

Advanced Chemistry and Its Impact on Disinfection

National Environmental Health Association's
EH2O Recreational Water Virtual Conference
18-19 January 2016

Roy D. Vore, Ph.D., NSPF®I, CPO® Certification, CPI™

BioLab Inc.

roy.vore@biolabinc.com

Since 1900 a few things have changed

- Filtration systems have changed – in more ways than recognized
- The focus of chlorination changed from oxidation to disinfection
- Test methods for chlorine have changed
- The list of pathogens have expanded
- The concentration of chlorine used has increased
- Water balance parameters have narrowed
- Now we have Model Aquatic Health Code (MAHC)
- Have we now arrived?

Status of rec water today – my view

- Operators are still focused on water quality with lesser concern about recreational water illnesses
- Inspectors are focused on comparing test results to rigid parameters

As we continue to revise our pool codes as well as the Model Aquatic Health Code I suggest we ask:

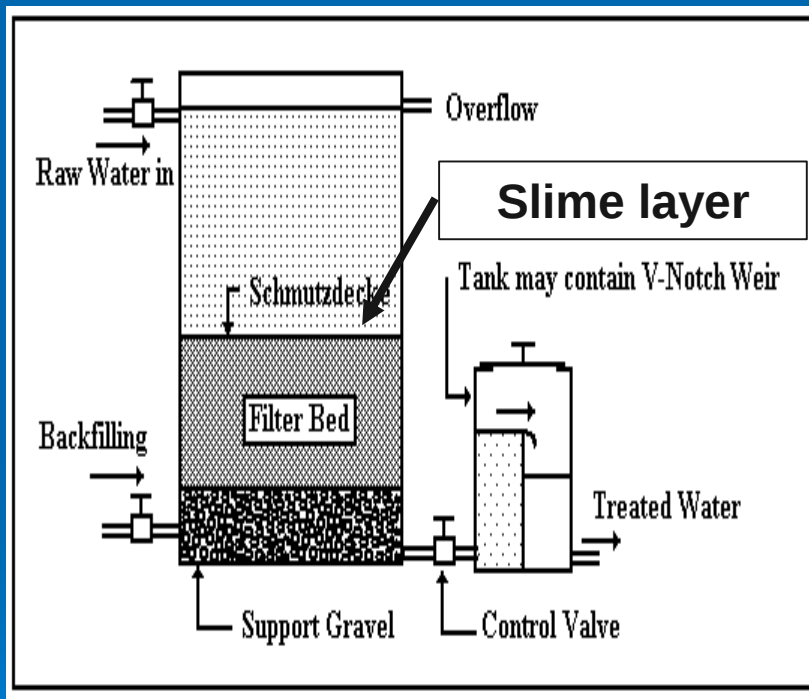
1. What lessons from the past have been lost?
2. Are our basic assumptions on treatment too restrictive?

Three areas I think we should revisit:

1. Examine how filtration has evolved
2. Investigate RWI outbreaks to see if we are using the correct pathogens as targets in establishing disinfection
3. Consider how normal variations in water parameters are impacting disinfection

Filtration

Slow rate sand filters – in the beginning



www.slideshare.net/drsanat81/water-filtration-plant

Slow rate sand filter

Gravity flow –very slow

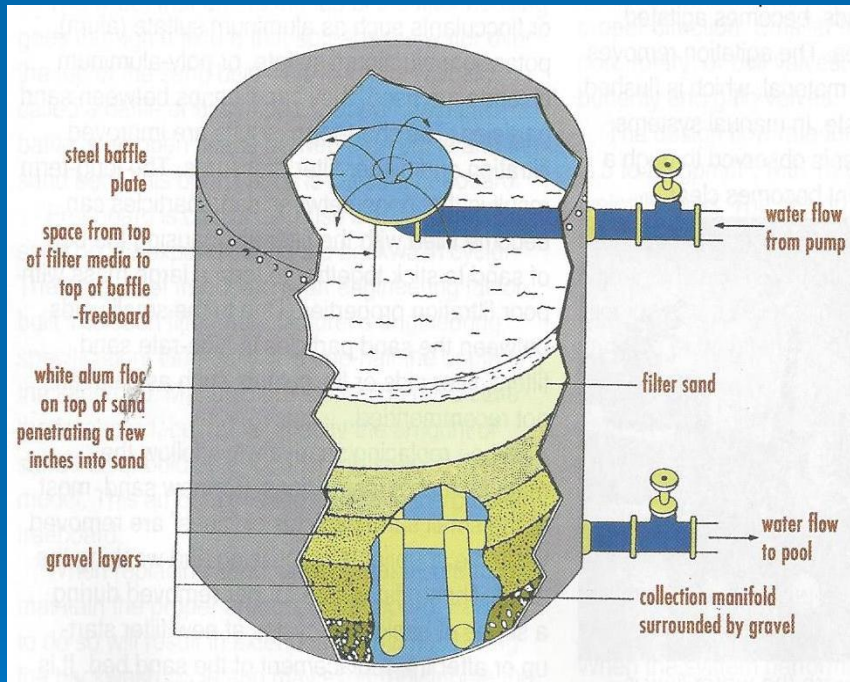
Multi-layers of fine sand, larger sand, and gravel (top to bottom)

