Chlorine Chemistry

Ernest "Chip" Blatchley III, Ph.D., P.E., BCEE, F. ASCE

Ernest (Chip) R. Blatchley III is a Professor at Purdue University with a joint appointment in the School of Civil Engineering and the Division of Environmental & Ecological Engineering. He received his B.S. in Civil Engineering from Purdue University, with M.S. and Ph.D. degrees from the University of California, Berkeley, also in Civil (Environmental) Engineering. Professor Blatchley and his students conduct research in the general area of Physico/Chemical Processes of Environmental Engineering, with particular emphasis on the fundamental behavior of disinfection processes.

Abstract

Chlorination (or more generally halogenation) has become a default practice in swimming pool operation and maintenance programs. Chlorine is known to be effective for control of most bacteria and viruses, and is also a powerful oxidant; both attributes can be beneficial in swimming pool settings. However, chlorine also reacts with a wide range of constituents that are introduced to swimming pools. The results of these reactions include formation of disinfection byproducts (DBPs) and decreases in the concentration of available free chlorine in a pool (i.e. chlorine demand). In addition, chlorine is known to be ineffective for control of protozoan parasites, such as Cryptosporidium parvum, that have been associated with a large fraction of recreational water illnesses of microbial origin.

This class will provide information about the chemistry that governs the behavior of chlorine in swimming pool settings as a disinfectant, as an oxidant, and as a precursor to DBP formation. Information will be presented to indicate the nature of the reaction products, the rates of these reactions, and their implications with regard to chlorine consumption in pools.
Chlorine Chemistry

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• Chlorine as a disinfectant
• Chlorine (halogen) chemistry
• Reactions in pools
  • Human body fluids
  • PPCPs
• Effects of chloride ion concentration
• Summary and conclusions

Overview

Chlorine as Disinfectant: History

From: http://rhtubs.com/resources/non-chlorine-shock-treatments-monopersulfate/
Chlorine as a Disinfectant: Ct Concept

• Basis: Chick-Watson (1908)
  \[ \frac{dN}{dt} = -\Lambda C^n N \]
  - \( n = 1 \)
  - Integrated form:
  \[ \ln \left( \frac{N}{N_0} \right) = -\Lambda t \]

\[ \text{HOCl} = H^+ + OCl^- \]

Crytposporidium Inactivation by Chlorine

• Remarkably resistant to chlorine
  - 4 log inactivation requires 5 days of exposure at 1 mg/L
  - Identified as etiologic agent in many outbreaks
  - Behavior of C. parvum may control management strategy


Inactivation of Bacteria by Chlorine

• Most bacteria (vegetative cells) are easily inactivated
• Rapid inactivation by free chlorine
• Chick-Watson is a reasonable first approximation

- Most viruses are easily inactivated by chlorine
- Chick-Watson is a reasonable first approximation
- Control of viruses should be effective with chlorination
- Water temperature affects inactivation kinetics

Chlorine Inactivation of Murine Norovirus and Coliphage MS2

\[ pH = 7.2, T = 5 \text{ or } 20^oC \]

<table>
<thead>
<tr>
<th>Virus Inactivation by Chlorine</th>
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Chlorine-Based Disinfection: Summary

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<tr>
<th>Microbe</th>
<th>Ct Required for 3 log10 Inactivation</th>
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<tr>
<td><em>Giardia lamblia</em></td>
<td>45-55 mg-min/L</td>
</tr>
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<td><em>Cryptosporidium parvum</em></td>
<td>~ 4500 mg-min/L</td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>~ 15 mg-min/L</td>
</tr>
<tr>
<td>Murine Norovirus</td>
<td>~ 0.18 mg-min/L</td>
</tr>
<tr>
<td>Coliphage MS2</td>
<td>~ 0.14 mg-min/L</td>
</tr>
</tbody>
</table>

Protozoa
Bacterium
Viruses

Protozoa
Bacterium
Viruses

FIGURE 4: Recreational Water-associated Outbreaks of Acute Gastrointestinal Illness, by Type of Exposure, Etiology, and Water Type — United States, 2011-2012

