This exploratory research finds that swimming pool water may be made safe without becoming irritating to the swimmer's eyes. This happy outcome is not achieved without difficulties: the method is by no means foolproof.

Development and Application of High-Free Residual Chlorination in the Treatment of Swimming Pool Water*

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HIGH-FREE residual chlorination of swimming pool water involves the application of the principles of break-point and superchlorination of public water supplies with modifications. Its development was stimulated by the need for a procedure of applying chlorine to swimming pool waters, particularly in pools located out-of-doors, in such quantities that at all times, when the pools are in use, the residual chlorine concentrations would be capable of maintaining bacterial densities below prescribed limits, and yet not be irritating to the eyes of swimmers.

Break-point and superchlorination have been used successfully for many years to control tastes and odors in drinking water caused by ammonia-nitrogen and chlorine. In 1925, Sir Alexander Houston [1] of the Metropolitan Water Board, London, England, and in 1926, Howard [2] of Toronto, Canada, observed reduction of tastes and odors in drinking water after superchlorination followed by dechlorination. Faber [3] and Griffin [4] demonstrated in their studies of superchlorination the presence of the "break-point" characteristic in the residual curves of practically all types of water. Calvert [5] showed that the "break" was a function of ammonia-nitrogen present in the water. Griffin and Chamberlain [6] verified these findings and observed that the pH of the solution determined, to a large degree, the extent of the reaction between the ammonium and chlorine ions, with the optimum values of pH between 7.0 and 8.0. These and other studies showed that ammonia-nitrogen was associated with some chlorinous tastes and odors in drinking water and that when the break-point occurred there was a reduction of the concentration of ammonia-nitrogen resulting in the formation of nitrogen (N_2) and the oxides of nitrogen and a reduction of tastes and odors. A decrease in amount of combined residual chlorine (chloramines) at and beyond the break-point was also observed.

These observations of the behavior of chlorine in drinking water containing ammonia-nitrogen led to the development of the theory that the principle causative agent of eye irritation of swimmers in pools that contained chlorinated water, was not chlorine but the combination of chlorine and ammonia-nitrogen. It was believed that, if taste and odors in drinking water could be controlled by the use of break-point chlorination, then swimming pool water could be

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made less irritating through the application of the same principles. In 1948, King[7] treated the water in a swimming pool in England with high concentrations of chlorine and observed that a free residual chlorine level of 2.0 ppm and a pH of 7.5, or higher, could be maintained without irritation to the eyes and skin of swimmers. Isherwood[8] made similar observations of the application of break-point chlorination in the treatment of swimming pool water and concluded that successful operation depended, in part, on the ability to maintain a minimum concentration of free residual chlorine of 1.0–2.0 ppm in excess of the value for combined residual chlorine.

In applying the principles of break-point chlorination to the treatment of swimming pool water which is recirculated continuously, it was found that the term "break-point" was no longer descriptive of the process. The characteristic "break" could not be demonstrated readily since ammonia-nitrogen was oxidized continuously as it was washed into the water from the bodies of the swimmers. The term "high-free residual chlorination" has been employed to characterize this newer process of treating swimming pool water with concentrations of chlorine sufficient to produce and maintain values of free residual chlorine equal to, or greater than, 1.00 ppm. It is differentiated from the older practice, commonly called "marginal chlorination," in which the free residual chlorine level was maintained between 0.4 and 0.6 ppm, as recommended by the Joint Committee on Bathing Places of the Conference of State Sanitary Engineers and the American Public Health Association.[9] This is consistent with common usage by waterworks men of the term "free residual chlorination" for break-point chlorination and superchlorination of drinking water.

To evaluate the behavior and efficiency of high-free residual chlorination in the treatment of swimming pool water, a research program was undertaken at Yale University. Earlier studies at Yale on the effect of residual chlorine and pH upon the eyes of swimmers indicated that within recommended limits of residual chlorine, the control of pH was found to be the more important of the two factors in reducing the amount of irritation of the eyes of swimmers.[10] All other conditions being equal pH 8.0 was less irritating than pH 7.0 at residual chlorine levels of 0.05 and 0.50 ppm. In order not to limit the scope of the research to the conditions found at the Yale University swimming pool, a program was developed to include the pools at Smith College, Northampton, Mass., and Colt Park, Hartford, Conn. The swimming pools at Yale University and Smith College are private institutional pools located in gymnasiums. The pool at Colt Park is a municipal pool, located out-of-doors in a public park. The three pools are of good design and are operated efficiently. They are of the continuous recirculation type and are operated 24 hours per day when in use. Sand and gravel pressure filters are used at the three installations with aluminum sulfate added as a coagulant and soda ash as a means to maintain the desired alkalinity.