Early 1900s, not used in pools today

Typically used with ammoniated alum $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$

Biologically active slime bed on top metabolized organics

Rapid rate sand filters – 2nd generation



NSPF

Rapid rate sand filter

3 gpm/square foot of filter area

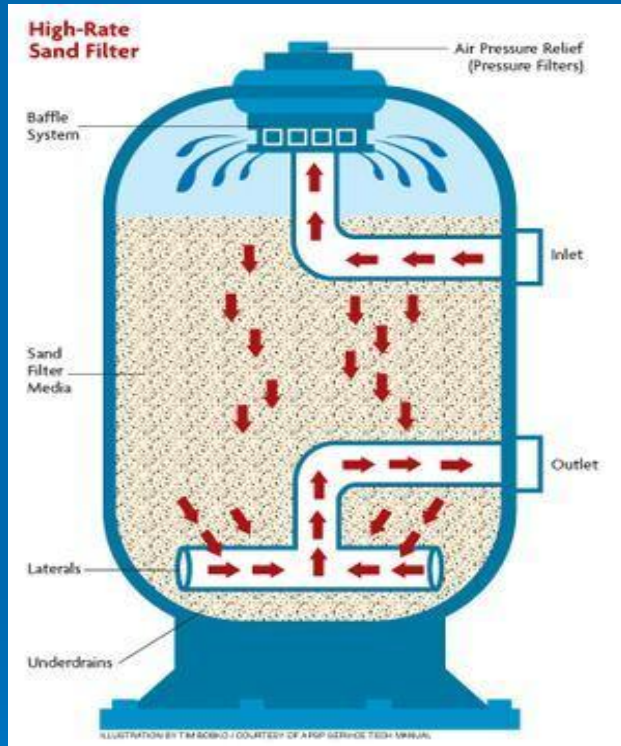
Multi-layers of gravel, sand, fine sand

Early 1900s, decreasing in use after 1950, still around but quite rare today

Commonly used with alum ($\text{Al}_2(\text{SO}_4)_3$)

Deep floc layer on top significantly improved filter efficiency

High rate sand filters – 3rd generation



www.poolspanews.com/

High-rate sand filter

5-20 gpm/ square foot of filter area

Single layer of sand of uniform size

Introduced in 1950s, dominate type used in pools today

Flocculants not typically used

Filter aids used only as needed to polish water

Summary of sand filters

Slow rate sand filter	Rapid rate sand filter	High-rate sand filter
Gravity flow –very slow	3 gpm/square foot of filter	5-20 gpm/ square foot of filter
Multi-layers of fine sand, larger sand, and gravel	Multi-layers of gravel, sand, fine sand	Single layer of sand of uniform size
Early 1900s, not in pool today	Early 1900s, decreasing after 1950, quite rare today	Introduced in 1950s, dominate type today
Typically used with ammoniated alum $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$	Commonly used with alum $(\text{Al}_2(\text{SO}_4)_3)$	Flocculants not typically used
Biologically active slime layer metabolized organics	Floc layer significantly improved filter efficiency	Filter aids used only as needed to polish water

Overview on sand filters

➤ What we know

- Filters work better being a little dirty, or with a flocculent
- Filters contain $>10^6$ bacteria per gram of sand
- Filters with microbial beds are called fixed-bed bioreactors
- Fixed-bed bioreactors are commonly used to bacteria digest organics
- Chlorinated organics are much more intractable to biological digestion than non-chlorinated organics

➤ What we might think about

- Would a slow-rate filter on a side stream increase DBP removal?
 - Would post-filter chlorination control *Pseudomonas* release?
 - Would post-filter chlorination increase DPBs?
- Would routinely using floc with current filters increase DBP removal?

