ODOR CONTROL METHODOLOGY FOR H₂S GENERATION

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Introduction

• Overview of Wastewater Odor Control Chemicals and Technologies
• Hydrogen Sulfide ($H_2S$) Generation
• Case Study
  – 1998 to 2008 Trial Data
  – 2009 to 2013 Two-Point Lime Application
  – 2013 Bioxide Trial
• Summary
• Questions
WastewaterOdorControlOverview

- Any process which wastewater is collected, conveyed, or treated has the potential to generate and release nuisance odors.
- Most often, these odors are generated as a result of an anaerobic or septic condition.
- This allows microbes, sulfate-reducing bacteria, to thrive and flourish.
- Odorous compounds such as mercaptans and amines – but $H_2S$ is the most prevalent.
Wastewater Odor Control Overview

• Solids handling facilities often release a combination of these compounds including ammonia and organic sulfides

• There are many different technologies to control odors; and these technologies can be divided into two main groups
  – Vapor-phase technologies
  – Liquid-phase technologies
Wastewater Odor Control Overview
Vapor-Phase Technologies

- Are used to control odorous compounds in the air or gas
- Are typically used in point-source applications,
- Designs are driven by the ventilation rate for headspace to be treated and the mass loading of the contaminant volatilized to the vapor phase
- Very efficient at preventing fugitive emissions from ventilated sources
Wastewater Odor Control Overview

Liquid-Phase Technologies

• Used to control odorous compounds in the liquid wastewater
• Typically are used in collection systems where control of both odors and corrosion are concerns
• Utilized for multiple point odor control such as manholes, air relief valves, and pumping stations
• Usually involve the addition of a chemical to the wastewater to control the formation of odorous compounds or react with those compounds after formation
Wastewater Odor Control Overview  
Vapor-phase versus Liquid-phase

**Vapor-phase**
- Driven by ventilation rates for headspace and mass loading of the contaminant volatilized from wastewater to the vapor phase
- Technologies within this group are Wet Air Scrubbing, Liquid redox technology, biofiltration, solid scavengers, and carbon adsorption

**Liquid-phase**
- Driven by wastewater flow rate and/or total mass loading of the contaminants within the liquid phase
- Technologies within this group are Iron Salts, Bioxide process, oxidizers, and anthraquinone
Vapor-Phase Technologies

Wet Air Scrubbing

• Most flexible and reliable technology for vapor-phase odor control
• Can be used to treat most water-soluble contaminants
• Very efficient for ammonia removal along with H$_2$S and organic odor removal
• Strictly a chemical reaction – not subject to upsets
• Application of multi-stage scrubbers target a wide range of contaminants for treatment
Vapor-Phase Technologies
Wet Air Scrubbing

• Major advantage is reliability and flexibility
• Major challenge is the minimization of chemical use and cost while maintaining complete treatment
• Most prevalent contaminant is H\textsubscript{2}S
• Multi-stage systems use sodium hydroxide to solubilize H\textsubscript{2}S, then sodium hypochlorite in last stage to treat other odor compounds
Vapor-Phase Technologies
Liquid Redox

- Long history of use
- Not widely used in odor control market
- Used in the petrochemical and natural gas industries
- Generally, too complicated and costly for odor control applications
- Use a chelated metal dissolved in water to remove H$_2$S from a gas stream then convert it catalytically to solid, elemental sulfur
- High capital costs
- Breakeven cost usually occurs when removal requirements exceed 200 – 300 lbs/day
- Only removes H$_2$S, therefore further polishing needed
Vapor-Phase Technologies

Biofiltration

• Can be used to treat a variety of biodegradable, water-soluble contaminants
• Odor contaminants are solubilized from vapor phase into an aqueous phase on the surface of an organic medium – compost, mulch, or peat
• Degradation by bacteriological population of the media
• Very effective at removing sulfur-based odors – not effective with nitrogen-based compounds
Vapor-Phase Technologies
Biofiltration

