Chlorine Safety: The Rest of the Story

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PA-AWWA
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Hershey, PA

Gary M. Lohse, P.E., Regional Sales Manager, Severn Trent Services
Topics to Be Covered

- Background
- Solid Chlorine
  - Calcium Hypochlorite
- Liquid Chlorine
  - Commercial (Bulk) Sodium Hypochlorite
  - On-Site Hypochlorite Generation
- Gas Chlorine
  - Gas Basics
  - Your Father’s Chlorine Safety
  - Containment Systems
  - Automatic Shut Off Valves
  - Emergency Scrubber Systems
- Summary
Potable Water Disinfection

- Chlorine Based
  - Calcium Hypochlorite
  - Commercial hypochlorite
  - Gas chlorination
  - On-site hypochlorite generation
  - Chlorination-De-chlorination
  - Chloramines
  - Chlorine dioxide

- Alternate
  - UV disinfection
  - Ozone
Calcium Hypochlorite Tablet Feeders

They are not complicated
Calcium Hypochlorite Tablet Feeders

- Safe and simple
- Low initial cost
- Low annual maintenance
- Typically used for smaller Systems
## Calcium Hypochlorite

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very effective at typical pH</td>
<td>Difficult to dose</td>
</tr>
<tr>
<td>Proven &amp; reliable</td>
<td>Reacts with ammonia</td>
</tr>
<tr>
<td>Leaves a residual</td>
<td>Effectiveness decreases at high pH</td>
</tr>
</tbody>
</table>

### Safety

<table>
<thead>
<tr>
<th></th>
<th>Safety</th>
<th>Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>•</td>
<td>Easily stored</td>
<td>Dust concerns</td>
</tr>
<tr>
<td>•</td>
<td>Stable as solid</td>
<td>Incompatibility with solvents</td>
</tr>
<tr>
<td>•</td>
<td>Not highly regulated</td>
<td>Safety issues often overlooked</td>
</tr>
</tbody>
</table>
Spontaneous fire in SUV caused by calcium hypochlorite mixing with a solvent which caused the death of two children
Commercial Sodium Hypochlorite

Typical Sodium Hypochlorite Dosing Station

Commercial Sodium Hypochlorite Highlights

- Delivered to site in usable liquid form
- Delivered as 12-15% chlorine
- Major system components include 1) storage tanks, 2) metering pumps 3) analytical instrumentation
## Commercial Sodium Hypochlorite

<table>
<thead>
<tr>
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<th>Disadvantages</th>
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<tr>
<td>Very effective at typical pH</td>
<td>Reacts with ammonia</td>
</tr>
<tr>
<td>Proven &amp; reliable</td>
<td>Effectiveness decreases at high pH</td>
</tr>
<tr>
<td>Widely used for water</td>
<td>Concentration decays quickly</td>
</tr>
<tr>
<td>Leaves a residual</td>
<td>THM Formation</td>
</tr>
<tr>
<td>Simple chemical feed system</td>
<td>High cost per pound</td>
</tr>
<tr>
<td>Low capital cost</td>
<td></td>
</tr>
</tbody>
</table>

### Safety

- Liquid safer & more familiar than Gas
- Can cause severe burns
- No make down required
- Potential for gas formation
- Not highly regulated
- Secondary Containment required
- Safety issues often overlooked
On-Site Sodium Hypochlorite Generation

On-site Sodium Hypochlorite Highlights

• Delivered to site as salt

• Sodium hypochlorite produced on-demand with minimum storage

• 0.8 % sodium hypochlorite solution produced

• Utilizes DC current, salt, water

Typical 24 lb On-Site Hypochlorite Generation System
On Site Sodium Hypochlorite Generation

\[ \text{NaCl} + \text{H}_2\text{O} + 2\text{E} = \text{NaOCl} + \text{H}_2 \]

- For each lb. equivalent of Cl₂:
  - Salt (NaCl) 3.0 lbs
  - Softened Water 15 gal
  - Electrical energy 2 kWh
- For each pound of Cl₂ equivalent produced:
  - (15 gallons of 0.8% concentration Sodium Hypochlorite)
  - 1/35 lb. of H₂ gas produced (5.6 ft³)
- H₂ gas Immediately diluted upon production with air blower 100:1 to reduce H₂ to 25% of LFL
On-site Sodium Hypochlorite Generation

