BABES: a better method than "BBB" for pools with a salt-water chlorine generator

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1.0 Summary

A swimming pool is an aqueous solution of interacting chemicals that determine appeal and safety for swimmers. The chemistry varies widely, depending on what is added to the pool. In recent decades, there has been an increasing trend towards domestic outdoor pools that use electrolytic salt-water chlorine generators for sanitation (SWC pools). These typically have cyanuric acid for photoprotection, and sometimes boric acid for improved pH buffering. Critical thinking about the chemistry indicates simple principles for efficient SWC pool maintenance, some of which differ from the traditional advice to non-salt pool operators. This article describes a simple approach built on the "BBB" tradition. The improved "BABES" method integrates the use of boric acid for pH buffering, hydrochloric (muriatic) acid to correct pH updrift from SWC operation, brushing to help prevent biofilms, electricity and common salt for sanitizer production. It explains the contribution of each of these components, then explores the scientific basis for the few additional compounds that should be considered, and those that should be avoided, for trouble-free SWC pool maintenance. Along the way it points out key myths and uncertainties to encourage deeper analysis. It ends with a simple set of operational guidelines that an SWC pool operator can adopt with confidence, or vary to suit their needs based on the scientific foundations in the article.

2.0 Introduction

For several decades, the BBB acronym has been a handy reminder of some of the key ingredients (Bleach, Borax and Baking soda) in an approach to use of readily-available materials and a few simple guidelines for 'trouble-free' maintenance of (domestic) swimming pools (Lion 2008; Powell 2010). Today, salt-water chlorine generators have proven to be probably the simplest and most reliable method to provide sanitizing chlorine levels in such pools. Thinking about the chemistry in SWC pools indicates how we can improve from the BBB background. Hence BABES: an approach to use of readily-available materials and a few simple guidelines for 'trouble-free' maintenance of (domestic) SWC swimming pools.

Borate: In a swimming pool, boron in solution will exist as pH-dependent equilibrium between boric acid and borate ions. At a suitable concentration (50 - 100 ppm boron equivalents), it provides the primary buffer against wild swings in pH that would create other problems such as scaling, corrosion, failure of sanitation, or irritation to swimmers. It can be added in several forms but the process will typically be simplest and cheapest if you can obtain boric acid in suitably pure form (> 99.5%); for example from some farm-supply stores. See the companion review (Birch 2013) for a detailed consideration of safety and efficacy of boric acid in swimming pool context.

Acid: Most owners of SWC pools find that pH is continuously drifting upwards during SWC operation. To maintain it in the desired working range (typically pH 7.5 - 8.2) you should add appropriate doses of the strong acid HCl (hydrochloric or muriatic acid). Concentrated HCl is highly corrosive: you must follow carefully the safety instructions on the package. HCl dissociates into H^+ and Cl^- ions that do not complicate other parts of salt-water pool chemistry. Other (boric and cyanuric) acids are used in the overall process, but you have a

target concentration for borate and cyanurate ions so these should not be used routinely for pH adjustment.

Brushing: There is no escaping the need for brushing of pool walls and floors to help disrupt the formation of microbial biofilms, which can become increasingly resistant to penetration and killing by your sanitizer (HOCl, hypochlorous acid). In warm pools which receive lots of sunlight, this is essential for control of algal (or cyanobacterial) growth. The challenge is greatest in porous areas, such as the concrete between pebbles in aged 'pebble-crete' finishes, where algae can grow into the surface. If a stiff brushing of the pool floor or steps kicks up a green cloud or flakes of algae, you need to do more to control algal biofilm development.

There is a partial trade-off between brushing and chlorine level. With sufficient HOCl and (Winter) conditions less favourable for algae, almost no brushing may be needed. Any lapse in HOCl levels will soon necessitate more brushing, and it is generally impractical to maintain sufficient HOCl to eliminate all need for brushing during (Summer) conditions favourable for algae. Some automated pool cleaners help to disrupt biofilm development (by suction, water jets and/or brushing), thereby reducing the need for manual effort. Most pools have areas (like steps or space behind ladders) not accessed by automated cleaners, and therefore entirely dependent on manual brushing. Brushing was the 'forgotten B' in the BBB acronym! It should be part of a maintenance regimen including regular checks of pool water chlorine and pH levels; along with cleaning of filters and periodic checks for scaling in the SWC cell. Brushing is also an excellent way to speed the mixing of pool water after the addition of acid, salt or other chemicals during pool maintenance.

Electricity: You will consume a little electricity in the SWC cell (which generates sanitizing HOCl from $H_2O + Cl^-$, the chloride ions normally supplied as NaCl); and a lot of electricity in the pump needed to (i) drive pool water through a suitable filter and SWC cell and (ii) maintain enough circulation to disperse the HOCl at an effective concentration throughout the pool. Single-speed pool pumps commonly use about four times as much power as the chlorinator. The total running cost for an SWC pool can sometimes be reduced substantially, by using a multi-speed pump at a lower speed for a longer chlorination period. In public pools, whenever there are swimmers there must be sufficient HOCl levels to prevent person-to-person transmission of pathogenic microbes. In domestic settings, it is usually most efficient to run the SWC cell at night. This is because HOCl (through its equilibrium product OCl^-) breaks down in sunlight, and HOCl has equal antimicrobial activity by day or night. This advantage is increased if you buy electricity at a cheaper night rate, but may be reversed if your electricity comes directly from your own solar panels. You will generally need to operate the SWC for long enough to maintain HOCl throughout the pool, somewhere above 0.05 ppm Cl_2 equivalents, for at least 12 hours per day. This typically means much longer run times in Summer than in Winter.

Salt: The amount needed varies with design of the SWC cell: somewhere between 3,000 - 8,000 ppm NaCl in the pool water. This will taste barely to noticeably salty. It is well below ocean concentration (~ 30,000 ppm of NaCl, plus many other salts at levels below 3,000 ppm). Salt is not depleted through evaporation or the SWC chlorination cycle, but like anything else you add, it will have to be replenished with any pool water lost through splashing, overflow after rain, backflushing filters or the like. Without such outflows, addition of bleach (NaOCl) sanitizer would eventually lead to NaCl levels above those used in SWC pools. Different rates of outflow lead to various salinity levels in 'fresh-water' pools.

3.0 Things you may also need at times

3.1 Test kit: You may find it convenient to have samples of your pool water tested at a pool store that you trust (and from whom you will probably buy other chemicals if they are needed). Just be aware that the pool shop's default maintenance strategy may differ substantially from the one you prefer. You may be able to explain this and obtain the pool shop's water test results to inform your own decisions about any chemicals required. Most likely, to take control of your pool maintenance you will need a high-quality pool water test kit, or a collection of selected components. Some of the tests sold in single or combination strip form are very good. Others are most reliable in liquid (especially titration-based) form.

The core tests needed at least every few days are free chlorine (FC) and pH. Tests for cyanuric acid (CYA) and boric acid will be needed occasionally. Check that the tests span your intended working range (if you have to dilute first you will need distilled water and an accurate means of measurement, which adds to cost and errors).

You may find a FAS-DPD titration (pink-clear) clearer to read than DPD alone (shades of cloudy pink), and applicable without dilution at the chlorine levels needed for sanitation in pools with CYA. DPD reagent is generally supplied with a high concentration of a buffer to bring the sample to pH 6.2 to 6.5, where interference from other oxidising compounds is minimised. Commonly the buffer is phosphate. Unfortunately, Ca and Mg phosphates are low in solubility, so a precipitate may form depending on pool ionic composition. This turbidity interferes more with visual colour matching than titration endpoint. By depleting the buffer, it can also take the reaction away from the ideal pH. This is not usually a major source of error for pool use, but some more expensive kits use other buffers to avoid the risk. Be aware that the ferrous iron titrant is relatively unstable, due to oxidation by air - so kit performance may change with age (Harp 2002).

Combined chlorine will probably never be an issue in a SWC pool, as discussed below. Tests for calcium hardness (CH) total hardness (TH) and total (or'titration') alkalinity (TA) can help when troubleshooting a pool with an unknown history of chemical addition (often meaning excessive calcium and bicarbonate levels), but their use to adjust 'water balance' to minimise 'aggressive' properties is moot, as discussed below. It may be possible to calculate concentrations of interest from these 'historical test' results (e.g. magnesium from TH minus CH).

'Alkalinity' whether bi/carbonate-derived (CA) or total (TA) is very useful in marine biology as an indicator of carbonate level (very important for organisms that make calcium carbonate shells). But the calibration depends a lot on pH, other compounds like borates, and even salt concentration. These factors are stable in ocean water, but they vary widely in pools. So while TA is easily measured, it is likely to be confusing in borate-buffered SWC pool management. For example, at pH 8 with 6,000 ppm salinity, 50 ppm borate (~21 ppm TA) and 50 ppm CYA (~18 ppm TA) a pool might be near CO_2 equilibrium (~1 mM HCO_3^-, ~55 ppm TA) at a TA reading around 94 ppm. But at pH 7.5 the equilibrium dissolved inorganic carbon (DIC) content would be much lower (~0.3 mM HCO_3^-) as would the measured TA (~ 7 + 16 + 16 = 39 ppm). Volatility (of CO_2) is peculiar to the carbonate system, but the relative contributions of all compounds to TA change with pH, because of their different pKa values. This can be seen by comparing the trends for borate, cyanurate and carbonate species in Table 1. The table assumes pKa values that would apply in a SWC pool near Watermaid recommendations (6,000 ppm NaCl, 60-100 ppm each of Mg^{++} and Ca^{++}) at 25 C.

Table 1. The effect of pH on contributions of key buffers to TA in an SWC pool (6,000 ppm NaCl) at 25 C

pH	Fraction of each major pool buffer present as the specified base (contributing to TA), at the specified pKa[†]				Equilibrium total DIC (mM) at 3.5x10^{-4} atm CO$_2$*
	Borate pKa = 9.0	Cyanurate pKa = 6.8	Bicarbonate DIC pKa = 6.0	Carbonate DIC pKa = 9.4	
7.4	0.02	0.80	0.95	0.01	0.27
7.5	0.03	0.83	0.96	0.01	0.34
7.6	0.04	0.86	0.96	0.02	0.42
7.7	0.05	0.89	0.96	0.02	0.53
7.8	0.06	0.91	0.96	0.02	0.67
7.9	0.07	0.93	0.96	0.03	0.84
8.0	0.09	0.94	0.95	0.04	1.07
8.1	**0.11**	**0.95**	**0.94**	**0.05**	**1.35**
8.2	0.14	0.96	0.93	0.06	1.72
8.3	0.17	0.97	0.92	0.07	2.19
8.4	0.20	0.98	0.91	0.09	2.80

[†] Calculated from the Henderson-Hasselbalch equation using academic.pgcc.edu/~ssinex/buffer_cap.xls
   pKa values will vary with temperature, and with pool solute composition due to specific ion-pairing
* Calculated from the data and equations of Mook (2000) and Millero et al. (2006). Without pH manipulation, such a pool would tend towards equilibrium with atmospheric CO$_2$ at pH 5.5 (without CaCO$_3$) or **pH 8.1** (in the presence of calcite CaCO$_3$).

Excluding volatility, buffers present in relatively high molar concentration, and with pKa within 1.5 pH units above the pool working pH range, will cause the greatest change in measured TA with variations in pool pH: borate is a case in point.