Pathogens in treated recreational water

Evolution of pathogens of concern

- Fecal indicators – the list came from drinking water
- *Staphylococcus* and coliforms – 1950s (White, 1972)
- *Shigella* – 1969
- *Pseudomonas* – 1978 (when hot tubs arrived) (CDC, 1978 WBDO report)
- *Legionella* – 1981 hot tub in VT (CDC, 1981 WBDO report)
- *Giardia* – 1985 (MMWR V47, SS-2)
- *E. coli* O157:H7 – 1998 Atlanta water park outbreak
- *Cryptosporidium* – 1992 (MMWR v 42; SS-5, 1993)
- Viruses have been mentioned for >60 years but less is known on their abundance or role in RWIs

Overview on pathogens of concern

➤ What we know

- CDC reports do not contain outbreaks of chlorine-sensitive pathogens when the free chlorine is >1.0 ppm
- This has been confirmed in an extensive field study (Esterman, 1984)
- Impacting bather behavior is very difficult - many still swim while ill
- Hyperchlorination is hard to employ, reactive, and not used until we are in the middle of a serious community health crisis

➤ What we might think about

1. Requiring full time on-site CPOs **or** remote monitoring for all facilities to reduce the incidence of chlorine-sensitive RWI outbreaks
2. Requiring secondary disinfection on **all** facilities to reduce *Crypto* outbreaks

Disinfection concentration

Chlorination type and levels

Pre-1941	1945-1969	1969-present
“Token” chlorination	“High free residual”	Current U.S. system
Measured by orthotolidine (O-T aka OTO)	Measured by orthotolidine (O-T aka OTO)	Measured by DPD
Used with ammonia supply	Total chlorine: 3.0 – 5.0 ppm	Combined chlorine <1.0 ppm, preferably <0.4 ppm
Total chlorine typical <1.0 ppm; monochloramine was primary disinfectant	Free chlorine: 1.0 – 2.0 ppm was primary disinfectant	Free chlorine: 1.0 – 4.0 ppm is mandated by EPA label
Limited ammonia supply in WWII reduced use	Required frequent superchlorination	Some states still listing <1.0 ppm free as minimum
Phased out once breakpoint was understood	Phased out because O-T is a carcinogen	MAHC 2016 lists: 1.0-10.0 ppm (without CYA) 2.0-10.0 ppm (with CYA)

Disinfection standards today

- Based on assumption that a broad-spectrum, rapid-acting disinfectant must be in the water at all times
- Disinfection testing method was drafted by USDA pesticides group (this was fore runner of US EPA)
- Method was published in 1964 (Ortenzio and Stuart, 1964)
- Method relied on the same bacteria used as indicators of fecal contamination of drinking water.
- Method was formalized as AOAC 965.13 and has not be updated since 1970

Conditions used in AOAC 965.13

Specified by US EPA in OCSPP 810.2600 as the laboratory presumptive method

- Glassware washed with chromic acid, triple rinsed and baked at 180°C for >2 hours
- Bacteria rinsed twice in a sterile solution and centrifuged to remove miscellaneous organic matter
- Sterilized distilled water with phosphate buffering
 - Plus it is treated to have ZERO chlorine demand
- Chlorine concentrations used:
 - 0.6 ppm at time zero
 - 0.4 ppm at ten minutes
- Kill times
 - *E. coli* 6 log reduction in ≤30 seconds
 - *Enterococcus faecium* 6 log reduction in ≤2 minutes

Before you adopt a 30 second kill rate

- Are your pool surfaces washed with chromic acid?
- Are your bacteria free of organic matter (e.g. feces, vomit, slime)?
- Did any soil get blown into the pool?
- Did any bather sweat or urinate in the pool?
- Did any bather carry sunscreen into the pool?
- In the official test method 1 bacteria is killed at 30 seconds and the other at 120 seconds. Why do we only quote 30 seconds as the performance standard?

Are you still certain that you want a rigid 30 seconds for a kill time in a real world setting?