• Two major challenges are
  – Stability of the media
  – Control of the biofiltration process
• Media prone to breakdown resulting in increased headloss through filter
• Biological population within filter is subject to upsets
• Engineered media can be used to meet a particular combination of organic material
• Media design assists in control issues – enclosed media to protect from temperature and humidity swings
• Modular design provides quick and easy construction of the system with easy media replacement
Vapor-Phase Technologies
Solid Scavengers

• Scavengers are solid or liquid materials that remove sulfur compounds from gas or liquid streams, reacting with them, and converting them to a stable compound
• Media is consumed – limited to low levels
• Solid scavengers are utilized in wastewater facilities
• Differ from carbon adsorbers in that the sulfur compounds actually react to form stable compounds
• Two types – organic substrate (iron sponge) or ceramic substrate
• Do not absorb carbon dioxide – ideal for treating biogas with moderate $\text{H}_2\text{S}$ levels
Vapor-Phase Technologies
Carbon Adsorption

• The air stream is passed over a bed of adsorbent (carbon)
• Odor compounds are attracted to and adhere to the surface of the adsorbent
• Sulfur-based compounds are removed effectively – but nitrogen-based compounds are not effectively treated
• Activated and impregnated carbon can be used independently or in combination to remove a wide variety of contaminants
Liquid-Phase Technologies
Iron Salts

- Iron salts are applied to wastewater to oxidize and/or precipitate dissolved sulfide
- Ferrous salts (Ferrous sulfate) precipitate sulfide as ferrous sulfide
- Ferric salts (Ferric chloride) oxidize sulfide to sulfur while reducing the ferric iron to ferrous iron – the remaining ferrous iron then reacts with dissolved sulfide to form the ferrous sulfide precipitate
- During aeration, the ferrous sulfide is dissociated – the sulfide is oxidized to sulfate and ferrous iron is oxidized to ferric iron
- Ferric iron can be used for chemical precipitation of phosphorous at the POTW
- Iron salts are classified as hazardous compounds required double-wall tankage and piping systems
Liquid-Phase Technologies
Bioxide Process

• Application of a nitrate solution to wastewater
• Patented process – proprietary
• Uses naturally occurring bacteria to biochemically oxidize dissolved sulfide in the presence of nitrate
• \[8\text{NO}_3^- + 5\text{H}_2\text{S} = 5\text{SO}_4^- + 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{H}^+\]
• Reaction takes place in the flow or upper zone of the slime layer
• Classified as non-hazardous compound
• Easy and safe to store, handle, and apply
Liquid-Phase Technologies
Oxidizing Agents

• Oxidation involves the application of a strong chemical oxidizing agent to wastewater
• Chemically reacts with dissolved sulfide, converting it to sulfate or sulfur
• May be used to treat other odorous compounds besides dissolved sulfide
• Application rates tend to be higher than those predicted by stoichiometry of the sulfide reaction
• All oxidizers for wastewater odor control are classified as hazardous
• Hydrogen peroxide is most commonly used oxidizer
Liquid-Phase Technologies
Anthraquinone

• Chemical compound that interrupts the sulfate reduction process of sulfate reducing bacteria (SRB) in anaerobic conditions
• Metabolic process occurs in the cytoplasmic membrane of the SRB
• Non-hazardous compound
• Specific to the control of sulfide
• Can be used in conjunction with bioxide process
Summary of Wastewater Odor Control Overview

• There is no “best” odor control technology
• Factors must be considered in the selection and design of any odor control technology
• Requires an odor control strategy which considers the following contentions
  – Existing or projected conditions
  – Treatment objectives
  – Economic restraints
Hydrogen Sulfide Generation

- Issue is corrosion of the infrastructure and odor complaints from citizens
- $\text{H}_2\text{S}$ is typically formed in the collection system – anaerobic conditions
- Sulfur compounds occur naturally in domestic wastewater; however, are increased by
  - Warm climates = warmer sewer temperatures
  - Low velocity = stagnation of wastestream $< 2$ ft/sec
- Wastewater collection systems downstream from certain industrial users discharge points contain higher levels of sulfides = more $\text{H}_2\text{S}$ generation
Hydrogen Sulfide Generation

