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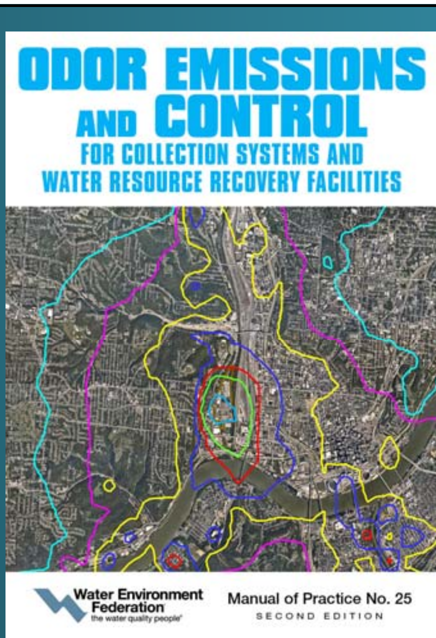

New edition addresses odor control for collection systems

Odor Emissions and Control for Collection Systems and Water Resource Recovery Facilities, MOP 25, Second Edition, offers guidance to help facility managers, operators, design engineers, and other decision-makers understand odors and air emissions and install effective odor control programs. This extensively revised second edition reflects the latest advances in odor testing and control and delivers contemporary knowledge on the odor control of water resource recovery facilities and collection systems. To order this resource, in print or eBook, visit www.wef.org/MOP25.

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Selection and Optimization of Liquid-Phase Odor Control Technologies

Thursday, April 30, 2020
1:00 – 2:30 PM ET

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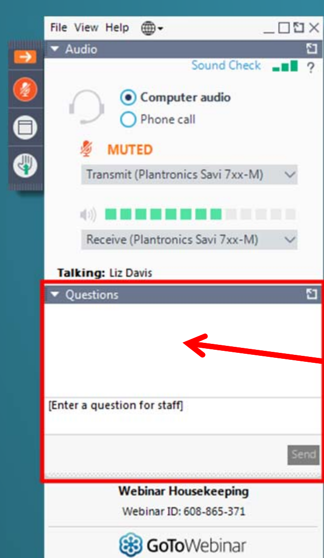
How to Participate Today



- **Audio Modes**
  - Listen using Mic & Speakers
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- **Submit your questions using the Questions pane.**
- **A recording will be available for replay shortly after this webcast.**

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Today's Moderators

Ali Trollier
Eastern Regional Manager
ECO2

Kevin Jameson
President
PureAir Filtration

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Dick Pope, P.E., BCEE

- Vice President & Odor Services Leader w/ Hazen and Sawyer
- 37-Years of Odor Assessment & Control
  - Focus on wastewater
  - Hands-on approach
  - More than 250 facilities/systems
  - 35 States and 10 countries
- Author, Presenter and Lecturer

Hazen

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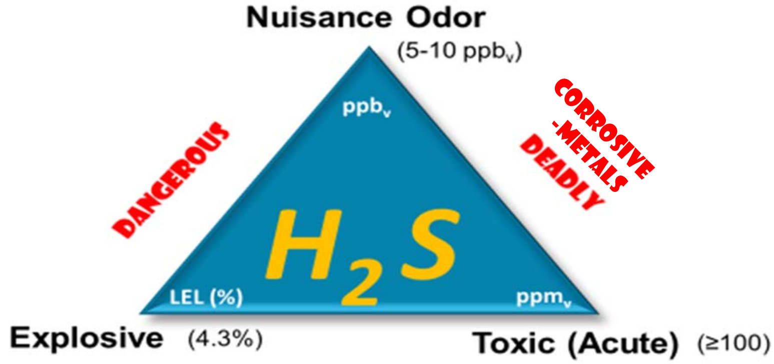
Health and Safety Moment

Be Careful of Hydrogen Sulfide - H_2S



Use Monitors
Be Aware of Concentrations
Err on the side of Caution

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Chemical Addition

- First and Foremost:
  - Wastewater Sulfide Mitigation
- Achieving:
  - Odor Reduction
  - Health and Safety Improvement
  - Infrastructure Corrosion Interruption

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Chemical Choices

Sodium Hypochlorite
STX
Sodium Hydroxide
Calcium Nitrate
Potassium Permanganate
Oxygen
Hydrogen Peroxide
Calcium Hydroxide
Ferric Sulfate
Ferric Chloride
Chlorinated Water
Ferrous Sulfate
Magnesium Hydroxide
Ferrous Chloride
Sodium Nitrate
Biological/Enzyme Additives

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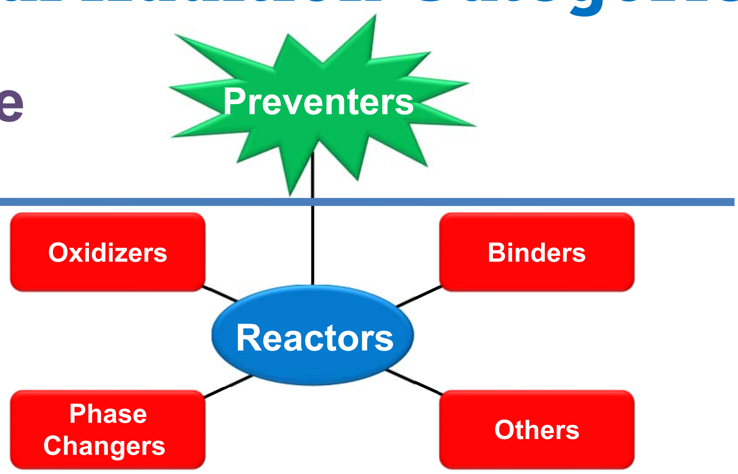
Chemical Addition Categories