Comparison of various codes/guidelines

Parameter	US EPA: use directions	MAHC (2016)	Nova Scotia (2014)	Alberta (2014)	BS EN 16713 (2016)
FC (no CYA)	1.0 - 4.0	1.0 – 10.0	2.0 - 4.0	>1.0 @ <30°C >2.0 @ >30°C	0.3 – 1.5
FC (+ CYA)	1.0 - 4.0	2.0 – 10.0	2.0 - 4.0	>1.0 @ <30°C >2.0 @ >30°C	1.0 – 3.0
CC	Not covered	≤0.4	≤0.4	Lowest possible	≤0.5
ORP (mV)	Not covered	Only specified with ozone	650 – 720	≥770 @ 0.3 ppm FC ≥700 @ 0.5 ppm FC	≥650
pH	7.2 - 7.8	7.2 - 7.8	7.2 - 7.8	6.8 – 7.6	6.8 – 7.6
Turbidity	Not covered	Must see bottom	Must see bottom	≤0.5 NTU	≤1.5 NTU
Flocculants	Not covered	Optional	Optional	Not covered	Optional
Bacteria testing	Not required (1)	Not required	Not required	Required	Optional

FC: free chlorine; CC: combined chlorine; (1) chlorine/bromine are grand fathered and efficacy data is not required for new formulations.

Comparison of various trade guidelines

Parameter	NSPF (2014)	APSP-11 (2009)	PWTAG (1999)
FC (no CYA)	1.0 - 5.0	1.0 - 4.0	0.5 - 2.0
FC (+ CYA)	1.0 - 5.0	1.0 - 4.0	2.5 - 5.0
CC	≤ 0.2	≤ 0.2	<50% of FC
ORP	“Calibrate to disinfectant level”	Not covered	Set per DPD results
pH	7.2 - 7.8	7.2 - 7.8	7.2 - 7.8
Turbidity	Drain clearly visible from deck	Bottom clearly visible	Not specified
Flocculants	Optional	Not covered	Optional
Bacteria tests	Not required	Not required	APC/coliforms recommended

FC: free chlorine; CC: combined chlorine;

Let's examine a hypothetical pool

➤ Assumptions:

- Chlorine source: pool bleach
- Free chlorine by DPD: 2.0 ppm
- Combined chlorine by DPD: 0.3 ppm
- pH (probe calibrated 1 hour ago): 7.5
- ORP (probe calibrated 1 hour ago): 780 mV
- Temperature: 77°F
- Cyanuric acid: 0.0 ppm
- TDS: 1000 ppm
- Ozone: not used
- Potassium monopersulfate: not used

Exactly what is your disinfectant level?

What happens if you keep the free chlorine at 2.0 ppm by DPD but your pH is unstable?

Free chlorine by DPD	pH	HOCl	OCl-	mV (Chemtrol)
2.0 ppm	6.6	1.77 ppm	0.23 ppm	849 mV
2.0 ppm	6.9	1.58 ppm	0.42 ppm	833 mV
2.0 ppm	7.2	1.31 ppm	0.69 ppm	815 mV
2.0 ppm	7.5	0.97 ppm	1.03 ppm	793 mV
2.0 ppm	7.8	0.64 ppm	1.36 ppm	766 mV
2.0 ppm	8.1	0.39 ppm	1.62 ppm	734 mV
2.0 ppm	8.4	0.21 ppm	1.79 ppm	694 mV

- As pH goes down HOCl and mV increase – and the kill rate increases accordingly
- As pH goes up HOCl and mV decrease – and the kill rate decreases accordingly

