chlorination

For most of the twentieth century there have traditionally been four major forms of chlorine used for swimming pool sterilization. All of them were in use by the middle of the century and, except for tanks of chlorine gas, continue to be widely used today. When certain chlorine compounds (or any oxidizer) are added to a pool, it oxidizes the organic materials and combines with certain inorganic species. The amount of oxidizing agent required to destroy the impurities present at the time of addition is the "chlorine demand" and the unchanged material is the "residual chlorine." Most pool chemical suppliers recommend keeping the residual chlorine at a concentration of no more than 2 ppm. "Shocking" a pool refers to adding excess chlorine (2.0 to 5.0 ppm) so that once the chlorine demand is met, a massive excess of chlorine "shocks" the water.

For very large pools the least expensive source of sterilizer has been compressed chlorine gas, which passes into the water at a measured rate. The tank usually sits on a scale so that the operator would know when it is running low. The problem with this method is that chlorine gas (Cl_2) is deadly and the tanks have to be checked regularly for leaks. Pool staff must know how to handle the steel tanks and need respirators in case of emergency (35). Over the years there have been a number of accidents involving this system. On July 14, 1965, 23 children were treated for chlorine gas exposure at the Rochelle Community Hospital in Rochelle Illinois, because excess gas had been released into the water after a chlorine tank valve had been left open (36). The other drawback to this system is the formation of HCl, in addition to hypochlorous acid, HOCl, when chlorine gas is added to water. HCl lowers the pools pH without appreciably contributing to sterilization. This system requires the addition of about one pound of soda ash (Na_2CO_3) for every pound of chlorine. (35)

The second method is "liquid chlorine," or more commonly, bleach. This material was sold in small bottles for home pools or in large drums for bigger operations. It is an approximately 10% to 15% solution of sodium hypochlorite. (37) Sodium hypochlorite is made by treating calcium hypochlorite with a solution of sodium hydroxide. After the reaction is complete, an excess of sodium hydroxide prevents breakdown of the product and the release of chlorine gas. The typical liquid chlorine product contains 13 g of NaOH per liter. This may or may not be a good thing. Sometimes this negates the need to add alkalinity-increasing chemicals to the water, but when the water is already alkaline, the pH may become unacceptably high (38). Because it is a liquid this product is easier to handle. It can be automatically fed into the water or simply poured in by hand. It does deteriorate in sunlight and warm temperatures, which are of course exactly the conditions where pools receive the most use. The other major drawback is that sodium hypochlorite cannot be used with hard water since it leaves calcium deposits. When these clog the automated feeders, a rinse with hydrochloric acid is necessary to clear them (37).

Figure 4. *Installed at the New Hyde Park Municipal Pool, in Hyde Park, New York, this late 1960s system automatically monitored and controlled chlorination, alkalinity, filtering, and water levels. Courtesy Council for National Cooperation in Aquatics*

Calcium hypochlorite, used in most private pools, has a number of advantages. A dry, white compound, it will release 70% of its weight as free chlorine when dissolved in water (37). Unlike chlorine gas and sodium hypochlorite, this compound will not appreciably change the pH of the pool water. Calcium hypochlorite is sold as a granular powder or pressed into slowly dissolving tablets (37).

By the middle of the twentieth century a new class of chlorinating compounds was available. These were compounds consisting of chlorine with cyanuric acid. Early experiments demonstrated that sodium dichloroisocyanurate and potassium dichloroisocyanurate are the most stable and have the best solubility of this class of compounds. Like earlier compounds, these materials function as a source of hypochlorous acid. The disadvantage of these materials is that the pool water must contain some cyanuric acid as a stabilizer. This prevents the chlorine from being lost to ultraviolet radiation. On a sunny day, as much as 70% of chlorine may be dissipated from an unstabilized pool (38). When used correctly the combination of dichloroisocyanurates and cyanuric acid stabilizer provides long lasting chlorine, good solubility, ease of application, and is unaffected pH (38). Today the typical residential pool owner uses a combination of isocyanurates pressed into slowly dissolving tablets for steady, long term chlorination and calcium hypochlorites for periodic "shock treatments."

Alternatives to Chlorine in Swimming Pools

From the outset there were those who objected to the odor of chlorine in their pools, and so a search began for alternatives. It should be pointed out that the so called "chlorine" odor found in pools is not in fact chlorine. The odor is that of chloramines, which are the reaction products of chlorine and nitrogen-containing organic compounds.

