Hydrogen Sulfide Control Methods

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What Is It - How Does It Affect Us? Complaints vs. Compliments!

Smell something - “Dial It Up”
Hydrogen Sulfide aka “Sewer Gas”

- Colorless
- Toxic
- Highly flammable gas
- Foul rotten egg odor
- Breakdown of organic matter by bacteria
Why The Concern?

$\text{H}_2\text{S}$
Why The Concern?

Low Levels
- Irritation to eyes, nose, throat and respiratory system
- Severe headaches
- Fatigue

Moderate Levels
- Severe irritation to eyes, nose, throat and respiratory system
- Dizziness and confusion
- Nausea and vomiting
- Difficulty breathing
- Possible loss of consciousness

High Levels
- Seizures and convulsion
- Inability to breathe
- Possible death
## Why The Concern?

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppm = 1/1000 of 1%</td>
<td>Can smell. Safe for 8 hours exposure.</td>
</tr>
<tr>
<td>100 ppm = 1/100 of 1%</td>
<td>Kills smell in 3-15 minutes. May sting eyes and throat.</td>
</tr>
<tr>
<td>200 ppm = 2/100 of 1%</td>
<td>Kills smell quickly. Stings eyes and throat.</td>
</tr>
<tr>
<td>500 ppm = 5/100 of 1%</td>
<td>Lose sense of reasoning and balance. Respiratory paralysis in 30-45 minutes. Needs prompt artificial resuscitation. Will become unconscious quickly (15 minutes maximum).</td>
</tr>
<tr>
<td>700 ppm = 7/10 of 1%</td>
<td>Breathing will stop and death will result if not rescued promptly. Immediate artificial resuscitation is required.</td>
</tr>
<tr>
<td>1000 ppm = 1/10 of 1%</td>
<td>Immediate unconsciousness. Permanent brain damage may result unless rescued promptly.</td>
</tr>
</tbody>
</table>
Why The Concern?

Odors and Corrosion are a Growing Concern for Wastewater Utilities

- Housing development encroaching on WWTPs
  - Suburban
  - Urban
- Water conservation and decreased I & I increases BOD and lowers flow:
  - Increased odors
  - Increased corrosion
- Aging infrastructure and desire to extend asset life by reducing sewer and equipment corrosion rates
Impacts of Hydrogen Sulfide Release

- Corrosion of sewers and treatment plant facilities
  - H2S converted to highly corrosive sulfuric acid

- Health and safety
  - Workers
  - Public - migration through dry traps etc.

- Nuisance Odors
  - Collection system
  - Wastewater treatment plants
Most wastewater odors caused by sulfides

- Generation of sulfides in sewers in simple terms:
  Sulfate (SO42-) + Anaerobic Bacteria Sulfides

- Sources of Sulfates
  - Potable water
  - Ground water infiltration into sewers
  - Sulfates from industrial, commercial and domestic source

- Sulfide generation almost always not limited by amount of sulfates in wastewater
Sulfide Generation in Sewer Pipes (simplified)

Sulfates converted to sulfides in anaerobic zone

Oxygen in aerobic zone oxidizes these sulfides

When oxygen insufficient (<0.1 - 1.0 mg/l), sulfides diffuse into wastewater
Parameters That Effect Sulfide Generation

- Velocity
- Sulfide Generation

Higher Velocity → Lower Sulfide Generation
Parameters That Effect Sulfide Generation

- Higher BOD Generation
- Higher Temperature
- Higher Detention Time

Sulfide Generation
Approach to Treatment

Quantify odors/H2S
- Sampling and measurements
- Collection system modeling

Establish Goals: Acceptable odor/Corrosion Impacts
- Air dispersion modeling
- Remaining useful life

Determine Impacts
- On receptors
- Corrosion rates

Evaluate Control Alternatives
- Vapor phase
- Liquid phase
- Control through design
- Operational controls

Establish Design Criteria for Controls
Data Collection and Analysis

Collect data
  - OdaLoggers
  - Surface pH readings
  - Flow rates

Analyze data
  - Highest H2S readings
  - Highest pH (corrosion) readings
  - Lowest Flow Areas
  - Longest Detention Times
  - Contributors near by (industrial)
Options for Corrosion & Odor Control
Options for Corrosion & Odor Control

**Vapor Phase**
- Biotechnology (biofilter, biotowers)
- Carbon Adsorption
- Thermal Treatment
- Chemical Scrubbers
- Ozone and Ionization
- Containment
- Ventilation
- Collection and Treatment
- Multi-Stage Treatment

**Liquid Phase**
- **Oxidation**
  - Hydrogen Peroxide
  - Chlorine (hypo)
  - Permanganate
  - Oxygen Injection
    - Air
    - Nitrate
    - Microbial fuel cells
    - Slow release solid phase oxygen
- **Change Equilibrium**
  - Magnesium hydroxide
  - Lime
- **Sequestration**
  - Ferrous
  - Ferric
  - PRISC
  - pH Control
- **Inhibition**
  - Free Nitrous Acid
  - FNA + H2O2
  - Calcium Nitrate
  - Anthraquinone
    - Enzymes
    - pH Shocking
    - Molybdate

**Prevention Through Design**
- Maintain Velocities
- Reduce Points of Turbulence
- Control/Alter Ventilation
- Line Pipes
- Concrete Additives
- Air Jumpers
Vapor Phase Control

- Biological
- Activated sludge diffusion
- Thermal Treatment
- Wet/Chemical Scrubbers
- Ozone
- Photoionization (UV/Carbon)
Odor Control - Liquid Phase (Chemicals)

Many options to choose from, best option will depend upon:

Wastewater characteristics
• EX: metals will precipitate with iron/impact iron effectiveness

Local chemical prices

Operating barriers (hazmat chemicals/safety)

Downstream impacts at WWTP:
• Additional solids production
• Benefits of precipitation
• VFA production in sewers/impact on bio-P
Prevention through proper design will always be the lowest cost!