Proactive

Reactive



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Preventers

Approach: Keep sulfides from being formed

Chemicals:

- Air/Oxygen
- Nitrates
- Caustic Scour

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Reactors

- **Binders**
  - Iron Salts
  - Polymeric Amine
- **Oxidizers**
  - Chlorine
  - Hydrogen Peroxide
  - Potassium Permanganate
- **pH Adjusters**
  - Caustic
  - Magnesium Hydroxide
  - Lime
- **Others**
  - Biological Additives
  - Enzyme Additives

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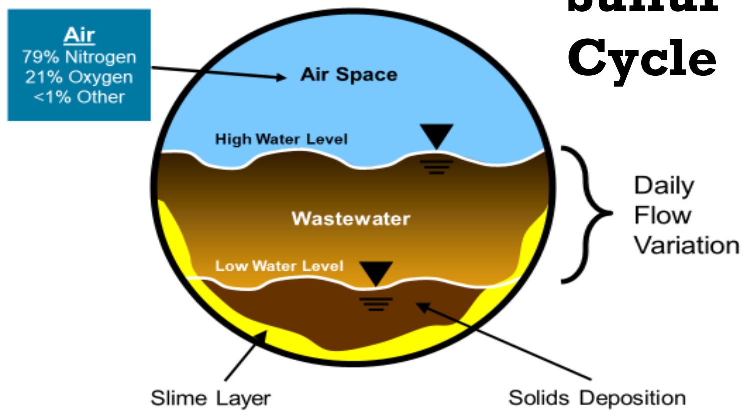
Where Does Production Take Place?

Gravity Pipe

- Where does Sulfide Form?
  - Slime layer
  - Wetted perimeter
- Wastewater D.O. dependent
  - D.O. > 0.5 mg/l – aerobic
  - D.O. < 0.5 mg/l – septic
- Airspace Oxygen varies

Sulfur Cycle



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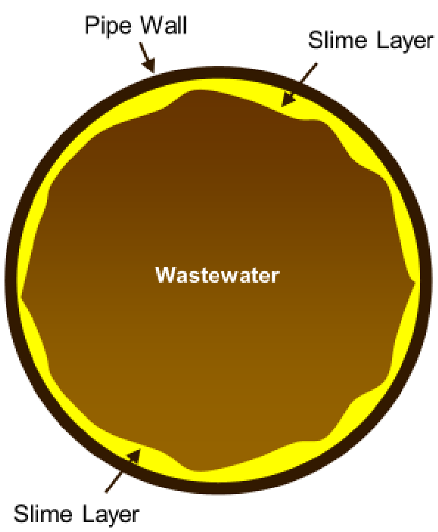
Where Does Production Take Place?

Force Main*

- Where does Sulfide Form?
  - Slime Layer
- Full pipe circumference slime layer
- No air space
  - No oxygen supply



*Includes surcharged line and inverted siphon.

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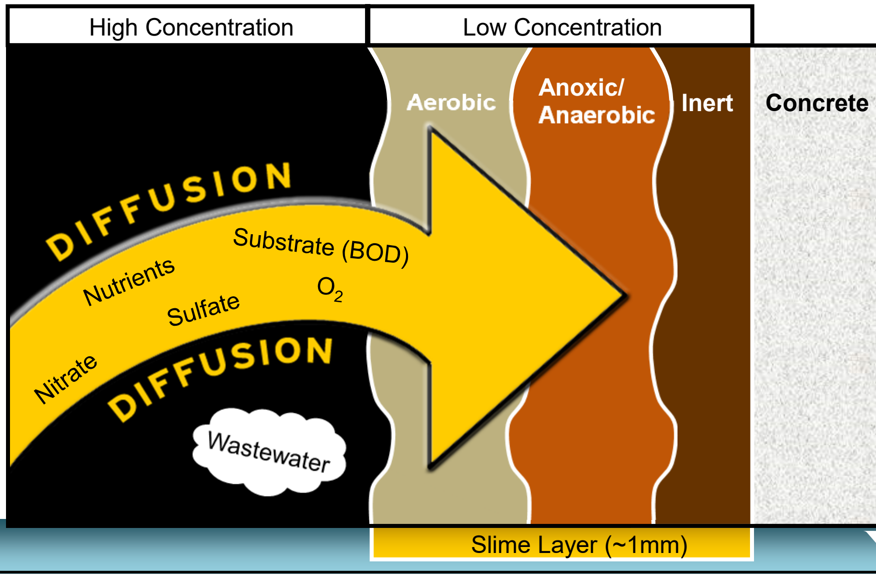
How Does Sulfide Form?



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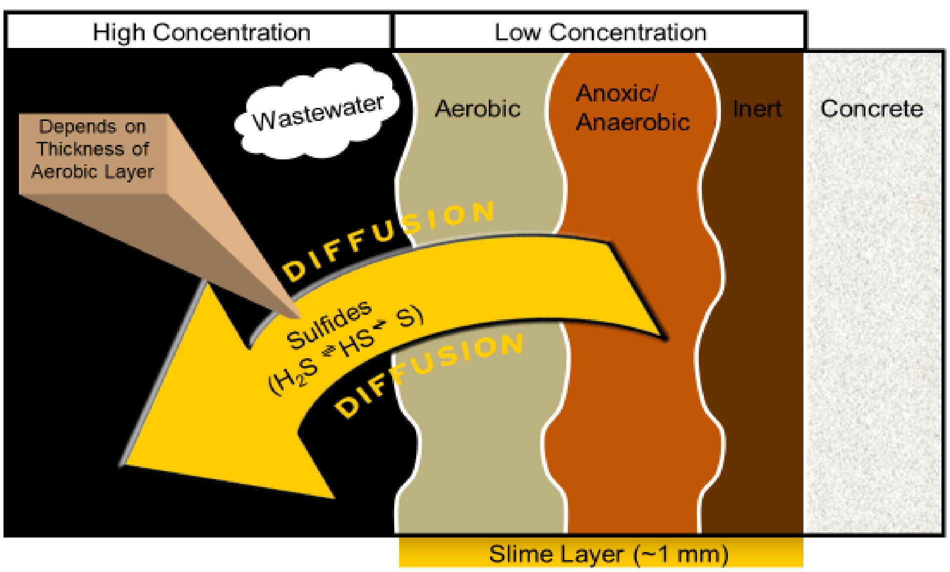
How Does Sulfide Form?