1. Water Softener
2. Brine Tank
3. Brine Injectors
4. Power Supply / Rectifier
5. Electrolytic Cells
6. NaOCl Tank
7. NaOCl Dosing System
8. Water Chiller / Heater
9. Hydrogen Dilution system
10. Control Panel

On-Site Hypochlorite Generation System Schematic
On-site Sodium Hypochlorite Generation
## On-Site Generated Sodium Hypochlorite

<table>
<thead>
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<tr>
<td>• Very effective at typical pH</td>
<td>• Reacts with ammonia</td>
</tr>
<tr>
<td>• Proven &amp; reliable</td>
<td>• Effectiveness decreases-high pH</td>
</tr>
<tr>
<td>• Often used for water</td>
<td>• THM Formation</td>
</tr>
<tr>
<td>• Leaves a residual</td>
<td>• More complex process than Bulk</td>
</tr>
<tr>
<td>• Minimal Concentration decay</td>
<td>• Higher capital cost than bulk</td>
</tr>
<tr>
<td>• Low cost per pound</td>
<td></td>
</tr>
</tbody>
</table>

### Safety

<table>
<thead>
<tr>
<th>Safety</th>
<th>Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 0.8% liquid safer than Bulk</td>
<td>• Can cause severe burns</td>
</tr>
<tr>
<td>• Deliver &amp; Store salt. Small quantity of chlorine on-site</td>
<td>• Potential for gas formation</td>
</tr>
<tr>
<td>• Not highly regulated</td>
<td>• Secondary Containment required</td>
</tr>
<tr>
<td>• Secondary containment not required</td>
<td>• Safety issues often overlooked</td>
</tr>
</tbody>
</table>
Chlorine Gas Feed Systems

Chlorine Gas System Highlights

- Delivered to site as gas in cylinders or containers or rail cars
- Stored on-site in original containers
- Chlorine removed from containers as liquid or gas
- Mixed with water prior to injection

Automatic control valve controlled by residual

Typical Chlorine Gas Feed System
**Gas Properties Comparisons**

<table>
<thead>
<tr>
<th></th>
<th>Chlorine (Cl₂)</th>
<th>Sulfur Dioxide (SO₂)</th>
<th>Ammonia (NH₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detectable Odor:</td>
<td>1.0 PPM</td>
<td>3 - 5 PPM</td>
<td>5 PPM</td>
</tr>
<tr>
<td>Throat Irritation:</td>
<td>5.0 PPM</td>
<td>8 - 12 PPM</td>
<td>400 PPM</td>
</tr>
<tr>
<td>Coughing:</td>
<td>20 PPM</td>
<td>20 PPM</td>
<td>1700 PPM</td>
</tr>
<tr>
<td>Dangerous in 30 - 60 Min.:</td>
<td>40 - 60 PPM</td>
<td>400 - 500 PPM</td>
<td>2500 - 4500 PPM</td>
</tr>
<tr>
<td>Specific Gravity (Air=1.0):</td>
<td>2.49:1</td>
<td>2.26:1</td>
<td>0.596:1</td>
</tr>
<tr>
<td>Color:</td>
<td>Yellow-Green</td>
<td>Colorless</td>
<td>Colorless</td>
</tr>
<tr>
<td>Solubility in Water (Lbs/Gal):</td>
<td>0.1216</td>
<td>1.9</td>
<td>4.417</td>
</tr>
<tr>
<td>Expansion Factor (Liquid/Gas):</td>
<td>1:457</td>
<td>1:73</td>
<td>1:146</td>
</tr>
</tbody>
</table>

- Of the three gases, Chlorine (Cl₂) is the most commonly used in the water and wastewater industry, followed by Sulfur Dioxide (SO₂), and Ammonia (NH₃).
How Gas Vacuum Feeders Work

- Discharge
- Ejector
- Water supply
- Ejector and check valve assembly
- Vacuum line
- Rate indicator
- Rate valve
- Vent check valve
- Regulating diaphragm assembly
- Inlet valve
- Lead gasket
- Valve cylinder
- Yoke clamp
- Inlet filter
- INLET VALVE
- LEAD GASKET
- CYLINDER VALVE
- YOKE CLAMP
- INLET FILTER
- CYLINDER VALVE
- Filter
- Chlorine gas
- Chlorine liquid
- Chlorine cylinder
- TO VENT
- VACUUM LINE
- WATER SUPPLY TO EJECTOR
- EJECTOR DISCHARGE
- R