Only minor changes of operation and no equipment changes were made to place the Yale University and the Smith College pools on a high-free residual chlorination schedule. At both pools there was sufficient chlorinator capacity, Yale using chlorine gas and Smith using high-test calcium hypochlorite. At Colt Park it was necessary to install a new gas chlorinator with a capacity to feed 100 pounds of chlorine gas per day to replace an older one of less capacity. Application of the chlorine solution at all three pools was made prior to filtration to permit thorough mixing.

The pH was adjusted to the desired

level by the addition of soda ash after filtration through proportioning, electrically operated chemical feed pumps. The filter plant operators made frequent tests each day of the water for residual chlorine and pH, using colorimetric methods, and made the necessary adjustments to maintain the values at the desired levels.

To set up standard conditions for measuring the amount of irritation of the eyes of swimmers following swimming, a group of 15 persons was selected at each pool who would swim for 15 minutes continuously on each test day using the crawl swimming stroke to get maximum exposure of the eyes to the pool water. After the swimming period, the swimmers recorded the immediate reaction of their eyes for the following sensations: (1) sensitivity to bright light, (2) stinging or smarting, (3) tearing or watering, (4) blurred vision, (5) appearance of rainbows or circles around sources of light, and (6) difficulty in keeping their eyes open. They were asked to record the sensations they felt as being: normal, slight, moderate, or severe. The following day the swimmers recorded their reactions to the same sensations of the eyes that occurred during the 24 hours following swimming.

The group of swimmers at Yale was composed of undergraduate and graduate male students. For the greater part, these men were competitive swimmers and swam with great speed during the study period. At Smith College, the group was made up of women who were either graduate students majoring in physical education or were members of the teaching staff in physical education. The group at Colt Park was a mixed group of nine men and six women who were either lifeguards or daily frequenters of the pool.

While the swimmers were in the water, samples were collected from the pool for analyses. They were analyzed daily for their residual chlorine content and pH level. Additional samples were collected at various intervals for chemical and bacteriological examinations. Residual chlorine determinations were made immediately after the collection of the sample with an amperometric titrator using the procedure recommended by Marks, Williams, and Glasgow.[11] The pH levels were measured potentiometrically with a glass electrode.

The data collected at the three pools during the testing period were analyzed in a standardized manner. The observations were grouped according to the pH and total residual chlorine values. The subdivisions that were used were selected empirically but the limits of values recommended by the Joint Committee on Bathing Places [9] were employed for one group.

In order to obtain a composite figure as a measure of the amount of irritation for a given condition of pH and residual chlorine, the data for the six measurements of eye irritation (i.e., sensitivity to bright light, stinging or smarting, tearing or watering, blurred vision, appearance of rainbows or circles around sources of light, and difficulty in keeping the eyes open) were grouped together. For each subdivision, the per cent of eye sensations, other than normal, was calculated and used as a measurement of the degree of eye irritation. Only the reactions felt immediately after swimming are recorded in this report as the reactions felt during the 24-hour period following swimming were usually normal and showed no significant distribution. This may be explained by the fact that at no time during the study was the water permitted to become irritating to a high degree. This was done intentionally to maintain the good will of the test swimmers.

The results of the observations made at the three pools are presented in Tables 1–3. The values obtained in one pool should not be compared directly

TABLE 1

Amount of Irritation of the Eyes Caused by Swimming in Water of an Indoor Pool (Yale University) Treated with Marginal and High-Free Residual Chlorination

Total Residual Chlorine in ppm	pH 7.0–7.5	pH 7.6–7.9	pH 8.0–8.4	pH 8.5–8.9
	Per cent	Per cent	Per cent	Per cent
0.0 –0.39	37		30	
0.40–0.60	38	27	30	
0.61–0.99		31		
1.0 –1.99		35		
2.0 –2.99		24	24	22
3.0 –3.99		45	20	
4.0 –4.99		54	17	

The per cent of irritating sensations for six criteria to the eyes of swimmers immediately after swimming in the Yale University Exhibition Swimmng Pool for the corresponding values of pH and total residual chlorine.