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Pipe Slime Layer – Sulfate/Sulfide Interaction

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How is H_2S Really Created in Sewer?

- Start with Sulfate ($SO_4^=$)
  - Typically present in wastewater
- Create anaerobic conditions
  - No available oxygen
- Grow anaerobic microorganisms
  - Sulfate Reducing Bacteria – SRB
  - Looking for an Oxygen Donor
- Combine with nutrients and substrate

$SO_4^=$	+	Anaerobic Microorganisms	=	Wastewater Sulfides

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How Does Sulfide Form?

$SO_4^{=}$ + Sulfate Reducing Bacteria = Wastewater Sulfide $H_2S \rightleftharpoons HS^- \rightleftharpoons S^{=}$

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How is H_2S Really Created in Sewer?

Wastewater sulfides exist as:

$H_2S \rightleftharpoons HS^- \rightleftharpoons S^{=}$

Which form(s) is (are) more prevalent?

Forms depend on wastewater pH!

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Why Are Sulfide Forms Important?

- **HS$^-$ and S$^=$ forms are soluble**
  - They remain in solution
  - Non-odorous
- **H_2S - only form that can**
  - Strip out of solution
  - Odorous
  - Corrosive

This is KEY!

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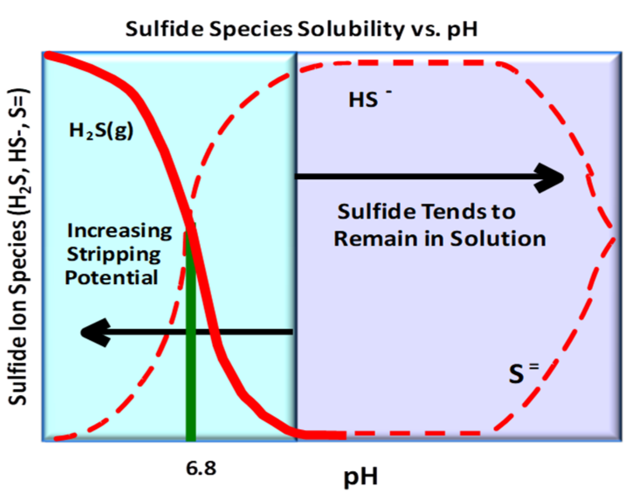
How Does Wastewater Sulfide Become an Odor Problem?



This relationship is critical to wastewater and vapor phase H_2S control!

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What are the Right Conditions for Odor Formation?

- Warm wastewater
- Low D.O.
- Lots of food (BOD) – soluble
- Long detention times
- Ample nutrients
- Sulfate
- Favorable support structure – pipe wall and deposition

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Critical Concept

Recognize

- Chemical Addition Focus: H_2S
- Other Odorous Compounds are Present
- Consider Their Importance

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Initial Steps

Review Existing Data/Systems

- Understanding Past & Current Conditions
- System Drawings
- Odor Complaints
- Previous Odor Studies
- System Hydraulic Model
- Identify Physical Sewer Attributes
- Meet with Staff

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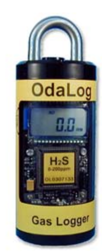
Field Investigations

Quantify Field Conditions

- Air
  - H_2S, Differential Pressure, Other Parameters
- Wastewater
  - Sulfide, BOD, Temp., pH, DO
- Other
  - Smoke Test



H_2S Data Logger

Field Test Kits

Smoke Candles

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Tools – Sewer Sulfide Modeling

- Hydraulic Model Base
- Collection System Simulation
- Physical & Operating Attributes
- Determinations
  - Sulfide Generation
  - H_2S Concentrations
  - ID Hot Spots
  - Chemical Addition Simulation
- MOP #25
  - Simplified equations
- Vendors

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Field Investigation – Bench Scale Testing

Chemical Jar Testing

- Viable Chemicals
- Dose Required
- Compare to:
  - Stoichiometric
  - Literature
  - Vendors

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What Chemicals Work Where?

- Site specific fit
- Depends on many variables
  - Desired goals
  - Application location/odor need
  - Length/Extent of effectiveness
  - Wastewater characteristics
  - Physical sewer attributes
  - Established criteria – Not 100%

    Ex.: 20 ppm H_2S & 0.2 – 0.5 mg/l Sulfide
  - Budget

Don't forget the Chemical Reaction Time!