Data courtesy of Richard Falk

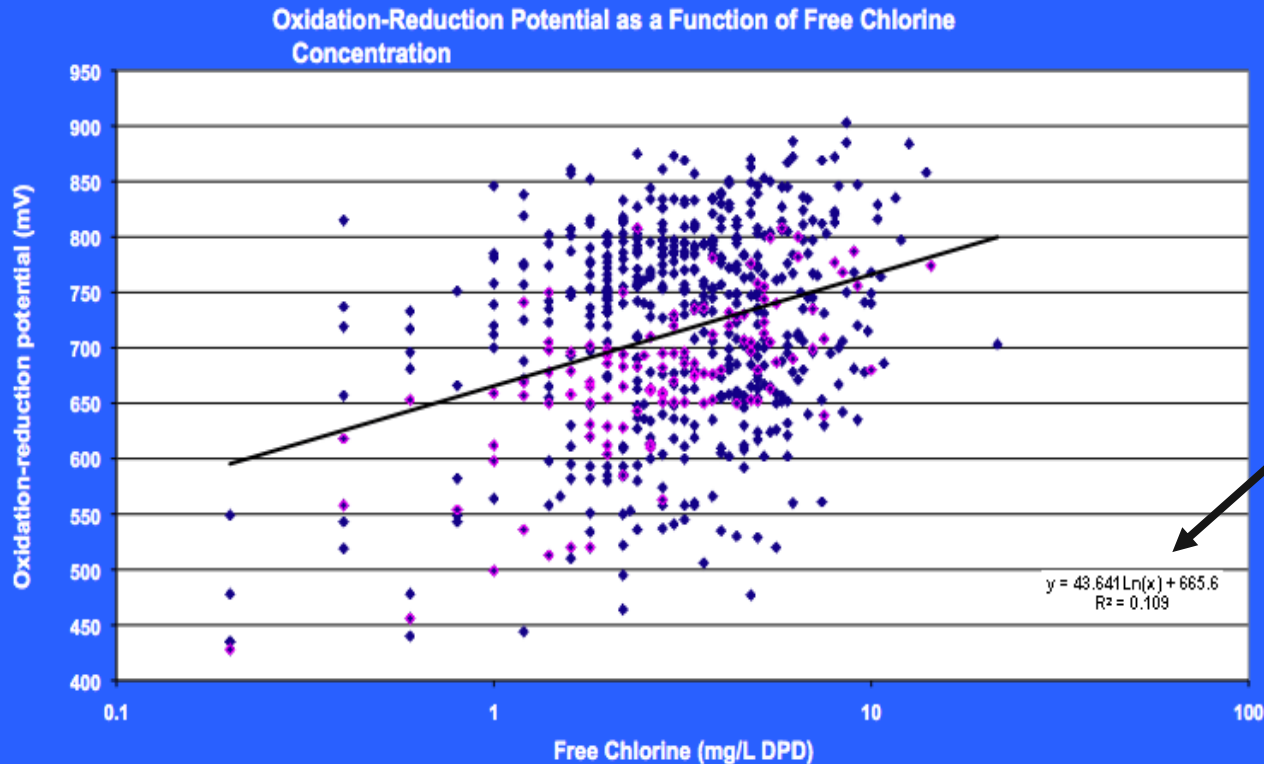
But ***you*** want to maintain HOCl at 1.0 ppm.
How do you adjust your DPD readings?

HOCl	pH	Free chlorine by DPD	OCl-	mV
1.0 ppm	6.6	1.13 ppm	0.13 ppm	799 mV
1.0 ppm	6.9	1.26 ppm	0.26 ppm	793 mV
1.0 ppm	7.2	1.53 ppm	0.53 ppm	786 mV
1.0 ppm	7.5	2.05 ppm	1.05 ppm	779 mV
1.0 ppm	7.8	3.10 ppm	2.10 ppm	773 mV
1.0 ppm	8.1	5.20 ppm	4.20 ppm	766 mV
1.0 ppm	8.4	9.37 ppm	8.37 ppm	759 mV

- In this case HOCl concentration is the dominant parameter
- *But* - you cannot directly measure HOCl. You calculate with a complex equation
- *Further* - the equation changes with changes in water chemistry parameters – and they are many

Data courtesy of Richard Falk

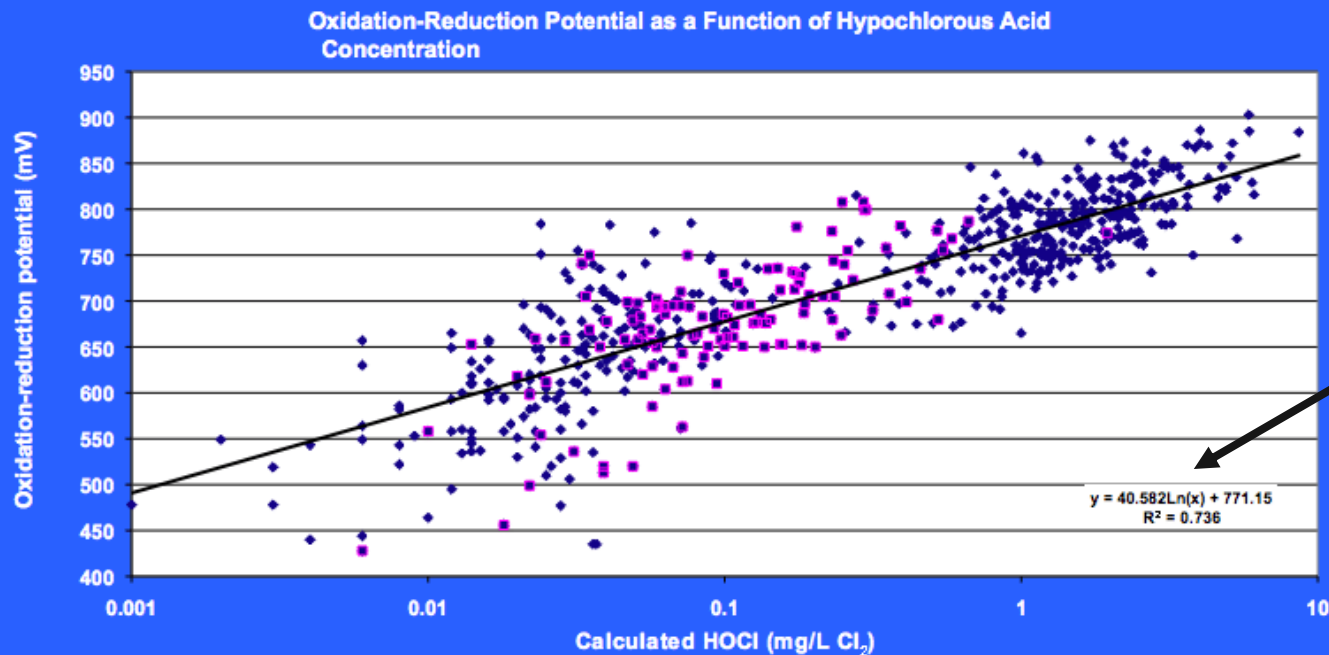
But we should not simplify this too much. Applying the same Free Chlorine vs. ORP curve to all pools will **NOT** work



