Suggestions for Improvement to 2009 CPO Handbook
by Richard A. Falk, 3/30/10

The 2009 "CPO® Handbook, National Swimming Pool Foundation®" with front cover title "Pool & Spa Operator™ Handbook" is very impressive (in the following sections I will simply refer to the Handbook). It is well organized, in full color, has many charts and examples, and a lot of very good information. The suggestions for improvement below are in no way an indication of the quality of the handbook. They are solely suggestions for improvement to make it even better.

Overall Suggestions
The Handbook appears to have been printed using inks that do not withstand rubbing. It's OK with moisture directly, but not with the pressure, heat and moisture combination from a finger. It behaves somewhat like an inkjet print or newsprint, even though the pages appear glossy. Given the use of the Handbook for reference, it would be better to have it printed using printing technology that would withstand smudging better.

Most of the detailed suggestions in the sections below are based on certain missing or incorrect items in the Handbook. I detail these in the following Trouble Free Pool forum web post with links to detailed references. I will not repeat those in this document.

Certified Pool Operator (CPO) training -- What is not taught

In the sections that follow, I quote existing and replacement text in indented paragraphs using ~~strikethrough~~ for deleted text and blue for added text.

Chapter 2. Regulations & Guidelines

ASSOCIATION OF POOL AND SPA PROFESSIONALS (APSP)
p. 18, 1st column – add the following to "The standards that apply to pool operators are:" section.

- ANSI/APSP-11 Standard for Water Quality in Public Pools and Spas
-

Chapter 4. Pool Water Contamination

NON-FECAL ILLNESSES – Pseudomonas aeruginosa
p. 40, 2nd column – mention something about how this bacteria can rapidly form biofilms. See Todar's Online Textbook of Bacteriology (or other numerous sources).

This is important because this bacterium must be killed quickly before it gets a chance to form such biofilms. Having the sanitizer too low for an extended period of time (more than an hour or so) can make it much harder to eliminate this bacterium. Perhaps the following is sufficient (note also the extra text that I have deleted).

> *Pseudomonas* grows in warm water and is more commonly associated with rashes from poorly maintained spas than swimming pools. The Spa & Therapy Operations chapter reviews the challenges for operators to maintain proper water chemistry in a spa. If the concentration of disinfection dips below proper operating levels, the environment becomes perfect for *Pseudomonas* growth. *Pseudomonas* also readily forms biofilms on surfaces that make it much more difficult to disinfect. This is why it is sometimes referred to as "Hot Tub Rash." Surrounding damp areas can also be can provide optimum growth conditions such as decks, benches, and drains. Normal disinfectant levels are sufficient to control *Pseudomonas.*

Trihalomethanes (THMs)
p. 46, Photo 4-6 – the water looks very cloudy and pale green. I suggest finding a better example of an indoor pool with good ventilation.
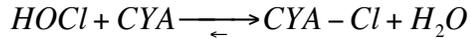
Chapter 5. Disinfection

CHLORINE CHEMISTRY
p. 48, 1st column – after "Hypochlorous acid is stable enough to maintain a residual concentration in the water over hours or even days" add "if there is no exposure to sunlight or high bather load."

> The most common disinfectants used to treat swimming pool water release "chlorine" (hypochlorous acid). Hypochlorous acid effectively kills or inactivates pathogens and algae. It also oxidizes (chemically destroys) other materials from the environment or users.   The terms "hypochlorous acid" and "chlorine" are often used interchangeably. Hypochlorous acid is stable enough to maintain a residual concentration in the water over hours or even days if there is no exposure to sunlight or high bather load. It also quickly inactivates almost all pathogens.

p.48, 2nd column – the diagram showing chlorine added to the water forming HOCl is misleading because it is not clear that the "By-product" when Cyanuric Acid (CYA) is present in the water can have most of the chlorine attached to it. I think the best way to show this is with an additional diagram right after the one the Handbook shows as "$XCl + H_2O$ ..." with the following (the formula is taken from ANSI/APSP-11 – I can't make that formula blue, but clearly it is added and not something already in the Handbook).

> When Cyanuric Acid (CyA), aka stabilizer or conditioner, is present, most of the chlorine is bound to CyA.
>
> $$HOCl + CYA \xrightleftharpoons{} CYA - Cl + H_2O$$
> Hypochlorous Acid + Cyanuric Acid ←→>> Chlorine bound to CYA + Water

(the text portion and be cleaned up to line up under the equation as was done in the handbook for the other equation). The main point to emphasize is the arrows that show that the bulk of chlorine is bound to CYA. This will be covered in more detail in a moved section on Cyanuric Acid (CYA) that should come right after the section on Hypochlorous Acid.

The following paragraph near the top of the 2nd column on p. 48 needs to be changed as follows.

> The hypochlorous acid, ~~and the~~ hypochlorite ion, and chlorine bound to CYA (if present), together, are called free chlorine (FC). Free chlorine is the reservoir of chlorine in the water that ~~is~~ can be made available for disinfection.   The HOCl is between 60 to 100 times more effective than the OCl⁻ at killing microorganisms and is over 100 times more effective than the chlorine bound to CYA. Chlorine testing measures FC and does not distinguish between the HOCl, ~~and~~ the OCl⁻ and the chlorine bound to CYA.

If preferred, one can use the term "chlorine reserve" instead of "reservoir of chlorine". Unfortunately, the historical terminology in the 1974 O'Brien paper used "free chlorine" to describe hypochlorous acid and hypochlorite ion while "reservoir chlorine" was FC plus chlorine bound to CYA. However, since the FC test is really a test for reservoir chlorine, I believe the above paragraph is reasonable since everyone today really associates the measurement of the FC test as what is meant by free chlorine. It really makes sense since the chlorine bound to CYA is released as hypochlorous acid gets used up, very similar to the shift from hypochlorite ion to hypochlorous acid (just slower, but still very fast). If one doesn't want to go this route and instead want free chlorine to mean only hypochlorous acid and hypochlorite ion, then one needs to explicitly say that chlorine testing doesn't really measure FC but rather reservoir chlorine. I think that's more confusing, personally.

Hypochlorous Acid

p. 48, 2nd column – Table 5-1 needs to say that this only applies when there is no CYA in the water. I'll give another table that can be used when CYA is present, but that will be in another section after this one called "Cyanuric Acid". Also, the chart from Lowry isn't quite correct though it isn't far off (it looks like he did not account for ionic strength). I get the following table results using temperature-dependent equilibrium constants and accounting for ionic strength (525 ppm TDS with 300 ppm CH and 100 ppm TA). I've also added a row showing 9.0 pH for consistency though really anything outside of the 7.0 to 8.0 range probably isn't necessary.

% Active HOCl	pH	% Less Active OCl⁻
~~97~~ 96	6.0	~~3~~ 4
~~91~~ 90	6.5	~~9~~ 10
~~76~~ 73	7.0	~~24~~ 27
~~66~~ 63	7.2	~~34~~ 37
~~50~~ 47	7.5	~~50~~ 53
~~33~~ 30	7.8	~~67~~ 70
~~24~~ 22	8.0	~~76~~ 78
~~9~~ 8	8.5	~~91~~ 92
3	9.0	97

Table 5-1. Active Chlorine vs. pH at 86ºF (when no CyA is present) ~~(reference R.W. Lowry, Pool Chlorination Facts)~~

I think that the entire section on Hypochlorous Acid needs to start out saying that the foregoing discussion applies when there is no CYA in the water. Either that or the hypochlorous acid and Cyanuric Acid discussions need to be combined somehow.

Cyanuric Acid

This is a moved section that should be added after Hypochlorous Acid and before Free Chlorine (i.e. move it out of the Disinfectants section and into the Chlorine Chemistry section). If one wants to take the parts about CYA that have to do with how to add it to the pool and put them in another CYA section under Disinfectants, then that would be fine, but the CYA effect on chlorine has to be done here under Chlorine Chemistry

> ~~The free chlorine (FC) provided by unstabilized chlorine compounds can be protected from the effects of UV light in sunlight by the addition of cyanuric acid (CyA), sometimes called stabilizer.~~

> Cyanuric Acid (CyA), sometimes called stabilizer or conditioner, is a compound that is either added directly or added indirectly via stabilized chlorine products (to be described later in the section on Disinfectants) and is typically used to protect chlorine from the effects of UV light in sunlight.

> Without CyA, half of the chlorine in water can be destroyed by sunlight in less than one hour. As a result, free chlorine (FC) concentrations can drop ~~below the recommended minimum~~ to near zero, risking disease transmission between people. When CyA is present in the water in sufficient concentrations, the FC residuals remain three to ten times longer than in water without CyA.

As described in the section on Chlorine Chemistry, CyA binds to most of the chlorine significantly reducing the hypochlorous acid (HOCl) concentration. The disinfection, oxidation and algae inhibition rates are significantly reduced when CyA is present. Fortunately, it takes a very small amount of hypochlorous acid to kill many pathogens. The CyA therefore moderates chlorine's strength while providing a reserve or reservoir of chlorine. This can help to reduce the oxidation of swimsuits, skin and hair and may reduce the production of some disinfection by-products (such as nitrogen trichloride). Cyanuric acid also buffers chlorine against changes in pH as shown in Table 5-2.

Cyanuric acid itself has no disinfection properties. ~~For optimum chlorine protection, the CyA level should be maintained between 30 and 50 ppm (mg/L).~~ In commercial/public pools where high bather load is typical, the CyA level need not be higher than 30 ppm (mg/L) as the chlorine usage from bather load will generally exceed that lost from sunlight. In residential pools that typically have lower bather loads, higher CYA levels up to 100 ppm can result in lower chlorine loss from sunlight. Many state and local codes limit the use of CyA, especially at indoor facilities. In the event of a diarrheal fecal accident occurs in water that contains CyA, higher chlorine concentrations or longer contact times may be needed to inactivate cryptosporidium, a common cause of water illness. The Pool Water Contamination chapter has more information.

CyA functions as a stabilizer for free chlorine and does not stabilize bromine. Excessive levels of CyA may lead to an increased risk of algae and lower disinfection and oxidation rates. The most common method of reducing CyA concentration is to partially drain and replace water with fresh potable water.