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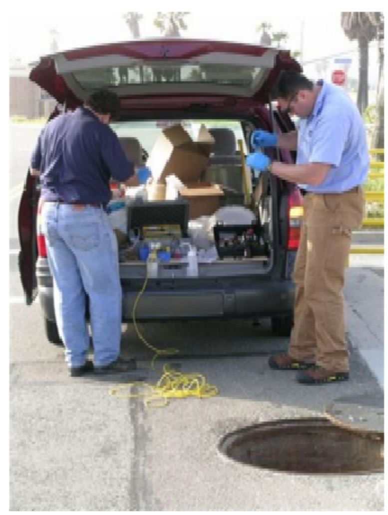
Chemical Control Considerations

- **Dosage almost never stoichiometric**
- **Chemicals have wide range of**
  - Quantities
  - Handling needs
  - Reaction times
  - Effectiveness
  - Cost
- **Some provide multiple benefits**
- **Some more effective when combined**



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Chemical Addition Challenges

- How much do I add, and when?
- Control approaches
  - Continuous addition
  - Flow paced
  - Air phase H_2S paced
- No commercially available sulfide probe

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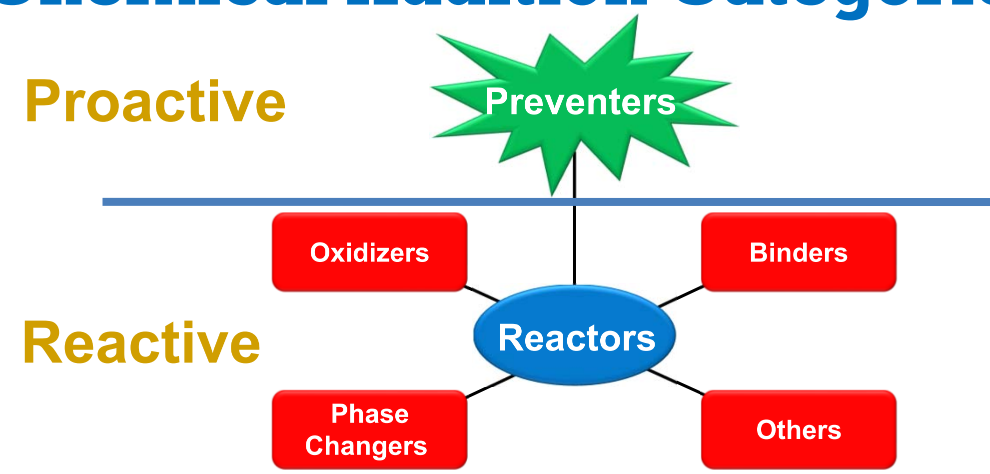
Chemical Addition Categories



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Chemical Discussion Breakdown

- **Dick Pope**
  - Preventer – Nitrates
  - Reactors – Binders and Oxidizers
- **Bruce Koetter**
  - Preventer – Oxygen
  - Reactors – pH Adjusters and Others

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Chemical Addition

NITRATES

Concept: Prevent sulfides from forming

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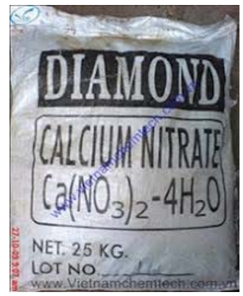
Nitrate Facts

- Nitrates are used to manufacture many items
  - Fertilizer
  - Food preservative
  - Explosives
- Non-hazardous:
  - Calcium Nitrate
  - Sodium Nitrate
- Stable solution – extended shelf life
- Worker H&S friendly
- Residual can add nitrogen to WRRF
- Nitrates act as
  - Preventers (slime layers)
  - Reactors (wastewater)



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Prevention Reaction Equation

Prevention Reaction Takes Place Here in Slime Laye

Prevention Reaction Equation

$$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 3N_2(g) + 7H_2O + 2OH^-$$

Oxygen Supplied by Nitrate

Microorganism Utilization Preference for Oxygen: $O_2 > NO_3^- > SO4=$

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Removal Reaction Equation

Removal Reaction Takes Place Here in Wastewater

Removal Reaction Equation

$$8NO_3^- + 5H_2S \rightarrow 5CO_2 + 5SO_4^{=} + 4N_2(g) + 4H_2O + 2H^+$$

Oxidizes Sulfide to Sulfate in Wastewater!

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Is It Safe?

- Non-Hazardous
- Neutral pH
- No Chronic Impacts
- No build-up
- Irritations to:
  - Skin
  - Eyes
  - Respiratory

Don't Dump On Ground!

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How To Protect Yourself?

- PPE
  - Gloves
  - Clothing to Protect Skin
  - Eyeglasses with Side Shields
- Safety Plan
- SPCC Plan

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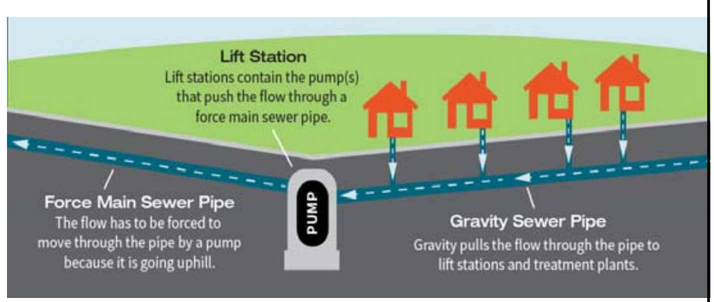
Where to Apply?

As Preventer

- Upstream
  - Where Concentrations reflect a need
- Force Main
- Long Siphon
- Extended Surcharged Line
- Takes time to acclimate slime
- Not effective-fast moving sewers
- Generates N_2 gas



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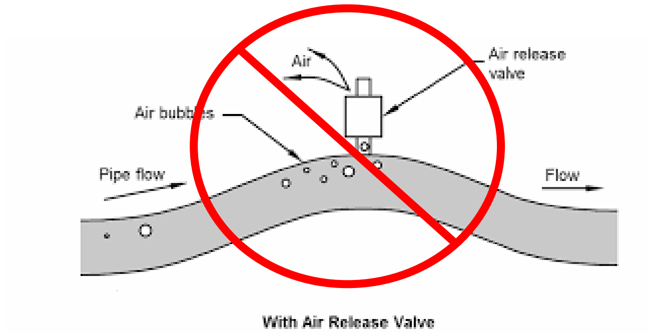
Where to Be Careful About Applying?

