Florida Rural Water Association
2016 Annual Conference
Daytona Beach, FL

Corrosion and Odor Control in Wastewater Systems
Topics to be covered

- Hydrogen Sulfide Formation and Consequences
- What has changed since the Clean Water Act
- Corrosion in Wastewater systems
- Liquid Phase Odor and Corrosion control
- Air Phase Odor control
- An comprehensive approach to Odor and Corrosion control
Hydrogen Sulfide Formation and Consequences

Hydrogen Sulfide (H₂S) is produced in sewer systems when dissolved oxygen is depleted and Sulfate reducing bacteria use the oxygen from Sulfate (SO₄) for their metabolism. The resultant product is hydrogen sulfide.
Other bacteria present in the water convert sulfates to sulfides. This causes the rotten egg smell, hydrogen sulfide gas ($H_2S$).

When the dissolved oxygen concentration falls below 0.1 mg/l, the water becomes septic.

Bacteria in the wastewater consume oxygen.
In water at pH 7, about 50% of the dissolved sulfide converts to $H_2S$ gas.
Acid corrosion then dissolves the infrastructure.

On the surfaces above the water, $\text{H}_2\text{S}$ gas is converted to strong sulfuric acid by *Thiobacillus* bacteria.

\[
\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{H}_2\text{SO}_4
\]
Once rebar is exposed, the sewer is structurally compromised.

Collapses routinely occur when preventable corrosion is allowed to continue unchecked.

\[
\begin{align*}
\text{Acid Attacks Concrete} \\
\text{SO}_4^{2-} &\rightarrow \text{HS}^- &\rightarrow &\ \text{H}_2\text{S}
\end{align*}
\]

\[
\text{H}_2\text{S} + \text{O}_2 = \text{H}_2\text{SO}_4
\]
What Has Changed Since the Clean Water Act Was Enacted??
Over the past 25 years, wastewater has changed.
DISSOLVED SULFIDE VS. TOTAL METALS
HYPERION WWTP

Corrosion Threshold

Metals
Sulfides

Courtesy of the City of Los Angeles
Relationship Between Total Sulfides and Gas That Can Be Released
According to the EPA, the primary reasons sulfide levels have risen are:

- **Pretreatment**

- **Longer Retention** – FM/grav. Centralization, lower flow plumbing

- **Higher BOD** - low flow plumbing, dewatering/transport strategies
Corrosion in Wastewater systems
Sulfide odor complaints are an indication that acid corrosion is occurring within your system.
Years of Life
(2” of sacrificial concrete)

Corrosion Range

Surface pH

Corrosion Rate (in./year)

7
6
5
4
3
2
1
0
0.001
0.01
0.1
1.0
100
20
8
L.A.County San Districts
When the surface pH falls below four, sewer life cycle cost assumptions are no longer valid.

For example, the difference in annual cost between surface pH 4 and 2 is...
Consequences of $\text{H}_2\text{S}$ Related Crown Corrosion
Corrosion at and above the spring line
Headworks Corrosion at and above the water line w/liner
Wetwells with Liners and Air Phase units
Manhole Corrosion
Acid corrosion, not "aging" is the primary cause of failing sewers. Bacteria cause odor and produce acid. Today, this phenomenon is much more commonly causing sewers to have surface pH of 2 or less.
Liquid Phase Odor and Corrosion control
Classes of Liquid Phase Treatment

- Oxidizers
- Metal Salts
- pH Control
- Hybrid Methods
- Biologics
Oxidizers

- Chlorine/Sodium Hypochlorite
- Aeration
- Oxygen Super Saturation
- Hydrogen Peroxide
- Nitrate Compounds
- Potassium Permanganate
Chlorine and Hypochlorite

- Abundantly available
- Can be hazardous to handle
- Can be corrosive
- Takes large quantities to oxidize the sulfides
  - Due to competing reactions may take as much as 10-15 parts by weight of chlorine to oxidize one part of sulfide
Aeration