At the usual levels of FC and CyA in pools, the amount of hypochlorous acid, and therefore the rate of disinfection, oxidation and algae inhibition, is proportional to the FC/CYA ratio (see Table 5-3). As the CyA level rises, the FC would need to be increased to maintain the same level of disinfection, oxidation and algae inhibition.

(note that this paragraph could be moved to the Disinfectants section, if desired) Depending on the size of the CyA granule, it may dissolve slowly taking as long as two days to go into full solution. Suspending CyA in a perforated plastic container into the surge or atmospheric tank allows for dissolution without closing the facility to users. Broadcasting cyanuric acid directly into the pool may cause a delay in reopening the pool to users to allow the CyA to dissolve completely.

The following table, similar to Table 5-1, should be near the Cyanuric Acid section that follows the Hypochlorous Acid section. I call it Table 5-2, but later tables in this

chapter need to be renumbered. Since the amount of active chlorine in the presence of CyA is very temperature dependent and since I am more confident in the O'Brien equilibrium constants at 77F than in the temperature-dependent numbers (based on activation energies from Wojtowicz), I use 77F below to be conservative.

% Active HOCl	pH	% Less Active OCl⁻	% Less Active CyA-Cl
6.5	6.0	0.2	93.3
3.3	6.5	0.3	96.4
1.9	7.0	0.6	97.5
1.6	7.2	0.8	97.5
1.4	7.5	1.4	97.2
1.3	7.8	2.6	96.1
1.2	8.0	3.9	94.9
1.0	8.5	10.7	88.3
0.8	9.0	25.5	73.7

Table 5-2. Active Chlorine vs. pH at 77ºF with 3 ppm FC and 30 ppm CyA

In addition to the above table, there should also be the following table which demonstrates how the active HOCl level is related to the FC/CYA ratio.

FC ppm	CyA ppm	FC as % of CyA	Active HOCl ppm
4	20	20	0.098
8	40	20	0.101
3	30	10	0.042
6	60	10	0.043
9	90	10	0.043
1.5	30	5	0.020
3	60	5	0.020
5	100	5	0.020

Table 5-3. Active Chlorine vs. FC/CYA ratio at 77ºF and pH 7.5

In fact, the entire point that is made about the strong dependence of HOCl concentration vs. pH when CyA is not present is a moot point since even at a pH of 9.0, the HOCl concentration with 1 ppm FC is around 0.03 ppm which is the same as the HOCl concentration when the FC is 7% of the CyA level. At normal pool pH of 7.5 with an FC as low as 1 ppm, the water is over-chlorinated with over 10 times more HOCl than found in a pool where the FC is 10% CyA level. As noted earlier, this leads to faster oxidation of swimsuits, skin and hair, may increase corrosion rates and may produce more disinfection by-products such as nitrogen trichloride.

Free Chlorine

The following paragraph in the 1st column on p. 49 needs modification as indicated:

Free Chlorine (FC) is the ~~active available disinfectant in the water~~ reservoir of chlorine in the water that can be made available for disinfection. It is the sum of the HOCl, ~~and~~ OCl⁻ and chlorine bound to CYA (if present) and it is the chlorine determined by the DPD test as discussed in the Chemical Testing chapter.

FC = HOCl + OCl⁻ + CYA-Cl
Free Chlorine = Hypochlorous Acid + Hypochlorite Ion + Chlorine bound to CYA

Combined Chlorine

The last sentence in the paragraph in the 2nd column of p. 49 should be modified as follows:

… It is important to know how much of the total chlorine is due to CC because CC is not an effective disinfectant, just as it is important to know the CyA level since CYA-Cl is also not an effective disinfectant.

The last paragraph in the 2nd column of p. 49 talks about the problems of combined chlorine and that chloramines evaporate and are irritating. There is no distinction between the different chloramines, which is unfortunate because some are far worse than others. Since there are no readily available poolside tests to distinguish between the different chloramines, this approach is understandable, but some day I believe a more balanced approach will be taken. For example, the hypochlorous acid odor threshold is around 0.28 mg/L so use of CyA can keep this amount below this threshold level (as shown in Table 5-3). The monochloramine odor threshold is around 0.65 mg/L though is typically not a more noticeable problem until up to 5 mg/L (typical drinking water has 1-2 mg/L monochloramine in many water systems). Dichloramine has an odor threshold of around 0.1 to 0.5 mg/L while it is nitrogen trichloride that is by far the most irritating with an odor threshold of 0.02 mg/L. I could not find the odor threshold for chlorourea, but it becomes an eye irritant at double the concentration of monochloramine that irritates with a clear reaction at 4 mg/L.

In the oxidation of ammonia by chlorine, the amount of nitrogen trichloride is roughly proportional to the hypochlorous acid level (all else constant) so the use of CyA can significantly reduce the amount of very irritating nitrogen trichloride. I don't expect this to be in the Handbook until this is validated by experiment and in real pools, but the theoretical chemistry from the breakpoint chlorination models (including Jafvert & Valentine 1992) show this effect.

DISINFECTANTS

The Table 5-2 "Characteristics of Disinfectants" has the second row below the headings say "% Active Strength", but the description in the 2nd column of p. 50 says "Active Chlorine Percentage". This needs to be reconciled.

The "% Active Strength" and the "% Available Chlorine Content" are incorrect for Sodium Hypochlorite. The "% Active Strength" or "Active Chlorine Percentage" is often quoted as a weight percentage of NaOCl for bleach but often quoted as a volume percentage of Available Chlorine (known as "Trade %") for chlorinating liquid. The relationships among these three quantities is as follows:

Weight % Available Chlorine (aka ACC) = Trade % / Specific Gravity = Weight % NaOCl * 0.9525

So, 12.5% (Trade %) chlorinating liquid with a density of 1.16 has a % Available Chlorine of 10.8% and a Weight % NaOCl of 10.3%. 6% (Weight % NaOCl) bleach with a density of 1.08 has a % Available Chlorine of 5.7% (and is listed as such on Clorox Regular bleach bottles) and a Trade % of 6.2%. The Trade % is a useful number because, being by volume, it allows simplified calculations such as 1 gallon of chlorinating liquid in 10,000 gallons yielding 12.5 ppm FC or 1 gallon of bleach yielding 6.2 ppm FC. These subtleties are probably beyond what should be in the Handbook.

The "pH Effect in Water" in Table 5-2 on p. 50 should have an "*" that says the following:

> *The effect on pH is for addition of the chlorine product to the water, but the consumption/usage of chlorine is acidic so the hypochlorite sources of chlorine are closer to pH neutral. The net pH rise from sodium hypochlorite comes from the excess sodium hydroxide (aka caustic soda or lye). Any additional pH rise is typically from the outgassing of carbon dioxide due to the Total Alkalinity (TA) being too high.

Unstabilized Disinfectants

The following statement in the first paragraph in this section in the 1st column of p. 51 should be changed:

> … Unstabilized disinfectants, with no separately added CyA in the water, are very sensitive to the UV radiation in sunlight.

Sodium Hypochlorite

The following paragraph at the end of the 1st and start of the 2nd column on p. 51 needs to be changed as indicated. Basically, the use of hypochlorite does not necessarily lead to a large rise in pH after chlorine consumption/usage is taken into account. It depends on the amount of excess lye. Also, one should not use only CO_2

for pH control of hypochlorite as the TA will rise over time and ultimately need a strong acid (such as Muriatic Acid) anyway.

>The hydroxide ion (OH$^-$) reacts with the pool or spa water to raise the pH initially upon addition, though this effect is reversed when the chlorine is broken down by sunlight or oxidizes ammonia or an organic compound. The strength as used at the pool or spa facility is 10% to 12% available chlorine content (ACC) and has a pH between 9 and 14. The pH ~~must~~ may need to be corrected by the addition of an acidic material such as muriatic acid ~~or the injection of CO₂~~. The amount of acid needed to control pH depends on the pH of the sodium hypochlorite. Sodium hypochlorite raises the water's total dissolved solids (TDS) by adding sodium (Na+) and chloride (Cl-) ions to the water. Sodium chloride does not have any negative effect on disinfection. Unfortunately, there is no easy way to differentiate between TDS due to salt and TDS due to less desirable contaminants. Therefore, dilution to lower TDS is recommended.

>… ~~The usual pH correction with muriatic acid (31%) involves using between 10 and 16 fluid ounces for every one gallon of sodium hypochlorite.~~

At 100 ppm TA and assuming 10,000 gallons, one gallon of 12.5% (Trade %) sodium hypochlorite with a pH of 12.5 would raise the pH from 7.5 to 8.15 upon addition and would raise the FC by 12.5 ppm. However, when this chlorine gets used/consumed by breakdown in sunlight or oxidation of ammonia or organics, the pH would drop down to 7.52 (if there were no carbon dioxide outgassing). The 10 to 16 fluid ounces of acid as indicated would initially have the pH be 7.80 to 7.60, respectively, BUT after chlorine consumption/usage, the pH would drop to 7.31 to 7.21, respectively. If one has the TA be lower to reduce the amount of carbon dioxide outgassing, then one can use far less acid. The only acid truly required is the amount to counteract the "excess lye" which in the example I gave is only 0.25%. 12.5% chlorinating liquid with a pH of 13.0 has a higher "excess lye" level of around 0.80% while a pH of 13.5 has 2.5% 6% Clorox Bleach has a pH of 11.9 and only 0.06% excess lye so results in minimal pH rise over time.

In my own pool, I add almost 4 gallons of 12.5% chlorinating liquid per month, but only need to add 2 cups (16 fluid ounces) of muriatic acid (31.45%) per month on average. My pool is covered except for 1-2 hours each day and longer on weekends so the rate of outgassing of CO2 is fairly low. I could lower the acid usage even more by having a lower TA (mine is around 120 ppm due to fill water with 80 ppm TA) since only around half of the rise is due to "excess lye".

It is very important to explain that the overall net pH rise from hypochlorite sources of chlorine is small unless the pH of chlorinating liquid is rather high – 13.0 or higher. If the pH is rising over time, then the TA is very likely to be too high and should be lowered as this will reduce the amount of acid that needs to be added over time. This is very counter-intuitive since TA buffers pH, but it is a true fact that

TA is a source of rising pH itself due to increased carbon dioxide outgassing (whose rate varies as the square of the TA).