with those obtained at another pool as the composition of the group and the style of swimming were not standardized between groups; rather the trends of increasing or decreasing eye irritation within the group should be studied. The values obtained at all three pools show a uniform trend. There is a definite amount of irritation at pH 7.0–7.5 for Yale (Table 1) and Colt Park studies (Table 3). At pH 7.6–7.9, the trend of increasing amounts of irritation with increasing residual chlorine levels is pronounced for the observations at Yale. If the study had ceased at this point, an erroneous conclusion might have been reached, that high concentrations of residual chlorine give rise to irritation of the eyes of swimmers. However, an analysis of the observations for values of pH 8.0–8.4 and of pH 8.5–8.9 do not support this conclusion. In these pH groupings, the benefits of high-free residual chlorination are first noted. The amount of decrease in irritation for observations made at Yale are not as pronounced as those for Smith College and Colt Park, but the trend is definite and similar in character.

Optimum results occurred in all pools at a value of pH 8.0, or higher, with residual chlorine levels greater than 1.0 ppm. This study does not indicate the relative importance of the pH of the water and the alkalinity expressed as ppm of $CaCO_3$. Since all three pools used soda ash to control the pH, an increase in the rate of application of soda ash increased the pH value and alkalinity simultaneously.

TABLE 2

Amount of Irritation of the Eyes Caused by Swimming in Water of an Indoor Pool (Smith College) Treated with Marginal and High-Free Residual Chlorination

Total Residual Chlorine in ppm	pH 7.0–7.5	pH 7.6–7.9	pH 8.0–8.4	pH 8.5–8.9
		Per cent	Per cent	
0.0 –0.39				
0.40–0.60			26	
0.61–0.99				
1.0 –1.99		14	18	
2.0 –2.99		11	11	
3.0 –3.99			13	
4.0 –4.99			21	

The per cent of irritating sensations for six criteria to the eyes of swimmers immediately after swimming in the Smith College swimming pool for the corresponding values of pH and total residual chlorine.

TABLE 3

Amount of Irritation of the Eyes Caused by Swimming in Water of an Out-of-door Pool (Colt Park) Treated with Marginal and High-Free Residual Chlorination

Total Residual Chlorine in ppm	*pH 7.0–7.5*	*pH 7.6–7.9*	*pH 8.0–8.4*	*pH 8.5–8.9*
	Per cent		*Per cent*	*Per cent*
0.0 –0.39	24			
0.40–0.60				
0.61–0.99				
1.0 –1.99	34		16	2
2.0 –2.99	65		10	8
3.0 –3.99			7	9
4.0 –4.99				

The per cent of irritating sensations for six criteria to the eyes of swimmers immediately after swimming in the Colt Park swimming pool for the corresponding values of pH and total residual chlorine.

A complete analysis of a portion of the study conducted at Smith College has been reported by Campbell.[12] While her analysis does not include all the data contained in Table 2, it does show the same trends and characteristics. Additional studies of use of high-free residuals for disinfection of swimming pool water are being conducted currently by the Department of Hygiene and Bacteriology, and the Department of Physical Education of Smith College.

It should be indicated that the amount of titratable combined residual chlorine remained uniformly constant for each pool throughout the study independent of the variations in the amount of free residual chlorine (Table 4). This is attributed in part to a concerted effort by the investigators to keep the ammonia-nitrogen fraction as low as possible at all times during the study. No attempt was made to increase the ammonia-nitrogen fraction through the addition of chemicals to increase the combined residual chlorine level and observe its effect. It can be assumed that the ratio of monochloramine to dichloramine varied according to the pH of the water as shown by Fair [13] and his associates in the study of the chemical action of chlorine and chlorine compounds.

