Stabilized Sanitizer Alternatives

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Innovative Water Care

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Laws and Codes

- Environmental Protection Agency (EPA)
  - The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)
  - Registration of products that kill and/or mitigate organisms
    - Sanitizers
    - Algaecides
- Occupational Safety and Health Administration (OSHA)
  - Personal Protective Equipment
  - Exposure Limits
- State and Local Government Agencies
  - Regulatory Codes
  - Code Inspection and Enforcement: Authority Having Jurisdiction (AHJ) (example: Health Inspectors)
National Standards

- The Centers for Disease Control and Prevention (CDC) Model Aquatic Health Code (MAHC)
  - [https://www.cdc.gov/mahc/editions/index.html](https://www.cdc.gov/mahc/editions/index.html)
  - Council for the Model Aquatic Health Code (CMAHC)

- Pool and Hot Tub Alliance (PHTA)
  - PHTA formed recently from two organizations
    - Association of Pool and Spa Professionals (APSP)- standards
    - National Swimming Pool Foundation (NSPF)- Certified Pool Operator (CPO) program
Stabilized Sanitizer Alternatives

- What is a stabilized sanitizer
- Why are stabilized sanitizer alternatives needed
- Stabilized sanitizer alternatives
  - Chlorine Gas
  - Sodium Hypochlorite
  - Chlorine Generator Systems
  - Calcium hypochlorite
    - Traditional
    - Slow dissolving
- New tool for making chlorine more effective
  - Biofilm control and remediation
Stabilized Sanitizers

- Stabilized sanitizers
  - Trichloroisocyanuric acid
    - 0.6 ppm cyanuric acid (CYA) per 1.0 ppm free available chlorine (FAC)
  - Sodium dichlorisocyanurate
    - 0.9 ppm CYA per 1.0 ppm FAC

\[
\text{Trichloroisocyanuric Acid} \quad 45.8\% \text{ Cl (91.6\% AvCl)} \\
54.2\% \text{ CYA}
\]

\[
\text{Isocyanuric Acid} \quad +3 \text{ HOCl}
\]
Free Chlorine Remaining After One Hour

Percent Free Chlorine Remaining After One Hour of Sunlight (Canelli 1974)

<table>
<thead>
<tr>
<th>CYA, ppm</th>
<th>% FAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25%</td>
</tr>
<tr>
<td>5</td>
<td>54%</td>
</tr>
<tr>
<td>10</td>
<td>65%</td>
</tr>
<tr>
<td>20</td>
<td>75%</td>
</tr>
<tr>
<td>25</td>
<td>77%</td>
</tr>
<tr>
<td>30</td>
<td>78%</td>
</tr>
<tr>
<td>100</td>
<td>82%</td>
</tr>
</tbody>
</table>
Why are stabilized sanitizer alternatives needed?

- HOCl is the primary sanitizer
- CYA decreases HOCl concentrations
- CYA can build quickly when stabilized sanitizers are used as the primary sanitizer
- CYA increases the time needed to kill pathogens
- Longer kill times for pathogens increase the risk of infection
Chlorine

Types of Chlorine Systems

- Hypochlorites
  - $\text{Ca}(\text{OCl})_2$ calcium hypochlorite (cal hypo)
  - NaOCl sodium hypochlorite (liquid bleach)
  - LiOCl lithium hypochlorite

- Isocyanurates
  - Sodium dichloroisocyanuric (dichlor)
  - Trichloroisocyanuric acid (trichlor)

- Chlorine gas (Cl$_2$)

- Chlorine Generator Systems (Salt Chlorinators)

All produce HOCl in the water

HOCl is the active sanitizer in a recreational water setting
Chlorine

Kill Times S. faecalis (Wojtowicz 1996)

- pH: 7 and 9
- CYA: 0 to 100 ppm
- FAC: 0.23 to 0.98 ppm
- Temp: 20°C

![Graph showing kill times vs disinfectant](image-url)
EPA Memorandum for Drinking Water


- In this Memo EPA defines free chlorine defined as "OCI and HOCl. Does not include chlorine bound to CYA

- National Primary Drinking Water Regulations (NPDWR)