Other chlorine types (calcium hypochlorite, lithium hypochlorite, chlorine gas)

The following table should go somewhere in the section describing the different sources of chlorine.

Type of Chlorine	FC	CYA	CH	Salt	Typical Dosage per 10,000 gallons per FC
Trichlor	10	6	0	8	14.6 oz. (109 grams)
Dichlor	10	9	0	8	24.1 oz. (181 grams) for Dichlor Dihydrate
Calcium Hypochlorite	10	0	7-8	10-12	20.7 oz. (155 grams) for Cal-Hypo 65%
Sodium Hypochlorite	10	0	0	17	102 fluid oz. (800 ml) for 12.5% (trade) chlorinating liquid
Lithium Hypochlorite	10	0	0	17	38.3 oz. (286 grams)
Chlorine Gas	10	0	0	8	13.4 oz. (100 grams)
Saltwater Chlorine Generator	10	0	0	0	N/A

Table 5-5. Net effect (in ppm increase) of adding 10 ppm Free Chlorine (FC) and in the case of salt, having that chlorine consumed/used.

Dichlor (NaCl$_2$C$_3$N$_3$O$_3$)

One needs to be careful about implying pH neutrality with Dichlor since in reality it is net acidic since chlorine usage/consumption is acidic. The following is on p.54, 2nd column. Note also the added "d" in "formulated". I am deleting the info on the effect of Dichlor on FC and CYA because this is now in the "Net effect…" table I just wrote above.

Sodium dichlor is unique among the disinfectants because its pH is almost neutral, being about 6.7. However, since the consumption/usage of chlorine is acidic, using Dichlor as a source of chlorine can have the pH drop if the TA is not high enough. It will also lower the TA over time if not adjusted with chemicals.

… ~~One pound (454 grams) of anhydrous dichlor or dichlor dihydrate per 10,000 gallons (37,843 liters) will provide about 7.4 ppm (mg/L) or 6.7 ppm (mg/L) of chlorine, respectively. This dosage will add about 7 ppm (mg/L) or 6 ppm (mg/L) stabilizer, respectively, for these two products.~~ Manufacturers have formulated dichlor with inert ingredients. …

Hypobromous Acid (HOBr)

The following modification starts on p. 55, 2nd column. Though it is true that CyA does not bind with bromine, it can still shield lower depths of water and in practice bromine pools with CyA don't lose bromine as quickly as described.

> The HOBr is destroyed by sunlight much like HOCl. About half of bromine can be destroyed by sunlight in 60 to 90 minutes. Cyanuric acid does not bind to bromine though can still shield lower depths for partial protection of HOBr from ultraviolet sunlight destruction. Once a brominating product is used, bromide will remain in the water. Adding a stronger oxidizer like a chlorinating chemical will cause the bromide to be oxidized to hypobroumous acid, consuming the hypochlorous acid. Therefore, cyanuric acid no longer stabilizes the chlorine once bromine has been used, since hypobromous acid will be present in place of hypochlorous acid as follows:

Chapter 6. Water Balance

The introductory paragraphs to this section describe water as the universal solvent. Though it is true that water that is not saturated with calcium carbonate will tend to dissolve calcium carbonate in plaster (cement), grout, etc., the water itself does not cause metal corrosion. Metal corrosion occurs primarily from an oxidizer (dissolved oxygen or chlorine), conductivity from dissolved salts, and low pH. Using CyA in the water significantly lowers the active chlorine (hypochlorous acid) concentration thereby significantly lowering the active oxidizer level and reducing the rate of corrosion. Some of the most rapid corrosion we've seen on pool forums has been with indoor saltwater chlorine generator (SWG) pools that did not use CyA and that had higher FC levels (3-5 ppm) where stainless steel would corrode within a year in spite of proper pH and saturation index levels. I'd leave the introductory section as is, but explain the distinction between dissolving plaster/grout vs. metal corrosion later.

On p. 61, 1st column, the recommended pH range is wrong and should be corrected as follows. I'm not sure why the recommended range was listed as 7.2 to 7.4 except perhaps the misconception that a lower pH is needed for much greater sanitation. As described earlier, this is not the case as pools with CyA are over-chlorinated while those with CyA are chlorine buffered against pH changes.

> The recommended pH of pool/spa water is slightly alkaline (7.2 – ~~7.4~~ 7.8). The pH of tears from a human eye is about 7.5. To assist in user comfort, the ideal range for pH is 7.4 to 7.6. ~~The acceptable range is 7.2 to 7.8.~~

In the "pH Related Pool Problems" Illustration 6.2 on pl 61, high pH should note under "Other Problems" metal staining as it is usually high pH that precipitates metal ions in the water. I don't know why it says "Chlorine Loss" at Low pH – why is there more chlorine loss at lower pH? If anything, the loss from sunlight is higher at

higher pH since the half-life of hypochlorite ion is around 20 minutes while that of hypochlorous acid is around 2 hours and 10 minutes (at pH 7.5 the balance between these two is a half-life of around 35 minutes). These are all half-lives at shallow 1 cm depths. In practice, overall half-life is longer since at 4-1/2 feet it's around 50 minutes (the chlorine in shallow depths somewhat shields lower depths). This all assumes no CyA in the water.

Also, I would remove "Chlorine inefficiency" from the "Other Problems" of High pH. As noted elsewhere, with no CyA in the water there is usually too much chlorine while with CyA in the water the drop from 7.5 to 8.0 is only 15% in active chlorine (hypochlorous acid) level.

Control of pH

The dilution of Muriatic Acid barely changes its very low pH. Full-strength muriatic acid (31.45% Hydrochloric Acid) has a pH of around -1.0 while diluting 50% to half-strength only increases the pH to -0.7. The acid is still very, very strong. The wording on p.61, 2nd column should be changed as follows.

> … If muriatic acid is used to lower the pH, it ~~is typically diluted with 50% water before it is fed into the pool or spa water~~ should be added slowly over a return flow, preferably at the deep end of the pool. To prevent pooling, the sides and bottom of the pool where the acid was added may be lightly brushed. This prevents the potential of corrosion in pool or spa equipment. Full-strength muriatic acid (31.45% Hydrochloric Acid) can fume so add the acid downwind or use half-strength that may fume less. If you prepare your own half-strength, remember the phrase "if you're doing what you ought'a, add the acid to the water" and should never add water to acid as it can splatter from a high heat of dilution.

On p. 62, 1st column, it incorrectly states that use of CO_2 increases bicarbonates that raise total alkalinity. Addition of CO_2 does not increase bicarbonate much at all – it mostly lowers pH and increases aqueous CO_2 (and slightly decreases carbonate which mostly offsets the slight increase in bicarbonate; the rest of the TA balance is with hydrogen and hydroxyl ions). The Total Alkalinity (TA) does not change when CO_2 is added to water nor when CO_2 is outgassed; only the pH changes. TA can rise from other sources such as from the "excess lye" in sodium hypochlorite or from evaporation and refill (since that adds to the pool water whatever is in the fill water, usually TA and CH) or the curing of plaster so using CO_2 instead of a strong acid in these situations will result in a rise in TA over time.

> ~~One by-product of the use of CO₂ to lower pH is the production of bicarbonates which raise the total alkalinity.~~ Addition of CO2 lowers the pH with no change in Total Alkalinity (TA) whereas addition of a strong acid (muriatic acid, sodium bisulfate, sulfuric acid) lowers both pH and TA. Therefore, using CO2 to lower pH can result in a rise in TA over time from alkaline sources such as the "excess lye" in sodium hypochlorite or the

increase in TA from evaporation and refill or from the curing of new plaster. Pools using ~~calcium~~ a hypochlorite source of chlorine as the primary disinfectant ~~and pools with source water high in total alkalinity or calcium hardness~~ may have problems with scale formation when using CO_2 as a result of the increase in TA over time.

In the section on p.62, 1st column on "To increase the pH", it talks about various bases, but does not include sodium tetraborate such as found in 20 Mule Team Borax (sodium tetraborate decahydrate). This is a base that will raise pH with about half as much rise in TA as with soda ash. It should not be used too heavily, however, as borates will build up in the water (which is a good thing up to a point, but normally shouldn't get much above 80 ppm). It should be noted that lye also increases pH with half the rise in TA. Basically, soda ash (sodium carbonate) is exactly like a combination of lye (sodium hydroxide) with baking soda (sodium bicarbonate) since $Na_2CO_3 + H_2O = NaHCO_3 + NaOH$. Sodium bicarbonate is not a strong base so should not be included in the list of bases. One can still recommend that it not be used to raise pH (in the subsequent paragraph).

To increase the pH, a basic material is added, the most common being sodium carbonate, known as soda ash (Na_2CO_3). Other bases for raising pH could be sodium hydroxide known as caustic soda or lye (NaOH), sodium sesquicarbonate ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$), and sodium tetraborate known as borax ($Na_2B_4O_7 \bullet 10H_2O$) ~~sodium bicarbonate (NaHCO₃)~~. When a base is added, there is an increase in the OH- ions and the pH as well as an increase in TA. Sodium carbonate increases TA by twice as much as sodium hydroxide while sodium sesquicarbonate increases TA even more. Sodium tetraborate increases the level of borates.

Since the outgassing of carbon dioxide tends to make the pH rise, the only time one usually needs to use a base to raise the pH is when using net acidic sources of chlorine such as Trichlor, Dichlor, or chlorine gas. In these situations, one usually has the TA be higher for additional pH buffering and to have more carbon dioxide outgas to keep the pH more stable (since it makes the pH rise, helping to counteract the drop in pH from the net acidic chlorine sources). So use of soda ash not only increases the pH, but increases the TA more as well helping to counteract the loss of carbon dioxide from outgassing. There is a sweet spot TA level where one can have the pH and TA both stable from the combination of chlorine and soda ash additions, assuming the aeration rate is constant.