CLAMP

17
Your Father’s Chlorine Gas Safety

- Pressurized systems
- Dangers Signs
- Ammonia bottle to find leaks
- Cylinders vertical, containers horizontal
- Chain cylinders together
- Keep cool and away from combustibles
- Eye wash
Modern Chlorine Gas Safety

- Significant Technical Advances
- Residual analyzer with feedback loop
- Non-pressurized vacuum systems
- Chlorine gas leak detector
- Alarm Systems / SCADA
- Automatic shut off valve
- Vega scrubber system for small leaks
- Scrubber system for gas containment
- Positive pressure breathing apparatus
- Specialized chlorine safety kits
- Fully automated system to contain leaks
- Federal, state and local regulations
- Written Emergency Procedures
Chlorine Gas Storage Cylinders

- Fusible Plug
- Capacity 1 to 150 lb
- 150 lb. predominate
- One opening - valve connection
- Standard cylinder valve with pressure relief device & fusible metal plug
- Fusible plug melts at 158-165°F
Ton Containers

- Capacity - 2000 lb.
- Two identical valves
- Can use as gas feed (upper valve)
- Can use as liquid feed with vaporizer (lower valve)
- Six (6) fusible plugs - three (3) in each end, melt at 158-165°F
ONE-TON CONTAINER LEAK SOURCES

- Sides and Heads of Container Fusible Plugs and Feed Valves
- Fusible Plug Core Fusible Plug Threads
- Valve Packing
- Valve Seat
- Valve Threads – In & Out & Nut
- Broken Valve – usually at container thread
# Chlorine Gas

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<thead>
<tr>
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<th>Disadvantages</th>
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<tr>
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<tr>
<td>• Widely used for water</td>
<td>• THM Formation</td>
</tr>
<tr>
<td>• Leaves a residual</td>
<td>• Leaves residual - potential dechlor</td>
</tr>
<tr>
<td>• Low Capital Cost</td>
<td></td>
</tr>
<tr>
<td>• Low cost per pound</td>
<td></td>
</tr>
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<table>
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<tr>
<th>Safety</th>
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<tbody>
<tr>
<td>• Smaller room area required</td>
<td>• Gas phase dangers</td>
</tr>
<tr>
<td>• Widely used in industry</td>
<td>• Higher risk -catastrophic accident</td>
</tr>
<tr>
<td>• Significant advances in safety systems decrease risk</td>
<td>• Highly regulated – OSHA, NFPA, USEPA, USDHS</td>
</tr>
<tr>
<td></td>
<td>• More training &amp; reporting required</td>
</tr>
</tbody>
</table>
Chlorine Containment Systems

Chlorine Containment Highlights

Steel shell containment system

Available for 150 lb. cylinders or one ton containers

Typical Chlorine Containment Systems for Ton Container
Chlorine Containment Systems - 150# Cylinder

Typical 150 Lb Cylinder Containment System
Chlorine Containment Systems

150 Lb Cylinder

One Ton Container
<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Often used for wastewater</td>
<td>Relatively Expensive</td>
</tr>
<tr>
<td>Proven &amp; reliable</td>
<td>One containment system required for each connection (cylinder or container)</td>
</tr>
<tr>
<td>Can reuse any chlorine captured</td>
<td>Extra time to change out cylinders or containers</td>
</tr>
<tr>
<td>Does not shut feed system down upon leak</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Safety</th>
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</tr>
</thead>
<tbody>
<tr>
<td>• Effective for leaks at tank</td>
<td>• No protection from leaks in line</td>
</tr>
<tr>
<td>• No release of chlorine at all for leaks at tank</td>
<td></td>
</tr>
<tr>
<td>• Can enter room after leak</td>
<td></td>
</tr>
</tbody>
</table>
Automatic Valve Shut Off Systems

Automatic Valve Shut off System Highlights

- Actuators mount directly to standard valve assemblies on ton containers and cylinders
- Fully automated system to automatically close the valves
- Can be activated by
  - Leak Detector
  - Panic or Emergency Button
  - SCADA and Fire Alarm System

Automatic Actuator - 150 Lb Cylinder
Mounting the Emergency Actuator

Note:
Multi Tank System Automatic Shutoff System
## Automatic Valve Shutoff Systems