- Close to plants
  - Residual Nitrate
- Force Main without Air Relief
  - Build-Up of N_2 (gas)



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What Dose to Apply?

- Prevention – Primary Use
  - Understand current formation
  - 7.2 kg of NO_3^- O / kg of Sulfide **Prevented**
- Reaction – Secondary Use
  - Understand current upstream level
  - 2.4 kg of NO_3^- O / kg of Sulfide **Removed**
- Literature suggests
  - Force Main
  - Maintain Residual Downstream at 0.4 to 0.8 mg/l
  - Consider 12 kg of NO_3^- O / kg of Sulfide **Prevented & Removed**
- Nitrates are system (slime layer) dependent
  - Actual Rates are Field Set

Trial and Error

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System Layout

- Tanks
  - High density, cross-linked polyester plastic
- Metering pumps
- Control Panel
- Containment
  - Double walled tanks
  - Containment area
- Piping
  - PVC
- Freeze Protection
  - Only if T< -10°F (-23°C)

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Monitoring (Typical)

- Purpose of Nitrate Addition
  - Mitigate Dissolved Sulfide & H_2S
- Monitor
  - Dissolved Sulfide - Grab Sample (Field/Lab)
  - H_2S - Grab or Continuous Data Logging
  - Nitrate - Grab Sample (Field/Lab)
- Downstream - Required
- Upstream – Necessary
- Frequency
  - H_2S - Continuous Preferred
  - DS & Nitrate - Routinely

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Chemical Addition

BINDERS (Iron Salts)

Concept: Tie up sulfide in a non-odorous compound

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Iron Salts Facts

- Widespread CS use
- Commercially available as:
  - Ferrous Chloride
  - Ferrous Sulfate
  - Ferric Chloride
  - Ferric Sulfate
- Available as pickle liquor
  - Waste product
  - Careful – heavy metal content
  - Inexpensive
- Forms black or reddish-brown floc
- Can react with Phosphate

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Iron Salts

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Iron Salts Facts

Iron Salt	Solution Color	Solution Strengths	pH	Freezing Point	Iron as Fe by Weight	Compatible Materials
Ferrous Chloride	Light Green	18 – 28%	< 1.0 – 2.0	-20 º C (-4 º F)	10%	FRP, Rubber Lined Steel
Ferrous sulfate	Light Green	8 – 16%	< 1.0 – 2.0	-2 º C (28 º F)	3 – 6%	FRP, High Density Cross Linked Polyethylene, Rubber Lined Steel
Ferric Chloride	Orange Brown	28 – 47 %	< 1.0 – 2.0	-50 º C (-58 º F)	13.8 %	Same as Ferrous Chloride
Ferric Sulfate	Orange Brown	35 - 50 %	< 1.0 – 2.0	-20 º C (-4 º F)	10%	Same as Ferrous Sulfate

Reaction Equations

- Ferrous (Fe^{++}) reactions:
  - Same for both Chloride and Sulfate
  - Anionic carrier does not enter reaction
  - Variety of iron-sulfide complexes formed
  - Simplest reaction:

$$Fe^{++} + HS^{-} \rightarrow FeS + H^{+}$$

- Stoichiometric iron amount: 1.6 kg Fe^{++}/kg sulfide

Reaction Equations

- Ferric (Fe^{+++}) reaction:
  - Simplest reaction:

$$Fe^{+++} + 3HS^{-} \rightarrow Fe_2S_3 + 3H^{+}$$

- Stoichiometric iron amount: 1.1 kg Fe^{+++}/kg sulfide

Is It Safe?

- Corrosive
  - Low pH (< 1-2)
- Irritant
- Careful

How To Protect Yourself?

- PPE
  - Gloves
  - Chemical goggles
  - Face shield
  - Protective apron
  - Boots, as necessary
- Eye wash station
- Safety shower
- Safety Plan
- SPCC Plan

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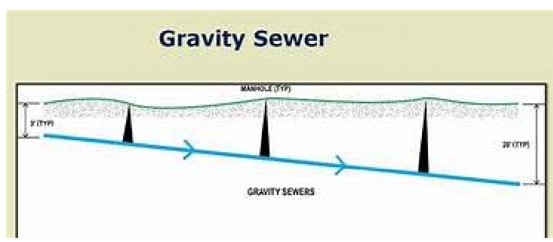
Where To Apply?

- Fast acting
- Does NOT react with organic material
- Greater benefits
  - Upstream
- Also added before plant
- Gravity line
  - Easier application



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Where To Be Careful Applying?

- FM
  - Requires pressure metering pump
  - Or – Add to wet well
- Low volume/flow areas
  - Dilute to avoid corrosion
- Avoid direct contact with
  - Concrete/Metal surfaces
  - Corrosive
  - Pipe to wastewater

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Iron Salts

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What Dose To Apply?