The effects on pKa of salinity and ion-pairing with divalent cations have been tested for borate (Owen and King 1943; Reardon 1976; Bassett 1980; Hershey *et al.* 1986) and carbonates (Millero and Roy 1997; Millero *et al.* 2006), but apparently not for cyanurate. Without an accurate pH meter and detailed knowledge of pool solute composition and its effects on pKa, there is limited scope to interpret 'alkalinity' in a borate-buffered pool. TA is an indication of buffer capacity against pH decrease, but the end-point around pH 4.5 is too low in pool management context (hence the separate acid demand test in comprehensive pool kits). For SWC pools, one is usually concerned with capacity to buffer against up-drift in pH, which is not predicted at all by TA (Fig. 1).

Specific tests for desired solutes (NaCl, magnesium or borate) make it easier to adjust for effects like pool overflows. They are absent from most pool combination kits, but available separately or in kits for marine aquarists. Unfortunately, kits sold for aquarium use may suffer interference from chemicals such as HOCl and CYA in pool water at concentrations far beyond their range in sea water, as discussed for
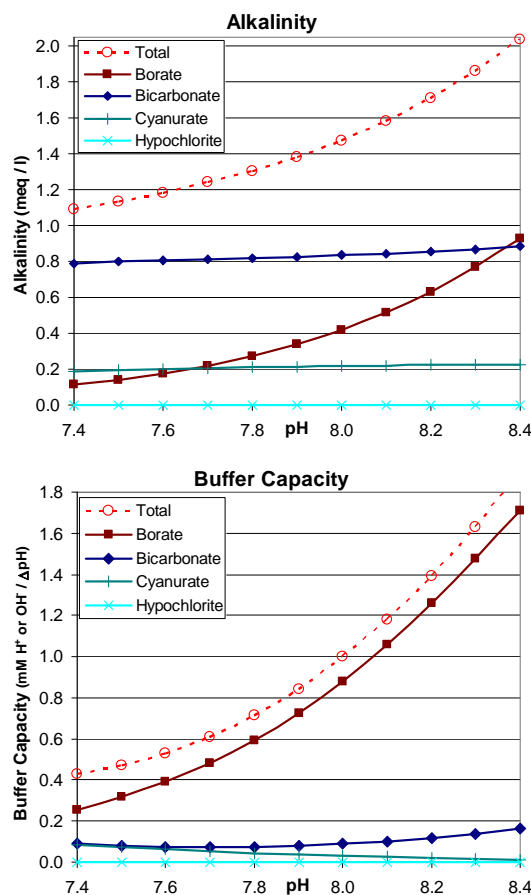

Fig. 1. Buffer capacity vs alkalinity from key acid-base pairs at typical concentrations in a borate-buffered SWC pool at 25 C: 4.62 mM borate (50 ppm B) and 0.32 mM cyanurate (30 ppm CYA). Bicarbonate is fixed at 0.82 mM assuming equilibrium with atmospheric CO$_2$ in a pool with 6,000 ppm NaCl held mostly at pH 7.9. Hypochlorite has little effect despite pKa around 7.4, because of low concentration (< 0.05 mM) in a swimming pool. Alkalinity to end-point pH 4 is given in meq / l and may be multiplied by 50 to approximate ppm CaCO$_3$ equivalents commonly measured using pool test kits. Data points can be derived using pKa values and tools referenced in Table 1. Buffer capacity is most important for pool management, but it is not easily predicted from alkalinity. Borate (at 50 ppm B) provides greater buffer capacity across this pH range than bicarbonate at levels commonly added to pools (up to 2.5 mM).

borate in the companion review (Birch 2013). Also be aware that the units of measurement used in the pool and aquarium fields may differ. For example: ppm Mg^{++} measured by some aquarium kits must be multiplied by 4.12 to yield hardness as ppm $CaCO_3$ equivalents in TH measured by some pool kits.

Don't attempt pool chemistry checks while superchlorinating. Many test reagents suffer interference from oxidation by HOCl or from the volume, salinity and pH change in a sample when HOCl is 'neutralized' by thiosulphate, yielding NaCl and bisulphate. More reliable results will be obtained if tests are conducted at a consistent and low FC level (not always easy to arrange in an outdoor SCW pool with sufficient CYA and FC for reliable sanitation).

The influence of ionic strength and interactions with specific ions present in some pool waters on the readings obtained from various tests is rarely documented. However, the effect can be substantial. For now it is 'the elephant in the room' of pool-water testing, and one reason that practices developed through experience with one pool may not be applicable to another pool with different solute composition. The aquarium industry is ahead of the swimming pool industry in this context, providing test kits calibrated separately for fresh *vs* ocean water (Fig. 2).
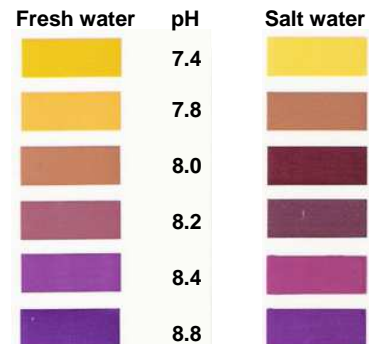
Fig. 2. Colour calibration differences for fresh *vs* (ocean) salt water in the API high-range pH test kit for aquarists. Pool managers face the added challenge of various salt levels preferred by various SWC manufacturers.

3.2 Sodium hypochlorite: Most pool test kits or strips provide a reading for "free chlorine" (FC), which is measured as oxidising power and expressed as ppm Cl_2. In this assay, HOCl, OCl^- and some reversible chlorine complexes such as monochlorocyanurate and hypochloritoborate all have the same oxidising power per molecule as Cl_2. But don't be fooled: all these molecules differ markedly in mass and in other key properties such as sanitizing power and photolability - so we often need to think about their ratios in a measured FC value. A "total chlorine" (TC) reading higher than FC indicates chlorine combined with ammonia (from a high bather load or urination in the pool), and a need for a period of much higher HOCl concentration (superchlorination or shock treatment) to remove the accumulated chloramines by oxidation to N_2 gas and chloride. Shock treatment may never be needed for chloramine removal in an SWC pool with low rates of ammonia contamination, because (i) circulating water is effectively superchlorinated as it passes through the SWC cell; (ii) bromamines are formed as discussed below; and /or (iii) volatile chloramines are driven off through increased aeration during SWC operation, especially in open outdoor pools.

Fig. 3. Percentage of chlorine present as HOCl as a function of pH and temperature, assuming zero ionic strength with HOCl and OCl^- as the only chlorine species present (Sugam and Helz 1976; Sinex 2007). HOCl as a percentage of measured 'free chlorine' is greatly reduced in the presence of CYA, as discussed below.

In aqueous solution, hypochlorous acid (HOCl) exists in a pH-dependent equilibrium with the hypochlorite ion (OCl^-) (Fig. 3). This is important because HOCl is the antimicrobial form, and OCl^- is unstable in sunlight. HOCl is also consumed while doing its work as a sanitizer, and it decomposes to chloride (or chlorate) faster as temperature increases, so it has to be replenished (White 2010).
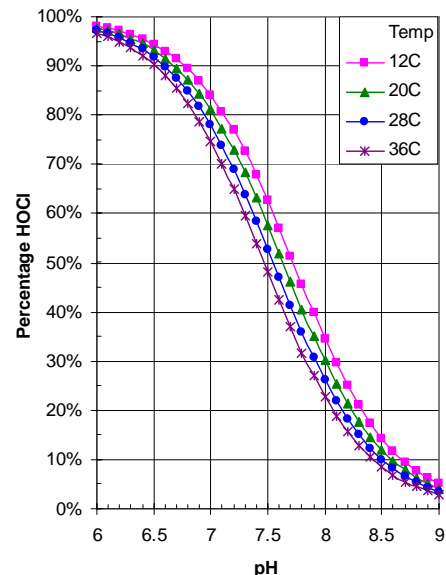
Replenishment of HOCl is conveniently achieved by an appropriate daily period of SWC cell operation. But there are many reasons why a SWC cell may fail at some time to provide the HOCl level needed for pool sanitation. Drinking-water treatment systems typically use 0.2 ppm Cl_2 equivalents (FC), and domestic pools need levels above 0.05 ppm Cl_2 equivalents (as HOCl) for control of planktonic microbes. The available HOCl level can drop because of SWC cell age, insufficient salt concentration, low temperature, increased swimmer or organic load, elevated pH, longer sunny days, or addition of other chemicals that interfere with the SWC cell or complex the chlorine in a form with less antimicrobial activity.

Not all of these causes are easy to correct quickly, or counteract with longer SWC run times. Then you may need to add supplementary HOCl. The supplement with fewest undesired side-effects on your pool chemistry is sodium hypochlorite (liquid pool chlorine or chlorine bleach). The only complication is that sodium hypochlorite solutions have been adjusted to high pH (typically by adding NaOH) to avoid rapid degradation through outgassing of Cl_2.

Although the NaOH concentration in bleach is typically low (<0.05% w/v) you may have to follow up with enough HCl to neutralise the added NaOH and restore your pool target pH.

3.2.1 Salt and HOCl: One more point deserves mention in context of HOCl concentration in salt-water pools. The pKa of HOCl is 7.54 at 25 C in pure water (zero ionic strength), but it declines with increasing ionic strength (Sugam and Helz 1976). Therefore, at any working pH, the ratio of HOCl to OCl^- will be a few percent lower in a salt-water pool (or the working pH will need to be about 0.1 unit lower than in a fresh-water pool for the same effective HOCl concentration) (Fig. 4).

As noted below, this effect can change dramatically in the presence of chlorine-complexing agents such as CYA, depending on the effects of pH (and ionic strength) on dissociation of the chlorine complexes.

3.2.2 Salt and pH: The apparent pK of any indicator dye will decrease with increasing salinity, so a pH-dye comparator calibrated for fresh water will read too high when used to test salt water. A salt pool could be 0.2 pH lower than indicated by a phenol red test calibrated for fresh water (Fig. 5). The extent varies between ionic species in the test solution (Sendroy and Hastings 1929). There is a possibility of further interference through specific ion pairing with divalent cations or borate in pool water, but investigation of this issue has not been reported. Fig. 2 is an example of salinity affecting (metacresol purple) pH indicator calibration.

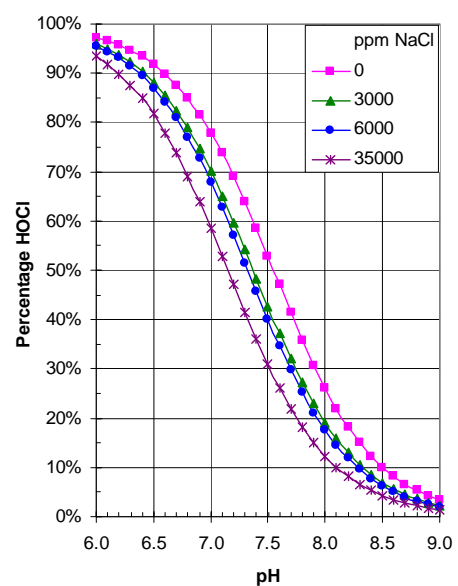To some extent, the effects of ionic strength on

Fig. 4. Percentage of chlorine present as HOCl as a function of pH and ionic strength, assuming 28 C with HOCl and OCl^- as the only chlorine species present (Sugam and Helz 1976; Sinex 2007). HOCl as a percentage of measured 'free chlorine' is greatly reduced in the presence of CYA, as discussed below.
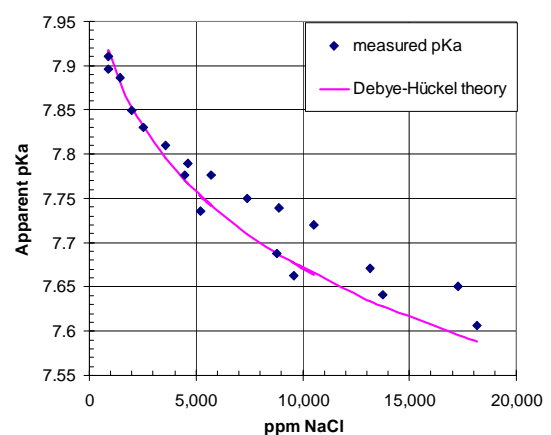
Fig. 5. Effect of NaCl salinity on apparent pKa of phenol red. Data points are from measurements in buffered NaCl solutions by Sendroy & Rodkey (1961). Line is from Debye-Hückel theory with ion-size correction.

colorimetric pH determination and HOCl dissociation cancel out, but this is not necessarily so for all pH-dependent processes in a pool.

