# A POSSIBLE STRATEGY FOR AMELIORATING CHLORINATION PROBLEMS IN SWIMMING POOLS

[This is offered by Richard Falk without comment from Dr. Rushall.]

From: Richard Falk <RichardFalk@comcast.net>

Date: Saturday, 19 August, 2006 (updated 20 December 2009)

Subject: ***Comments on chlorinated pools and asthma***

Dr. Rushall:

I read with interest your web page *http://coachsci.sdsu.edu/swimming/chlorine/chlorine.htm* summarizing studies and anecdotes on competitive swimming, the use of chlorine (especially in indoor pools) and asthma or related health effects.

Though it appears that the greater problem is with indoor pools, what is not so clear is exactly why. Part of the problem is the lower amount of air circulation indoors, though as one study showed, you can absorb THMs (trihalomethanes) through the skin. The other difference between indoor and outdoor pools is that outdoor pools are often exposed to sunlight and the ultraviolet radiation may breakdown some chlorinated organic compounds (combined chlorine) and certainly appears to be the case with the inorganic chloramine nitrogen trichloride.

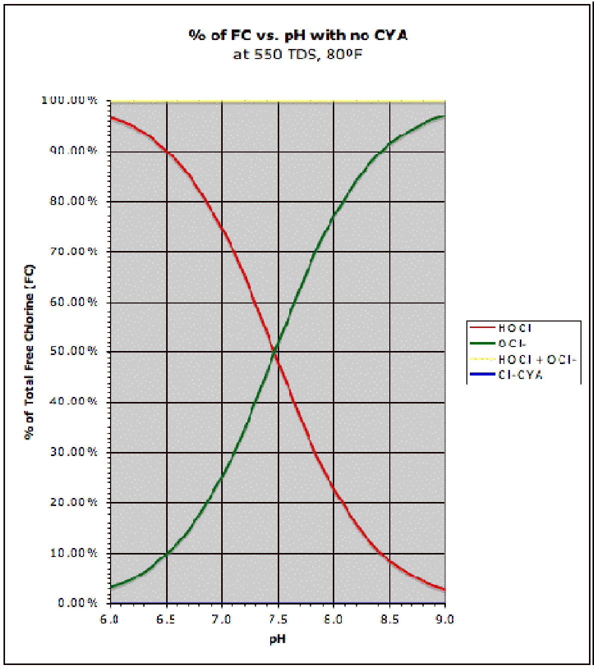
One other reason that outdoor pools may not pose as much of a health threat is an indirect relation to the exposure to sunlight. To prevent the breakdown of chlorine from sunlight, specifically from ultraviolet radiation, most outdoor pools have cyanuric acid (CYA) added to them as a "stabilizer" or "conditioner". Without cyanuric acid, half of the chlorine in a pool can be lost through breakdown from noontime sunlight in about a half-hour. When cyanuric acid is present in pool water, it extends the half-life of chlorine to over six hours. However, by combining with the disinfecting form of chlorine (HOCl) and its related form (OCl-) as chlorinated cyanurates, the chlorine's effectiveness as a disinfectant and oxidizer is significantly reduced. The net effect is that the effective active chlorine level is significantly reduced. The definitive O'Brien (1974) paper describing the chlorine/CYA relationship is at the following link:

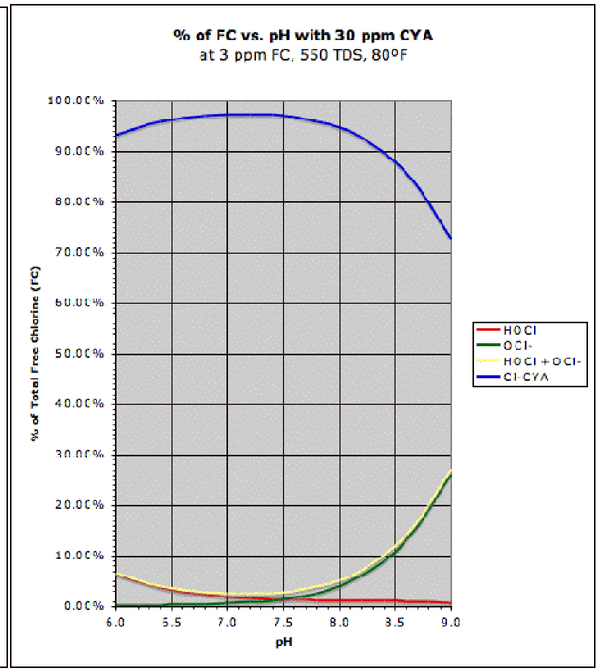
http://richardfalk.home.comcast.net/~richardfalk/pool/OBrien.htm