Ultraviolet sterilization was an early alternative to chlorination. In 1919 the Hotel Pennsylvania was advertising that its two swimming pools were "filtered clean, and then purified by violet rays. No Chlorine, no Chemicals (39)." (The hotel's women's bath was open daily except Sunday 10 to 7, and the men's bath was "always open.") The hotel also offered "all electric treatments," baths, manicures, chiropody, and massage, all by "Highly expert operators (39)."

W.A. Manheimer, Ph.D., was the secretary of the American Association for Promoting Hygiene and Public Baths. In the early 1920s he conducted water purification experiments at the research laboratories of the New York State Department of Health. As a result of these experiments and subsequent field trials, Manheimer concluded that ozone was superior to chlorine for swimming pools. Chlorine was unsuited to waters with high concentrations of organic matter because of the odor problem. He went on to point out that since ozone is insoluble in water, there were no upper limits on the amounts that could be introduced. (40)

In 1934 a chemist named C. H. Brandes developed a method of introducing silver ions into a pool as a sterilizer (41), but the cost of treating pools by the electrolytic production of silver ions was considerably higher than that with chlorine. The effectiveness is also limited by the presence of interfering compounds in the water (42). The use of an electric current to create ions for bacteria and algae control is gaining in popularity, and there are a number of these systems available to pool owners today.

The Postwar Period

How many Americans knew how to swim at the start of WWII? Although an exact count is impossible, some statistics are available. A survey of seniors at Kansas City high schools revealed that 90% of the boys and 72% of the girls could swim (43). Swimming as a competitive sport, especially for women, gained popularity after the establishment of the modern Olympic Games in 1896. The sport received another boost when, during WWII, thousands of men and women were taught to swim as part of their military training.

Aside from advances in chlorine chemistry, the most important innovation in pool purification technology was the introduction of diatomaceous earth as a filter medium. It gained widespread use after WWII. The tiny skeletons of one-cell organisms make an excellent filter medium; it has been estimated that as much as 95% of the bacteria in water can be removed by filtration through this material (44). Another important change to filtration technologies was the introduction of new types of skimmers. The Paddock Pool Company of San Mateo, California, invented a floating skimmer during WWII. This device was followed by a skimmer built into the pool wall, introduced in 1952. The impetus behind these innovations was the introduction of the free-form pool, which could not be fitted with scum gutters. (12)

With the outbreak of the Korean War in June, 1950, the economy went back on a wartime footing, and strategic materials were once again rationed. In January, 1951 the National Production Authority ordered producers to supply public health authorities (waterworks and sewage treatment plants) with the same quantities of chlorine as they had in 1950. The availability of chlorine for pools was described as "doubtful." The needs of swimming pool operators and owners were specifically excluded from the definition of public health (45). At the time, US chlorine production was 6,000 tons per day, while chlorine demand was estimated at 10,000 tons (45). Twenty years later US chlorine production would reach 26,000 tons per day, and in 2005 it was up to 35,000 tons per day (46).

Polio was the dark cloud hanging over what should have been the carefree summer days of the immediate postwar period. Although the disease was first identified at the end of the 1800s, and the first serious outbreaks in the United States occurred at the time of WWI, polio was most common in the period between 1942 and 1953. The epidemic peaked in the summer of 1952 with 60,000 cases reported. (47) Because polio outbreaks were most common in the summer months, anything associated with summer were suspect: flies, mosquitoes, sunshine, heat, strenuous exercise, and even drinking cola (48). Swimming was especially suspect because people remembered that President Roosevelt first exhibited symptoms of polio after swimming in an icy bay at his family's vacation home in Maine. Lakes, beaches, and public pools were frequently closed (49). Some people felt safe swimming in pools while others distrusted them. Cold water was suspect as was cloudy water. Some parents forbade swimming in pools but allowed children into woodland creeks and lakes (49). For many, it must have been a relief when in 1946 announcements were made clearing the swimming pool as a potential source of the virus. The University of Michigan School of Public Health announced that conventional means of sterilization, including chlorine or "chlorine dioxide" rendered the virus inactive. G. M. Ridenour and R. S. Ingols studied the viability of the poliomyelitis virus in waters used for both drinking and bathing. They concluded that chlorine levels low enough to keep the water palatable were still high enough to inactivate the virus (50). In January, 1946 *The Journal of Pediatrics* published a study on the means by which polio was transmitted. Although polio would continue to resist all prevention efforts of both laypersons and the medical community, a few useful facts did emerge. The authors concluded that there was no evidence that "water supplies, milk supplies, or swimming pools were means by which the disease was disseminated (51)."