3.2.3 Salt and bromide: Another complication arises from the presence of bromide in seawater (and therefore in sea salt used in many salt-water pools). Bromide reacts with phenol red, changing pH indicator properties (Basel *et al.* 1982). More importantly, bromide undergoes a rapid quantitative reaction with HOCl to form hypobromous acid (HOBr) plus chloride (Margerum and Hartz 2002). The sanitizing reactions of HOBr are analogous to those of HOCl (Elsmore 1994; White 2010). Seawater (at 35,000 ppm salinity) contains approximately 67 ppm (0.84 mM) bromine, and in chlorinated seawater the predominant biocide is HOBr (Macalady *et al.* 1977). A swimming pool adjusted to 6,000 ppm salinity using sea water will have around 0.14 mM bromide. Ocean-derived 'pool salt' supplies may have lower proportions of trace chemicals including bromide, as a result of the evaporation and washing steps in their manufacture. A typical analysis provided by one manufacturer indicates Br at 150 mg/kg, which will give about 0.011 mM bromide at 6,000 ppm salinity. In some geographic locations, even drinking water supplies have sufficient bromide for substantial formation of HOBr during chlorination (Richardson *et al.* 2010).

The common FC tests respond to all of the oxidizers listed below, so (to a first approximation) the combined level of $HOCl + OCl^- + chlorocyanurate + HOBr + OBr^- + bromamine = 0.14$ mM at 10 ppm FC, or 0.014 mM at 1 ppm FC. Depending on the salt source and salinity level used in a salt-water pool, HOBr can be a substantial part of the sanitizing hypohalogen after HOCl addition. This may result in better than expected sanitation for several reasons.

Firstly, HOBr gives a less intense colour than HOCl (by a factor of about 2.25 according to Taylor Technologies) with DPD and OT reagents, so you may underestimate the sanitizing hypohalogen level if you use a chlorine comparator. Secondly, the pKa for dissociation of HOBr is 8.66 at 25 C in pure water, so sanitation at pH 8 may be more effective than anticipated (because HOBr remains 82% in sanitizing form, in contrast to 26% for HOCl) (Fig. 6). Thirdly, combined bromine (bromamine) retains much greater oxidative and germicidal activity than chloramine. Bromamines rapidly oxidise organic material, in the process yielding bromide (Johannesson 1960; Elsmore 1994; White 2010). This fast spontaneous reaction generally eliminates any need for superchlorination to remove bromamines, in contrast to chloramines (White 2010). Further interesting effects may occur in photostability of the sanitizer, and in differential loss of halides through volatile disinfection byproducts, as discussed in sections below.
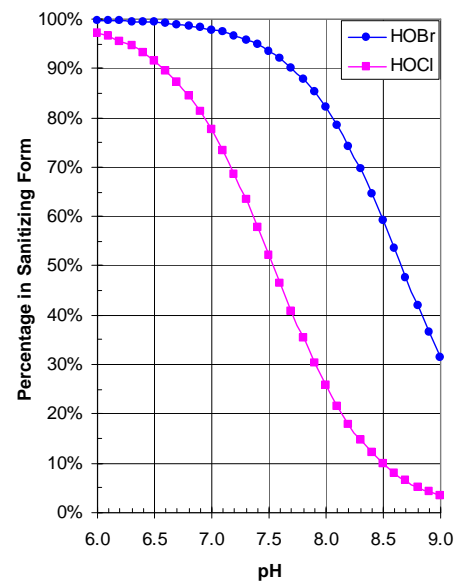

Fig. 6. Percentage of sanitizer present in active (photostable) form as a function of pH assuming 25 C, zero ionic strength and no CYA, based on pK_a values for HOCl and HOBr from Bousher (1987). Values would be slightly lower in a salt-water pool.

3.3 Cyanuric acid (CYA): OCl^- absorbs UV radiation at wavelengths 300-400 nm that are abundant in sunlight reaching the earth's surface, and it is destroyed rapidly by photolysis in strong sunlight (Buxton and Subhani 1972; Pinsky and Hu 1981; Nowell and Hoigne 1992; Cooper *et al.* 2007; Watts and Linden 2007) (Fig. 7).

This is a big problem because it can be hard to maintain a sufficient concentration and even distribution of HOCl for reliable sanitation in outdoor pools. There tend to be wild swings: too much HOCl when and where it is added, and not enough HOCl later or elsewhere in the pool. Continuous replenishment from an operational SWC unit can help, but the unit may not be able to keep up with the rate of photolysis in strong sunlight.

CYA (shown as H_2CY^- in the equation below) forms reversible complexes with HOCl. For example: $2\ OCl^- + 2\ H^+ + H_2CY^- \leftrightharpoons 2\ HOCl + H_2CY^- \leftrightharpoons 2\ H_2O + Cl_2CY^-$ (dichlorocyanurate) (Fig. 8). The chlorocyanurate complexes show practically no photolysis by sunlight at the earth's surface, but they also have little antimicrobial activity (Wojtowicz 1996b). Effectively the CYA provides a buffer of complexed (non-sanitizing) chlorine from which free (sanitizing) HOCl is released to replenish the amounts lost through photolysis in a rapid equilibrium throughout the pool. Overall, the negative effect is that more HOCl has to be supplied to achieve the same free (sanitizing) HOCl level in darkness, but the benefit is that the chlorocyanurate reservoir can sustain higher and evenly-distributed free HOCl levels during daylight hours - until the reservoir is depleted by photolysis of all the released HOCl. The dissociation of chlorocyanurate complexes is not very sensitive to salinity, but it increases with temperature and pH, increasing the proportion of free HOCl but decreasing the amount of photoprotection (Gardiner 1973; O'Brien *et al.* 1974; Pinsky and Hu 1981).
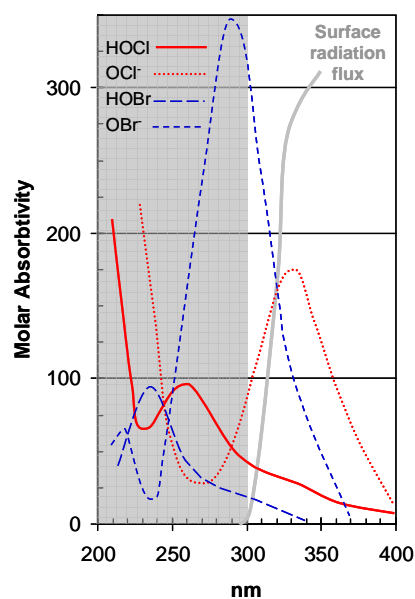

Fig. 7. Absorption spectra of aqueous hypochlorite and hypobromite species, relative to earth surface radiation. Data from Anbar & Dostrovsky (1954), Madronich et al. (1998) and references therein.
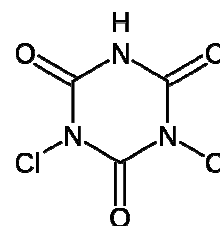
Fig. 8. Dichlorocyanurate. (Image from Wikipedia)

CYA appears to increase the rate of FC decline in indoor pools (Wojtowicz 2004b), and is not recommended for use there.

3.3.1 CYA as a pH buffer: CYA also contributes to pH buffering. At 25 C the pKa of CYA is 6.9 in pure water, and it will be somewhat lower in an SWC pool (the extent of any ion-pairing effect has not been documented). Contribution to buffering is a function of both molar concentration and proximity to pKa. The pKa of CYA is well-suited, but in the usual concentration range around 0.4 mM (50 ppm), CYA will not contribute much to overall pH buffering. Compare this with 4.6 mM of boric acid for 50 ppm boron equivalents. As discussed below, you will <u>not</u> want to increase CYA concentration to achieve stronger pH buffering: this can lead to an impossibly high FC requirement for effective sanitation.

Early SWC manuals indicated that their operation would gradually deplete CYA. High pH and hypochlorite concentration in a SWC cell are ideal for CYA decomposition, especially at a high pool temperature (Wojtowicz 2001a). In practice, CYA declines over a period of months at a rate faster than expected from pool outflows, so its concentration should occasionally be tested and adjusted. Loss of 5-10 ppm CYA / month is commonly observed.

3.3.2 CYA and the HOCl : FC ratio: The chlorocyanurate equilibrium depends on pH in a way that alters the widely-publicised relationship between pH and ratio of HOCl to FC.

In the absence of CYA (or any other compound that forms reversible complexes with hypochlorite), FC measures HOCl plus OCl⁻ (which is far less antimicrobial and far more photosensitive). The fraction present as HOCl drops steeply (from about 78% to 26% in pure water) as pH rises from 7.0 - 8.0 (Fig. 3). Increasing pH, temperature and ionic strength all increase the ratio of OCl⁻ to HOCl (Fig. 4). Therefore a lot of emphasis is commonly put on keeping (non-CYA) pools pH below 7.5, to ensure that measured FC is a reasonable indicator of (sanitizing) HOCl.

In the presence of CYA, FC measures HOCl + OCl⁻ + chlorocyanurates. The fraction present as HOCl depends a lot on CYA concentration (Fig. 9), and far less on pH (Figs. 10-11). The hydrolysis of chlorocyanurate to release HOCl also increases steeply with temperature (Wojtowicz 1996b; Wojtowicz 2004b). Unfortunately, many recommendations about target FC levels for pool operation take no account of CYA concentration. Such recommendations (typically in the range 1 - 5 ppm FC) yield vastly different HOCl levels in pools with different CYA levels - which is not a rational approach to pool sanitation!

Fig. 9. Effect of CYA concentration on sanitizing chlorine (HOCl) concentration at at 10 ppm FC. Calculated in Falk's (2008) spreadsheet using dissociation constants estimated by O'Brien (1972).

But the relationship between CYA concentration and fraction of FC present as HOCl in a swimming pool is not known exactly. The reason for this lingering ignorance is that it is hard to measure HOCl, OCl⁻ and chlorocyanurates independently at the concentrations used in pools. Estimates of dissociation constants for chloroisocyanurates vary between studies, with substantial effects on downstream calculation of HOCl under various conditions (Wojtowicz 1996a). Moreover, there is some evidence for differential effects of temperature on the various constants, but data are scant above 25 C (Pinsky and Hu 1981; Wojtowicz 1996a).