- "The NPDWRs-approved DPD (N,N-diethyl-p-phenylenediamine ) and indophenol methods cannot measure free chlorine residual in the presence of cyanuric acid when Dichlor or Trichlor are being used for primary disinfection"

- "This has raised concerns that the inactivation determined based on chlorine residual measurements using the approved DPD and indophenol methods, in the presence of cyanuric acid in Dichlor and Trichlor, may not be sufficient to meet Ground Water Rule (GWR) since free chlorine is not being measured"

- Developed a web-based calculator to determine free chlorine residual [https://usepaord.shinyapps.io/cyanuric/](https://usepaord.shinyapps.io/cyanuric/)

- Presentation: [https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=534533](https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=534533)
HOCl as a Function of CYA

pH 7.5, 85 °F, 800 ppm TDS

Equilibrium constants from O’Brien 1972

- pH change from 7.2 to 7.8
- HOCl% changes from 69% to 35%
- Δ 34%
CYA Build Up

Compared To Calcium Hardness (CH) Build Up

Build Up With 3 ppm FAC Per Day
CYA - Trichlor; Ca - Cal Hypo

MAHC Limits

ppm CYA

Days

ppm CH

Trichlor
Cal Hypo

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Effect of CYA on Chlorine Kill Rates
### Effect of CYA on Cryptosporidium

(pH 7.5, 25°C) (Murphy et al. 2015)

<table>
<thead>
<tr>
<th>Average FC conc. (mg/L)</th>
<th>Average CYA conc. (mg/L)</th>
<th>Average time $3\text{-log}_{10}$ inactivation (hr)</th>
<th>Average Estimated $3\text{-log}_{10}$ CT value (mg·min/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.6</td>
<td>0</td>
<td>8.2</td>
<td>10,500</td>
</tr>
<tr>
<td>21.1</td>
<td>8</td>
<td>14.1</td>
<td>17,800</td>
</tr>
<tr>
<td>19.1</td>
<td>16</td>
<td>27.5</td>
<td>31,500</td>
</tr>
<tr>
<td>40.6</td>
<td>0</td>
<td>5.1</td>
<td>12,400</td>
</tr>
<tr>
<td>40.9</td>
<td>9</td>
<td>6.2</td>
<td>15,300</td>
</tr>
<tr>
<td>38.3</td>
<td>15</td>
<td>8.4</td>
<td>19,400</td>
</tr>
</tbody>
</table>

3-log inactivation was not achieved with 50 or 100 ppm CYA
Stabilized Chlorine Systems

Recommended CYA Limits

- MAHC (2018): 90 ppm maximum (15 ppm or less during crypto remediation)
- CMAHC Ad Hoc CYA Committee: Ratio 20 to 1 (ppm CYA to ppm FAC) maximum (Falk 2019)
- ANSI/PHTA-11. (2019): 100 ppm maximum

Possible Toxicology Limits:

- WHO: 117 ppm (11.7 mg Tolerable Daily Intake for a 10 kg child, swallowing 100 ml of water) (WHO 2006)
- NSF Memorandum (2019): Estimates the maximum allowable concentration in pool water to be 305 ppm, based on the Average Daily Dose (ADD) for competitive adult swimmers
Staying in Control of CYA

- Option 1: Use non-stabilized chlorine as primary sanitizer
  - Manually dose CYA for outdoor pools

- Option 2: Use stabilized chlorine as primary sanitizer, and...
  - Use non-stabilized chlorine for contamination remediation (MAHC 6.5.2.3)
  - Dilution (drain and refill water)
    - If 3 ppm FAC is added daily, when using trichlor
    - Drain 2% of the water every day to keep the CYA below 90 ppm.
    - Water loss due to splash out and back washing helps
    - Water loss from evaporation does not
Staying in Control of CYA

Continued...