Some of the historians with whom the author has corresponded think the polio outbreaks of this period were responsible for replacing the natural swimming hole in favor of the man made pool. In the final analysis though, postwar affluence had far more to do with the rising popularity of swimming pools. The increasing popularity of pools prompted both the American Public Health Association and the US Public Health Service to develop standards for their care. The latter agency developed a model ordinance governing the construction and use of public pools. It was intended to be adopted by municipalities but was not binding. The Health Service hoped soon to complete a comparable ordinance for private residential pools (52). The American Public Health Association devoted much of its annual meeting to creating a set of guidelines for swimming pool care. Meeting in Detroit's Cobo Hall in November, 1961, the association invited representatives of the pool industry, a decision that sometimes resulted in heated debate (52). Eric W. Mood of the New Haven, Connecticut, Health Department chaired a subcommittee on water disinfection. The Committee issued a recommendation that residual chlorine should be maintained at 0.4 ppm and that for killing algae, copper sulfate should be added at a level of 1.4 ppm. Mood warned that copper sulfate should not be used daily, lest it turn blonde hair green (52)! Dr. Walter L. Mallmann, professor of bacteriology at Michigan State University, reported at the meeting that streptococcus was discovered at "otherwise adequately chlorinated pools." The conditions, however, were those of crowded pools and none of the bacteria was found in empty pools. Since the bacteria were characteristic of the respiratory tract, Mallmann believed that they escaped from the noses and mouths of swimmers and survived long enough to infect others (52).

The health recommendations came at an opportune time. According to *Life* magazine, Americans were spending $250,000,000 on private pools in 1960 (53). Chlorinating these pools with tablets had become easier when, in 1956, Olin Mathieson introduced a floating polyethylene mesh basket that could be suspended in a pool and allow chlorination tablets to dissolve (54). The chemistry choices confronting the pool owner or operator of the early 1960s were about the same as those of today. The five categories of products were those for disinfection, pH control, algae control, stabilizers, and flocculating agents (55). Liquid chlorine (or more properly an alkaline solution of 10 to 15% sodium hypochlorite) was among the most popular types of chlorine at that time, but an average sized pool required as much as one gallon per day. Lithium hypochlorite had also recently come onto the market. This material released only 35% available chlorine compared to the 70% released by calcium hypochlorite. These two materials were the most popular types of solid chlorine products (55). The chlorinated isocyanurates were also relatively new; and while they were more resistant to photodegradation than other forms of chlorine, their effectiveness as biocides was still being debated. Bromine, iodine, and silver ions were available but not widely used. Chlorine in one form or another was used to disinfect some 95% of pools in 1963 (55). Algae control formulations based on quaternary ammonium compounds were also introduced, but they did not entirely replace copper sulfate. (Swimmer's hair continued to turn green.) Pool owners were advised to maintain pH between 7.2 and 7.6, as they still are today (55).

By 1963 advances in pool construction techniques lowered the price of residential pools from $10,000 - $20,000 to an average of $4,000. Homeowners willing to buy do-it-yourself kits could have a respectable backyard pool for as low as $1,000. About 15% of pools were lined with plastic (53). It was estimated that by 1970, there would be 1,000,000 pools in the US and 550,000 would be in private hands (53). The estimates proved low. Over 1,000,000 above-ground pools were installed in the country by 1969, and it was projected that another 275,000 above-ground pools 12-feet and larger would be sold that year (56). In 1986 there were 2,569,000 in-ground residential pools and at least another 2,000,000 above-ground residential pools (57). According to the market research firm of PK Data of Duluth, Georgia, in the early years of the 21st century, 8,000,000 US households have swimming pools, about half being above-ground units. (Sales of above-ground pools have tripled since 1980.) There are another 5,000,000 hot tubs in the United States (3, 58).