What you
can't read
says, " $R^2 =$
 0.109 "

Data courtesy of Richard Falk and Jeff Luedeman

If you can develop a method to compare HOCl to ORP the fit is much better



The R^2 improves substantially to “ $R^2 = 0.736$ ”

Data courtesy of Richard Falk and Jeff Luedeman

Overview on disinfection

➤ What we know

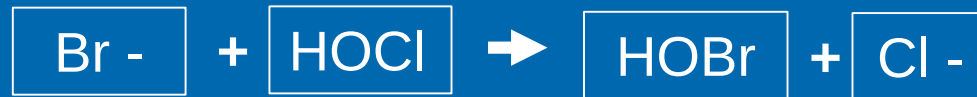
- In chlorine treated pools, HOCl is the only chlorinated species that is an effective disinfectant
- Using old studies is problematic because different test methods (OT, thiosulfate, DPD) were used at various times
- The disinfectant concentration, HOCl in our case, is impacted by numerous parameters including sunlight, temperature, pH, and organics
- Measuring HOCl is very difficult but it can be calculated, if you factor in the appropriate parameters

➤ What we might think about

1. Focusing on HOCl, not free chlorine as measured by DPD
2. Considering wider water parameters that recognize HOCl chemistry

Issues with *Crypto* in bromine pools

Methods to produce hypobromous acid



Regardless of the source, HOBr is the *primary* disinfectant

Reactions of bromine during disinfection



The ONLY way to eliminate the bromide salt (Br-) is to COMPLETELY drain and refill the pool.

Hyperchlorinating a bromine pool



- Adding chlorine results in the regeneration of hypobromous acid
 - This reaction occurs almost instantaneously
 - Because there is so much Br⁻ this reaction continues until all the hypochlorous acid is depleted
- The net result: it is extremely unlikely that you would ever be able to establish any appreciable amount of free chlorine in a bromine pool

White, Handbook of Chlorination, 4th ed

Hyperchlorinating a bromine pool

- If the Br- to HOBr reaction consumes all the HOCl then you are hyperbrominating *NOT* hyperchlorinating the pool
- DPD *cannot* distinguish HOBr, combined chlorine, and combined bromamines easily or quickly
- If you have a *Crypto* outbreak in a bromine pool and decide to treat it with chlorine, how do you test to ensure that you have achieved the correct CT target?
- *You cannot!*
- For *Crypto* you have only two effective options
 - A *COMPLETE* drain and refill (partial refills may not be effective)
 - Secondary disinfection systems

Finally, five thoughts to consider

1. If someone proposes a filtration system that has demonstrated DPB reduction would you consider it? What if it's unconventional?
2. If a pool is operating well at pH 6.6, zero cyanuric acid, has balanced water and 1.1 ppm free chlorine by DPD with no eye/skin complaints should it be closed by an inspector? If yes, why?
3. If a pool is operating well at pH 8.1, zero cyanuric acid, has balanced water and 5.2 ppm free chlorine by DPD with no eye/skin complaints should it be closed by an inspector? If yes, why?
4. How do you treat a *Crypto* outbreak in an outdoor bromine pool?
5. What if 2, 3, or 4 occurred in a splash pad with a UV system?

References

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