- When CYA is in the water maintain a higher FAC
  - PHTA
    - Without CYA: Pools: 1-4 ppm Spas: 2-5 ppm
    - With CYA: Pools: 2-4 ppm if CYA > 50 ppm Spas: 3-5 ppm if CYA >50 ppm
  - MAHC:
    - Without CYA: Pools:1 - 10 ppm
    - With CYA: Pools: 2-10 ppm Spas: Prohibited
  - CMAHC Chlorine Stabilizers Ad Hoc Committee: CYA to FAC Ratio (20 ppm CYA for every 1 ppm FAC) when CYA > 0 ppm
  - EPA*:
    - Without CYA Pools: 1-4 ppm Spas: 2-5 ppm
    - With CYA Pools: 1-4 ppm Spas: 2-5 ppm

*Based on survey of EPA Labels. “It is a violation of Federal law to use this product in a manner inconsistent with its labeling.”
Implementing the 20:1 CYA:FAC Ratio

- In practice:
  - EPA Labels: 1 to 4 ppm FAC
    - “It is a violation of Federal Law to use this product in a manner inconsistent with its labeling”
  - Calculate limits:
    - \( \text{Min. FAC ppm} = \frac{\text{Max. CYA ppm}}{20} \)
    - \( \text{Max. CYA ppm} = \text{Min. FAC ppm} \times 20 \)
  - Set Static Limits; or
  - Set Dynamic Limits

### Static Limits

<table>
<thead>
<tr>
<th>FAC ppm</th>
<th>CYA ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>2.0</td>
<td>40</td>
</tr>
<tr>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td>3.0</td>
<td>60</td>
</tr>
<tr>
<td>3.5</td>
<td>70</td>
</tr>
<tr>
<td>4.0</td>
<td>80</td>
</tr>
</tbody>
</table>

### Dynamic Limits

<table>
<thead>
<tr>
<th>Date</th>
<th>CYA ppm</th>
<th>FAC ppm</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/1/2019</td>
<td>20.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>6/8/2019</td>
<td>32.6</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>6/15/2019</td>
<td>45.2</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>6/15/2019</td>
<td>22.6</td>
<td>1.1</td>
<td>Drain/Refill 50%</td>
</tr>
<tr>
<td>6/22/2019</td>
<td>35.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>6/28/2019</td>
<td>47.8</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>6/28/2019</td>
<td>23.9</td>
<td>1.2</td>
<td>Drain/Refill 50%</td>
</tr>
<tr>
<td>7/6/2019</td>
<td>36.5</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>
Benefits

- Low set up costs
- Low maintenance
- Slow dissolving tablets
- 99% Trichlor = 90% FAC
Dissolving Rate

Trichlor Tablets: Internal Test Results

* pH: 7.6 ± 0.1; Water Temp: 80.3 ± 0.9 °F; Flow Rate: 20.0 ±0.0 GPM, 8 Hrs./Day
Challenges

- Low pH: 2.9 – 3.5 @ 25°C (1% solution)
  - Corrosion
  - Adjustment chemicals
- CYA build up
  - Slows chlorine’s ability to disinfect
  - Water must be drained and refilled
- Incompatibility
Non-stabilized Chlorine Products

- Chlorine Gas
- Sodium Hypochlorite
- Saltwater Chlorine Generators
- Calcium Hypochlorite
Benefits

- Raw chemical cost
- 100% Cl₂ = 100% FAC
- Well metered dosage

Challenges

- Risk of chlorine gas release
  - Permissible Exposure Limit (PEL) 1 ppm (in air) (OSHA 2018)
- More stringent regulation compared to other forms of chlorine
  - Bans on ton-cylinders becoming more frequent
  - Department of Homeland Security (DHS)-Chemical Facility Anti-Terrorism Standard (CFATS)
- Training/monitoring costs
- Lowers pH at injector site
- MAHC 4.7.3.2.4.1 Chlorine gas prohibited in new construction
**Benefits**
- Low cost per pound
- 10% to 16% FAC
- Well metered dosage

**Challenges**
- Poor shelf stability (can lose 1/3 its strength in 30 days)
- Heavy, bulky containers
- Capital costs for storage (tanks and containment)
- Highly alkaline/caustic (pH~12)
- Secondary containment (leaks/spray)
- Dose changes (tubing wears out, change in strength) Tubing needs changing often
- Contributes more TDS than chlorine gas or calcium hypochlorite

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Sodium Hypochlorite Systems

**Diagram**

- Hypo Storage Tank
- Peristaltic Pump and tubing
- Pump
- Return
Saltwater Chlorine Generators

