Peracetic Acid
Can it work at your WRRF?

Brian Hilts, PE
Outline

- Background of PAA
- Evaluating PAA
- Design Considerations
- Life Cycle Evaluations
- Summary
Background

History of Usage

- Disinfection for the food industry (early 1990’s)
  - Hard surfaces in dairy, beverage, brewery, winery, egg, food processing plants and other clean-in-place (CIP) processes
- Food, meat, fish, fruit and vegetables (early 2000’s)
  - Food products can be put through spray, dip and brush wash
- Pulp & paper
  - Used to eliminate odor in paper mills and as a bleaching agent for pulp and paper
- Laundry (early 2000’s)
- Medical device sterilization (1980’s)
- Cooling towers water treatment (1990’s)
Background

**WRRF Disinfectants**

![Oxidation Potential (Volts) Chart]

- Chlorine Dioxide
- Chlorine
- Permanganate
- Hydrogen Peroxide
- Peracetic Acid
- Ozone
- Ferrate
- Hydroxyl Radical
Background

What is PAA?

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Colorless Liquid</td>
</tr>
<tr>
<td>Odor</td>
<td>Pungent, vinegar-like</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.16 g/cm³</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>108°C (226°F)</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>22 mm Hg at 25°C</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-49°C (-59°F)</td>
</tr>
<tr>
<td>Shelf Life</td>
<td>~12 months</td>
</tr>
</tbody>
</table>
## Background
### What is PAA?

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Vigorox® WWT II</th>
<th>Proxitane® WW-12</th>
<th>Peragreen® 22WW</th>
<th>SaniDate® 15.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peracetic Acid (CH₃COOOH)</strong></td>
<td>15%</td>
<td>12%</td>
<td>22%</td>
<td>15%</td>
</tr>
<tr>
<td><strong>Hydrogen Peroxide (H₂O₂)</strong></td>
<td>23%</td>
<td>18.5%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td><strong>Acetic Acid (CH₃COOH)</strong></td>
<td>16%</td>
<td>20%</td>
<td>42-50%</td>
<td>40%</td>
</tr>
<tr>
<td><strong>Sulfuric Acid (H₂SO₄)</strong></td>
<td>&lt;1%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Water (free)</strong></td>
<td>45%</td>
<td>balance</td>
<td>balance</td>
<td>35%</td>
</tr>
</tbody>
</table>
Background

How PAA Works

- Antimicrobial mode of action has chemical specificity\(^1\)
  - Active oxygen disrupts sulfhydryl (-SH) and disulfide (S-S) bonds in enzymes and proteins in cell membranes
  - PAA also reacts with the base pairs in DNA and RNA

- This reaction specificity results in low doses of chemical for disinfection

PAA is a viable and cost-effective disinfection alternative for NPDES compliance with numerous ongoing projects.
Evaluating PAA

*When is PAA Viable?*

**Process Operations Perspective**
- Disinfection by-products are a concern
- Water has widely variable water quality considerations
- Water has high color, high TSS, or low UVT
- In CSO applications where chlorine is stored for long periods of time without use
- Safety – Move away from chlorine gas

**Cost Perspective**
- Capital costs are a primary driver
- Existing infrastructure supports easy conversion to PAA
Evaluating PAA
Advantages/Disadvantages

**Advantages**
- Typically requires low dose
- Typically quenching not required
- Not impacted by Ammonia & Nitrite
- Long shelf life
- Short contact time
- No DBP formation
- Low capital cost delivery options
- EPA approval as WW & CSO disinfectant

**Disadvantages**
- High chemical costs
- Adds BOD to effluent
- State regulatory approval is limited
Evaluating PAA

Regulatory Acceptance

- US EPA has approved PAA as a primary WW disinfectant
- Individual States also provide approval

Disinfection Application
- Approved Water Reclamation Modified Permit
- In-Process Water Reclamation Permit Modification
- Approved Combined Sewer Overflow Modified Permit
Evaluating PAA

**Testing**

**Bench Testing**
- Identifies preliminary PAA dose
- Establishes dose-response and demand/decay

**Pilot Testing**
- Scaled or full-scale
- Refines dose-response based upon effluent variability

**Data Collection**
- Flow
- pH, TSS, Pre-BOD & Post-BOD
- Color, UVT
- Influent, effluent pathogens
- Dose and residual
Evaluating PAA

Dose Determination

- Determine C*T (mg*min/L) value required for Log Inactivation
- Develop inactivation model
  - Many models available, most are variations of the Chick-Watson model with adjustments for first-order kinetics

Homs Model

\[
\ln\left(\frac{N}{N_0}\right) = -kCt
\]

- \(N\) = Organism concentration
- \(N_0\) = Initial organism concentration
- \(K\) = Disinfection rate constant
- \(C\) = PAA concentration
- \(n, m\) = weighting factors
- \(t\) = time

Double Exponential Model

\[
N = N_o \cdot f_{Nd} \cdot e^{-kd \cdot CT} + N_o \cdot f_{Np} \cdot e^{-kp \cdot CT}
\]

- \(N\) = Organism concentration
- \(N_0\) = Initial organism concentration
- \(f_{Nd}\) = the fraction of the organism population that is “easy to inactive”
- \(k_d\) = the specific decay rate of the “easy to inactive” organism
- \(f_{Np}\) = the fraction of the organism population that is “hard to inactive”
- \(k_d\) = the specific decay rate of the “hard to inactive” organism
- \(t\) = time
- \(C\) = PAA concentration
Evaluating PAA

*Dose Determination*

![Graph](image)