Total Alkalinity

On p. 62, Illustration 6-4 "Total Alkalinity Related Pool Problems" says that Low Total Alkalinity has "pH Bounce" which can result in Etching of pool/spa surface, Staining of surface walls, and Heater failure. The first of these can be true since a low TA without other adjustments can make the saturation index low. The other two are not true since surface walls do not stain from low TA (they get metal stains from higher pH or sometimes high TA or high CYA as well). Heater failure, from

metal corrosion, is mostly from low pH (and high TDS and high oxidizer levels). High Total Alkalinity says "pH Lock", but this is not true. It is really more "pH Buffered" so takes more acid or base to move the pH, but the pH is not "locked" because a higher TA when using hypochlorite sources of chlorine (or not using any chlorine at all, for that matter) results in a rising pH over time due to carbon dioxide outgasssing. This rate roughly varies with the square of the carbonate portion of the TA level. The negative effects listed under "pH Lock" are correct and are a result of the saturation index being too high.

One can have a TA as low as 50 ppm (assuming 30 ppm CYA) when using hypochorite sources of chlorine, though usually in a pool it is not necessary to go much below 70 ppm. If there is a lot of aeration, then a lower TA works better (when hypochlorite sources of chlorine are being used). If additional pH buffering is desired, then one can use 50 ppm Borates though in a commercial/public pool the amount needed can get expensive. For residential pools and especially for spas, it works quite well. One can often get pH stability in a spa in spite of the strong aeration and use of bleach (after Dichlor is initially used to raise the CyA to 30 ppm) if one lowers the TA to 50 ppm and uses 50 ppm Borates and by targeting a pH of 7.7 instead of trying to fight to stay at 7.5.

On p. 63, 1st column, the recommended TA range is not appropriate for all sources of chlorine if one wants to have greater pH and TA stability over time and use less acid, base and baking soda to compensate.

> The ideal level for total alkalinity depends on the source of chlorine that is used and is generally 80 to 120 ppm (mg/L). High pH disinfectants (the hypochlorites) will usually require a total alkalinity in the lower part of this range, and in some situations even lower (as low as 50 ppm) when there is significant aeration and churning of the water. Remember that higher TA is a source of rising pH due to carbon dioxide outgassing. Low pH disinfectants (dichlor, trichlor, BCDMH bromine, and gas chlorine) require a total alkalinity in the higher part of this range.

Low Total Alkalinity

On p. 63, 1st column, I would delete the sentence that says "Low alkalinity may result in water with a green tint if iron or copper are in the water." A green tint from these metal ions occurs when they form oxides or hydroxides as would occur from a higher pH or when they form carbonates as would occur from a high TA (or high TA and pH combination). A purple color can result from copper and a high CYA level.

> When there are not enough bicarbonate ions to provide buffering of the pH, the pool or spa water will exhibit pH bounce. Small amounts of chemical additions can make this occur. Acid rains or high user loads may cause the pH to fluctuate. ~~Low alkalinity may result in water with a green tint if iron or copper are in the water.~~ Low alkalinity may also cause corrosion/etching of pool/spa surfaces. ...

High Total Alkalinity

It is very important to describe, again, how TA (specifically the carbonates portion of TA, not the CyA or borates portion) is a source of rising pH itself due to carbon dioxide outgassing. Add this info to the 2nd column on p. 63 as follows.

> At higher levels of total alkalinity, the pH is usually higher than ideal and becomes very difficult to change. Higher total alkalinity is a source of rising pH itself, due to carbon dioxide outgassing, and this becomes apparent when using a hypochlorite source of chlorine since acidic sources of chlorine obscure this effect. Cloudy water due to calcium carbonate suspended in the water is a very real possibility with high total alkalinity conditions

Calcium Hardness

The statement that the terms "soft water" and "hard water" are an indication of the water's calcium content is incorrect. These terms refer to total hardness that includes magnesium. It should be stated that it is the calcium level that is of concern since plaster/gunite/grout contains calcium carbonate and that calcium carbonate scale forms well before magnesium carbonate (at all but virtually unheard of magnesium levels). On the 2nd column of p.63 the following should be changed as indicated.

> Total hardness and calcium hardness are two different but related entities. Total hardness is the sum of calcium and magnesium and is sometimes expressed in grains of hardness (1 grain = 17.1 ppm or mg/L). The terms "soft water" and "hard water" are an indication of the water's ~~calcium content~~ total hardness. In pools and spas, it is the calcium hardness, not total hardness, that is important to achieve a balanced saturation index so that calcium carbonate is neither dissolved from plaster/gunite/grout nor deposited as scale. Low calcium hardness is a major contributor to foaming in spas. A calcium hardness level of 120 ppm or higher will usually minimize such foaming.

In Illustration 6-5 "Calcium Hardness Related Pool Problems" at the bottom of p. 63, it says that low calcium hardness levels can result in "staining of surface walls" or in "heater failure". This is not correct and should be removed. Metal staining occurs from metal ions in the water combined with hydroxide (from higher pH) or carbonates (from higher TA as well as pH) or from cyanurate (from higher CyA). Heater failure from metal corrosion occurs most commonly from low pH or from higher oxidizer levels (such as high FC with no CyA) or increased conductivity (from higher TDS or salt levels).

Total Dissolved Solids

Since conductivity only measures ions and not neutral molecules, it can only approximately measure TDS and this is written in a later sentence. So I would change the following paragraph as indicated in the 1st column of p. 65.
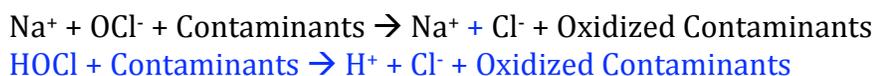
Total Dissolved Solids (TDS) is the total weight of all soluble matter in the water. The TDS concentration can be approximately derived by measuring the electrical conductivity of the water. Dissolved charged ions add to the water's conductivity. Contaminants that are neutral are not measured using the conductivity method. The lower the water's conductance, the more "pure" the water.

The discussion on sodium hypochlorite and the effects from inert ingredients in the 1st column of p. 65 are only half-true. This is because the amount of excess lye varies by product and can be quite low and because salt (chloride ion) is produced from **any** source of chlorine when the chlorine is consumed/used (be it oxidation of ammonia or an organic or from breakdown from the UV in sunlight). One can refer back to the chart I made earlier showing the net increases in CyA, CH and salt from each source of chlorine accounting for chlorine consumption/usage. I would replace most of what is written in the 1st column of p. 65 as shown below.

Disinfection chemicals added to pool/spa water contribute to the increase in TDS, mostly as salt. As an example, when sodium hypochlorite is added to water, ~~a substantial amount of~~ inert ingredients, ~~like~~ including a substantial amount of salt (NaCl) and some amount of sodium hydroxide (caustic), ~~and salt (NaCl)~~ are present as a result of the bleach manufacturing process. These inert ingredients are introduced into the water with the bleach. In addition, the bleach (NaOCl) disinfectant is introduced into the water and the pH rises as a result of the following reaction ~~takes place~~:

$NaOCl + H_2O \rightarrow HOCl + NaOH$
Sodium Hypochlorite + Water $\rightarrow$ Hypochlorous Acid + Sodium Hydroxide

$HOCl \leftrightarrow OCl^- + H^+$
Hypochlorous Acid $\leftrightarrow$ Hypochlorite Ion + Hydrogen Ion

$NaOH \rightarrow Na^+ + OH^-$
Sodium Hydroxide $\rightarrow$ Sodium ion + Hydroxide Ion

After the hypochlorous acid and hypochlorite ion ~~reacts~~ with contaminants in the water (or break down from the UV in sunlight), ~~it~~ they ~~leaves~~ a chloride ion (Cl^-) and sodium ion (Na^+) as shown in the reaction below and in the case of hypochlorous acid, the pH drops so the net result of adding sodium hypochlorite and having it consumed/used is no change in pH except from the excess sodium hydroxide (caustic):

$Na^+ + OCl^- + Contaminants \rightarrow Na^+ + Cl^- + Oxidized Contaminants$
$HOCl + Contaminants \rightarrow H^+ + Cl^- + Oxidized Contaminants$

The ions from the bleach and the inert ingredients do not evaporate and are only removed when water is removed from the pool (back washing, splash

16

out, carry out, etc.). The ions build up as TDS as more disinfectant is added over time. Similarly, other disinfectants introduce salts and inert ingredients. All sources of chlorine result in an increase in sodium chloride salt over time with the amount shown in Table 5-5 (the "Net Effect..." table in the Disinfectants section).

The paragraph in the 2nd column of p. 65 regarding TDS and the "age" of water should be changed as follows to distinguish between higher bather load situations vs. low bather load and the type of chlorine that is used.

TDS is in some manner a measurement of the "age" of the water when the bather load is moderate-to-high. As TDS increases, the amount of partially oxidized and unoxidized organic contaminants also increases. Included in this would be nitrogenous contaminants from user waste. Much of this material is uncharged or neutral and therefore does not contribute to ~~measurable~~ TDS as measured by conductivity. This added material may increase the consumption of disinfectant by fueling the growth rates of algae and bacteria. There are expensive and time-consuming methods of testing for these items, but TDS is generally accepted as a good indicator of "tired" water. When TDS is high, the organic contamination may also be judged high except in low-bather load situations where the TDS rise is mostly associated with salt buildup from chorine breakdown by the UV in sunlight.

Illustration 6-6 in the 2nd column of p. 65 that shows TDS, organic contaminants, and conductance vs. time should be removed. The scale makes no sense for the other two items and will vary by bather load.

Galvanic Corrosion

The risk of metal corrosion increases with increasing conductivity. There is no magic number where corrosion suddenly occurs since it depends on a variety of variables including the type of metals involved, the amount of oxidizer present (dissolved oxygen or chlorine), the pH, the temperature, and other factors. So I would not give a specific level where the probability increases. Also, the guideline of not exceeding 1500 ppm higher than the TDS when the pool or spa was started up hides the fact that a saltwater chlorine generator (SWG) pool starting with 3000 ppm is already at greater probability with metal corrosion right away. These increased risks can be mitigated. Finally, it's not just galvanic corrosion, but direct oxidation of metal by oxidizers that can also occur (via other forms of corrosion such as uniform attack, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion corrosion and stress corrosion), depending on conditions. I would change the 2nd column on p. 65 and the 1st column on p.66 as follows and would also change the title of this section from "Galvanic Corrosion" to "Metal Corrosion".