- Experience demonstrates:
  - Optimal dose for wastewater applications

3.5 kg Fe/kg Sulfide

- Generally can control to between:
  - 0.05 and 0.1 mg/l sulfide
- Typical target criteria:
  - 0.2 -0.5 mg/l sulfide

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System Layout

- Similar to Nitrates
- Tank containment
- Best to flow pace
  - Avoids acid build-up
- Aluminum, Brass and Stainless Steel
  - Readily Attacked
  - Not recommended

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Iron Salts

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Binders – Polymeric Amine

Approach:
Tie up sulfide in non-odorous compound

Another Example:

- Polymeric Amine Condensate
  - From Petroleum Industry
  - Is water soluble/non-volatile
  - Selective to sulfides
  - More effective in Force Mains
  - Dosage range 3.5-8 : 1 (sulfide)
  - Non-hazardous
  - Expensive

Another alternative

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Chemical Addition

OXIDANTS
(Chlorine)

Concept: Convert sulfide to non-odorous forms

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Chlorine Facts

- Common Plant chemical
- Staff familiarity
- Available as
  - Pure gas
  - Hypochlorite solution *
  - Hypochlorite granules/tablets
- Powerful oxidant
- Reactive component
  - Hypochlorite ion

* Most Common: Sodium Hypochlorite and Calcium Hypochlorite

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Chlorin

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Hypochlorite Facts

- Sodium Hypochlorite Solution
- Greenish-yellow in color
- Freezing: (12%) -12.5 ⁰ C (9.5 ⁰ F)
- pH: 11.5 – 13.0
- Avoid temperatures >40 ⁰ C
- Avoid ammonia, oxidizable materials
- Non-flammable
- Reacts with other compounds

Reaction Equations

SO4=

- Acidic pH

$$HS^- + 4Cl_2 + 4H_2O \rightarrow SO_4{=} + 9H^+ + 8Cl^-$$

Requires 8.9kg chlorine/kg sulfide

- Basic pH

$$HS^- + Cl_2 \rightarrow S + H^+ + 2Cl^-$$

Requires 2.2kg chlorine/kg sulfide

Is It Safe?

- Hypochlorite is a hazardous material
  - Any use must include Health and Safety
- Corrosive
- Strong oxidant
- Non-Flammable
- Typically available in 12.5% solution
  - Caustic added to retard off-gassing
- 2-3 X as strong as household bleach

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How To Protect Yourself?

- PPE
  - Gloves
  - Chemical goggles
  - Face Shield
  - Boots as necessary
  - Protective apron
- Eye wash station
- Safety shower
- Safety Plan
- SPCC Plan

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Where To Apply?

- Reacts very quickly
- Apply upstream of need
- Generally closer to WRRF
  - Avoid reconversion of SO_4^{-2}
- Non-Selective bactericide
  - Potential impact on WRRF

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What Dose To Apply?

- In practice:
  5 - 15kg chlorine/kg sulfide
- Competing side reactions
- Indiscriminately oxidizes any reduced compound

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System Layout

- Common chemical addition arrangement
- Tank containment
- System make-up
  - Polyethylene tank
  - Metering Pumps
  - Controls
  - Instrumentation
- Careful of off-gassing
- Subject to degradation
  - Shelf life around 28-days
- Freezes (12%) at -12.5º C (9.5º F)
- Avoid oxidizable materials, ammonia

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Chemical Addition

OXIDANTS

(Hydrogen Peroxide)

Concept: Convert sulfide to non-odorous forms

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Hydrogen Peroxide Facts

- Commonly used oxidant
  - Gravity and FMs
- Medical use (lower strength)
- Colorless liquid
- Strong oxidizer
  - H_2S
  - Organic matter
- Decomposes to water and oxygen
  - No chemical residual
  - Safe to WRRFs
- Freezes (35%) at -34º C (-29º F)

Reaction Equations

- pH < 8.5

$H_2S + H_2O_2 \rightarrow S + 2H_2O$

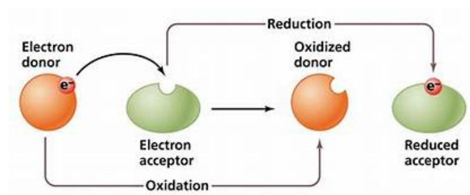
Requires 1 part peroxide/1 part sulfide

Develops light floc

- pH > 8.5

$S^{-} + 4H_2O_2 \rightarrow SO_4^{-2} + 4H_2O$

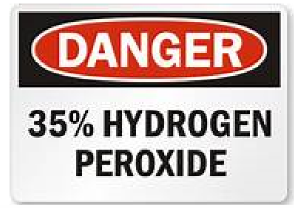
Requires 4 parts peroxide/1 part sulfide



Wastewater pH is generally <8.5.

Is It Safe?

- Strong Oxidizer
- May cause fire or explosion
- Causes severe skin burns & eye damage
- Don't breathe mist
- Hazard labels:
  - Oxidizer
  - Corrosive
  - Poison



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How To Protect Yourself?

- PPE
  - Gloves
  - Chemical goggles
  - Face shield
  - Protective clothing
  - Boots as necessary
- Eye wash station
- Shower station
- Safety Plan
- SPCC Plan

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Where To Apply?

- Full reaction delay
  - Up to 20 minutes
- Upstream of need
- No by-products
- No WRRF impacts

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What Dose To Apply?

- In practice
  - Dose of 2 – 4 peroxide: 1 sulfide is typical
- Reacts with organic material
  - Higher than stoichiometric dose required

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System Layout

- Common chemical addition arrangement
- Tank containment
- Common strengths: 35% and 50%
- Storage tank MOC
  - Stainless Steel
  - High Purity Aluminum
  - Polyethylene (Lower concentrations)

  } Higher Concentrations (Stainless Steel, High Purity Aluminum)
- Piping:
  - Typically PVC
- Wetted pump parts:
  - PTFE
  - Stainless Steel

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System Layout

- Materials to avoid
  - Metals
  - Organic materials
  - Reducing agents
  - Combustible materials

- Installation
  - All wetted surfaces
  - Prepared by Passivation

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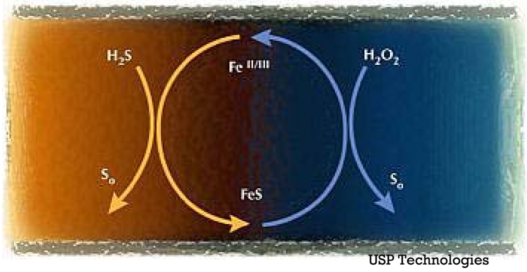
Common Chemical Combination

- Combining Iron Salts and Hydrogen Peroxide
  - Gravity lines
  - Iron (Primary Control) added upstream
  - Peroxide added downstream
  - Spent Iron (FeS) regenerated
  - Elemental sulfide produced
  - Proprietary process



USP Technologies

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Speaker Information

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- President of Webster Environmental Associates, Inc.
- Purdue Boilermaker
- 27 years of odor control experience

ENVIRONMENTAL WEBSTER ASSOCIATES, INC.