By one interpretation (Falk 2007b), at 28 C and 50 ppm CYA, to obtain 0.1 ppm HOCl requires 8 - 10 ppm FC over the range pH 7 - 8 (Fig. 10). In practice, many SWC systems will struggle to achieve 10 ppm FC over Summer in an uncovered pool. For 0.05 ppm HOCl (a reasonable minimum for reliable sanitation and control of suspended algae in a domestic pool) the corresponding calculations

Fig. 10. Effect of CYA concentration on FC level required to supply sanitizing chlorine (HOCl) at 0.1 or 0,05 ppm Cl₂ equivalents in a pool with 5,000 ppm TDS at 28 C. Data points calculated as in Fig. 9.

indicate a need for 4 - 6 ppm FC with 30 - 50 ppm CYA. Interested readers can explore the modelled CYA : HOCl relationship further using PoolEquations.xls (Falk 2008).
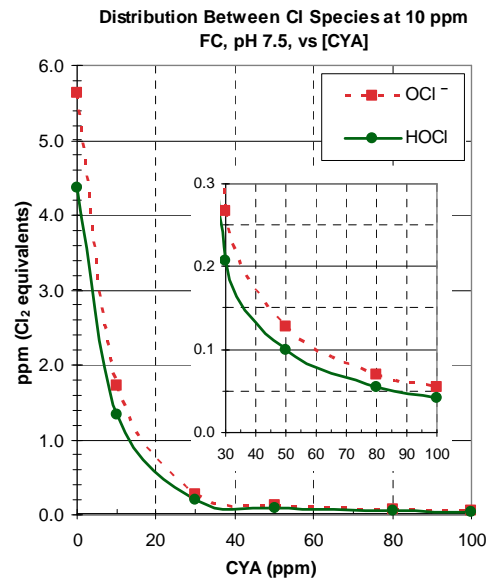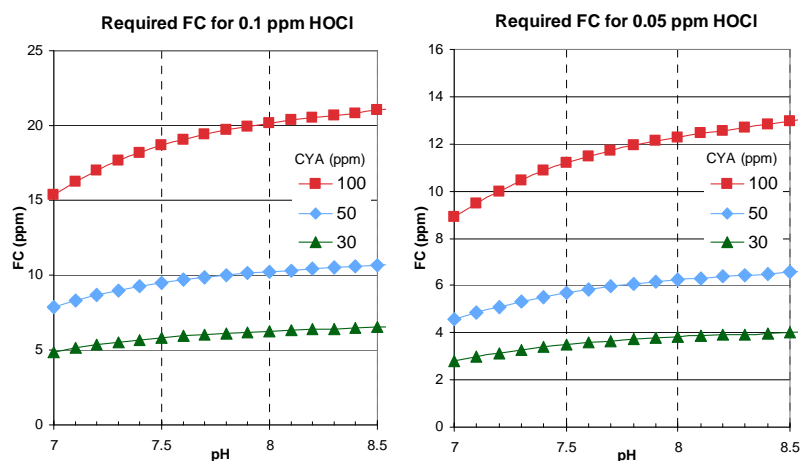
3.3.3 CYA and optimal pool pH: From Fig. 10, and considering only instantaneous HOCl concentrations, with CYA there seems less reason to "fight" a pool that tends to equilibrate near pH 8 (perhaps through SWC activity).

But high pH also increases the ratio of OCl$^-$ to HOCl (Fig. 11). Because OCl$^-$ is more light-sensitive (Nowell and Hoigne 1992) and less microbicidal than HOCl, the trade-off between photodegradation and sanitation will be less favourable at high pH, even in the presence of CYA (Fuchs and Lichtman 1961). More chlorine will have to be supplied to replenish losses through photolysis at pH 8 than at pH 7. The estimated amounts of this increase vary, over the range 1.3- to 3-fold in fresh-water pools (Fuchs and Lichtman 1961; Nowell and Hoigne 1992; Cooper *et al.* 2007). The pH effect will be less noticeable in the presence of bromide (Cooper *et al.* 2007), as discussed in other sections. The absolute losses of sanitizer through photolysis in the presence of CYA increase with temperature, light intensity, daylength, shorter (UV) wavelengths, amount of shallow water (pool SA : vol ratio), pH and presence of bromide. A 3-fold increase in sanitizer loss due to photolysis may be trivial under some conditions (such as a covered pool in Winter), but expensive (in electricity for pump operation) or impractical to replenish from a domestic SWC system during Summer.
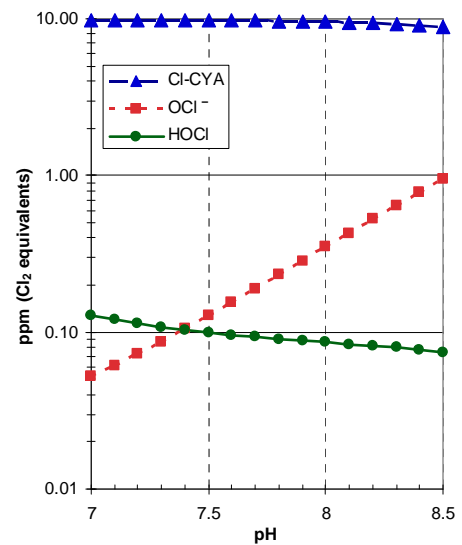

Fig. 11. Components of measured 'free chlorine' in the presence of 50 ppm CYA. Note the logarithmic scale. Data points calculated as in Fig. 8 (at 28 C, 6000 ppm NaCl and 10 ppm FC in this example).

3.3.4 CYA and superchlorination: SWC systems can be effective for clean and safe water at relatively low pool FC levels, because of super-chlorination in the plumbing downstream of the SWC cell. This commonly eliminates the need for periodic chlorine 'shock' treatments needed to eliminate chloramines in non-SWC pools. But control of biofilms in the pool depends on HOCl throughout the pool, and is more challenging than control of suspended microbes (Goeres *et al.* 2004). Algal growth on an SWC pool floor with crystal-clear water and FC levels around 5 ppm for most of the day can be a sign of excessive CYA. If there has been no preceding lapse in brushing or FC levels, it is time test CYA level.

During summer, some pool operators use periodic superchlorination (10 ppm HOCl in the pool water for at least 4 hrs) to help prevent algal films on the pool floor, especially in porous areas such as the concrete between pebbles. This becomes impractical at higher CYA levels (10 ppm HOCl requires >50 ppm FC in the presence of 30 ppm CYA at pH 7.5). CYA will decompose over a period of months in pools. Before replenishing it, consider superchlorinating (preferably in the evening, followed by use of the pool cover) and allowing at least a day for the high free HOCl level to do its work. Some algal species (including cyanobacteria commonly referred to as 'black algae' by pool operators) are relatively chlorine-resistant and able to develop protective surface layers. Once established, these need repeated brushing and high HOCl levels over many days or weeks to control. Spot treatment with 'granular chlorine' is effective to kill algae on the pool floor, but it is important to check whether other components (such as calcium or CYA) in the product are consistent with the target concentration ranges for these components in the overall pool management strategy.

While the SWC approach reduces daily maintenance for chlorine addition, by now it will be clear that SWC pool operators still need (i) target concentration ranges for key pool solutes,

(ii) a strategy for control of algal biofilms and (iii) a maintenance regimen including regular checks of FC and pH; along with brushing, cleaning of filters and periodic checks for scaling in the SWC cell.

3.3.5 CYA and SWC operation: CYA also helps to make the SWC cell an efficient generator of HOCl, with minimal wasted outgassing of Cl_2 gas. Reactions at the electrode surfaces have been summarised well by Falk (2007b). In a SWC cell:

At the anode (positive electrode): $2\ Cl^- \rightarrow Cl_2(gas) + 2\ e^-$
At the cathode (negative electrode): $2\ H_2O + 2\ e^- \rightarrow H_2(gas) + 2\ OH^-$

Chlorine gas dissolves in water (in the cell or downstream plumbing) to give HOCl:
$Cl_2(gas) + H_2O \leftrightarrows Cl_2(dissolved) + H_2O \leftrightarrows HOCl + H^+ + Cl^- \leftrightarrows OCl^- + 2\ H^+ + Cl^-$

The hydrolysis of dissolved chlorine, yielding HOCl, is extremely rapid at low chlorine concentration and pH at or above neutral (as in swimming-pool water). It is favoured by high pH in the electrolytic cell, and under such conditions is virtually complete within 1 sec (White 2010). Other bubbling such as $H_2(gas)$ production in the SWC cell may tend to favour outgassing of Cl_2; but there is a substantial turbulent flow path in which to redissolve any Cl_2 before return to the pool. When your SWC unit is operating, you will probably see bubbling at the pool water returns. If you catch a little of this gas you can confirm that it contains H_2, because it explodes on ignition. Substantial Cl_2 content would make the gas (or at least the heavier-than-air layer) irritating to breathe and bleaching on wet indicator paper.

By rapidly complexing HOCl, CYA helps to avoid potential outgassing of Cl_2 in two ways: (i) it drives the above reaction to the right; and (ii) it avoids high local HOCl concentrations in the SWC cell that might allow $HOCl + Cl^- \rightarrow Cl_2(gas) + OH^-$ (or $OCl^- + H^+ + Cl^- \rightarrow Cl_2(gas) + OH^-$). These reactions to form $Cl_2(gas)$ are favoured at low pH (< 5) and high Cl^- (White 2010). Such conditions may also exist transiently within a salt-water pool, for example if HCl used to counter upward drift in pH is added without rapid mixing.

Overall, during HOCl production from an SWC, pool pH is expected to rise because of the net increase in OH^-. Combining the above equations and noting that $H^+ + OH^- \rightarrow H_2O$:
$2\ H_2O + Cl^- \rightarrow HOCl + OH^- + H_2(gas)$. From the standard oxidation potentials for the half-reactions at the electrodes and the hydrolysis of chlorine, only a low voltage is needed to drive the overall reaction in the desired direction ($E^0 \approx$ -2.5 V) but a high DC current will be needed for sufficient production of HOCl: this is the task of the SWC power supply. For every moleule of H_2 bubbled off, one molecule of HOCl is introduced to the pool. One day someone will work out how to trap all that H_2 and we will use it to run our cars instead of wasting much of the energy used for electrolytic chlorination of our swimming pools.

Provided all of the Cl_2 is indeed converted to HOCl, and all of the HOCl is consumed within the pool, the net OH^- produced in the SWC can be balanced by H^+ produced during the consumption of HOCl. At the same time, the $H_2(gas)$ lost from H_2O during electrolysis is balanced by $O_2(gas)$ lost during HOCl consumption, and the chloride ion concentration is restored. For example, by photolysis: $2\ HOCl \leftrightarrows 2\ H^+ + 2\ OCl^- \rightarrow 2\ H^+ + O_2(gas) + 2\ Cl^-$. Or in complete oxidation of ammonia: $2\ NH_3 + 3\ HOCl \rightarrow N_2(gas) + 3\ H^+ + 3\ Cl^- + 3\ H_2O$.

In reality, such balance is exceedingly unlikely. HOCl will be lost through splashing, backflushing etc; altering the above balance in the direction of increased pH. Sparging the pool with all those H_2 bubbles from SWC operation will also facilitate the removal of any

other dissolved gasses in the pool water (including any dissolved Cl_2 and CO_2). Diverse chlorine-containing compounds will be formed in the pool (Richardson *et al.* 2010) and not all of the associated reactions balance OH^- production in the SWC cell. For example, especially in outdoor pools, volatile compounds like trichloromethane and chloroform formed by reaction of HOCl with nitrogenous and organic matter will be lost as gasses in substantial quantity before they can be completely oxidised by 'superchlorination' in the SWC cell. Indeed, reactions that balance pH through breakdown of many major disinfection byproducts (such as organohalides) are not known (Deborde and von Gunten 2008; White 2010).