As TDS increases ~~above 2,000 ppm (mg/L)~~, there is a greater probability of galvanic corrosion when there are dissimilar metals within the system. For example, if a pool has a copper heat exchanger and other metals in the

plumbing, light fixtures, or metal pump impellers, then galvanic corrosion can occur. Galvanic corrosion would be observed by the discoloration of metal parts in the water. Other forms of more direct metal corrosion also have a greater probability to occur due to the greater conductivity of the water at higher TDS levels.

It is commonly recommended that the TDS should not exceed 1,500 ppm (mg/L) higher than the TDS when the pool or spa was started up. There is no minimum or maximum. The start-up level includes the TDS of the source water as well as any inorganic salt used by chlorine generation systems. Note that this implies that water with higher initial salt levels is at greater risk of metal corrosion and may need to be mitigated through appropriate use of more corrosion-resistant materials (such as cupro-nickel or titanium heat exchangers and high-quality stainless steel) and through use of a sacrificial anode (zinc or magnesium) connected to the bonding wire and buried in moist soil, particularly when aluminum is in contact with the water (as with some vanishing automatic pool cover header bars).

SATURATION INDEX

The "divide by 3" rule for adjusting the Total Alkalinity (TA) by the Cyanuric Acid (CyA) concentration to calculate the Carbonate Alkalinity used in the Saturation Index (SI) formula only really applies when the pH is near 7.5. The more complete Taylor test kits (K-2005, K-2006) contain a chart of CyA adjustment factors for TA based on pH and one could include the same in the Handbook. However, for normal pool and spa pH values in the 7.2 to 7.8 range, the 1/3rd rule is close enough so the following table is just FYI.

pH	Adjustment Factor
6.0	0.07
6.5	0.14
7.0	0.24
7.2	0.28
7.5	0.32
7.8	0.35
8.0	0.37
8.5	0.39
9.0	0.40

Table 6-?. CyA adjustment factor for TA

The TDS factors in the Handbook are too simplistic since the factor according to APSP-11 at 3000 ppm is 12.35. The following is the table of TDS factors from the ANSI/APSP-11 standard.

TDS	Factor
< 1000	12.10
1000	12.19
2000	12.29
3000	12.35
4000	12.41
5000	12.44

Table 6-?. Total Dissolved Solid Factors

My own analysis of the saturation index based on the best thermodynamic values I could find for the carbonate equilibria result in a somewhat different temperature dependence. Wojtowicz has different values as well based on Ksp and K2 values from Plummer and Busenberg (1982). The temperature factor range from 32F to 105F in the Handbook and ANSI/APSP-11 is 0.9, but from my calculations using CODATA thermodynamic values it is 0.63 while from Plummer and Busenberg it is 0.57. In the more relevant range from 76F to 105F, the factors range from 0.3, 0.22 and 0.20, respectively, so this isn't a terribly big deal though I would say that the Handbook and ANSI/APSP-11 values are probably wrong and based on old data from Langelier. They somewhat overstate the scaling potential at higher temperatures and understate it at colder temperatures.

As for TDS, my own ionic strength calculations result in a somewhat different TDS dependence. The ANSI/APSP-11 range from < 1000 (say, 525 ppm) to 5000 has a difference in factor of 0.34 while my calculations give a difference in factor of 0.29. This is reasonably close enough.

At a typical combination of values of pH 7.5, TA 100, CYA 30, CH 300, TDS 1000, Temp 84F, the ANSI/APSP-11 factors give a saturation index of +0.11 while my calculation results in +0.0 and the Plummer and Busenberg values result in +0.14. All are reasonably close so my only recommendation for the Handbook is to include the Total Dissolved Solid Factors table so that saltwater chlorine generator (SWG) pools with 3000 ppm salt will correctly get the extra 0.15 lowering of the saturation index properly reflecting the greater tendency to dissolve plaster in higher TDS pools (all else equal).

Chapter 7: Pool & Spa Water Problems

COMBINED CHLORINE: WATER & AIR QUALITY

What follows is a discussion that I'm not sure how to summarize in the Handbook since it requires a shift in thinking about Combined Chlorine (CC). For now, perhaps, leave the Handbook as is, but think about how to handle this in the future.

As I had noted in an earlier discussion of Combined Chlorine in Chapter 5 on Disinfection, there are many different kinds of CC and they are not all irritating at

the same levels. In fact, since at pool water temperatures chlorine slowly reacts with the largest component (other than water) in sweat and urine, namely urea, to form chlorourea (usually within an hour) and takes even longer (usually many hours to days) to fully oxidize, there may be seemingly persistent readings of CC in pools with higher bather loads, yet the water not be irritating since chlorourea, and even monochloramine, at low ppm levels (< 3 ppm) is not an irritant. Drinking water today often has monochloramine in it at levels of around 1 ppm. A rule to keep CC at or below 0.2 ppm can be very impractical and really misses the point.

It is far more important to limit the most irritating and volatile components, most specifically nitrogen trichloride since it's odor threshold is as low as 0.02 ppm and it is the chemical indicated in airway irritation and possibly a trigger for asthma, though that is not conclusive. The theoretical models of breakpoint chlorination (chlorine oxidation of ammonia), Wei & Morris (1972), Selleck & Saunier (1976, 1979), Jafvert & Valentine (1992) and Vikesland, Ozekin, Valentine (2000) all show that there is greater production of nitrogen trichloride when the hypochlorous acid concentration is higher and the more recent models show that the rate and final endpoint amounts of nitrogen trichloride are roughly proportional to that hypochlorous acid concentration (if maintained at a roughly constant concentration). Therefore, the use of CyA in indoor pools should theoretically significantly reduce nitrogen trichloride concentration by orders-of-magnitude. The tradeoff is that the monochloramine and dichloramine concentrations will be proportionately higher, but a sweet spot might balance these three at their odor and irritation threshold limits at around an FC that is 20% of the CyA level, such as 4 ppm FC with 20 ppm CyA.

There is no accepted model for the chlorine oxidation of urea, though there have been some proposals. In these proposals, dichloramine and nitrogen trichloride are formed as oxidation products from a quadchlorourea. If something like this is what happens, then the same reasoning for limiting nitrogen trichloride by lowering hypochlorous acid concentration could apply to chlorine oxidation of urea. Funding of research in this area to confirm or refute this hypothesis would be very worthwhile.

Breakpoint Chlorination (BPC)
In the link I gave at the beginning of this document I describe in more detail why the traditional pool/spa industry breakpoint chlorination rule of using 10x the CC level is wrong on two counts. First, it does not account for the fact that 1 of the 1.5 chlorine needed to oxidize ammonia on a molar basis is already accounted for in the CC reading (assuming it is monochloramine) and second, it does not account for the differing units of measurement between ammonia (measured in ppm N) and FC or CC (both measured in ppm Cl_2). The 10x rule comes from the 3 chlorine to 2 ammonia molar ratio (i.e. 1.5 ratio) with the factor of 5 measurement unit difference between chlorine and ammonia which results in a net 7.6 factor. It takes somewhat more chlorine to get over the hump of reactions so it's usually quoted as 8-10x from which the 10x was taken as the "rule" for BPC. The correct rule, when starting from

CC, is that it only takes at least 0.5x and at the most 1x the CC level to complete the BPC reaction, at least for monochloramine.

When considering urea, and assuming that the CC is measuring monochlorourea, then it takes a minimum of 2x and at the most 3x the CC level to complete the BPC reaction. So the 10x rule is not the correct minimum, though any higher level of chlorine than these minimums simply results in a faster reaction time, but also may produce higher levels of irritating and volatile nitrogen trichloride.

In the 1st column of p. 76, the Handbook says that "inorganic chloramines may have evaporated from the water and then redissolved." This is highly unlikely since chemical equilibrium do not reverse themselves. It is true that if the volatility were extremely high and if subsequently the chemicals in the water continued to be oxidized (i.e. eliminated), then such a reversal could happen, but it is far more likely that any persistent CC is due to organic chloramines including chlorourea. The levels of dichloramine and nitrogen trichloride are so low during BPC that it is unlikely they get measured in a CC test. The models show that dichloramine is typically 1/10th the level of monochloramine (the model does not account for volatization and assumes all chemicals remain in the water). Monochloramine is by far the most dominant inorganic chloramine. This is also demonstrated in the real pool measurements in the paper "Volatile disinfection by-product analysis from chlorinated indoor swimming pools" by Weaver, Li, Wen, Johnston, M. Blatchley, E. Blatchley (2009) where dichloramine was usually a factor of 3 lower in concentration than monochloramine while nitrogen trichloride was in the ballpark same concentration as dichloramine. These pools presumably were not using CYA. If they were, then I would expect the monochloramine and dichloramine to be much higher and the nitrogen trichloride to be much lower.

So the formulas under "Achieving Breakpoint Chlorination" are wrong in terms of the minimum amount of chlorine needed. Also, not achieving breakpoint does not get anything stuck – one can simply add more chlorine and continue. So long as there is measurable FC, reactions are continuing – BPC is continuous when FC is always present and the only issue with the FC level is in determining reaction rates and in the relative concentrations of monochloramine, dichloramine and nitrogen trichloride.

The Handbook says that "Some test kits measure the monochloramine directly. If one of these tests are used, then the desired change is five times the monochloramine level." Where did this number come from? Except for the organic chloramines that can measure as CC, the CC test also measures monochloramine so why the difference in the CC rule vs. the monochloramine rule? Is there an assumption of how much CC is organic chloramines? As noted above, the factor for monochlorurea would be 3x and this is all a bit moot anyway since one just needs to keep adding chlorine to have measurable FC.

Indoor Air Handling

Trichloramine and nitrogen trichloride are synonyms for the same compound so perhaps was meant was dichloramine so the following in the 2nd column on p. 76 should be changed as indicated. Also, regarding evaporation and redissolving, Henry's Law determines the best-case complete equilibrium concentrations between water and air for the different chemical species. For hypochlorous acid, 1 ppm in water would be in equilibrium with 22 ppbV in air. For monochloramine, 1 ppm in water would be in equilibrium with 155 ppbV (about 0.16 ppmV) in air. For dichloramine, 1 ppm in water would be in equilibrium with 486 ppbV (about 0.5 ppmV) in air. For nitrogen trichloride, 1 ppm in water would be in equilibrium with 141,000 ppbV (141 ppmV) in air. For whatever reason, the attainment of equilibrium with air is slow for nitrogen trichloride and possibly for some of the other compounds so the evaporation and redissolving argument seems very weak to me.