Methods of automatic chlorination, especially for the homeowner, became a popular accessory and a number of inventors produced devices for this purpose. Dr. Frank Schneider of Part Washington, Long Island, was a retired professor of chemistry at the time he was awarded US Patent 3,622,479 for a small-scale electrical device that turned sodium chloride into chlorine. Schneider's partner in the project was a retired chemical manufacturer, Albert Young, of Fort Lauderdale, Florida (59). Called the Electrochlor, the device was one of the first to use salt water as its feed stock; it was intended for use in potable water sterilization as well as swimming pools. What made the Electrochlor unique was that it "fragmented" the water before it came in contact with the electrodes (59). According to the patent application, spinning disks threw droplets of water from a continuous stream into a chamber with a hydrophobic coating. This chamber's interior had a hydrophobic coating. This prevented the droplets from coalescing and thus provided a continuous electrical path from the electrodes to a swimmer (60). At the bottom of the chamber the salt solution is allowed to coalesce and come in contact with the electrodes. Hydrogen gas is drawn off from one aperture and the dissolved chlorine is drained off through another. (60). Operation of the device required that dilute sodium chloride be dissolved in the pool water and when used for potable water treatment, a separate source of salt water had to be provided (60). The Electrochlor was an early version of a system that is widely popular today. Presently in Australia, more than 95 % of homeowners use a salt water-chlorine system for their residential pools. The benefits of this system are said to include lower maintenance of the pool, cleaner, silkier water, and reduced skin and eye irritation compared to a conventional system of chlorination (61). However, in 2005, the Los Angeles County Sanitation District banned the use of salt water systems in Santa Clarita. According to officials, the waste salt pollutes freshwater when it is drained into local sewers (62).

Chlorine Safety and Chlorination Byproducts

The first fissures in the summer love affair between chlorine and swimming came in 1974 when chemists first discovered that halogens could react with organic material in drinking water to create chloroform and other trihalomethanes (63). As research continued into this subject, additional reaction products were discovered including known carcinogens such as bromodichloromethane, chlorinated acetic acids, and 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (64). It was discovered in 1990 that shortly after exercise, swimmers using indoor pools had elevated levels of chloroform in their blood (65). The hunt for a "chemical free" pool took on added urgency, but the question remained whether the average swimmer should be concerned about chloroform exposure. Speaking in 1993, Dr. Eric W. Mood, by then an Associate Professor at Yale University Medical School, stated that while it was possible to generate chloroform in swimming pools, it was not possible to "form much of it in connection with sanitizing swimming pool water (66)." In the same year Joe Thornton, a research analyst at Greenpeace's Seattle office, warned that chloroform and chlorinated acids are very toxic. Greenpeace was not, however, lobbying against the use of chlorine in swimming pools. Instead the group was concentrating its efforts on industrial uses. (66)

While chronic effects were being debated, everyone agreed that acute effects from chlorine misuse are potentially serious. In the mid-1980s, the New York City Department of Health Poison Control Center received about a dozen calls every summer resulting from misuse of pool chemicals. People have been known to splash the chemicals in their eyes, be overcome with fumes while mixing chemicals in their pool houses, and burn their legs by standing in the pool while adding chemicals to it (66). The acute effects of chlorine exposure from swimming in pools are generally not considered serious health risks. Hair can turn dry and brittle. Chlorine from pools, or salt from the ocean, can dry out the skin (67). Dr. Jeffrey R. Haag and Dr. Richard G. Gieser of the Loyola University Medical Center reported that two-thirds of swimmers exposed to chlorine in pool water experienced a swelling of the cornea, and almost all of them showed some erosion of the cornea. This problem can be avoided with the proper use of high quality goggles (67). A recent Belgian study found that regular attendance at indoor chlorinated pools can increase the risk of developing asthma in children. The main cause is believed to be trichloramines (68).

Environmental Effects

According to Scott Klarich, an environmental protection specialist with the Colorado Department of Public Health and Environment Water Quality Control Division, when swimming pool or hot tub water runs off into ponds, lakes, rivers, and oceans, the high chlorine concentration can prove to be harmful to fish and other aquatic life. Even a concentration as low as 0.011 ppm can be detrimental to organisms in the water. Therefore, owners are urged to take precautions when draining the chlorine-contaminated water from pools (69).