Therefore, the upward pH drift commonly observed in SWC pools can be attributed to some combination of (i) unavoidable loss of HOCl with any pool overflow; (ii) outgassing of Cl_2, which is less likely with sufficient CYA; (iii) reactions yielding various compounds from HOCl without stoichiometric H^+ production; (iv) effects of carbonate scale in the electrolytic cell (see Box 2); and (v) increased aeration through the effects of H_2 production and longer pump run-times for SWC operation, causing increased outgassing of CO_2 from bicarbonate added to many pools. The latter process consumes H^+: $HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2(dissolved) + H_2O \rightarrow CO_2(atmospheric) + H_2O$. While outgassing of CO_2 is by no means limited to salt-water pools (Wojtowicz 1995), it is exacerbated by H_2 bubbling and prolonged pump operation in SWC pools. Switching from bicarbonate to borate for pH buffering eliminates cause (v) but not causes (i) - (iv).

So CYA concentration is very important for an outdoor SWC pool. Too little CYA (arguably < 30 ppm) and: (i) the chlorocyanurate reservoir may be too small to sustain an effective HOCl level through hours of sunlight; (ii) loss of some Cl_2 gas may exacerbate the upward drift in pool pH. Borate may help to reduce these undesired effects, but it is expected to be much less effective than CYA based on lower affinity for hypochlorite. When I have used the crude tests above on gas from SWC operation, expelled through the water returns in a clean pool with 20-35 ppm CYA, pH 7.8 - 8.0 and boron around 50 ppm, it has always been positive for H_2 and negative for Cl_2. Under these conditions, effect (ii) was undetectable.

Too much CYA (arguably > 50 ppm) and the SWC may not be able to achieve an effective free HOCl level, even with continuous operation of that electricity-consuming pump. Then you end up buying hypochlorite to supplement the SWC. At higher FC levels, more hypochlorite will be lost with any pool overflow, disrupting the cycle that balances H^+ to OH^- within the pool, and exacerbating the upward drift in pool pH.

Indeed, by reducing the proportion of HOCl lost through photolysis (which balances OH^- production during electrolytic chlorination) and increasing the proportion consumed in reactions that oxidise organic and nitrogenous compounds (which sometimes fail to balance pH); any effective level of CYA may increase the need for HCl addition to balance electrolytic OH^- production. This is unavoidable in practical outdoor SWC pool management.

3.3.6 CYA and HOBr: A complicating factor in a salt-water pool is the likely presence of bromide, as discussed in a previous section. The presence of bromide ions will further reduce the chance of outgassing of Cl_2, by rapid consumption of HOCl to produce sanitizing HOBr. The estimated rate constants for HOCl removal ($M^{-1} sec^{-1}$ at 25 C) are 7.4 x 10^4 with CYA (Matte *et al.* 1990) and 6.8 x 10^3 with bromide (Bousher *et al.* 1986). Key reactions in the elimination of chloramines are presumably even faster (White 2010), under the common assertion that breakpoint chlorination occurs in the SWC. Conversion of HOCl to HOBr does not interfere directly with the anticipated pH balance, because the breakdown reactions of the

hypohalites are equivalent. For example, by photolysis 2 HOBr $\leftrightharpoons$ 2 H$^+$ + 2 OBr$^-$ $\rightarrow$ 2 H$^+$ + O$_2$(gas) + 2Br$^-$ (Farkas and Klein 1948; Macalady *et al.* 1977). The bromide ions remain in the pool to be converted back to HOBr by the next dose of HOCl.

There are counteracting factors in the relative photostability of the two hypohalous acids (Figs. 6-7). HOBr undergoes less dissociation into light-sensitive halite across the pool pH range (Anbar and Dostrovsky 1954), but OBr$^-$ absorbs more than OCl$^-$ in the highest-energy wavelength range (300-320 nm) of sunlight at the earth surface (Madronich *et al.* 1998). The measured half-life of HOBr/OBr$^-$ was longer than that of HOCl/OCl$^-$ under conditions relevant to photodecay in outdoor swimming pools without CYA, by about 1.5-fold at pH 7 or 2.3-fold at pH 9 (Cooper *et al.* 2007). But in the presence of CYA, photolysis of HOBr/OBr$^-$ will be much faster than that of HOCl/OCl$^-$.

Bromoisocyanurates are reportedly formed in swimming pools by reaction of HOBr with CYA (Wojtowicz 2004a) but impractically high CYA levels are required for photostability (Wojtowicz 2001b). Because of the rapid conversion of HOCl to HOBr, the presence of bromide ions can greatly reduce the photoprotection of HOCl by CYA. There are no well-documented experiments, but the increase in photodecay rate could be in the order of 5-fold based on one reported test probably conducted around pH 7.5 (Wojtowicz 2001b). Nothing has been reported about the effects of CYA on germicidal activity of HOBr. The assumption appears to be that lack of photoprotection indicates lack of binding and therefore lack of effect on sanitation by HOBr. This deserves testing, given the prevalence of CYA-treated SWC pools. Bromo-dimethyl-hydantoin derivatives such as BCDMH are sometimes described as 'stabilized bromine', but they do not seem to provide a practical level of photostability in pools (Wojtowicz 2001b).

HOBr with borate reversibly forms complexes that are likely to be photostable. From the stability constants estimated by Bousher et al. (1987), at typical SWC pool concentrations (< 0.01 M B(OH)$_3$ and < 10 ppm FC in the presence of bromide) the hypobromitoborate complex will comprise < 4% of FC; even lower at pH 7.5 (Fig. 12). This is not enough for substantial photoprotection.

It should by now be obvious that with the rise in prevalence of outdoor SWC pools, more work is warranted on effective photostabilizers for HOBr.

The combination of bromide with stabilised chlorine has been envisaged in patent literature as an improved sanitizer (Shim *et al.* 2001). However, the balance of the complex reactions involving hypohalogens, including mutually accelerated decomposition to halates, depends substantially on concentrations of these compounds and ammonia, pH and light intensity (Macalady *et al.* 1977; Richardson *et al.* 1981; Bousher *et al.* 1990; Margerum and Hartz 2002). The chemical equilibrium and rate constants, needed reliably to model the outcomes under pool scenarios, are not all known. Moreover, the bromide content of a salt-water pool may decline in a saw-tooth pattern depending on the pattern of salt addition and loss of volatile by-products, as discussed in Box 1 below.
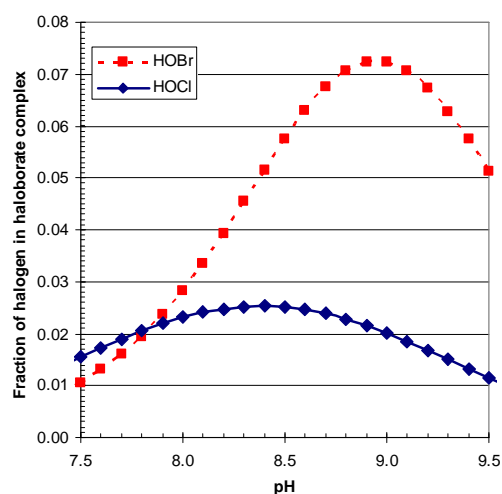

Fig. 12. pH-dependent formation of photoprotected hypohaloborate complex in a pool with 100 ppm borate and 1 ppm 'free halogen' (without CYA), based on pKa values of 9.24 for B(OH)$_3$, 8.66 for HOBr, and 7.54 for HOCl, with stability constants of 68 for B(OH)$_3$OBr$^-$ and 178 for B(OH)$_3$OCl$^-$, as estimated by Bousher et al. (1987).

Because SWC pools operate with diverse organic loads, at diverse salinities achieved using diverse salt sources with diverse bromide contents, they vary markedly in the degree of protection conferred by various CYA levels, at various pH levels. This may help to explain some of the very different observations on this subject from different pool operators. There is no simple test to measure bromide in a pool with a high chloride level, though these two halides can be distinguished using methods such as ion-selective electrodes. A simple test to guide practical responses in individual pools is suggested under "Operational tips".

3.4 Magnesium chloride: This chemical is available in bulk as the hexahydrate $MgCl_2.6H_2O$ used for de-icing, dust control and an equine feed supplement. Food grade material is expensive, but for pool use a technical-grade white product with > 98% purity should be sufficient (~$40 for 25 kg from some farm-supply stores). There should be no smell of ammonia, which is a sign of lower purity. Some SWC manufacturers including Watermaid recommend use at about 0.5 kg / kl = 2.459 mM = 60 ppm Mg^{++} equivalents = 245 ppm "total hardness" (TH, in $CaCO_3$ equivalents). This makes the Na^+ : Mg^{++} ratio in a pool more like sea water. Substituting some Mg^{++} for Ca^{++} in measured TH reduces problems including the formation of hard $CaCO_3$ scale in SWC cells. The Mg^{++} ions may need to be periodically replenished as they are depleted in (softer) scale formation in SWC cells. Another effect that has not been fully explored in swimming pool chemistry is ion pairing with borate and carbonate. The effect is that apparent pKa of these buffers is lowered more than expected from ionic strength alone, in the presence of Na^+, and particularly Ca^{++} and Mg^{++} ions.
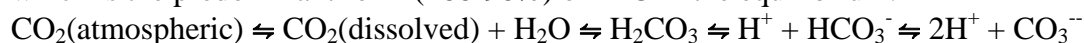
3.5 Sodium hydroxide: If you ever need to increase pool pH (which is extremely unlikely in an SWC pool unless you have added an acid) this is the best chemical for the purpose. NaOH (caustic soda, sold in pure solid form as a drain cleaner) dissociates in water to Na^+ and OH^- ions, which do not complicate other parts of salt-water pool chemistry. If you ever need to add NaOH to increase pH, you can dissolve some of the solid in water, pour it in front of the pool water returns, and allow time for thorough pool mixing with the pump running before re-checking pH. This is much the same method (requiring all the precautions in handling corrosive concentrates) used when adding HCl to reduce pH.

Do not get into a cycle of alternating acid (HCl) and alkali (NaOH) addition for tight pH control. Big swings in pH are a sign of insufficient buffering. Borate, CYA and carbonates can all provide buffering. SWC operation has a tendency to increase pH - so you probably never need to add anything to increase alkalinity. See the discussion below about bicarbonate.

4.0 Things you should <u>not</u> add without careful thought

4.1 Bicarbonate or carbonate: This may be a controversial part of the recommendation to improve the BBB method, because it eliminates one of those Bs (Baking soda).