> Inorganic chloramines like ~~tr~~dichloramine and nitrogen trichloride are volatile and will evaporate. These chloramines are the cause of the "chlorine like" smell in indoor pools. ~~These gasses may also dissolve back into the pool water. As a result~~ For bather comfort and safety, it is important that indoor aquatic facilities are designed and operated so that part of the air is replaced with fresh air to remove chloramines ~~so they do not redissolve into the water~~. Additional information about indoor air quality is addressed in Heating & Air Circulation chapter and the Facility Safety chapter.

OXIDATION

The Handbook should mention that shocking with a chlorine product will also substantially increase the side effect components for the particular type of chlorine used. For example, it is a bad idea to use Dichlor for shocking since it will substantially increase CyA. Trichlor powder should also be used judiciously. Cal-Hypo as well. The earlier table showing the side effects of different types of chlorine can be used as a guide, but generally speaking shocking with sodium hypochlorite is best. "Shock" is a verb, not a noun. The chlorine disinfection products repackaged and called "shock" are no different than their non-shock counterparts. It is only the so-called non-chlorine shock products, such as potassium monopersulfate, that are truly unique.

It should also be noted that if one properly maintains the appropriate FC/CYA ratio, and in high bather load pools uses means to remove organic precursors (e.g. ozone, coagulation/filtration/backwashing) then shocking may be rarely needed. This is certainly the case in low-bather load situations as with most residential pools. Oxidation is a continual process so shocking merely accelerates this process, but at the cost of producing more nitrogen trichloride.

> … If the water looks dull or hazy, treating the water with an oxidizer often helps improve water clarity.

If one maintains an appropriate sanitizer level (Free Chlorine, FC) relative to the stabilizer level (Cyanuric Acid, CyA), then the rate of oxidation may be sufficient to handle bather waste under low and possibly moderate bather loads. For higher bather loads, some form of supplemental oxidation is usually required.

The process of removing contaminants from the water can be improved by a variety of oxidizer products. Some oxidizers are also disinfectants. For example, a product that releases a high dose of chlorine both oxidizes contaminants in the water and disinfects the water. ~~Products that both oxidize and disinfect are commonly called "shock" or "superchlorination" products.~~ The chlorine disinfectants described in the Disinfection chapter can be used to shock or superchlorinate the water. Note that such products often have additional side effects such as increasing CyA or CH levels as described in Table 5-5. If an operator intends to kill microorganisms or algae, the product must contain a disinfectant. It is important for operators to review the product labels to ensure that the products they are using contain written claims for their intended use.

Potassium Monopersulfate

I do not understand the statement about oxidation increasing the contaminant's relative negative charge thus promoting their removal by the filter. Oxidation of ammonia results in hydrochloric acid and nitrogen gas while oxidation of urea results in carbon dioxide, hydrochloric acid and nitrogen gas. Even partial oxidation of many organic compounds often results in neutral molecules. Are there specific examples where oxidation produces compounds typically found in pools that have a negative charge? It is true that oxidation of a compound increases the oxidation state (number of electrons), but that does not necessarily result in a more negative charge because the resulting compounds have different atoms (number of protons) as well. The ammonia and urea examples all start and end with neutral molecules or charge balanced ions. For example, with MPS a double bond may be converted to two single bonds with an oxygen bridge (i.e. epoxidation of olefins).

It should be noted that continued use of monopersulfate substantially increases the level of sulfates in the water. This can cause problems for chlorine generator systems in terms of reducing the life of certain plate coatings and can also increase the rate of stone deterioration via splash-out and re-crystallization of magnesium sulfate (which has far higher re-crystallization pressure than sodium chloride). In the 1st column on p. 77, the following can be added as indicated.

... The recommended dose is one pound (0.45 kg) of monopersulfate per 10,000 gallons (38,000 L) based on an active strength of 42.8%. Once the monopersulfate is dissolved, users may enter the water. Monopersulfate will reduce the water's pH. Some formulations of monopersulfate contain ~~a~~ less active ingredient with additional pH balancing ingredients and a more desirable, neutral pH. The recommended dose of monopersulfate raises the

sulfate level by 7.5 ppm so if added each week the sulfates will build up over time unless there is significant water dilution with water that is low in sulfates.

COLORED WATER

This section correctly states how "corrosive water, usually caused by low pH, can dissolve these items" referring to metal components. Yet earlier, the illustrations on low TA and low CH said "staining of surface walls" which is something I want removed from those illustrations.

In the 2nd column on p. 78, the Handbook says that when metal sequestrants break down, "they deposit much of the metals on the filter." Is this really true? How does this work? When metal sequestrants break down from being oxidized by chlorine, they release their metal ions. Why would these then get caught in the filter? This would only happen if the metal ions precipitated into metal hydroxides, oxides, carbonates, cyanurates, but why would they get caught in the filter rather than stain a plaster pool surface?

The Handbook should probably note somewhere that EDTA-based metal sequestrants tend to break down more quickly (i.e. they get oxidized by chlorine faster) so require more frequent maintenance doses and create a higher chlorine demand compared to HEDP and other phosphorous-based metal sequestrants. When these phosphorous-based metal sequestrants break down, they eventually result in higher orthophosphate levels. This can be managed through proper FC/CYA ratio control, but at lower ratios algae growth can accelerate from the increased nutrient level. This isn't a reason not to use such sequestrants, but is more a reminder to have a sufficient FC/CYA ratio to prevent algae growth (or to use some other supplemental algaecide, if desired).

STAINS

One might mention how reducing agents, such as ascorbic acid and oxalic acid, can be used to help remove metal stains, particularly iron stains where the ferric ion (Fe^{3+}) needs to be reduced to ferrous ion (Fe^{2+}) to be bound to metal sequestrants or chelating agents.

SCALE

In the 1st column on p. 80, there is a typo to be corrected as follows. Also, scale comes from over-saturation of calcium carbonate so it is not necessary to reduce TDS to reduce the likelihood of scale. In fact, higher TDS makes it less likely for scale to form due to higher ionic strength that tends to shift the equilibrium more towards calcium and carbonate ions and away from calcium carbonate solid.

> To prevent scale, the alkalinity, calcium hardness, pH ~~and total dissolved solids (TDS)~~ must be brought into proper balance. A portion of the pool water may need to be drained and replaced with fresh source water that is lower in hardness ~~and TDS~~. ...

CLOUDY WATER

Usually, with a proper functioning filter and with sufficient chlorine levels, a clarifier is not needed. Though it can speed up clearing, chlorine alone at a shock level that is around 40% of the CYA level will kill an algae bloom reasonably quickly and clear it over several days (up to a week, if circulation is poor).

The Handbook should also note that the filter should be cleaned or backwashed (as appropriate) to remove the caught material. This will also reduce the chlorine demand since the chlorine will continue to oxidize material that is caught in the filter.

FOAMING

One should note that unlike quaternary algaecides, PolyQuat does not foam. That's one of its main benefits, along with also being somewhat of a clarifier. It's more expensive, but that's the price/performance tradeoff.

ALGAE

The Handbood states that "some algae have the ability to reproduce rapidly if the conditions are favorable turning a clear pool to green in less than a day." Only bacteria reproduce quickly enough (15-60 minute generation time) to turn pool water that quickly though there is a bacteria which in the pool industry is called "pink algae" or "pink slime". Blue-green algae are actually cyanobacteria, but from what I can find, their generation time is in the 8-24 hour range. Most algae have a generation time under ideal conditions of around 3-8 hours so would not turn a pool green in one day. The pool water might turn dull after 24 hours, cloudy after two days, and become a full-fledged bloom after 3 days. Usually when it seems as if pool water has turned quickly, it was actually in a nascent algae bloom for a day or two and was not noticed.

Prevention of Algae

In addition to "constant, sufficient levels of disinfection" one should reiterate the importance of maintaining a minimum FC/CYA ratio as it is the hypochlorous acid concentration that is relevant in preventing algae growth. If a proper FC/CYA ratio is maintained, the use of supplemental algaecide and routine superchlorination are unnecessary. Generally speaking, SWG pools require a minimum FC that is 5% of the CYA level while manually dosed pools need a minimum FC that is 7.5% of the CYA level. Since commercial/public pools should probably have an FC that is around 20% of the CYA level for sufficient oxidation and disinfection rates, they get algae prevention for free (assuming regular brushing, good circulation and filtration are present).

> … Operating factors such as proper filtration, circulation flow, elimination of dead spots, and constant, sufficient levels of disinfection (FC/CYA ratio in pools with CYA) can be managed. Routine superchlorination and the use of an algicide on a maintenance basis are useful tools in the prevention of algae when an insufficient FC/CYA level is being maintained. Brushing the

pool/spa walls on a routine basis is an important preventative measure. It is far easier to prevent algae than to remove algae.

Metallic Algicides

The Handbook should also describe purple copper cyanurate stains. Also, it is incorrect to say that chlorine oxidizes copper. Copper is already oxidized as a copper ion and in algaecides is already a copper ion. Chlorine does oxidize solid copper to copper ion (Cu^{2+}) and also oxidizes solid iron to ferrous ion (Fe^{2+}) and then to ferric ion (Fe^{3+}). It is higher pH that can form oxides, hydroxides and carbonates (if TA is also high) of copper (and iron) to produce stains. Usually it is the hydroxide or carbonate that is first formed and then a water or carbon dioxide is released to form the oxide as with the following chemical reactions:

Cu^{2+} + 2OH⁻ → $Cu(OH)_2$(s)
$Cu(OH)_2$(s) → CuO(s) + H_2O
Cu^{2+} + CO_3^{2-} → $CuCO_3$(s)
$CuCO_3$(s) → CuO + CO_2
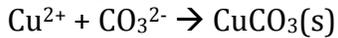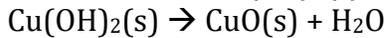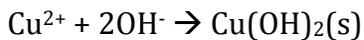
The biggest disadvantage is that the copper ions (Cu^{2+}) ~~in the copper algicide are not stable in the presence of chlorine. Chlorine can oxidize copper to produce black stains on the pool surface~~ can stain pool surfaces. Higher pH can have copper form oxides that can produce black stains and hydroxides that can produce pale blue stains, respectively. In addition, copper can form a bond with the high concentration of carbonate (total alkalinity; see the Water Balance chapter) and stain plaster surfaces to a blue-green color. When CYA is present at high levels, copper can form a bond with the high concentration of cyanurate (cyanuric acid; see the Water Balance chapter) and stain plaster surfaces to a purple (amethyst) color. High copper ion concentrations can give blond hair a greenish tint.