<table>
<thead>
<tr>
<th>Advantages</th>
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</tr>
</thead>
<tbody>
<tr>
<td>• Fully automatic system</td>
<td>• One system required for each tank in service</td>
</tr>
<tr>
<td>• Simple to operate and maintain</td>
<td>• Increases time to change out tank</td>
</tr>
<tr>
<td>• Available for cylinders and containers</td>
<td></td>
</tr>
</tbody>
</table>

### Safety

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>• Protect against line leaks</td>
<td>• Does not protect against plug or tank failure</td>
</tr>
<tr>
<td>• Completely automated</td>
<td>• Some gas leaks in room prior to automatic closure</td>
</tr>
<tr>
<td>• Battery operated – will operate in power outage</td>
<td></td>
</tr>
</tbody>
</table>
Emergency Chlorine Scrubbers

Wet or Dry Scrubbers Available

Major Components: 1) Instrumentation for activation 2) Exhaust Blower, 3) Treatment System 4) Vents to Atmosphere

Fully automatic – Start and stop based

Chlorine Room Design Very Important

Typical Emergency Chlorine Scrubbers System
Emergency Chlorine Scrubber History

ADVANCEMENTS IN CHLORINE ABATEMENT TECHNOLOGY

I  SOLUTION BY DILUTION
   ONE ROOM VOLUME
   CHANGE IN 1 OR 2 MINUTES
   NEGATIVE ROOM PRESSURE

II  DILUTION RATES WITH
    SLOW START TOWERS
    POSITIVE TO NEGATIVE
    ROOM PRESSURE

III  RECYCLE GAS
     SYSTEM WITH EJECTOR VENTURI
     SCRUBBER
     POSITIVE ROOM PRESSURE

IV  ONCE THROUGH GAS
    SYSTEM WITH EJECTOR AND TOWER
    EMISSIONS LESS THAN 1/2 IDLH
    NEGATIVE ROOM PRESSURE

V  LOW PROFILE ONCE THROUGH GAS
    MULTI VENTURI PACKLESS SCRUBBER WITH 8' OVERALL
    HEIGHT ELIMINATES PACKED TOWER SCRUBBER
    EMISSIONS @1/2 IDLH & NEGATIVE ROOM PRESSURE
Emergency Chlorine Scrubber Design

FUSIBLE PLUG WORST-CASE

- Melts at approximately 160 °F
- $\text{Cl}_2$ at 80 °F = 117 psia vapor pressure
- $\text{Cl}_2$ at 160 °F = 325 psia vapor pressure
- 0.34” diameter orifice = 437 lbs/min at 160 °F
- Ton Container liquid plug empties ~ 5 minutes
- 437 lbs/min = 2380 scfm

Keep room at negative pressure

- Trend is to specify 3,000 scfm systems for one-ton containers.
- 150 lb Cylinders: Gas Leak Rate is 20 lbs/min = 110 scfm
- Scrubber Rate: Typically 250 cfm
Gas Chlorine Room Design

Room Containment Design Considerations

- Chlorine gas is heavier than air
- Must Contain gas and Liquid Chlorine
- Pick up duct should be 12-18 inches above floor
- Slope floors – confined corner sump
- Step down doorways, gratings covered
- Flood room to check for liquid escape routes
- Gas Detector 12 inches off floor
- Dual Rooms – Dual Intakes

Typical Gas Chlorine Room
Emergency Chlorine Scrubbers

Types of Emergency Chlorine Scrubber Systems

1. Wet Packed Emergency Chlorine Scrubber Systems
   - Utilizes caustic to neutralize chlorine
   - \[ \text{Cl}_2 + 2 \text{NaOH} \Rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} + 628 \text{ BTU/lb } \text{Cl}_2(\text{g}) \]
   - Upwards airflow, downwards chemical flow
   - Produces hazardous waste material

2. Wet Pack-less Emergency Chlorine Scrubber Systems
   - Same chemical reaction as packed tower
   - \[ \text{Cl}_2 + 2 \text{NaOH} \Rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} + 628 \text{ BTU/lb } \text{Cl}_2(\text{g}) \]
   - Utilizes ejector venturi
   - Produces hazardous waste material
Emergency Chlorine Scrubbers

High Performance Packing Media

Typical Wet Ejector Venturi / Packed Tower
3. Dry Emergency Chlorine Scrubber Systems

- Latest innovation in emergency scrubbers
- Utilize dry 4 mm impregnated activated alumina beads