A combination of the concerns about health effects from exposure of chlorine byproducts and from pool water discharge has prompted the creation of biological treatment systems. These have been popular in continental Europe for 20 years and are becoming increasingly common in the United Kingdom. At this time only a few have been installed in the United States (70). This system consists of two artificial pools that are connected. One is for swimming and the other is for growing plants that purify the water (70). Pumping water between the two basins is required as are occasional chemical treatments. Plants used for purification are divided into three categories. The emergent category includes sedges, lesser cattails, aquatic irises, and rushes. Submergent plants such as the common waterweed and Hornwort are valued for their high oxygen output. The floating plants category includes pondweeds and common duckweed (71).

A Final Note

There can be no more enthusiastic endorsement of the public's faith in chlorine than the attempt made in 1989 to sterilize an ocean beach by using chlorine tablets. At 4 am on Thursday, July 20th, 1989, the mayor of Wildwood Crest, New Jersey, received a request from five local businessmen to throw chlorine tablets into the ocean. Because it was not clear at the time exactly what the men were planning to do, the call was referred to the town's Public Works Director, Arthur Schard (72). Although chlorine tablets were not mentioned in the conversation, Schard gave the men permission to accompany the town's work crew on their early morning daily beach cleanup. At around 5 am, county inspectors spotted the men throwing chlorine tablets into the ocean. Six days later, Robert Drewnowski, Joseph Salerno, Daniel MacElrevey, Robert Belansen, and Joseph Jablonski were presented with a civil summons for placing "deleterious substances" in tidal waters (72). Wildwood Crest has always been proud of its 100-yard wide beach, but that summer business was down by some 28 to 30% from pervious years. Health inspectors had spent the two days gathering water samples. Some of the samples revealed bacteria levels that were high enough to force four town beaches to close (72). Everyone agreed that the five men were responsible local businessmen who were trying to do what was best for the town, but beyond that, opinion was divided. "It seems like a senseless thing to do," said one resident; and "They tried to do right for the whole town," said another. Mayor Joyce P. Gould said that the tablet throwing "really wasn't sanctioned by the town government." She went on to call the action "futile and ludicrous," but she strongly defended the men in her public statement. "They genuinely felt a concern for the beach," according to the mayor (72). The decision to use chlorine tablets in the surf was not entirely without precedent. Twice a week the town's public works crews would suspend baskets of tablets in the storm drains. Any bacteria accumulating in there would be killed before rainwater washed it out to sea. It is not clear from the press reports whether the five men took their idea from this practice (72).

Conclusions

Chlorine has been providing a means of protecting human health by sterilizing swimming pool water for almost a century. During that time effectiveness and ease of use have been steadily increasing. While initial opposition to chlorine use was due to objectionable odors, since the 1970s there have been an increasing number of concerns over human exposure to chlorinated organic byproducts as well as the release of inorganic chlorine compounds to the environment. There will certainly be an increase in the number of large pools purified with ozone technology but it remains to be seen what alternatives will prove popular among residential pool owners. Despite the increasing concerns over safety, chlorine in one form or another is expected to remain in widespread use in the foreseeable future.

APPENDIX: How does Pool Chlorine Work?

"Chlorine" in swimming pools is something of a misnomer. The active sanitizing agent is hypochlorous acid. When chlorine gas is bubbled into water, or some other source of hypochlorous acid is dissolved in the water, an equilibrium forms with Cl_2, HOCl, and HCl:

$$H_2O + Cl_2 \rightleftharpoons HOCl + HCl$$

The active sterilizing agent is the hypochlorous acid and not the diatomic chlorine. This equilibrium is pH-dependent and the available sanitizer is maximized under slightly acidic conditions. However, even slightly acidic water would damage the pool and so a pH 7.4 to 7.6 is considered optimal. The formation of hydrochloric acid may require addition of an alkaline material to increase the pH.

Meanwhile solar radiation of the water is causing the hypochlorous acid to break down:

$$HOCl \rightarrow Cl_2 + O_2 + \text{small amounts of } ClO_3$$

For this reason stabilizers are added to chlorine tablets, which function as a sort of sunscreen to prevent the photodegradation reaction. The Cl_2 escapes from the surface of the water; when pools are overly chlorinated, it can cause breathing difficulties. Shock treatment formulations contain a source of hypochlorous acid but often without any stabilizer, which is why many manufacturers recommend adding them at night.

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