Other Algicide Types

It should be noted that ammonium sulfate combines with chlorine to form monochloramine and that this is the killing agent against algae. Both monochloramine and bromine are effective when CYA levels are high because neither are moderated in strength by CYA.

When ammonium sulfate is used as an algicide, the chemical requires the water pH to be adjusted to about 8.0. The ammonia combines with chlorine to form monochloramine which kills algae. Monochloramine does not combine with cyanuric acid (CyA) so is not moderated in its strength so is most useful when CyA levels are too high to raise the Free Chlorine (FC) level high enough to kill algae effectively. After the algae have been killed, superchlorination is required to remove the ammonia from the water. The pH has to be checked and may need to be readjusted.

When sodium bromide is used, the bromide is oxidized by chlorine to hypobromous acid (HOBr), which is effective at killing algae. Bromine does not combine with cyanuric acid (CyA) so is not moderated in its strength so is most useful when CyA levels are too high to raise the Free Chlorine (FC) level high enough to kill algae effectively. The presence of bromide cancels out cyanuric acid's ability to protect chlorine from being broken down by sunlight.

Some products recommend that a source of boron like sodium tetraborate or boric acid be added to achieve 30 to 80 ppm (mg/L) of boron to inhibit algae growth in the water.

Phosphates and Nitrates

It should be noted that nitrates are a (minor) byproduct of the chlorine oxidation of ammonia and nitrogenous organics. This section seems very biased against phosphate removers by implying that because phosphate is stored in algae, that lowering phosphate levels will not affect phosphate growth. Phosphate removers only remove orthophosphate, not organic phosphates, but the uptake rate of organic phosphates by algae (though not bacteria) is far slower than for orthophosphate. Also, once one kills and removes algae from a pool (including oxidation of any remaining by chlorine), one can lower the phosphate level and with maintenance doses can keep it low. This can take the edge off of algae growth in a similar manner as other algaecides (such as quats and PolyQuat) that still require chlorine as the primary disinfectant and algae killer. Though one does not really need algaecide nor phosphate remover if one maintains an appropriate FC/CYA ratio, these products are certainly OK to use and one should not be biased against any one type (one should just note the downsides, as was done with copper algaecide).

One common source of nitrogen, a nutrient needed by algae and bacteria, is nitrate. Nitrate sources are similar to those that contain phosphate. In addition, sweat and urine contain some nitrogen and the chlorine oxidation of ammonia and nitrogenous organics can produce nitrate as a minor byproduct. …

Since all the nutrients that algae needs, including phosphate and nitrate, are commonly available in pool water or are stored within algae, it is very important that disinfectant residuals (a sufficient FC/CYA ratio if cyanuric acid is used) be maintained at all times to prevent the growth of algae.

BIOFIOM

It should be noted that biofilm can be prevented by killing bacteria before they get a chance to form biofilms. Consistent disinfection, along with proper circulation to ensure disinfectant levels are well distributed, can therefore prevent biofilm formation.

ENZYMES

It is not true that when proteins are in a 3-D arrangement, they are enzymes. Most proteins have a 3-D arrangement, but not all proteins are enzymes. Many proteins are simply transport carriers across membranes or solutions (where they have a specific 3-D shape for these binding activities) or are simply structural. Only a subset of proteins are enzymes. The definition of an enzyme is a chemical catalyst – a chemical that reduces the activation energy of a reaction to speed it up while not being consumed in the process.

> Living cells in plants and animals make proteins from long strings of different amino acids. Cells bend and twist proteins into a specific three-dimensional arrangement. When in that arrangement, some of these proteins are called "enzymes" because they ~~cause~~ accelerate (catalyze) chemical reactions ~~(catalysts)~~ required by the body for life to exist. For example, the food we eat is broken down in part ~~by~~ with the assistance of enzymes. Pool and spa enzyme products are made from living cells that are broken apart and claim to contain enzymes that react with and degrade contaminants in water.

Chapter 8: Chemical Testing

Dip-and-Read Test Strips

There are no test strips that I am aware of that can measure Calcium Hardness (CH) as opposed to Total Hardness (TH). Also, test strips typically have an accuracy of +/- 40 ppm compared to +/- 10 ppm for most drop-based (titrametric) test kits.

TEST PROCEDURES

In the 1st column of p. 89, the Handbook talks about holding the comparator to the northern horizon, but it should be noted that this is for the northern hemisphere and that the southern horizon should be used in the southern hemisphere.

TESTING FREQUENCY

Total Alkalinity

As noted earlier in the Disinfection section, when CYA is present, the variation of hypochlorous acid vs. pH is minimal (15% drop from 7.5 to 8.0) so the paragraph on the importance of TA to keep pH stable to provide disinfection should be deleted. TA is still important for the saturation index and to provide some pH buffering, but should generally be kept lower if using hypochlorite sources of chlorine and if the pH tends to rise over time (especially if adding acid causes the TA to drop over time – this is a clear indicator of carbon dioxide outgassing because adding acid to compensate for a base simply gets you back where you started with both pH and TA).

DISINFECTANT TESTING

False DPD Readings

In the 1st column of p. 92, the sentence "The chlorine activity is much lower at a high pH, and the DPD will not "bleach out"" is not true since it does not take into account that the DPD test is not measuring hypochlorous acid directly and that hypochlorite ion will convert to hypochlorous acid as the latter gets used up by oxidizing the DPD to become a visible dye (CYA-Cl will also release hypochlorous acid in the same way). The following is a description of the DPD test from "Current Technology of Chlorine Analysis for Water and Wastewater" from the "Technical Information Series – Booklet No. 17" by Daniel L. Harp for Hach Company in 2002.

The DPD amine is oxidized by chlorine to two oxidation products. At a near neutral pH, the primary oxidation product is a semi-quinoid cationic compound known as Würster dye. This relatively stable free radical species accounts for the magenta color in the DPD colorimetric test. DPD can be further oxidized to a relatively unstable, colorless imine compound. When DPD reacts with small amounts of chlorine at near neutral pH, the Würster dye is the principal oxidation product. At higher oxidant levels, the formation of the unstable colorless imine is favored – resulting in apparent "fading" of the colored solution.

In other words, it is the relative amounts of dye vs. free chlorine (FC) that determine whether only the first oxidation step takes place producing the colored Würster dye or whether there is an excess of chlorine that will oxidize this dye to another compound that is colorless. It is possible that there are reaction rate dependencies that are a function of pH or hypochlorous acid concentration, but it seems more likely that this effect is mostly a stoichiometric one since the bleaching out of DPD can occur in high FC pools that have CYA and therefore have very low hypochlorous acid concentrations (thus showing that this concentration is not the relevant factor – though pH might still be a factor on its own).

FAS – DPD Titration testing

The comment about MPS oxidizing the DPD #3 reagent (i.e. oxidizing potassium iodide to iodine) also applies to the DPD test so should be mentioned there as well.

Oxidation Reduction Potential (ORP) Testing

In the 2nd column on p. 93, the statement that "... many chemicals used in water impact the ORP reading (potassium monopersulfate, cyanuric acid, dirt, etc.)." is true, but the effect cyanuric acid has is directly related to its significant reduction of hypochlorous acid concentration, not any direct oxidation effect.

In the 1st column of p. 94, the Handbook says "It is difficult for an operator to determine how much the ORP is lowered due to cyanuric acid lowering the oxidation potential of the chlorine and how much is due to probe fouling." It is actually quite possible to calculate the hypochlorous acid concentration in the water given various water parameters (mostly FC, CYA, temp., TDS), but relating these to

ORP is difficult since different sensors are not consistent in their ORP reading – not only in their absolute ORP, but in their slopes (ORP mV per doubling of hypochlorous acid concentration) as well.

WATER BALANCE TESTING

In the 1st column on p. 94 the Handbood says, "Pools and spas are normally operated at a slightly alkaline pH, with an ideal pH range o 7.4 to 7.6. Earlier on p. 61, 1st column, the recommended range was given as 7.2 to 7.4 which was assumed to be a typo that should have been 7.2 to 7.8. These two ranges need to be reconciled – perhaps recommended is 7.2 to 7.8 with "ideal" being 7.4 to 7.6 and one can cross-reference these two statements.

Cyanuric Acid Testing

The Handbood earlier talked about the effect of CYA on sanitation and on the prevention of algae, so that can be repeated here as well.

> The effect of cyanuric acid increases as more is added to the water. Many health departments limit cyanuric acid to 100 ppm (mg/L), although some allow less and others allow more. Testing and control of cyanuric acid is important to comply with state and local codes. Cyanuric acid significantly lowers the hypochlorous acid level and the rates of disinfection, algae prevention and oxidation, though fortunately it takes very low levels of hypochlorous acid to kill most pathogens. See the section on Cyanuric Acid in the chapter on Disinfection for more details.

Testing for Hydrogen Peroxide

Hydrogen peroxide is degraded by sunlight, though not as quickly as the degradation of chlorine.

Chapter 9: Chemical Feed & Control

Addition by Broadcast Method

The advice I wrote earlier should be repeated here.

> Slowly pour the chemical broadly over the water's surface. Keep the packaging near the water's surface and away from your face and body. To spread the chemicals throughout the water, in particular for acid and chlorine, kneel down and pour some of the chemical into the pool water close to a return fitting (preferably in the deep end if adding to a residential pool). Add the chemical slowly into the water flow and after you are done, lightly brush the side and bottom of the pool in the area of chemical addition to ensure thorough mixing (this is especially important in vinyl pools).