DID YOU KNOW???
Preventative maintenance coatings to protect infrastructure add layer to prevent corrosion and will “stop time”

Magnesium Hydroxide Surface Spray
- lowers surface pH
- protective layer between concrete and acids
- spray at release points (manholes, wet wells)
Corrosion Control

Corrosion rate is dependent on multiple factors:

- H2S Concentration
- Alkalinity
- Surface pH
- Wall Thickness
- Concrete Mix/Blend
- Oxygen
- Humidity
- Other Factors
Impacts of Hydrogen Sulfide Release

H$_2$S Vs the Life Expectancy of Reinforced Concrete Pipes

<table>
<thead>
<tr>
<th>Dissolved Sulfide (mg/L)</th>
<th>Pipe Diameter (Feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 5 Years</td>
<td>1  1.5  2  3  4  5  6  7  8</td>
</tr>
<tr>
<td>5-10 Years</td>
<td>1  1.5  2  3  4  5  6  7  8</td>
</tr>
<tr>
<td>10-25 Years</td>
<td>1  1.5  2  3  4  5  6  7  8</td>
</tr>
<tr>
<td>25-50 Years</td>
<td>1  1.5  2  3  4  5  6  7  8</td>
</tr>
<tr>
<td>&gt; 50 Years</td>
<td>1  1.5  2  3  4  5  6  7  8</td>
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Sulfide Species are a Function of pH
Factors that Affect H2S Release

**Generation**
- Organic Material (BOD)
- Dissolved Oxygen (DO)
- Temperature

**Release**
- pH
- Turbulence
Common Liquid Treatments

Precipitants

Oxidizers
- Chemicals
- Oxygen

Nitrates
- Calcium Nitrate
- Aluminum Nitrate
Common Controls Odorous Air Treatments

- Carbon Absorbers
- Biological Treatment
  - Bioscrubber
  - Oxygen
- Chemical Scrubbers
  - Calcium Nitrate
  - Aluminum Nitrate
Chemicals Used for H2S Control

**Most Common:**

- Bioxides / Calcium Nitrate
- Iron Salts
- Magnesium Hydroxide
- Sodium Hydroxide
# Chemical Treatment

## Advantages
- Ease of installation (often turnkey)
- Low capital cost (typically)

## Disadvantages
- High annual costs
- Some chemicals hazardous to handle
- Deliveries of chemicals hard in some areas (neighborhoods)

Closer added to the wwtp = more careful considerations
## Liquid Phase Treatments

<table>
<thead>
<tr>
<th>Precipitation</th>
<th>pH Elevation</th>
<th>Prevention</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Salts</td>
<td>Sodium Hydroxide (shock treatment)</td>
<td>Nitrate formulations</td>
<td>Air injection</td>
</tr>
<tr>
<td></td>
<td>Magnesium Hydroxide</td>
<td></td>
<td>Oxygen injection</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrogen peroxide</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Sodium hypochlorite</td>
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<tr>
<td></td>
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<td>Potassium permanganate</td>
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</tbody>
</table>
Iron Salts

Chemicals used
• Ferrous/ferric chloride
• Ferrous/ferric sulfate

Removal mechanisms
• Bind with dissolved sulfide and precipitate
• Reduce Sulfate Reducing Bacteria activity by 50%
• Provided as solution with low pH (1 to 2+)
• Typical dose rates ~ 3.5 lb Fe/lb sulfide
• Quick reaction times
Iron Salts

ADVANTAGES
• Sulfide specific
• Sulfide fully react (not re-released)

DISADVANTAGES
• Corrosive
• Hazardous materials a concern in neighborhoods
• Adds solids to wastewater
• Darkens wastewater: issue for UV systems
• Residual sulfide 0.1-0.2 mg/L
Nitrates

Calcium nitrate most common
• Non-hazardous

Prevention mode
• Provides substitute food source for microbes when oxygen depleted
• Typical dose ~ 2.1 gal/lb sulfide

Removal mode
• Nitrate biochemically oxidizes sulfide
• Typical dose ~ 0.7 lb gal/lb sulfide
• Long reaction time needed (1-2 hrs)
Iron Salts

ADVANTAGES

• Non-hazardous chemical
• Provides prevention and treatment
• Reduces sulfide to very low level
• No solids added to system

DISADVANTAGES

• High costs
• Detention time (for removal)
• Some issues with nitrates at WWTP
Magnesium Hydroxide

- Dosing independent of sulfide concentration
- Economical for high (>5 mg/L) sulfide levels
- Maintains pH at 8-8.5, inhibits SRB activity
- Adds alkalinity
- Generally requires mixer to maintain slurry in suspension
Magnesium Hydroxide

ADVANTAGES

• Non-hazardous chemical
• Can provide downstream benefits (alkalinity, etc.)
• Reduces sulfide to very low level
• No solids added to system

DISADVANTAGES

• Holds sulfide in suspension - inflows may reduce pH and release H2S
• Not generally cost effective for low sulfide streams (under 5 mg/l)
• Mixing required
Important Considerations

Acidic pH = Corrosion!!!

Odor is merely the symptom.

Corrosion is the real cancer!
References:

Michigan DEQ - Operator Training and Certification Unit

David Proctor, Chemist and Wastewater Operator

US EPA, Hydrogen Sulfide Control Methodologies
Questions?

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