However, two qualitative observations

TABLE 4

Average Amount of Residual Chlorine Found as Combined Residual Chlorine in the Titratable Total Residual Chlorine Value

Titratable Total Residual Chlorine in ppm	*Average Titratable Combined Residual Chlorine Included in the Titratable Total Residual Chlorine, in ppm*											
	pH = 7.0–7.5			*pH = 7.6–7.9*			*pH = 8.0–8.4*			*pH = 8.5–8.9*		
	Yale Univ.	*Smith Coll.*	*Colt Park*	*Yale Univ.*	*Smith Coll.*	*Colt Park*	*Yale Univ.*	*Smith Coll.*	*Colt Park*	*Yale Univ.*	*Smith Coll.*	*Colt Park*
0.00–0.39	0.02 *		0.30 †				0.02 *					
0.00–0.39	0.02		0.30				0.02					
0.40–0.60	0.23			0.27			0.22					
0.61–0.99				0.27								
1.00–1.99			0.28	0.30	0.32			0.29	0.26			0.25
2.00–2.99			0.25	0.33	0.28		0.24	0.23	0.26	0.26		0.25
3.00–3.99				0.37			0.27	0.29	0.27			0.27
4.00–4.99				0.34			0.26	0.28				

* Average total titratable residual chlorine values = 0.05 ppm
† Average of total titratable residual chlorine values = 0.30 ppm

The average amount of combined residual chlorine found in the swimming pool waters at Yale University, Smith College, and Colt Park as compared with the titratable total residual chlorine level and pH.

were made during the study of the effect of a sudden increase in the ammonia-nitrogen fraction. The water in two pools, not included in this study but which were operating with high-free residual chlorination, suddenly became irritating to the eyes of swimmers. In one pool chlorine was applied in the form of a hypochlorite solution. Initially calcium hypochlorite was applied at this pool with excellent operating results. The chemical was changed to sodium hypochlorite and with this change the water became irritating. A sharp increase in the combined residual chlorine level was observed. Eventually, this was traced to the sodium hypochlorite which had been stabilized by the manufacturer with ammonium salts. When this chemical was discontinued and ammonia-free calcium hypochlorite was used in its stead, the irritation of the eyes was reduced and the combined residual chlorine level declined to its previous value. In the case of the second pool, the conditions were slightly different. This pool was a large, new, indoor pool in which chlorine gas was used. High-free residual chlorination was introduced and excellent results were obtained. The residual chlorine level was kept at 2.0–3.0 ppm with a pH of 8.0 and no irritation to the eyes of swimmers was observed. Inadvertently, one night a large quantity of waste water found its way into the pool. This waste water was evidently high in its ammonia-nitrogen content as it changed all of the free residual chlorine to combined residual chlorine and caused the water in the pool to be unbearable for swimming because of the intense amount of eye irritation produced. When this water in the pool was dumped and the pool refilled with fresh water with a low ammonia-nitrogen fraction and treated with high-free residual chlorination, excellent results were again obtained.

Extremely low bacterial densities of swimming pool water treated with high-free residual chlorination have been reported.[14] These studies were conducted concurrently with the observations of irritation to the eyes of swimmers. The combination of low bacterial densities, the absence of algae, and the presence at all times of high concentrations of free residual chlorine, causes the water to remain crystal clear. In the case of the Colt Park pool, it was possible to view under water a swimmer at one end of the pool from the opposite end, 120 feet away. The water in the pools always remained light blue in color without any tint of green. Esthetically, the pools treated with high-free residual chlorine have been very appealing to the swimmers.

High-free residual chlorination cannot be applied to every pool. Observations to date indicate that successful use of this method of water disinfection is limited in part by the following conditions:

1. The water in the pool must be recirculated and filtered continuously.
2. The arrangements of inlets and outlets to the pool must be of good design to permit uniform flow of water through the pool.
3. The capacity of the chlorinating equipment must be sufficient to maintain the desired free residual chlorine levels.
4. The continuous application of chlorine, even when the pool is not in use, at a rate to permit the oxidation of the ammonia-nitrogen fraction.
5. The complete turnover of water in the pool through the filters must occur at least approximately once every eight hours.
6. The use of ammonia-free chemicals must be applied at uniform rates under controlled conditions.

CONCLUSIONS

High-free residual chlorination for the disinfection of swimming pool water presents many new problems. The studies discussed in this paper were not exhaustive but rather exploratory to illustrate the benefits of high-free residual chlorination over marginal chlorination in reducing eye irritation to swimmers and to define areas for future studies.

From the data that are available the following conclusions are drawn:

1. High-free residual chlorination of swimming pool water reduces the amount of irritation to the eyes of swimmers when compared with marginal chlorination.

2. Optimum conditions of the swimming pool which cause minimal amounts of irritation to the eyes of swimmers are found when the pH of the water is 8.0–8.9 and the residual chlorine level is 1.0–3.99 ppm with the principal portion of the fraction as free residual chlorine.

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