Chapter 10. Water Circulation

Turnover Rate

I'm not sure where the filtration percentages based on number of turnovers came from since they are incorrect. For continuous circulation, mixing and filtration one turnover has all but $e^{-1} = 0.368$ or 37% of the water molecules, having 63% of them go through the filter. For two turnovers this is all but $e^{-2} = 0.135$ or 14% and for three turnovers this is all but $e^{-3} = 0.0497$ or 5% and for four turnovers it is $e^{-4} = 0.0183$ or 2%. So the Handbook should be changed as follows in the 2nd column of p. 118 as well as the corresponding pie charts.

> The mathematical model standard for one turnover is the filtration of ~~42%~~ 63% of the water molecules, leaving ~~58%~~ 37% of the water unfiltered. A second turnover reduces the unfiltered level to ~~16%~~ 14%. After a third turnover, the unfiltered water is 5%. It is only after four turnovers that the amount of unfiltered water is reduced to 2%, which many codes require on a daily basis. For this reason, the turnover rate requirement or code standard for most commercial swimming pool operations is six hours.

Chapter 11: Pool & Spa Filtration

FILTER MEDIA

In the 2nd column of p. 137, one could add the micron range for the size of particles a sand filter will filter since the Handbook describes a 10 to 25 micron range for cartridge and 2 to 6 micron range for D.E. and Illustration 11-1 has a 25 to 100 micron range for sand filters (based on what is written in the 1st column of p. 142).

Zeolite

The statement about zeolite absorbing ammonia may be true, but is misleading since any pool with measurable Free Chlorine (FC) will have chlorine combine with ammonia to form monochloramine in seconds to a minute, long before any ammonia gets a chance to circulate through the Zeolite filter. Furthermore, the filter does not absorb monochloramine and the reaction of monochloramine converting to ammonia is too slow for the filter to reduce the monochloramine level in any reasonable time. So I would modify what is in the Handbook in the 1st column of p. 145 as follows.

> Zeolite is a granular volcanic material that is extremely porous and is capable of removing particles down to five microns in size. Manufacturers claim that activated zeolite has the capability to absorb ammonia from the pool water. ~~Removal of this contaminant is desirable since chlorine reacts with ammonia to form chloramines that are irritating to users' eyes and has a pungent odor that impacts the indoor air quality.~~ However, in a pool with chlorine, any ammonia will quickly combine with chlorine to form monochloramine which the filter will not remove.

Chapter 12: Heating & Air Circulation

Pool and Spa Covers

The handbook says that a pool cover will reduce heat los from thermal radiation, but that generally is not true since the pool cover often equilibrates in temperature to something close to the water temperature so still radiates heat to the sky. It is definitely true that heat loss from evaporation is cut down considerably and heat from convection is also cut down since the cover is insulating so heat transfer from the pool water through the cover is slowed down. So in the 1ˢᵗ column on p. 153 I'd change the following.

> The use of a pool cover reduces the heat loss due to evaporation, ~~thermal radiation,~~ and convection, which account for about ~~95%~~ 70% of the losses. …

HEAT GAINS

It is not true that 90% of the sunlight that reaches the surface of a pool is absorbed. This only happens if the pool surface (colored plaster or vinyl) is black. For a white plaster surface and an average 4.5 foot (3 to 6 foot) depth pool, there is 60% net absorption of sunlight. About 25% is absorbed within the first inch of water and about 40% in the first foot and is mostly infrared. So I would change the 2ⁿᵈ column on p. 153 to the following.

> Swimming pools gain heat in three ways. The first is natural sunlight, absorbed directly by the water. About ~~90%~~ 60% of the sunlight that reaches the surface of a pool is absorbed in pools with white plaster while around 90% is absorbed in pools with black surfaces. …

Chapter 13: Spa & Therapy Operations

Hot Water Diseases

I'm not sure if you want to reiterate the tendency of *Pseudomonas aeruginosa* to rapidly form biofilms so that it is important to have this bacteria killed quickly and that means not having too low an FC/CYA ratio (some regs say not to use any CYA, but that has the chlorine generally be too strong). A limit of 30 ppm CYA is probably reasonable for spas – the hotter water temperature has a higher active chlorine (hypochlorous acid) level at the same FC/CYA ratio as compared to cooler temps in pools.

Disinfectants

The Handbook in the 1ˢᵗ column of p. 168 says that "A greater percentage of spas use bromine to disinfect the water. This is due to bromine's superior disinfectant performance at higher pH." This is not true because as I described earlier the active chlorine level is very high to begin with and if CYA is used it is buffered against changes in pH so remains very effective. Bromine is more likely to be used because

it tends to outgas more slowly so is retained longer, and it is more convenient in having bromine tabs (at least for residential spas). The rest of what is written in the Handbook is true in that the bromamines are still reasonable disinfectants and are not as irritating as chloramines.

pH
The Handbook talks about carbon dioxide evaporation (outgassing) here, but does not relate this to the same effect with pools earlier. Though the outgassing of carbon dioxide increases the pH, it does not decrease the alkalinity. It is the subsequent adding of acid to lower the pH that also lowers the TA. So the Handbook should be corrected as follows.

> The aeration typically found in spas and therapy pools~~,~~ causes carbon dioxide to evaporate from the water. The loss of carbon dioxide will increase the pH ~~and decrease~~ while subsequent acid addition to lower the pH will also lower the alkalinity. Much as a can of soda loses its fizz and is no longer acidic to the stomach, the pH of a hot water facility has a tendency to rise. …

Total Alkalinity
It should be noted again that TA is a source of pH rise itself. If one uses a hypochlorite source of chlorine, then a lower TA will result in a slower pH rise, though the use of 50 ppm Borates is helpful as an additional pH buffer.

Total Dissolved Solids
Increasing TDS does not directly affect disinfection unless the TDS rise is associated with a rise in CYA level. The chlorine demand may rise if there are unoxidized organics building up in the water, but that does not reduce chlorine's effectiveness so long as the FC level is maintained.

Cyanuric Acid
If chlorinated isocyanurates are used, the CYA level can build up much faster than you might think. In a residential spa (usually around 350 gallons), a daily chlorine usage of 4 ppm FC using Dichlor results in an increase in CYA of 30*4*0.91 = 109 ppm per month.

Chemical Overdosing
It is very interesting that the Handbook says that "High chlorine levels are no more effective at inactivating most pathogens, but more potentially toxic disinfection byproducts may form. Bleaching of swim suits and hair becomes more likely at high disinfectant levels." This is very true, but it doesn't just apply to a high FC level alone since that is not related to the hypochlorous acid concentration unless one also accounts for the pH and CYA (and temperature). How can such a true statement be made, yet one ignore the order-of-magnitude differences in hypochlorous acid concentration between a pool with no CYA vs. one with CYA? Remember that at typical pool temperatures, an FC that is around 10% of the CYA level has a hypochlorous acid concentration of 0.043 ppm which is over 20 times lower than the hypochlorous acid concentration with 2 ppm FC and no CYA. So not

CPO Handbook Suggestions

using any CYA at all is a significant over-chlorination of the water leading to the same problems described in the Handbook in this section.

Foaming

It should be mentioned here (as it is elsewhere in the Handbook) that raising the Calcium Hardness (CH) to 100 ppm or more can help to reduce foaming.

References

In Table B-1 Water Chemistry Guidelines on p. 258, the low end of the Total Alkalinity range for hypochlorite sources of chlorine should be lower – as low as 50 ppm though a supplemental pH buffer (such as 50 ppm Borates) would be beneficial if the TA is below 70 ppm.

In the Glossary on p. 265, the definition of Cyanuric Acid should talk about its lowering disinfection and oxidation rates as follows.

> **Cyanuric Acid** ($C_3N_3O_3H_3$) (a.k.a. Stabilizer, conditioner, or 2,4,6-trihydroxy-s-triazine) – A white, granular solid chemical that reduces the loss of chlorine due to the ultraviolet rays from sunlight and significantly reduces the hypochlorous acid (HOCl) concentration thereby reducing chlorine's disinfection and oxidation rates.

Exercises for CPO Classes

Some of the principles can be taught in CPO classes using fun exercises or experiments. Some examples are below.

Disinfection Rate vs. Chlorine Reserve (FC)

Many people mistakenly assume that the release of more hypochlorous acid from CYA (or converted from hypochlorite ion) means that bacterial kill rates and oxidation rates are not slowed down. One can illustrate why this is wrong and that it is the instantaneous concentration of HOCl that is relevant by doing an exercise that has a few members of the class represent HOCl and most members stand behind them as chlorine reserve (either chlorine bound to CYA or as hypochlorite ion). Only the few members of the class that are HOCl can kill bacteria quickly.

An analogy can be made to fighting a war with only the front line having weapons, but having plenty of people in reserve to take the place of members of the front line who are killed (that is, HOCl that kill bacteria and get used up in the process). It should be pretty clear that the rate of killing the enemy depends on how many people are on the front line with rifles and not on the number in reserve.   Where the reserve becomes important is in not running out of people before all of the enemy is

killed – that is, the reserve is a capacity for how long one can continue to fight and not the rate of killing itself.

Total Alkalinity and Carbon Dioxide Outgassing

This can be illustrated with glasses of water, baking soda, acid (vinegar, which is acetic acid, is fine) and wide-range pH and TA strips. One adds baking soda to the water and measures the pH and TA. Then one adds some acid and measures the pH and TA again (both should be lower, especially the pH).

One can then wait and do something else in the class and then have people measure the pH and TA again and see that the pH may have risen a small amount. Then have the class stir the water in the glass vigorously for 30 seconds and measure the pH and TA again and see that the pH has risen with no change in TA. Then have them blow bubbles through a straw and see the same effect though the rate of pH slows down as the pH rises (this is in spite of one's blowing bubbles having higher levels of carbon dioxide 100 times higher than in air – the TA levels in the experiment have far higher levels of carbon dioxide in the water than in air, but the princple is the same as that in pools – just accelerated).

One can add acid again and see that pH and TA drop and that blowing bubbles or stirring has the pH rise again. One can see that this cycle of aeration and acid addition results in a lowering of TA.