• Septic conditions do not allow sulfides to be oxidized, so the sulfides combine with hydrogen = hydrogen sulfide gas
• Gas released to headspace of sewer results in aerobic bacteria to oxidize $\text{H}_2\text{S} = \text{H}_2\text{SO}_4$
• $\text{H}_2\text{SO}_4$ attacks calcium carbonate in concrete resulting in milky appearance on surface at crown
• $\text{H}_2\text{S}$ Triangle: Contain three characteristics
• Presence of sulfur, low pH, high temperature
Hydrogen Sulfide Generation

• Corrosion issues can be resolved by increased ventilation, chemical addition, biological treatment, and application of protective coatings

• Odor issues often are resolved by chemical addition, biological treatment, ventilation, pollution prevention/source reduction
Case Study

• Twenty years of data in regarding to H₂S generation, trial methodology, and trial data/results

• Generation of H₂S is predominately a result of an Industrial User (IU) with @ 4.1 MGD flow, BOD loadings average @50,000 lbs/day (ranging from 30,000 lbs/day – 83,000 lbs/day), TSS loadings average @25,000 lbs/day (ranging from 10,000 lbs/day – 41,000 lbs/day)

• Sulfide concentration average = @1 mg/L

• Sulfate concentration average = @350 mg/L
Case Study

1998-2008 Cargill Self-Monitoring Field Data, Site 4 (Kettering Field) - Water Temperature
Case Study

1998-2008 Industrial User Self-Monitoring Field Data, Site E (Embury Park) and Site 4 (Kettering Field) - H₂S

- Goal (10 ppm)
- Magnesium hydroxide
- Sulfa Clear
- Two-Point Lime
- Bixide
- Ferric sulfate
- Hydrogen peroxide
- Anthraquinone
- Surfactant
- Sodium hypochlorite
- Sodium hydroxide
- Carbide Lime
- Ferric chloride
- 30 ppm Max. Avg. (H₂S Site 4 - Inside Manhole)
- 30 ppm Max. Avg. (H₂S Site E - Inside Manhole)
Case Study

January 2009 through February 2013 IU Self-Monitoring Field Data - Dissolved Sulfide
Two-Point Lime Application - Embury Park
Case Study

January 2009 through February 2013 IU Self-Monitoring Field Data - Dissolved Sulfide
Two-Point Lime Application - Kettering Field
Case Study

January 2009 through February 2013 IU Self-Monitoring Field Data - pH
Two-Point Lime Application - Embury Park
Case Study

January 2009 through February 2013 IU Self-Monitoring Field Data - H2S
Two-Point Lime Application - Embury Park
Case Study

January 2009 through February 2013 IU Self-Monitoring Field Data - H2S
Two-Point Lime Application - Kettering Field
Case Study

February 14, 2013 through April 12, 2013 IU Self-Monitoring Field Data - Dissolved Sulfide
Bioxide Trial - Embury Park

Dissolved Sulfide (mg/L) vs Date
Case Study

February 14, 2013 through April 12, 2013 IU Self-Monitoring Field Data - Dissolved Sulfide Biocide Trial - Kettering Field
February 14, 2013 through April 12, 2013 IU Self-Monitoring Field Data - pH
Bioxide Trial - Embury Park
Case Study

February 14, 2013 through April 12, 2013 IU Self-Monitoring Field Data - pH
Bioxide Trial - Kettering Field
Case Study

February 14, 2013 through April 12, 2013 IU Self-Monitoring Field Data - H2S
Bioxide Trial - Embury Park
Summary

• Many odor control methodologies have been tried – some more successfully than others

• Select the best-fit methodology for specific applications – some things work better under certain scenarios

• Case Study: Two-Point Lime Application has been most effective at controlling H₂S generation but with some undesirable consequences
Questions

Contact Information

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THANK YOU!
References

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