It is commonly recommended to add sodium bicarbonate (baking soda) or sodium carbonate (soda ash) to pool water, to assist with pH buffering (total alkalinity) or to raise pH. There is a slow equilibrium between atmospheric CO_2 and dissolved CO_2, H_2CO_3 (carbonic acid), HCO_3^- (bicarbonate) and CO_3^{--} (carbonate) ions. The dissolved inorganic carbon (DIC) equilibrium reactions are shown below. The slow reaction is the hydration of dissolved CO_2 to produce carbonic acid. Borate actually catalyses this step, and it might enhance the rate of CO_2 exchange by about 10% at typical pool borate concentrations (Guo *et al.* 2011). At typical swimming-pool pH (7.2-8.1) carbonic acid rapidly dissociates to yield bicarbonate ion which is the predominant form (~88-98%) of DIC in the equilibrium:
$$CO_2(\text{atmospheric}) \leftrightharpoons CO_2(\text{dissolved}) + H_2O \leftrightharpoons H_2CO_3 \leftrightharpoons H^+ + HCO_3^- \leftrightharpoons 2H^+ + CO_3^{--}$$

At 25 C, the apparent pKa for the production of bicarbonate from CO_2 is 6.35 in pure water or about 6.0 in a salt pool. To achieve sufficient pH buffering strength, pools are commonly adjusted to far above the equilibrium levels of bicarbonate. For example, in equilibrium with atmospheric CO_2, rain water at 25 C is expected to have pH 5.65 and DIC ($CO_{2(aq)}$ + H_2CO_3 + HCO_3^-) at 0.014 mM. The equilibrium with atmospheric CO_2 is slower and more complex in large bodies of water; with effects such as salinity, vertical temperature and concentration gradients, contact with solid carbonate species, biological carbon cycling and various feedback phenomena (Roether 1980; Mook 2000). In a swimming pool without a solid carbonate reservoir, the level of bicarbonate at equilibrium with atmospheric CO_2 will depend substantially on temperature, salinity and pH. Provided that pool pH is controlled by means other than (bi)carbonate addition, the equilibrium concentration can be estimated using data and equations presented by Mook (2000) and Millero et al. (2006) to remain below 1 mM across the conditions normally encountered in swimming pools (from ~0.1 mM in fresh water at pH 7.2 to ~1 mM with 6,000 ppm salt at pH 8.0; at 25 C and 350 ppm atmospheric CO_2).

Ocean surface water has near-saturating [CO_3^{--}], which is replenished from geological sources such as the dissolution of limestone. There the reaction: CO_2(dissolved) + CO_3^{--} + H_2O ⇋ 2 HCO_3^- results in much higher levels of bicarbonate (~1.8 mM) and pH (~8.1) at equilibrium with atmospheric CO_2. Many swimming pool operators also adjust calcium (CH) and/or carbonate (CA or TA) levels to achieve a "water balance" near saturation for $CaCO_3$. In most SWC pools, water circulates over $CaCO_3$ scale deposited in the electrolytic cell. Thus SWC pool carbonate chemistry usually resembles that in the ocean, with pH drifting to an equilibrium above 8 in a system open to both atmospheric CO_2 and solid $CaCO_3$ (see Box 2).

Swimming pools commonly have added bicarbonate around 2 mM (to achieve TA around 100 ppm $CaCO_3$ equivalents). There are two problems with the addition of bicarbonate (or carbonate) as a pool pH buffer. One problem is that carbonate salts are relatively insoluble. Calcium and calcium-magnesium carbonates are the major causes of scale formation at high pH, and in SWC cells. Some SWC units use methods such as polarity reversal to reduce scale build-up, but these can be overwhelmed at high Ca^{++} or CO_3^{--} levels.

The other problem is that in pools with added bicarbonate or carbonate, the DIC equilibrium reactions naturally flow to the left, towards equilibrium with atmospheric CO_2. With aeration (which is enhanced by SWC operation) to drive outgassing of excess dissolved CO_2, this inexorable flow towards equilibrium consumes protons (H^+ ions) causing upward drift in pool pH. To replace the protons consumed by outgassing all of the CO_2 from 1 kg $NaHCO_3$ requires only 1.3 litres of 33% (w/v) HCl. But the bicarbonate-buffered pool operator faces an endless cycle of acid addition to replenish the lost protons and bicarbonate addition to restore buffering strength (commonly measured as TA). Volatility of one of the components is a big disadvantage in the bicarbonate buffering system, which is not the case for borate and cyanurate buffers. So ideally, an SWC pool operator would like to achieve sufficient pH buffering through a combination of borate at a safe level for swimmers, CYA to a level that does not preclude effective sanitation, and bicarbonate in equilibrium with atmospheric CO_2.

Taking those levels as borate 100 ppm (9.25 mM), CYA 50 ppm (0.39 mM), bicarbonate <1 mM (in equilibrium with the atmosphere), in a pool with NaCl at 6,000 ppm (103 mM), Mg at 60 ppm (2.5 mM), pH 7.5 - 8.0 and 25 C, the water will likely be non-corrosive to pool hardware, without any added calcium; and it will provide workable pH buffering without any added carbonates. Note that the trick of aerating to increase pH actually depends on driving CO_2 outgassing from added bicarbonate back towards equilibrium with atmospheric CO_2: it

will not work in a pool already at CO_2 equilibrium. If for some strange reason you needed to increase pH in an established borate-buffered SWC pool, NaOH addition would usually be the best choice to avoid interference with other elements of pool chemistry.

Box 1: So why does pH keep rising in a borate-buffered SWC pool?

In at least some geographic areas, pH will continue to drift upwards in a borate-buffered SWC pool, long after the cumulative amount of added HCl has completely countered the effects of any previously-added bicarbonate. Under these conditions, the SWC-mediated pH rise can not be due to outgassing of CO_2, and with at least 30 ppm CYA it seems unlikely to be due to outgassing of Cl_2 in the SWC cell. Although the chloride concentration throughout a salt-water pool satisfies one requirement for $HOCl + Cl^- \rightarrow Cl_2(gas) + OH^-$, it is hard to envisage conditions that would cause sufficiently low pH (<5) for long enough to drive substantial outgassing of Cl_2 from HOCl in the pool (White 2010). This leaves HOCl loss through pool outflows, HOCl reactions that do not balance OH^- production in the SWC cell, and carbonate scale reactions (see Box 2), as plausible mechanisms. The rate of pH drift is typically proportional to SWC operation time (which increases both water flow over solid $CaCO_3$ in the electrolytic cell and the potential for unbalanced OH^- production in the cell).

Every molecule of HOCl lost through pool overflow (or outgassing of Cl_2) effectively removes one H^+. At 10 ppm FC (0.14 mM Cl_2 oxidising equivalents, so less than 0.14 mM HOCl), a maximum of 16 ml of HCl (33% w/v = 9.05 M) is needed to compensate for each kl of pool outflow (e.g. from 25 mm of rain into an 8 x 5 m pool). Many domestic SWC pools require more than 100 ml of added HCl per week (and a litre per week is not unusual), so there must be causes in addition to pool overflow.

Chlorination results in diverse disinfection byproducts (White 2010), some of which are volatile (Richardson *et al.* 2010) and many of which are not known to decay through reactions that balance OH^- production in the SWC cell (Deborde and von Gunten 2008). Indeed, some organochlorines are produced much faster at high chlorine concentrations used for chloramine elimination (White 2010). The composition of byproducts may vary between salt-and fresh-water pools (Beech *et al.* 1980), with brominated products expected from pools using sea salt (Deborde and von Gunten 2008, White 2010). It is clear from the studies cited above that volatile compounds like NCl_3 and trihalomethanes are formed in substantial quantities, and lost as gasses especially from outdoor pools. Even monochloramine is sufficiently volatile to be lost as a gas from an aerated outdoor pool (Holzwarth *et al.* 1984). While some of the reactions yielding volatile byproducts consume OH^- ions (like the haloform reaction that produces trihalomethanes from ketones), in other cases the loss of Cl or Br moieties in gasses is effectively accompanied by loss of H^+ ions, which would have formed if oxidation of these byproducts progressed to the release of halide ions in the pool.

While many factors can be envisaged to affect flux (which has not directly been measured), this mechanism has the potential to be a major driver of overall H^+ depletion in some pools. There is a continuous rain of organic matter into outdoor pools, probably explaining why pH continues to climb in the absence of bathers (another source of N and C compounds). The magnitude will vary between pools and over time, depending on local factors such as the type and proximity of nearby trees in relation to prevailing winds. Use of a pool cover may help, but much of the organic matter that falls on the cover still ends up in contact (and reaction) with pool water around the edges of floating covers. Capture of organic material in filters through which chlorinated pool water is pumped provides an ideal reaction matrix.

It makes sense to reduce the total organic load and exposure time (e.g. by prompt removal of leaves and cleaning of filters), to reduce both HOCl consumption and H^+ depletion. In practice the upward pH drift is then managed by regular pH testing, and timely addition of HCl to keep pool pH within the chosen working range. Coincidentally this adds chloride ions, which are needed for electrolytic production of HOCl, but gradually depleted through formation of volatile organochlorine compounds. Because bromide ions are lost in volatile disinfection byproducts, but not replenished during pH adjustment, the Br^- : Cl^- ratio in an SWC pool is expected to drop progressively below that in the source 'pool salt'.

4.2 Calcium salts: Calcium carbonate is the major form of scale to build up on SWC cell electrodes, requiring troublesome cleaning and/or shortening cell life. Perhaps counter-intuitively, Ca^{++} solubility is increased by higher atmospheric CO_2, in open equilibrium. This is because increased CO_2 decreases pH and the concentration of dissolved CO_3^{--} in favour of HCO_3^-; and $Ca(HCO_3)_2$ is far more soluble than $CaCO_3$ (http://en.wikipedia.org/wiki/Calcium_carbonate). But in swimming pools where pH and DIC are adjusted far from equilibrium with atmospheric CO_2, addition of HCO_3^- will also increase CO_3^{--} and potential for $CaCO_3$ precipitation. In a pool at 25 C and 5,000 ppm salinity with 1 mM HCO_3^-, based on solubility and dissociation constants from Mook (2000) for $CaCO_3$ (4.74×10^{-8}) and HCO_3^- (3.29×10^{-10}), the maximum Ca^{++} level before precipitation of $CaCO_3$ is about 14 mM Ca^{++} (CH 1400 ppm) at pH 7 or 1.4 mM Ca^{++} (CH 140 ppm) at pH 8. These values (approximations ignoring supersaturation and interactions with Mg^{++}, $B(OH)_4^-$ or other ions in the pool) are about twice those in pure fresh water, because salinity increases solubility of $CaCO_3$ more than it increases concentration of CO_3^{--}. Thus salt-water pools can be slightly less prone to scaling in the pool, but they have an Achilles heel in the SWC cell.

If you find soft white flakes settling in the pool, inspect the electrolytic cell for build-up of scale. A small amount of soft scale washing back to the pool is common and harmless. But if a hard layer covers the electrode, scaling can become an autocatalytic process (which increases temperature in the SWC cell and is enhanced at high temperature and pH in the cell). It also reduces the efficiency of chlorine production, and can progress to a level that damages the cell, so follow the manufacturer's instructions about timing and methods of cleaning that do not themselves severely shorten cell life.

One theory is that you need to add calcium to avoid damage through leaching out of pool concrete. But some calcium is almost invariably present in pool fill water (except rain water) and it will leach from the surfaces of any new concrete pool into the water. So unless you are draining and refilling with rainwater, addition of calcium to an SWC pool is likely to be counter-productive. If you increase CH (Ca^{++} concentration expressed as ppm $CaCO_3$) above 60 you will simply increase scaling in the SWC cell until that process reduces CH to below the problem level for the cell. Even SWC units that use methods such as polarity reversal to reduce scale build-up can be overwhelmed at high calcium levels. Avoid products like calcium chloride (water hardener) and calcium hypochlorite (granular chlorine).

Great emphasis is sometimes put on an 'index' of 'water balance' calculated from measured temperature, pH, ionic strength (generally estimated poorly as TDS - assuming a pure NaCl solution), CH and TA. These calculations derive from work by Langelier (1936) to estimate the saturation point for $CaCO_3$ in water under various industrial conditions, because a little precipitation of $CaCO_3$ can help to protect surfaces from some forms of corrosion, but too much precipitation of $CaCO_3$ (excessive scale formation) causes other problems such as

blockages in water systems. But Langelier's brief was to reduce pitting in cast-iron water pipes, a far cry from the challenge of ideal solute composition for a SWC swimming pool!