- Wetwell aeration
  - Can only raise DO to near saturation
  - May release sulfides and other odors in the wetwell during aeration
  - DO does not last long enough for effective long-term downstream odor control
Oxygen Supersaturation

- Provides oxygen for as an oxidizer and DO source
- Provides oxygen for a longer period of time in the sewer than wetwell aeration.
- Requires high purity oxygen source – O₂ production facility or liquid oxygen storage and vaporization facility.
- Financial analysis is needed
Hydrogen Peroxide

- Effectively oxidizes Sulfides
- Provides DO to wastewater
- Once DO is depleted there is no more preventative power
- Should be added fairly close to odor problem
- Must be added at multiple locations on long sewer lines to be effective.
- Hazardous material and requires special handling and storage
Nitrate Compounds

- Provide a combined Oxygen Source to control the H2S production by the Sulfate Reducing Bacteria
- Oxygen from nitrates (NO₃) is preferentially used before sulfate (SO₄) reduction begins
- Once all the oxygen is consumed from the NO₃ nitrogen gas is released and there is no residual action
- Very effective for short problem forcemains.
- If large amounts of nitrate is used, there have been instances of gas binding in force mains due to excessive N₂ release due to denitrification.
- Is not effective for long distances
Potassium Permanganate

- Very strong oxidizer
- Effective for sulfide oxidization
- Stains all surfaces it touches
- Difficult to handle
- No long term preventative power
Iron Salts

- Ferrous Sulfate  \( \text{Fe} (\text{SO}_4) \)
- Ferric Sulfate  \( \text{Fe}_2 (\text{SO}_4)_3 \)
- Ferric Chloride  \( \text{Fe} \text{Cl}_3 \)
- Ferrous Chloride  \( \text{FeCl}_2 \)

FeSO\(_4\) + H\(_2\)S \(\rightarrow\) FeS↓ + H\(_2\)SO\(_4\)

SO\(_4\) + HS\(^-\) \(\rightarrow\) H\(_2\)S↑
Negatives of Iron Salts

- 4.5 lbs. of ferrous sulfate to remove 1 pound of H2S.
- Many times 2-3 times that amount is necessary for sulfide reduction
- Why, there are competing reactions in wastewater that will consume iron. Phosphorus, chlorides, sulfates, hydroxide, carbonate, oxygen and other common compounds compete for the iron especially in wastewaters high in saltwater infiltration.
- Byproducts – acid and precipitate
- Unintended consequence – More sulfide production
pH Control

- Lime Addition
- Sodium Hydroxide addition
- Magnesium Hydroxide addition
- The only Liquid phase treatment that will not consume VFA needed for Anaerobic Selectors in BNR
### Chemical Properties of Commercial Alkali's

<table>
<thead>
<tr>
<th>Property</th>
<th>50% NaOH</th>
<th>30% Ca(OH)$_2$</th>
<th>60% Mg(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Hydroxide</td>
<td>42.5</td>
<td>45.9</td>
<td>60.3</td>
</tr>
<tr>
<td>Solubility ($\text{H}_2\text{O}, \text{g}/100\text{ml}$)</td>
<td>42</td>
<td>0.185</td>
<td>0.0009</td>
</tr>
<tr>
<td>Per million gallons</td>
<td>1750 tons</td>
<td>7.7 tons</td>
<td>75 lbs</td>
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<tr>
<td>Reactive pH</td>
<td>14</td>
<td>12.5</td>
<td>9.0</td>
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<tr>
<td>Freezing Point °F</td>
<td>61</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Weight Equivalency</td>
<td>1.37</td>
<td>1.25</td>
<td>1</td>
</tr>
</tbody>
</table>
Sodium Hydroxide (Caustic Soda)

- Can be used to “burn out slime layers in pipes”
- Can be used to raise pH to between 8-9 for H2S control (has a reactive pH of 14.0)
- Hazardous Chemical requiring special storage and handling
- Raises pH very quickly
- Can create hot spots if not mixed well
- Must be carefully controlled to prevent scaling and corrosion
Lime