- $\text{Cl}_2 + \text{STS media} \Rightarrow \text{NaCl (Salt)}$
- No liquid chemicals required – media lasts forever
- Produces non-hazardous waste material – landfill
- Automatic operation - minimum maintenance
Dry Media Scrubber Features & Benefits as Compared to Traditional Caustic Scrubbers

- No chemical maintenance
- New as well as exhausted media is non-hazardous
- One moving part - blower
- No chemical pumps
- Chemical leak containment is not required
- No heaters required in cold climates
- Safe
- User-friendly
- Dependable operation
- Tested and certified
- Low cost of ownership

Type “STS” 4 mm impregnated activated alumina beads
Dry Media Scrubber (one ton container)
Skid Mounted Dry Scrubber for 150 Lb Cylinder

See reverse side for parts description
150 # Cylinder Scrubber Installed In Storage Room

- Flanged Lid
- Sample Ports
- Suction Duct
- Rubber Pad
- Exhaust Fan - outside the storage room other side of wall
Dry Scrubber Installed Outside Storage Room

Scrubber

150# Cylinder Room
Dry Scrubber Skidded Assembly

- Suction Duct
- Differential Pressure
- No-Loss Discharge Stack
- 4 Sample Ports
- Drain
- 2 Hp Fan
- FRP Skid
Scrubber Dry Media Refill
VENT EXHAUST GAS ARRESTOR

- Treat vacuum regulator vent line
- Reduces room corrosion and outside releases
- Five gallon HDPE disposable bucket
- Dimensions are 10” Square x 15” Tall
- Passive – No fans required
- Pressure loss is less than same length of tubing
- Weighs 35 pounds with ‘STS’ 4 mm media beads
- Scrubs over 3 pounds of chlorine
- Media is non-toxic in fresh or spent forms
- Stackable for gas-side series mounting
- Visible Exhaustion Indicating Strips
## Emergency Chlorine Dry Scrubbers

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Fully automatic systems</td>
<td>• Like insurance – often are never used because not needed</td>
</tr>
<tr>
<td>• Dry media scrubbers require minimum maintenance</td>
<td>• Room design considerations</td>
</tr>
<tr>
<td>• Medium capital cost</td>
<td></td>
</tr>
<tr>
<td>• Cost benefit to using gas significant</td>
<td></td>
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</table>

### Safety

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<tr>
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<tbody>
<tr>
<td>• Recommended by Ten States</td>
<td>• Cannot enter room without safety equipment until cleared</td>
</tr>
<tr>
<td>• Reduce liability significantly</td>
<td></td>
</tr>
<tr>
<td>• Proven safe and reliable</td>
<td></td>
</tr>
</tbody>
</table>
## Safety Option Matrix – Cost vs Benefit

<table>
<thead>
<tr>
<th>Safety Option</th>
<th>Description</th>
<th>Capital Cost</th>
<th>O&amp;M Costs</th>
<th>Cost of Chlorine</th>
<th>Room Coverage</th>
<th>Ease of Operation</th>
<th>Operator Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gas - Auto Value</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Valve Only</td>
<td>Easy</td>
<td>Medium</td>
</tr>
<tr>
<td>2</td>
<td>Gas – Container System</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Cylinder</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>3</td>
<td>Gas- Wet Scrubber</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Full Room</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>4</td>
<td>Gas - Dry Scrubber</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>Full Room</td>
<td>Easy</td>
<td>High</td>
</tr>
<tr>
<td>5</td>
<td>Commercial Sodium Hypochlorite</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>None</td>
<td>Easy</td>
<td>High</td>
</tr>
<tr>
<td>6</td>
<td>On-site Hypochlorite Generation</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>None</td>
<td>Easy</td>
<td>High</td>
</tr>
</tbody>
</table>
Summary

- Chlorine gas, commercial hypochlorite and on-site hypochlorite are all very effective methods of disinfecting wastewater.
- Commercial hypochlorite avoids many of the safety issues associated with chlorine gas but the cost is significantly more per pound of chlorine.
- On-Site hypochlorite generation also avoids many of the safety issues associated with chlorine gas but with a lower cost per pound of chlorine than commercial hypochlorite.
- There are various methods to improve chlorine gas safety including containment systems, automatic shutoff valves and emergency scrubbers.
- Dry media emergency scrubbers have significantly less operation and maintenance costs compared to wet scrubbers.
- A life cycle cost analysis should be completed to properly assess the costs and benefits of each safety solution.
THANK YOU!

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