- Etiology: Untreated Water
- Etiology: Treated Water

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Protozoa
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Protozoa
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**Chlorine Chemistry: Equilibria**

\[ \text{Cl}_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \]
\[ \text{HOCl} = H^+ + OCl^- \]

\[ \text{FAC} = [\text{Cl}_2] + [\text{HOCl}] + [\text{OCl}^-] \]

\[ \text{HOCl} + \text{HOCl} = \text{Cl}_2O + H_2O \]

- Reactions are fast in both directions!
- Equilibrium established quickly
- Forms of FAC differ in terms of reactivity
- Distribution of FAC among forms governed by:
  - pH
  - [Cl^-]
  - T

**Chlorine Distribution (20°C)**

<table>
<thead>
<tr>
<th>pH</th>
<th>Distribution Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
</tr>
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**Reactivity of FAC: Substitution and Redox**

- Cl\(_2\) (and Cl\(_2\)O) are more effective substituting agents than HOCl, OCl\(^-\)
- Cl\(_2\) (and Cl\(_2\)O) are generally present at much lower concentrations than HOCl, OCl\(^-\)
- Factors that affect distribution of FAC will influence reactions

**Standard Redox Potentials (25°C)**

- \( \text{HOCl} + H^+ + 2e^- \rightarrow Cl^- + H_2O \) \( 1.49 \text{ V} \)
- \( \text{Cl}_2 + 2e^- \rightarrow 2Cl^- \) \( 1.36 \text{ V} \)
- \( \text{OCl}^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \) \( 0.90 \text{ V} \)
Chlorine Reactions With Ammonia: Breakpoint and Chloramination

- Substitution reactions are rapid and reversible
- Many redox reactions! (not shown)
- All proceed (directly or indirectly) through NHCl₂
- Any process that promotes NHCl₂ formation will promote chloramine instability
  - Low pH
  - High Cl:N ratio

Inorganic Chloramines in Pools: Where Do They Come From?

- Only trace quantities of NH₃ in pools
- Reduced-N in pools
  - Urine
  - Sweat
  - Urea
  - Creatinine
  - Uric acid
  - Amino acids

Formation of Inorganic Chloramines from Urea: t = 5 hr
Residual Chlorine Dynamics: Chlorination of Urea: pH=6.5; T=30°C; Cl:P=2

Urea:Chlorine "Breakpoint" Experiment
pH=7.5; [urea]₀=1.0 x 10⁻⁵ M; T=25°C

Urea:Chlorine "Breakpoint" Experiment
pH=7.5; [urea]₀=1.0 x 10⁻⁵ M; T=25°C

Chlorination of Urea: Reaction Products

\[
\text{Urea} + \text{Cl}_2 \leftrightarrow \text{NCl}_2 + \text{OH}^- + \text{Cl}^- \\
\text{Monochloro-urea} + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{NCl}_2 + \text{HOCl} \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{H}_2\text{O} \rightarrow \text{NH}_2\text{Cl} + \text{HOCI} \\
\text{HOCI} + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{Cl} + \text{HOCI} \\
\text{NOCI} + \text{H}_2\text{O} \rightarrow \text{NHCl}_2 + \text{HOCI} \\
\text{NOCI} + \text{HOCI} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \\
\text{Hydrolysis} \\
\]

Urea: Chlorine Summary: “Shock” Chlorination?

- Urea represents majority of reduced-N in pools
- Urea reacts slowly with free chlorine
- Products:
  - NCl\(_2\), NHCl\(_2\), NH\(_2\)Cl
  - NO\(_3\)\(_2\)
- Fates of reduced-N unclear
  - Inorganic chloramines → Oxidation via breakpoint reactions (Cl:N ≥ 1.6; mass ratio ≥ 10)
  - Organic chloramines → Oxidation incomplete; Chemistry, products, toxicology undefined
Chlorination of Glycine


Chlorination of L-Histidine


Effects of Chloride Ion on DBP Formation in Chlorinated Swimming Pools

• Traditional focus of halide ion effects on bromide (Br^-)
  \[ \text{HOCl} + \text{Br}^- \rightarrow \text{HOB} + \text{Cl}^- \]

• Effects of chloride (Cl^-) largely uninvestigated
  \[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \]