Benefits

- No transportation/storage of sanitizer
- Costs tied to electric costs

Challenges

- High capital costs
- Maintenance (cleaning and replacing cell)
- Raises pH (NaOH)
- MAHC 4.7.3.2.2.2 – all feeders/inline generators must be designed to maintain FAC concentrations at all times of operation.
- CMAHC group working on formula to size
**Traditional Calcium Hypochlorite Systems**

**Benefits**
- Shelf life
- Total operating costs
- Well metered dosage
- Calcium based
- Solid chemical (no secondary containment)
- Storage (no large chemical tanks)
- Lower shipping costs than bleach

**Challenges**
- Scale
- pH ~ 10.4-10.8
- Maintenance (descale)
- Slightly alkaline
- Always adding calcium hardness
Slow Dissolve Calcium Hypochlorite Systems

Benefits
- Same as other calcium hypochlorite systems
- Slow dissolving
- Low capital costs
- More dilute solutions than traditional cal hypo, less likely to build scale
- Feed generated by pressure differential

Challenges
- pH ~ 10.4-10.8
- Always adding calcium hardness
Percent Dissolved: Trichlor and Slow Dissolve Cal Hypo

- 3" Trichlor Tab...
- 3" Slow Dissolve Cal Hypo Tab...

*pH: 7.6 ± 0.1; Water Temp: 80.3 ± 0.9 °F; Flow Rate: 20.0 ± 0.0 GPM, 8 Hrs./Day
Feeder Technology – Output Control

- **Pool Feed Rates**
  - 0.5 to 7.0 pounds of available chlorine per day per feeder

- **Spa Feed Rates**
  - 0.5 to 5.5 pounds of available chlorine per day per feeder

- A maximum of three feeders can be installed in parallel to increase the total output rate

<table>
<thead>
<tr>
<th>Recommended Pool Size</th>
<th>Indoor</th>
<th>Outdoor Stabilized</th>
<th>Outdoor Un-Stabilized</th>
<th>Commercial Spa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,000 to 60,000 gallons</td>
<td>1,000 to 40,000 gallons</td>
<td>1,000 to 25,000 gallons</td>
<td>500 to 5,000 gallons</td>
</tr>
<tr>
<td></td>
<td>[3,785.4 to 227,124.7 liters]</td>
<td>[3,785.4 to 151,416.5 liters]</td>
<td>[3,785.4 to 94,635.30 liters]</td>
<td>[1,892.7 to 18,927.1 liters]</td>
</tr>
</tbody>
</table>

CDC/ Dr. Edwin P. Ewing, Jr.
Chlorine Gas Exposures

- MAHC Annex: 4.7.3.2.1
  - Bathers have been exposed to chlorine gas when;
    - Circulation pump is off or has low flow
    - Hypochlorite solution and acid are pumped into the return line
    - Chlorine and acid mix, generating chlorine gas
    - Circulation pump is turned on when bathers are present
MAHC 4.7.3.2.1.3

- All chemical control and feed systems shall be provided with an automatic means to disable chemical feeders in the event of low or no flow

MAHC 4.7.3.2.1.3

- Two of the following interlocks:
  - Recirculation pump power monitor,
  - Flow meter/flow switch in the return line,
  - Flow meter/flow switch at the chemical controller

- Slow dissolve cal hypo feeders use the pressure differential across the filter. No flow in the main recirculation line stops flow to the feeder
How can we make chlorine more effective

- Use cyanuric acid sparingly
- pH control
- Biofilm remediation and prevention

CDC/ Janice Haney Carr
Biofilms

Prevention

- Maintain the proper chlorine residual in all parts of the water at all times
- “Biofilms are communities of organisms that are held together by a sticky extracellular (polymeric) matrix.” (Josowitz 2011)
- Warm water and nutrients make spas good breeding grounds for biofilms
- Once a biofilm forms, it can protect pathogens from disinfectants

- *Legionella pneumophila*
- *Pseudomonas aeruginosa*
- Various Algae
- Various Molds
Biofilm Remediation