- **Fecal Coliform Log Inactivation** vs **PAA Residual Concentration (mg/L)**

- **Hom’s Model**

- Time points: 5 minutes, 10 minutes, 25 minutes, 35 minutes, 43.5 minutes
Evaluating PAA

Dose Determination

Double Exponential Model

Log Inactivation E. Coli

CT (mg/L*min)

LI Exp  LI Model
Evaluating PAA Impact on BOD

Rate of BOD Formation (mg/L BOD/mg/L PAA) vs. PAA Dose (mg/L)

- Manufacturer A
- Manufacturer B
- Manufacturer C
Evaluating PAA

**Discharge limits**

- Some states have established limits for residual disinfectant
- The Vigorox® WWTII label includes recommended limits for discharge
  - 1 mg/L or a calculation based on the 7Q10 of the receiving stream
- WET testing to verify environmental impact
- Quenching?
  - Not typically, but testing is required to confirm
- **BE CAREFUL OF YOUR PERMIT!**
  - PAA interferes with chlorine tests

- **EXAMPLE: Metro Vancouver**
  - Doses < 5.2 / 5.9 mg/L resulted in residual concentration less than LC50
  - 40 WET tests were conducted during piloting and ALL met the criteria
  - Method: EPS 1/RM/13 “Biological Test”
Evaluating PAA Costs

- Procurement method options:
  - Purchase chemical only
  - Lease equipment and purchase chemical
  - Lease equipment, purchase chemical, and third-party operations

- Capital cost varies by site and application

- Costs for chemical vary based on amount purchased
  - $8.20 to $9.70 per gallon of solution (includes leased equipment) is a typical planning level range for a 3-5 year lease
  - Actual costs can be less
Evaluating PAA Costs

Aspects of System Procurement:

- Preconstruction services
- CFD modeling to confirm mixing efficacy
- Shop drawings
- Equipment procurement
- Feed pumps
- Tanks
- Controls & Analyzers
- Chemical purchase
- Duration
- Storage requirements
- System maintenance (preventive and/or reactive)
- System operation
Evaluating PAA

**Safety**

- Check local building and fire codes
- NFPA
  - Health Hazard – 3
  - Flammability – 1
  - Stability – 2
  - Special Hazards - OX
- WHMIS Hazard Class
  - B3 – Combustible liquid
  - C – Oxidizing materials
  - E – Corrosive material
  - D2B – Toxic materials
- No RMP required
- > 500 gallons = H-4 Occupancy
Design Considerations

- PAA Tank
- PAA Feed Pumps
- Contact Basin
- Sodium Bisulfite (If Necessary)
Design Considerations

Materials of Construction

<table>
<thead>
<tr>
<th>Material</th>
<th>Component</th>
<th>Compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passivated 304L/316L SS</td>
<td>Storage Tank/Piping</td>
<td>Very Good</td>
</tr>
<tr>
<td>HDPE</td>
<td>Storage Tank</td>
<td>Moderate</td>
</tr>
<tr>
<td>Teflon</td>
<td>Wetted Parts</td>
<td>Very Good</td>
</tr>
<tr>
<td>Kalrez</td>
<td>Wetted Parts</td>
<td>Very Good</td>
</tr>
<tr>
<td>Kynar</td>
<td>Wetted Parts</td>
<td>Very Good</td>
</tr>
</tbody>
</table>
Design Considerations

Storage & Pumping

- Chemical storage system
  - 14 days of storage at average conditions
  - Storage in delivery totes or bulk
  - Chemical venting/scrubbers – *Strongly recommend*
  - Does not need a heated space

- Chemical feed and transfer pumps
  - Redundancy
  - Transfer pumps
    - Air Diaphragm or Centrifugal
  - Feed Pumps
    - Peristaltic or Gear Pumps
  - PRVs included in all segments of piping that can be isolated by valves
Design Considerations

Mixing

- Chemical mixing or induction system similar to hypochlorite
- Mechanical or static mixing
- Do not use dilution water for mixing
- There is a possibility to install a system without mixing
- Consider CFD modeling
Design Considerations

**Process Control & Analyzers**

**Process Control**
- Dose-response is site-specific
- Various process control parameters (UVT, color, COD)
- Several process control approaches are feasible

**Analyzers**
- Location is dependent upon control
- Similar units to chlorine analyzers with proprietary PAA analysis equations.
- Tests field samples for PAA concentration
PAA Costs and Lifecycle Analysis

Case Study 1

- Conventional Activated Sludge Facility
  - Tertiary Filters w/post aeration
  - Bulk Chlorination/Dechlorination
  - Violating DBP in Permit
  - Tight effluent hydraulics
- ADF (mgd) = 5.5/10
- PHF (mgd) = 25
PAA Costs and Lifecycle Analysis

Case Study 2

- Conventional Activated Sludge Facility
  - Gaseous Chlorination/Dechlorination
  - Moving to new technology because of safety concerns

- ADF (mgd) = 25
- PHF (mgd) = 63
PAA Costs and Lifecycle Analysis

Case Study 3

- Solid Contact Stabilization Facility
  - Trickling Filters ahead of aeration
  - High industrial loading
  - No disinfection
  - Chlorine not an option
  - High color/decreasing UVT

- ADF (mgd) = 90
- PHF (mgd) = 170
Summary

PAA is a viable disinfection alternative for permit compliance

Site specific parameters identified through testing

Proper basis of design considerations needed for accurate sizing of system for alternative evaluation

Challenges Remain

- Regulatory acceptance
- Process control strategies for variable effluent quality
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