In swimming pool context, the usual calculations of a '$CaCO_3$ saturation index' are far from accurate because they ignore factors such as ion-pairing with borate and effects of other solutes in the pool (Wojtowicz 1998). Also in this context, $CaCO_3$ saturation is far from a perfect indicator of the various types of 'corrosiveness' that might be relevant to different pool types (depending, for example, on pool wall coatings and composition of the plumbing). Roman concrete baths and aqueducts have lasted thousands of years without supplementing water Ca^{++}. There is no strong indication from experience that any calcium saturation index is important in modern pool concrete etching (Powell 1997; Falk 2007a).

In fact, concrete is damaged by the formation of $CaCO_3$, through reaction of carbonic acid with bonding agents including calcium silicate hydrates. The risk depends on the composition of the cement (or plaster or grout) and on physical factors such as porosity, which depend on both composition and technique when laying the concrete (Lewis 1995; Fibertex Co. 2003; L&M Construction Chemicals 2006). Hopefully the concrete pool surface was treated during construction to minimise penetration by carbonic acid. Even so, it makes more sense to reduce carbonic acid concentration in SWC pool water (by use of borate buffer to allow reduced total carbonate level, and by avoiding low pH) than to add calcium salts in any effort to avoid etching of pool concrete.

Most concrete pools have an overflow drain, typically set about 60 - 90 cm below the wall capping. Do not plug this drain in an effort to reduce loss of pool chemicals with overflow during the wet season. Concrete around the top and outside of the pool wall is probably not designed for constant exposure to salty pool water. Seepage into this vulnerable concrete through prolonged over-filling may lead to serious corrosion problems in the concrete and metal reinforcing, and eventual structural failure.

As mentioned above, magnesium chloride may be added to SWC pools to make subsequent SWC cell cleaning easier. Magnesium can also substitute for calcium in contribution to total water hardness. If the protection from 'balanced water' is primarily from a protective surface coating of $CaCO_3$, then $MgCO_3$ or other low-solubility salts may be similarly effective. Whether it makes sense to measure TH (most test strips), or CH (by titration methods), or both, or neither, in routine SWC swimming pool maintenance is moot.

Box 2: More about optimal pH range for a pool

Low pH is a greater risk than low Ca^{++} for corrosiveness of pool water towards any exposed metals in the pumping system, and towards well-installed concrete. Lower Ca^{++} and carbonate concentrations also reduce the tendency for excess scale formation at higher operating pH. Therefore, an SWC-pool operator using low CH (< 100 ppm $CaCO_3$ equivalents), along with 30 - 50 ppm CYA and 50 - 100 ppm borate for buffering, may prefer a working pH range around 7.8 - 8.2 (where borate buffers better). Metal corrosion is electrochemically less favoured at higher pH, and borates may also assist the passivation of metal surfaces (Schubert 2011). Higher pH will enhance any side benefits mediated by the borate ion. Conversely, precipitation of insoluble carbonates is more likely at higher pH.

There are many simultaneous chemical reactions in any pool. Most of these reactions affect pH, and are affected by pH. Under some conditions, the consequence is that a pool tends to equilibrate at a particular pH.

Calculations based on carbonate chemistry indicate that at 25 C water containing 6,000 ppm salinity, in open contact with the atmosphere and calcite, is expected to equilibrate at pH 8.1 - 8.2 with CA around 82 ppm. The equation (corrected from section 9.5.3 in Mook 2000) is:

$$(K_0*K_1/h + 2*K_0*K_1*K_2/h^2)*(P_{CO2})^2 + (K_w/h - h)*P_{CO2} - 2*K_{cal}*h^2/(K_0*K_1*K_2) = 0.$$

P_{CO2} is taken as 0.000355 atm. Values for K_0, K_1, K_2, K_w and K_{cal} at any temperature and salinity can be calculated using formulae from Millero *et al.* (1995, 2006) and Mook (2000); with the equation then solved by iteration for equilibrium pH ($-\log_{10}h$). The assumptions of this model may be challenged if there are sources of calcium and/or carbonates other than $CaCO_3$ and atmospheric CO_2 (as added by some pool operators). More soluble forms of carbonate scale (such as high-magnesium calcites) will increase the equilibrium pH and CA. While solubilities of the various forms of carbonate scale that form in electrolytic cells under various pool chemistries are unknown, it seems unlikely that there will be a substantial carbonate residue with solubility higher than six times that of calcite (Morse *et al.* 2006). Under the pool conditions specified above, this gives an expected equilibrium at pH 8.3 - 8.4. The equilibrium calculated from carbonate reactions should not be anticipated if pH is otherwise manipulated, for example by unbalanced OH^- production accompanying SWC.

If an 'equilibrium pH' is reached, within a workable range for pool management (arguably up to pH 8.2), it may be sensible to operate there rather than perpetually fighting the pool by adjustment to a generic recommendation about 'optimal pH' (typically around pH 7.5). As noted above, attempts to maintain a pH below 8.1 in a SWC pool with $CaCO_3$ scale in the electrolytic cell (which is a normal situation) are fighting an equilibrium predicted from carbonate chemistry. Whether increased loss of sanitizer at a higher pH ends up costing more than HCl usage to maintain a lower pH will depend on many environmental and economic factors (daylength and light intensity, borate and bromide concentrations, organic load, temperature, pool cover type and usage pattern, aeration, SWC cell cost and life, SWC chlorination rate, target FC level -- which depends on CYA level, automatic and manual FC boost thresholds, electricity cost, HCl cost, supplementary bleach cost, time cost for monitoring etc). Other considerations such as risk of staining are mentioned in other sections.

More likely an open SWC pool will continue to drift upwards in pH into an unacceptable range (well above pH 8.2) without stopping at any apparent 'equilibrium pH'. So it is more common for SWC pool owners to find that they settle into a fairly predictable rate of HCl addition (such as 'my pool consumes on average 1 l of HCl per week throughout Summer' or 'my pool consumes about 25 ml of HCl for each hour of SWC cell operation'); with a wary eye on conditions that can change that usage rate, and regular checks that pH is being maintained in the desired working range.

If there is no carbonate scale in the system, it may prove better to work to a target around pH 7.5. IF loss of volatile byproducts is unaffected by pH, no more acid will be required over time at pH 7.5 than at pH 8 to balance OH^- production in the SWC. (You can test this big IF by monitoring HCl use over time at different target pH levels in your own pool, with as few other seasonal variables as possible). There may be a benefit at pH 7.5 vs pH 8 in effective sanitizer dose (area under the HOCl + HOBr concentration vs daylight time curve) from the same SWC regimen, which may help in control of algal biofilms. Just be careful when adjusting pH not to overshoot with too much acid: use an acid-demand test to estimate the required amount and add this in several stages with pH tests in between. The capacity of borate to buffer against pH decrease becomes lower as we move further below its pKa, and the equilibrium concentration of buffering bi/carbonate species also declines with pH.

Ben Powell (1998) has provided a useful practical analysis of cautions before deciding to

adopt a higher pH working range for a swimming pool. Anyone who has swum in the ocean knows that pH 8 is not a cause of skin or eye irritation. It is sometimes argued that working pH needs to be in the easily-distinguished colour transition range of the most commonly-used pool pH indicator dye. But this is putting the cart before the horse. Phenol red used in many pool kits suits a working range of pH 6.8 - 7.8. Other dyes suit other working ranges: cresol red for pH 7.4 - 8.4 or metacresol purple for pH 7.8 - 8.8 (Senese 2001). Kits with matching comparators are available from several major pool-water test manufacturers, and are also widely used by salt-water aquarists (Fig. 2). The complication that calibration depends on ionic composition of the tested solution is discussed in a previous section. Some people find narrow-range pH paper easier to read, but beware the potential for interference from bleaching by HOCl. Resolution from any visual test is unlikely to exceed +/- 0.2 pH units. A glass-electrode pH meter with 0.1 pH resolution is becoming a realistic option, as the cost of a meter with calibration buffers approaches that of a quality pool-water test kit.

Unfortunately, multiple pH scales are in use which differ by more than 0.1 pH unit under common test conditions (Sigel *et al.* 1991; Waters and Millero 2013). Interpreting advice about pH-dependant pool phenomena at this resolution requires consideration of which pH scale and calibration method is being referenced - but this is rarely explicit.

*4.3 Metal ions and algaecides***:** Regular brushing, combined with a sustained HOCl level above 0.05 ppm Cl_2 equivalents, typically prevents any visible algal development in a pool. However, a lapse in these measures, particularly during hot sunny weather with increased bather or leaf load, can allow more resistant species such as cyanobacterial 'black algae' to gain a foothold. A more serious lapse may allow a green algal bloom in the water. Then a lot of supplementary chlorine or an algaecide treatment is likely to be needed (along with more brushing and possibly flocculation and vacuuming the settled debris to waste) to restore order. While copper (in the form of cupric ion, Cu^{++}) at about 1 ppm is an effective algaecide, it also interferes with delivery of HOCl from an SWC, by accelerating the decomposition of chlorine (or HOCl) into hydrochloric acid and oxygen: $2\ Cl_2 + 2\ H_2O \rightarrow 4\ HCl + O_2$ (or $2\ HOCl \rightarrow 2\ HCl + O_2$). Other pathways of hypohalous acid decay, including halate formation, are also catalyzed by compounds like CuO (Liu *et al.* 2012).

Some SWC manufacturers recommend copper treatment in desperation for treatment of algal outbreaks. Continuous SWC operation may then be needed until the copper is depleted. High carbonate levels will accelerate depletion via insoluble $CuCO_3$. Various reactions between copper ions and hypochlorous acid can also form insoluble salts; e.g.: $CuCl_2 + 2\ H_2O \leftrightharpoons Cu(OH)_2 + 2\ HCl; 2\ Cu(OH)_2 + 4\ HOCl \rightarrow 2\ CuCl_2.Cu(OH)_2 + 2\ H_2O + O_2$. Flocculent precipitates may be removed by settling and vacuuming to waste.

Some pool sanitiser formulations are intended to provide effective concentrations of both Cu^{++} and HOCl, but this approach is harder to manage with SWC systems. Staining from metal oxide formation becomes an increased risk at higher pH (and higher oxidising HOCl concentration) - conditions which also prevail locally in the SWC cell. Adding copper algaecide to a pool with a working pH above 7.8 may create more problems than it solves.

Quaternary ammonium algaecides can consume hypochlorite through formation of dangerous gasses including chloramines or nitrogen chloride. Polyquat algaecides are sometimes claimed not to deplete pool chlorine, without reference to independent scientific tests. Like most organic compounds, polyquats are oxidized by HOCl. Oxidation is faster during superchlorination (and in the SWC cell). This reaction depletes HOCl, as reported by some

polyquat users (www.troublefreepool.com/poly-quat-question-t939.html). Likewise complexes such as copper polyacrylate are claimed to overcome some limitations of free ionic forms (Patent US6387415), but data on interactions with HOCl are scarce (and would be needed over sufficient time for loss of the organic moiety while leaving the metal ions).

Hypohalous acids are the most effective, broad-spectrum algaecides (Adamson & Sommerfeld 1980) and there is little evidence of synergy with other approved pool biocides (Fitzgerald & DerVartanian 1969). Local super-chlorination after brushing, by rubbing with a trichlor puck or by applying a layer of 'granular chlorine' over the affected area with circulation off, can be effective against algal films. For SWC systems, granular calcium hypochlorite has a disadvantage of added calcium ions. Granular trichlor (with borate in some products) is effective, provided you can manage the consequent change to CYA (and borate) concentration. Magnesium hypochlorite has appeal for SWC pool use, but it does not seem to be available commercially and there are conflicting reports on stability.