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pH Adjusters, Oxygen Injection and Others

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pH Adjusters

- pH Maintenance vs Shock Dosing
  - pH Maintenance – Dose chemical at a rate to maintain wastewater pH at 8.0 – 9.5.
  - Shock Dosing – Elevate pH to 12.5 - 13 for 30 minutes to inactivate sulfate reducing bacteria in slime layer for 3-7 days

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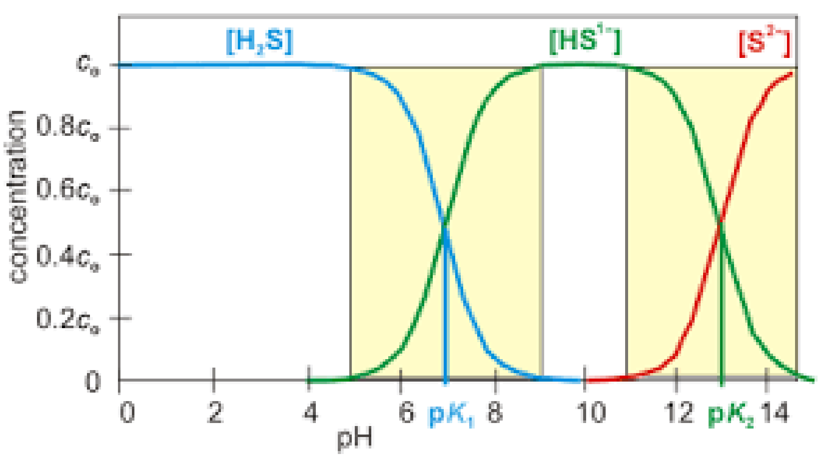
pH Maintenance ($(H_2S)_g \rightarrow HS^-$)



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pH Maintenance

- Magnesium hydroxide (Thioguard®)
- Calcium hydroxide (Alkagen® - A lime/nitrate solution)

pH Maintenance (Mag Hydroxide)

- Process is patented
- Non-hazardous buffer
- Buffers at pH ≈ 9
- Gradual pH shift
- Maintain pH between 8.0 – 8.5
- Rule of thumb is 50 - 100 gal/million

pH Maintenance (Mag Hydroxide)

- Magnesium hydroxide
  - Freezes at 32°F
  - Storage tank must be mixed, insulated/heat traced to prevent coagulation
  - Dissolves as needed
  - Effective FOG control
  - Struvite formation

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pH Maintenance (Lime/Nitrate)

- Calcium hydroxide/nitrate solution
  - Non-hazardous
  - Quick dissolving/fast acting (seconds)
  - Effective FOG control
  - Buffered at 12.4 pH
  - Can achieve pH >8.5
  - No Struvite formation associated with magnesium

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pH Maintenance (Lime/Nitrate)

- Calcium hydroxide/nitrate solution
  - Often effective on long FM with high sulfides
  - May enhance BNR at plants
  - Freezes at 32°F
  - Storage tank must be mixed and insulated/heat traced

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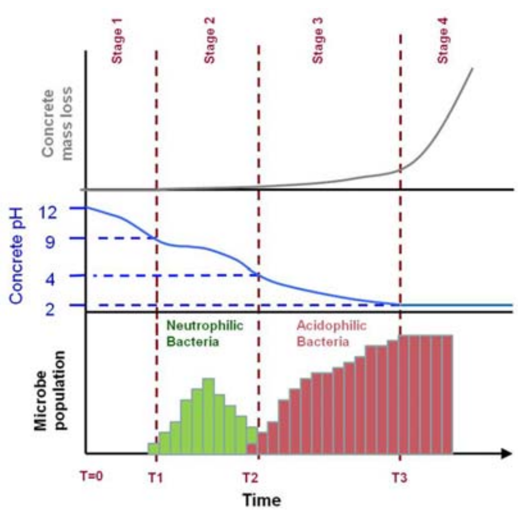
Corrosion Control



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Shock Dosing

- Sodium Hydroxide (caustic soda)
  - Inactivates sulfate reducing bacteria in slime layer
  - Temporary elevation of pH to 12.5 – 13.0
  - Short term duration (30 minutes)
  - Effective for 3-7 days
  - Highly corrosive

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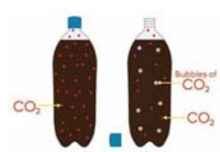
Oxygenation – What is it?