I have a spreadsheet that calculates all of the equilibrium equations so that one can calculate the active chlorine (hypochlorous acid) concentration at various Free Chlorine (FC) and CYA levels here:

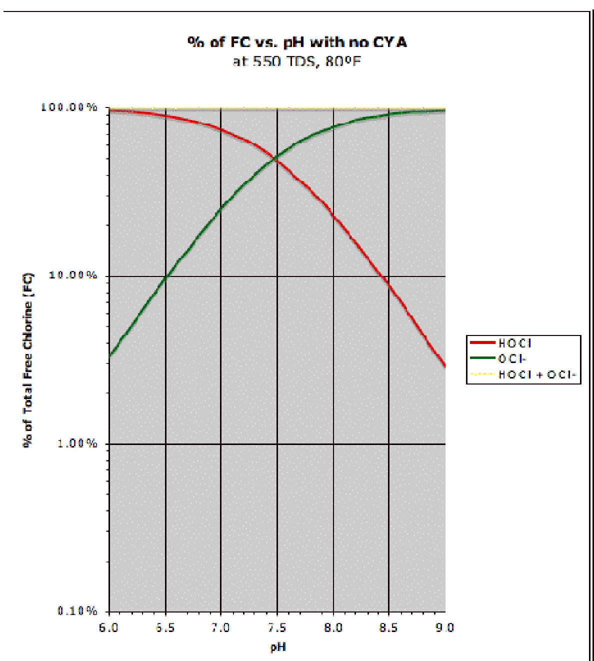
http://richardfalk.home.comcast.net/~richardfalk/pool/PoolEquations.xls

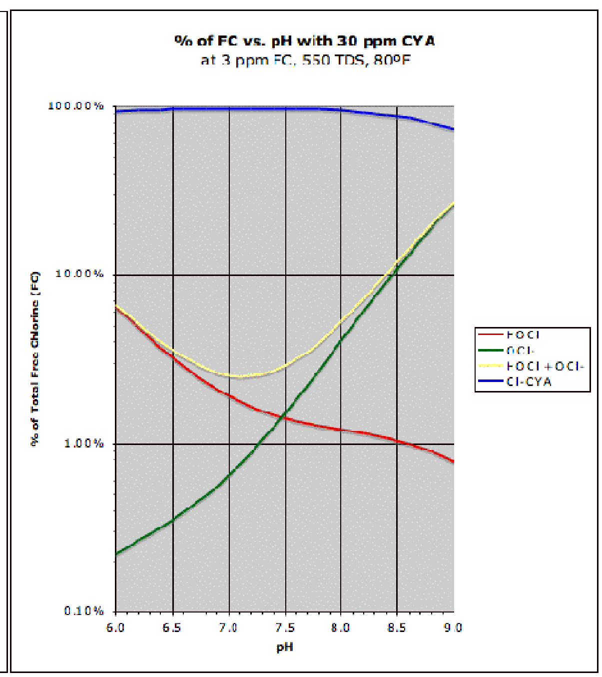
Using this spreadsheet, I created the following charts showing the traditional active chlorine levels vs. pH on the left and the actual levels vs. pH in the presence of 30 ppm CYA on the right.




In particular, notice how with even 30 ppm cyanuric acid, the chlorine concentration is reduced by a factor of about 30 so that a pool with 3 ppm Free Chlorine with 30 ppm cyanuric acid is roughly equivalent to a pool with 0.1 ppm without cyanuric acid. In order to see the relationship of chlorine vs. pH more clearly, take a look at the following log graphs of the same data as above with no CYA on the left and 30 ppm CYA on the right.