Sometimes pool maintenance requires a choice of the 'lesser of two evils'. For example, in an area prone to 'black algae' in Summer, the most effective approach might be to treat once or twice during the problem season with a 'granular chlorine' distributed over the pool floor. With circulation off, this gives very high chlorine levels around the dissolving granules, killing the biofilm bugs. Then manage the side effects: exclude swimmers until the FC level is safe (which may take days if a lot of chlorine was added and CYA levels were high). If calcium hypochlorite is used, be ready to clean scale from the SWC cell until calcium levels are depleted. Or if CYA (and borate) levels have fallen below the target range, it may be preferable to use 'trichlor' (or 'hy-tech') granular chlorine products, to avoid Ca^{++} addition.

Borate forms complexes with ions of metals including Cu at much higher affinity than Na, Mg or Ca (Bassett 1980), but it is not clear how this affects the above activities of Cu relevant to algaecidal activity, chlorination or staining in swimming pool scenarios. Reports that "copper borates" are very insoluble, unless accompanied by elemental analysis of the precipitate, need to be interpreted with the possibility in mind that other products such as $Cu(OH)_2$ were formed in the reaction mixtures.

4.4 Sulphates: Sulphate (sulfate) is more prone than other pool anions (like chloride or carbonate) to form expanding crystals under suitable conditions (Lamond and Pielert 2006). So sulphate increases the risk that evaporation at small cracks in a concrete pool will form crystals that force the cracks to widen. In a concrete pool, avoid products like sodium bisulphate (dry acid) and magnesium sulphate (Epsom salts).

4.5 Trichlor or dichlor: While the HOCl is consumed, the CYA remains in your pool; so unless you need to replenish CYA these products should be avoided. Small amounts rubbed or sprinkled onto individual algal colonies will not measurably alter pool CYA levels.

5.0 Operational tips

A pool-maintenance strategy that does not make sense in terms of underlying chemical principles is unlikely to be efficient or effective. But no great knowledge of chemical theory is required to follow a simple and effective maintenance strategy. Anyone can enjoy and maintain a well-designed domestic SWC pool by following a few simple guidelines.

1. Keep salt levels and any SWC cell adjustment at the maximum safe level recommended by

the manufacturer. During summer, in a pool with CYA, you will likely need maximum available chlorine production from the SWC to achieve an effective free HOCl level. Doing this by prolonged operation at a lower SWC setting will increase the cost of electricity, because a typical single-speed pool-water pump consumes much more than the electrolytic cell. For the same reason, it is false economy to install a SWC system at the 'lower limit' of capacity for the pool. If you pay for electricity, the cost for prolonged pump operation will soon outweigh the 'saving' from the smaller SWC system.

It is worth considering a multi-speed pool pump. Single-speed pool pumps typically operate well into the zone of diminishing return (Enine 2007), to deliver continuously a high flow rate needed only occasionally by the pool manager. Back-pressure in the filter rises with increasing flow rate, and is typically a key factor limiting the flow rate at high pump speeds. In such cases, half of the peak pump speed can deliver more than half of the peak flow rate. The lower flow rate may be more than sufficient for filtration and chlorination, at below half of the electricity consumption rate. Chlorination rate will typically be undiminished: most cells show optimal efficiency at a flow rate below that from a single-speed pool pump. Filtration can be more efficient, but requires longer to process the pool volume. Therefore, running costs may be minimised by using a lower pump speed for a longer time to achieve sufficient filtration and improved chlorination; using higher speeds only when needed for backwashing a filter, vacuuming or operating a pool cleaner. Just be sure that the pump speed used is sufficient to avoid any build-up of hydrogen gas from the SWC cell, even when a dirty filter slows water flow. Depending on overall system plumbing, this typically requires a water flow of 80-160 litres per minute through 40 mm pressure tubing. Check the specifications for your particular chlorinator. There should be a stream of tiny bubbles in the exiting water flow, and no expanding gas bubble at the top of the SWC cell during operation. Also check that the water returns in the pool are directed to maintain good mixing throughout the pool. This generally involves pointing 'eyeball' outlets below horizontal. Where noise is an issue, the quieter operation of multi-speed pumps at low speed may also be appreciated.

2. Use boric acid (at 50 - 100 ppm boron) for the convenience of buffering against rising pH from SWC operation (and some side-benefits through formation of complexes between borate ions and metals, divalent cations, hypochlorite etc). Advise people not to drink your pool water (more than a cup per day).

If you use boric acid (at 50 - 100 ppm boron) do not add bicarbonate (or carbonate). They will merely increase the problem of rising pH, through outgassing of CO_2 accompanied by H^+ consumption until your pool returns to equilibrium with atmospheric CO_2. Even so, you will probably need to add HCl periodically to counter rising pH from unbalanced OH^- production in the SWC cell.

3. Use reliable pH and FC tests regularly. A working pH range from 7.4 - 7.8 is fine, and will typically be maintained by regular addition of HCl (about once a week depending on local conditions). HOBr is likely to be a substantial fraction of the free sanitizer in many SWC pools, and it retains far more activity than HOCl at higher pH. So you might consider a higher working pH range like 7.8 - 8.2 for enhanced borate buffer strength (especially if your pool equilibrates in this range). If you do this, be aware that you need to adjust other elements of 'pool chemistry' accordingly (use a pH test that spans your working range; be alert to increased loss of sanitizing chlorine under sunlight; avoid copper algaecides - these may precipitate as stains; avoid calcium products - these may precipitate as scale). Anywhere across this pH range, you do not need to add calcium or bicarbonate to raise CH or TA factors, or otherwise adjust 'water balance' to minimise 'corrosive potential'.

4. In an outdoor pool, use CYA at 30 - 50 ppm to provide a reservoir of chlorine that can

replenish losses through photolysis by sunlight. Note that this requires an increase in FC to provide the same instantaneous concentration of sanitizing free HOCl. Typically you will need 4 - 6 ppm FC at the end of the SWC cycle (about the limit for many domestic SWC systems). At this CYA level, 8 - 12 ppm FC is not excessive, and may be needed to control algal biofilms. Even with the protective effects of CYA, FC will be depleted by photolysis, and depletion will be faster at high temperature (which increases the hydrolysis of chlorocyanurate to HOCl) and high pH (which increases the ratio of photolabile OCl^- in equilibrium with HOCl). This relationship is complicated by the bromide content in many SWC pools. The chemistry is not resolved enough for reliable modelling, but you can do a simple practical test.

If your clean pool shows a dramatic (> 90%) drop in FC over the course of a sunny day (with no other activities to add or deplete HOCl), it is a good candidate for addition of CYA to a final concentration of 30 - 50 ppm (and a working pH around pH 7.5). If this does not help, it is likely that your pool bromide content is resulting in HOBr as the major sanitizer. Running the SWC cell from late afternoon may be your best strategy, to maximise the daily period of effective sanitizer concentration (especially if you get cheaper electricity at night and can run your pump then without annoying your neighbours).

5. Consider the addition of $MgCl_2$ to about 2.5 mM (60 ppm Mg^{++} equivalents), to reduce the difficulty of cleaning scale formed on the SWC cell electrodes (and some possible side-benefits through substitution for Ca^{++} when CH is kept low). Do <u>not</u> add any calcium products unless pool CH is below 60 ppm.

6. Take account of organic load (particularly bather load and cleanliness), which with longer and warmer days can have a dramatic effect on chlorine consumption in the swimming season. Train your swimmers to shower first and not urinate in your pool. Prefer a sun shirt to sun cream. Remove leaves promptly. Brush the pool floor and walls regularly to disrupt formation of algal films. In summer, increase SWC and filter operation times as necessary to maintain FC, and be alert that pH drift may increase. You may never need to 'superchlorinate' to eliminate combined chlorine (because this is accomplished in the SWC cell if the rate of combined chlorine formation is not excessive).

In an outdoor pool during summer, periodic superchlorination may help to prevent algal films on the pool floor, but it requires high chlorine doses to be effective in the presence of CYA (10 ppm HOCl would require >70 ppm FC at 50 ppm CYA and pH 7.5). At higher CYA levels, it can take a many days for FC to decline to a swimmer-friendly range after superchlorination. An unpleasant bitter taste and stinging eyes are common effects of excessive FC levels.

Spot treatment with 'granular chlorine' is an option to kill algae on the pool floor, if other components (such as calcium or CYA) in the product are consistent with your target concentration ranges for these components, or if you can manage their side effects.

7. Most pool owners find that some kind of 'automatic pool cleaner' is worthwhile compared to regular manual vacuuming or scoop-netting of debris from the pool floor. Just be sure that the cleaner is designed not to damage your pool surface type. An effective cleaner may even reduce the need for manual brushing, or allow you to focus manual brushing on areas not sufficiently accessed by the machine: commonly the steps, tight corners and some walls.

8. Keep leaf filters clean. Organic matter consumes HOCl, driving pH up in the process. Regularly check for build-up of scale indicating it is time to clean out the SWC cell, and for pressure rise indicating the need to backflush any sand filter. Follow the manufacturer guidelines for these routine maintenance procedures on your specific pool equipment.

9. To stay in the intended working ranges, you will occasionally need to replenish the chemicals mentioned above, in proportion to loss through splashing, backflushing or overflow of pool water after rain. But don't add any other chemical to your pool without very careful thought! Effective management of pH and HOCl (and/or HOBr) levels really are the keys to a 'trouble-free pool'. Any additional chemicals probably confer no benefit (except to those who sell them) and may cause problems (to you in pool maintenance).

10. Adjust your maintenance to suit local conditions. For example, in areas with a wet summer, check and replenish salt levels more frequently to ensure that NaCl concentration stays in the optimal range for HOCl production in the SWC cell. In areas with a dry winter, a pool cover may extend the swimming season, and save costs through reduced water loss, SWC and filter operation times.

Table 2 shows recommended working ranges for some key variables in (domestic) outdoor, borate-buffered, salt-water chlorinated swimming pools, based on the analysis provided in previous sections.

Enjoy your pool.

Table 2. Suggested Operating Range for Outdoor SWC Swimming Pools*

Variable	Unit	Range
Free Chlorine	ppm Cl_2 equivalents	6 - 12[†]
pH	- $\log_{10}$ [H^+]	7.4 - 8.2[Δ]
Cyanuric Acid	ppm Cyanuric Acid	30 -50
Borate	ppm Boron equivalents	50 - 100
Calcium Hardness	ppm $CaCO_3$ equivalents	60 - 100
Magnesium Hardness	ppm $CaCO_3$ equivalents (in TH)	250 - 400
NaCl	ppm NaCl	SWC Manufacturer Specification
Combined Chlorine	ppm Cl_2 equivalents	NA[‡] (0)
Total Alkalinity	ppm $CaCO_3$ equivalents	NA[‡] (40-150)

* Statutory requirements prevail in the event of conflict.

[†] Spot treat algal colonies using granular chlorine as required.

[Δ] Prefer HCl over 'dry acid' to reduce pH (adds Cl^- not SO_4^{2-}).

[‡] Not applicable (typical levels are indicated, but measurement and adjustment are not recommended). SWC operation will gradually deplete excess Ca^{2+} (by scaling on the electrode) and drive CO_3^{2-}/HCO_3^- towards equilibrium with atmospheric CO_2. Do not add more of these chemicals to a borate-buffered pool.

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