Definition	 To supply, treat, charge, or enrich with oxygen $2O_2 + H_2S \rightarrow H_2SO_4$
Henry's Law	**Henry's law** states that the amount of dissolved gas in liquid is proportional to its partial pressure above the liquid.  Soda

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Wastewater Applications

- WWTPs
  - Headworks
  - Primary clarifiers
  - Sludge holding tanks
  - Plant Effluent (to oxygenate downstream waterway)
- Collection Systems
  - Long Force Mains
  - Low velocities
  - Long HRT
  - Downstream odor complaints/sensitive areas
  - Corrosion issues/infrastructure damage
  - Perhaps gravity lines

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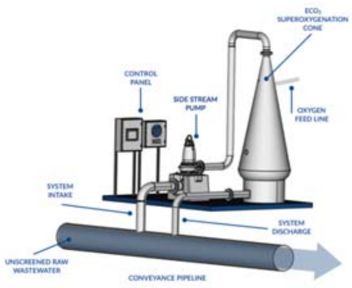
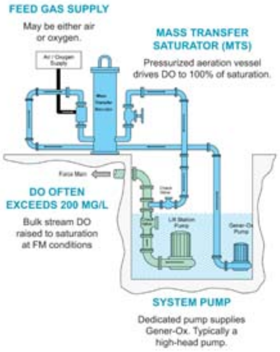
Oxygenation System Manufacturers

ECO2



BlueInGreen

Gener-Ox™



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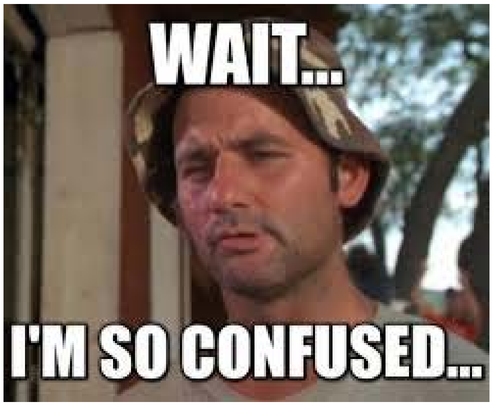
How do you know if oxygenation is right for your application?



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How much oxygen is required?

- Oxygen Demand = OUR * HRT
  - OUR for Wastewater = 5-10 mg/L/hr is common
  - HRT of Force main

- Example:

O2 Demand = 10 mg/L/hr * 10 hrs = 100 mg/L

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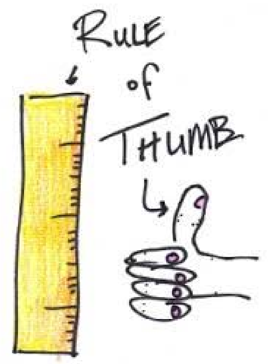
Additional O2 Demand

- Sulfides that are already in solution need to be oxidized
  - Existing sulfides are oxidized 5-20 minutes after oxic conditions are established
  - Rule of thumb – 2 mg/L oxygen per 1 mg/L of DS
  - Oxygen required to oxidize existing sulfides added to OUR demand

OUR Demand	= 100 mg/L
Existing DS Demand	= 6 mg/L
Desired Residual DO	= 5 mg/L (at discharge)
Total O2 Required	= 111 mg/L



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Saturation Capacity

- **How much oxygen can we dissolve into the water?**
- **Rule of Thumb: 1 mg/L O_2/ft pressure**

Example:
- **115 ft (50 psi) of pressure at pump discharge**
- **Csat = 115 ft *1 mg/L/ft of head pressure = 115 mg/L**
- **If O2 Demand < Csat, then OK – Proceed with evaluation**
- **If O2 Demand >Csat, then poor application or two systems in series may be needed**

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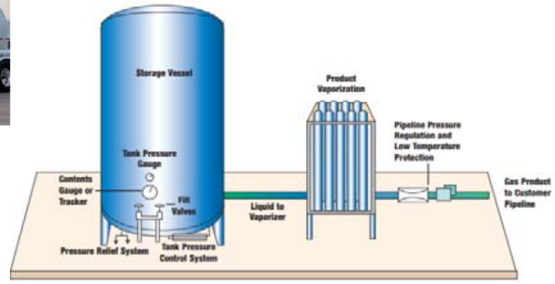
LOX or On-Site Generation?



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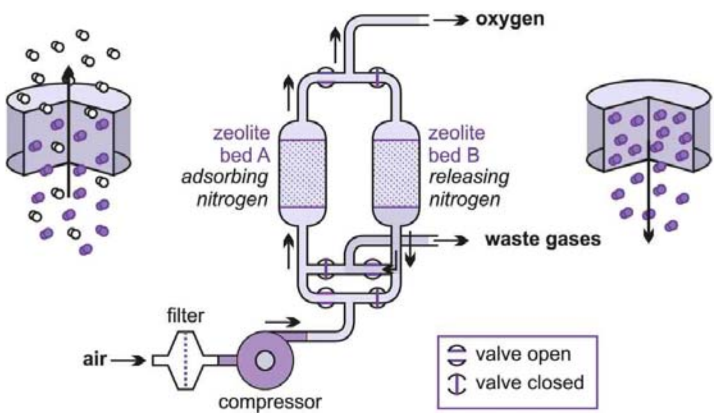
On-Site Generation

(Pressure/Vacuum Swing Adsorption)



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Oxygen Injection – Key Design Details

- O_2 Demand vs Saturation Capacity
- Feed location(s)
- LOX or On-site generation
- LOX delivery considerations
- Side-stream flow rate
- Oxygen feed control method
  - DO Meters
  - Raw sewage flow meters
  - # of RS pumps in operation

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Other Liquid Phase Treatment Alternatives

- Biological/Enzymes
- Potassium Permanganate
- Combos
  - Iron salts + hydrogen peroxide (Prisc)
  - Oxygen Injection + nitrate polishing
- Gas-Phase Treatment Alternatives

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Liquid Phase Odor Control Selection Considerations

- Control location
- Liquid sulfide concentrations
- H_2S concentrations
- Hydraulic residence time
- Site restrictions and limitations
- Safety
- Aesthetics
- Corrosion control
- Wastewater treatment processes
- Costs

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Summary

- There are many liquid-phase odor control options
- Selecting the best solution requires:
  - Knowing system parameters
  - Testing of your system
  - Knowledge of alternatives
  - Knowledge of local preferences

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Questions?

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