• Cl^- a common product of redox reactions with chlorine

• Cl^- accumulates in pools
  • Non-volatile
  • Largely non-reactive
  • Infrequent water replacement

• Cl_2 (and Cl_O)
  • Present at relatively low concentrations
  • Much more effective chlorinating agents than HOCl, OCl^-

Cl- a common product of redox reactions with chlorine
Effects of Chloride Ion on DBP Formation in Chlorinated Swimming Pools: FIC Consumption

Body Fluid Analog (BFA)

Effects of Chloride Ion on DBP Formation in Chlorinated Swimming Pools: DBP Formation

DBP Production from Chlorination of BFA

CHCl₃ Formation from Citric Acid

Effects of Chloride Ion Concentration on DBP Formation in Pools

NCl₃ Formation as a Function of Chloride Ion Concentration

CHCl₃ Formation as a Function of Chloride Ion Concentration

Pharmaceuticals and Personal Care Products (PPCPs)

- Vast group of chemical compounds
  - Drugs and veterinary products
  - Lotions, sunscreen, fragrances, and cosmetics

- Pathway to enter aqueous environment
  - Directly release to water treatment system
  - Inappropriate disposal

- Route to swimming pools
  - Wash-off during swimming
  - Excretion from bathers

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Pharmaceuticals
- Acetaminophen
- Budesonide
- Caffeine
- Ibuprofen
- Naproxen
- 16-alpha-hydroxyprednisolone
- Acetaminophen glucuronide
- Norfentanyl
- O-desmethylapronoxen
- 1-methyluric acid

Pharmaceutical metabolites
- 16-alpha-hydroxyprednisolone
- Acetaminophen glucuronide
- Norfentanyl
- O-desmethylapronoxen
- 1-methyluric acid

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Acknowledgement: Professor Markus Lill
Results and Discussion (Lotion)


Results and Discussion (Sunscreen)
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- **Acetaminophen** (Pain Reliever, Fever Reduced)
- **Budesonide** (Corticosteroid Hormone)
- **Caffeine** (CNS Stimulant)
- **Ibuprofen** (Nonsteroidal Anti-Inflammatory)
- **Naproxen** (Nonsteroidal Anti-Inflammatory)


Results and Discussion – Pharmaceuticals
Results and Discussion (Pharmaceuticals)

(T=25°C, pH=7.5, Cl:P=10)

- Acetaminophen
- Butorphanol
- Caffeine
- Naproxen
- Blank

Results and Discussion (Pharmaceuticals)

(T=25°C, pH=7.5, Cl:P=10)

- Acetaminophen
- Butorphanol
- Caffeine
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Results and Discussion (Pharmaceuticals)

(T=25°C, pH=7.5, Cl:P=10)

16-alpha-hydroxyprednisolone
Acetaminophen
Acetaminophen glucuronide
1-methyluric acid
Norfentanyl
O-desmethylnaproxen
Results and Discussion (Pharmaceutical metabolites)

\( T = 25^\circ C, \ pH = 7.5, \ Cl:P = 10 \)

Results and Discussion (Pharmaceutical metabolites)

\( T = 25^\circ C, \ pH = 7.5, \ Cl:P = 10 \)

Results and Discussion (Pharmaceutical metabolites)

\( T = 25^\circ C, \ pH = 7.5, \ Cl:P = 10 \)
Summary: Effects of Pharmaceuticals on DBP Formation in Pools

- Acetaminophen and acetaminophen glucuronide show significant DBP formation after chlorination
  - CNCl and CNCHCl₂
- 1-methyluric acid and uric acid
  - Inorganic chloramines
  - CNCl, CH₃NCl₂, and CNCHCl₂

Summary: Conclusions, Recommendations

- Proper bather hygiene
  - Reduction of DBP precursors
  - Reduction of chlorine demand
  - Improved water and air quality
- Wide range of (volatile) DBPs produced
- Chloride ion concentration affects water/air chemistry
- PPCPs contribute to DBP burden in pools
- Bather hygiene education, enforcement (culture change)
  - Bathroom breaks
  - Showers
- Water replacement is important to water/air quality
  - Accumulation of "stable" entities
    - Cl⁻
    - NO₃⁻
    - Others

Thank you! Questions?

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