- Can be used to raise pH to 8-9 in sewers for odor control
- Has a reactive pH of 12.5
- Must be controlled to keep from increasing pH above 9.0
- Has no residual effectiveness for downstream odor control
- Every pound of lime added creates 4.5 pounds of sludge
Magnesium Hydroxide

- Can be used to raise the pH to between 8 and 9 for odor prevention and control.
- Is non hazardous and safe to handle
- Has a reactive pH of 9.0
- Solubilizes over long periods of time and remains effective in the down stream collection system.
- Prevents sulfate reducing bacteria (SRB) growth.
- Mg$^{++}$ combines with HS- to form a soluble complex
SRB Growth

![Graph showing SRB Growth Rate vs. Average pH]

- SRB Growth Rate at 6.23 is significantly higher compared to other pH values.
- The growth rate decreases as the pH increases to 7.16, 8.07, and 9.18.
Unlike iron salts however, there are no appreciable reaction precipitants.

\[ \text{Mg}^{2+} + \text{HS}^- \Leftrightarrow \text{MgHS}^+ \Leftrightarrow \text{Mg}_2(\text{HS}) \]
Hybrid Liquid Phase Treatment

- Peroxide regenerated Iron Treatment
- Nitrate treatment enhanced with alkali
- Iron treatment enhanced with Magnesium Hydroxide
- Lime treatment enhanced with Anthraquinone
- Sulfur scavengers (amine compounds)
Biologics

- Anthraquinone
- Bacteria Addition
- Enzymes
Air Phase Odor Control
Air Phase Unit Operation

- Units placed at the site of an odor problem as a method to remove odors from the air being discharged from a Wastewater Facility
- Do not prevent odors from forming
- Do not prevent corrosion at the structure being treated
- Does nothing for upstream corrosion or odor control
- While the cost appears to be less than liquid phase treatment, if replacement capital costs are considered this treatment may not be the bargain it appears to be.
Types of Air Phase Treatment

- Chemical Scrubbers
- Biofilters
- Carbon Adsorbers
- Impregnated media filters
Chemical Scrubbers

- Most common type use plastic media, caustic soda, and bleach
- The chemical is sprayed at the top of the tower and allowed to contact the air to be treated as it trickles down through the media.
- Caustic Soda (NaOH) is usually used in the first stage and controlled by pH monitoring
- Bleach is used in the second stage and is controlled by ORP control. ORP must remain positive.
- Magnesium Hydroxide has been used successfully as a replacement for Caustic Soda
- Sulfur Scavengers have also been used successfully to remove sulfides.
Biofilters

- The most common type of Air Phase Unit in the Marketplace
- The unit depends on a biological growth that is promoted on media in the filter housing
- A nutrient solution is sprayed on the media to promote the growth
- The units are effective in removing sulfides but often have other organic odors in the exhaust that require polishing
Biofilters Continued

- The units operate at a pH between 1.7 and 2.4 which is also the pH of the drainage from the filter that is discharged back to the sewer.
- The media varies greatly from mulch to sea shells.
- Some units are not in fiberglass tanks but are large beds of mulch.
Carbon Adsorbers

- H₂S adsorbs on the activated carbon
- Other odors also adsorb on the carbon
- Effective until there is H₂S or other odor break-through
- Some carbons can be regenerated chemically
- Some carbon can be thermally regenerated
- Most is landfilled and replaced
- Very effective as polishing units downstream of liquid phase treatment.
Carbon Adsorbers
Impregnated Medias
A Comprehensive Approach to Odor and Corrosion Control

- Use an effective liquid phase odor and corrosion control program in the collection system.
- Supplement the liquid phase treatment with air phase polishing.
- Institute physical and structural methods to minimize gas release.
  - Eliminate aeration and agitation from cascading flows, harsh transitions, splashing, etc.
  - Use liners where effective as a back-up to the above
  - Use non Corrosive materials
Questions