The graph on the right is essentially the same as Figure 14.5 of the O'Brien paper (except that I show a narrower pH range and have combined the chlorinated cyanurate species into one curve). You can see that the pH dependence on chlorine concentration is significantly altered in the presence of CYA. Instead of the active chlorine (hypochlorous acid) concentration dropping roughly in half from a pH of 7.5 to 8.0, it only drops by around 15% with 30 ppm CYA.

All of the models of chlorine oxidation of ammonia [ Wei & Morris (1992), Selleck & Saunier (1976, 1979), Jafvert & Valentine (1992), Vikesland, Ozekin, Valentine (2000) ] show that the amount of nitrogen trichloride that is produced when there is a sufficient excess of chlorine to ammonia is roughly proportional to the hypochlorous acid concentration, all else equal. There is no definitive model for chlorine oxidation of urea, though Wojtowicz has proposed the formation of a quadchlorourea followed by oxidation by chlorine to form dichloramine and nitrogen trichloride (and carbon dioxide) that would then follow the standard models. I have a spreadsheet with these various models at the following link:

http://richardfalk.home.comcast.net/~richardfalk/pool/Breakpoint.xls

There is no free lunch here. While the amount of irritating and volatile nitrogen trichloride can be reduced by orders of magnitude through use of a small amount of CYA (say, 20 ppm in indoor pools), the amount of monochloramine and dichloramine is increased by roughly that same proportion and persists for a longer period of time, though it still does become oxidized (mostly to nitrogen gas). In heavy bather load pools, supplemental oxidation or breakdown of chlorinated compounds, such as by UV or ozone, combined with a low active chlorine level may be a way to significantly reduce disinfection by-products. The German DIN 19743 standard accomplishes this by specifying low chlorine levels of 0.3 to 0.6 ppm FC with no CYA, though also completely removes chlorine and chlorinated by-products during filtration via activated carbon followed by optional ozone and then re-injects chlorine. In what I am proposing with 4 ppm FC and 20 ppm CYA, one has the equivalent of roughly 0.2 ppm FC with no CYA, but has plenty of reserve of chlorine to not run out under local high bather insult (such as urination from children).

It should be noted that one result of a lower active chlorine concentration is the longer persistence of Combined Chlorine (CC), but of forms that may be far less of a problem. The bulk of CC will generally be monochlorourea (or possibly dichlorourea) since urea is by far the largest component of sweat and urine and oxidizes rather slowly by chlorine (except at higher temperatures as in spas). So having a higher CC is not necessarily a problem since clear reactions to eye irritation (in rabbits) for chlorourea starts at 10 ppm while for monochloramine it starts at 4 ppm (for Free Chlorine, it starts at 16 ppm, but that is with no CYA in the water) and these compounds are not indicated in the problems of asthma or other health issues as are nitrogen trichloride and chloroform (a trihalomethane, THM). If there is CC and no CYA, then this is far more indicative of a problem due to likely higher nitrogen trichloride levels, but CC with CYA is not necessarily a problem, at least not at the 0.5 ppm threshold most commercial/public pools or even higher, especially if there is no noticeable odor.

Therefore, in addition to some of the alternatives listed on your web page, another possibility is to use a small amount of cyanuric acid in indoor pools, probably not more than 20 ppm CYA with 4 ppm FC since one wants some reasonable oxidation capability. In high bather load situations, supplemental oxidation is strongly recommended.

Thank you for your attention,

Richard Falk

**REFERENCES**

J. E. O'Brien, J. C. Morris and J. N. Butler, "Equilibria in Aqueous Solutions of Chlorinated Isocyanurate", Chapter 14 in Alan J. Rubin, ed., *Chemistry of Water Supply, Treatment and Distribution*, 1973 Symposium, (published 1974), Ann Arbor Science Publishers, Ann Arbor, MI, pp. 333-358. ISBN 0-250-40036-7

Chad T. Jafvert, Richard L. Valentine, "Reaction Scheme for the Chlorination of Ammoniacal Water", *Environmental Science & Technology*, 1992, Vol. 26, No. 3, pp. 577-586.

Peter J. Vikesland, Kenan Ozekin, Richard L. Valentine, "Monochloramine Decay in Model and Distribution System Waters", *Water Research*, 2000, Vol. 35, No. 7, pp. 1766-1776.