- MAHC 6.5.3.6 *Legionella* Contamination Remediation
  - Close
  - Test for *Legionella*, contact/inform Authority Having Jurisdiction (AHJ)
  - Scrub all surfaces with 5 ppm FAC or greater, rinse with clean water
  - Rinse with clean water, drain all water
  - Replace filters, make any necessary repairs
  - Refill, hyperchlorinate with 20 ppm FAC, 10 hours
  - Repeat until tests are negative for *Legionella*
Biofilm Removal

- First utilized as a remediation biocide and cleaner to eliminate slime and fouling in cooling towers
- EPA Reg. 63761-8
  - Patented technology
    - 6% quat
    - 6.3% hydrogen peroxide
      - 12.3% active ingredients
- EPA Registered Claims
  - For use in pools and spas
  - Biofilm removal
  - Kills biofilm bacteria
Hydroperoxide ion-phase transfer catalyst (HPI-PTC)

The combination of these ions enables them to transfer into the biofilm, lyse the biofilm organisms, and break down the lipid-based soils.

Inside the biofilm,

- The anion of hydroperoxide reacts with acetyl esters to produce peroxy-acids,
- which produce hydroxyl radicals
- Very reactive
- Decompose cell material efficiently

\[
\text{H}_2\text{O}_2 + \text{Quat}^+ X^- \rightarrow [\text{Quat}^+ -\text{OOH}] \rightarrow \text{OOH}^- + \text{Quat}^+ X^-
\]
Field Study #1

Corporate center central utility plant HVAC –

- 20,000 gal water in cooling tower
- DBDMH continuous feed (0.1 – 0.3 ppm free halogen)
- Prior improvements to microbial control program showed insufficient improvement
- Nov. 2, 2009, weekly THPS treatment was replaced with 9 ppm active dose of EPA Reg. 63761-8
- Observed a drastic reduction in slime Forming Bacteria (SFB) counts
- During trial green foam that had been plaguing the system was eliminated

EPA Reg. 63761-8 dosing started

[Graph showing SFB reduction from 7/21/2009 to 12/21/2009]
Use Instructions

CLEANING AND DISINFECTION OF WHIRLPOOL BATHTUBS, JACUZZIS, SPAS, POOLS, AND FOOTBATHS

- After using unit, drain and fill with a use solution of
  - 12.8 – 16.0 fl. oz. cleaner solution (EPA Reg. 63761-8),
  - 12.8 – 16.0 fl. oz. activator solution
- per gallon of water (1:1:10 – 1:1:8), with enough to cover the intake valve
- Start the pump to circulate the solution
- Wash down any related equipment with a clean swab, brush or sponge
- Treated surfaces must remain wet for a minimum of 10 minutes
- Drain the solution from the unit and rinse disinfected surfaces with fresh water
- Repeat for heavily soiled units
Thank you!
Resources

- Centers for Disease Control and Prevention (CDC)
  - [http://www.cdc.gov/healthyswimming/](http://www.cdc.gov/healthyswimming/)

- Pool and Hot Tub Alliance
  - Information bulletins on pathogens, contamination response, sanitizers
  - Standards
    - [http://www.apsp.org](http://www.apsp.org)

- Environmental Protection Agency (EPA)
  - EPA Registrations
Resources

- OSHA Chemical Database:

- Department of Homeland Defense Chemical Facility Anti-Terrorism Standards

- The Chlorine Institute
  - Pamphlet 82. Recommendation for Using 100 and 150 Pound Chlorine Cylinders at Swimming Pools 3rd Edition

- California Department of Pesticide Regulations
  - California Pesticide Illness Query (CalPIQ)
    - https://apps.cdpr.ca.gov/calpiq/calpiq_input.cfm
References

References

- Murphy, J. L., Arrowood, M.J., Lu, X., Hlavsa, M.C., Beach, M.J., Hill, V.R., Effect of Cyanuric Acid on the Inactivation of Cryptosporidium parvum under Hyperchlorination Conditions, Environmental Science and Technology, 2015, 49(12), 7348-7355

- Canelli, E.D., Chemical, bacteriological, and toxicological properties of cyanuric acid and chlorinated isocyanurates as applied to swimming pool disinfection, a review, AJPH February 1974, 64(2) 155-162.


References

