### Sulfide Modeling as a Practical Asset Management Tool Prabhu Chandrasekeran, PE



## Introduction





# WSSC's Collection System

- Collection System Evaluation Program
  - Consent Decree requirements
  - Currently in Phase-III
- Critical Asset Condition Assessment
  - Anacostia Sewer (102")
  - Trunk Sewers
  - Microbial Induced Corrosion (MIC) issues
  - How can we predict and be proactive?



#### This Presentation Describes The Sewer Sulfide Modeling As A Practical Asset Management Tool

- Sulfide generation and corrosion mechanisms
  - How does sulfide generate within collection system?
  - How does corrosion occur?
  - How does hydraulics affect corrosion?
  - What is sulfur cycle?
- How can we predict corrosion within sewer system?
  - Basic approaches and complex modeling tools
  - Limitation of various approaches
- Application of Model
  - What factors were found to affect corrosion?
  - How can a model be used as a predictive tool?



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# Sulfide Generation, Sulfide Transfer and Corrosion Mechanisms



- High Sulfates High H<sub>2</sub>S
- High BOD High H<sub>2</sub>S
- Low DO High H<sub>2</sub>S (Anaerobic conditions)
  - Non-limiting  $O_2$  (<1.0 mg/L)
  - Flat sewers (Trunk Sewers)
- More Surface area More slime layer More H<sub>2</sub>S
  - Debris increases surface area
- High temperature High H<sub>2</sub>S
- High Detention Time High H<sub>2</sub>S
- SRBs can exist between pH 5.5 to 9



# Sulfide Generation, Sulfide Transfer and Corrosion Mechanisms



- DO concentration and sulfide oxidizing bacteria
- Liquid/Gas phase H<sub>2</sub>S equilibrium (Henry's Law)
- Higher the dissolved  $H_2S$ , higher the headspace  $H_2S$
- Higher the temperature higher the concentration of H<sub>2</sub>S in headspace



# Sulfide Generation, Sulfide Transfer and Corrosion Mechanisms

- Sulfide is a weak-acid and pH dependent
- Only the unionized H<sub>2</sub>S is a soluble gas



# Sulfide Generation, Sulfide Transfer and Corrosion Mechanisms



- Gaseous H2S is oxidized to sulfuric acid
- Impact to different pipe materials
- pH of Concrete
- Sulfuric acid runs back into the sewage
- Depletes alkalinity and become sulfates
- CYCLE STARTS AGAIN



# Sulfide Generation, Sulfide Transfer and Corrosion Mechanisms



- Air velocity profile within a sewer
- Air moves at different velocities based on the distance from the wastewater
- Point of H<sub>2</sub>S release is not necessarily the point of corrosion



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# Prediction of Sulfide Generation And Corrosion In Sewer Networks

- Empirical Equations
  - Yes-or-No Answers
- Qualitative Indicators
  - Pomeroy Method for Pressure Sewers
  - Pomeroy and Parkhurst Method for Gravity Sewers
  - Z-Formula
- Mechanistic Modeling
  - WATS Wastewater Aerobic/Anaerobic Transformations in Sewers
  - Adaptation of the WATS Model



### Mechanistic Modeling Is Akin To Biological Process Modeling, Reflecting As Many Important Transformations As Practical

- Mechanistic Modeling
  - WATS Wastewater Aerobic/Anaerobic Transformation in Sewers
  - Akin to IWA's ASM No. 1 for Activated Sludge





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#### Mechanistic Modeling Requires Significant Computational Power And Expertise Of A Software Operator/Programmer

Processes	x <sub>s{-11}</sub>	S <sub>s[-11]</sub>	So	pH <sub>2</sub> S	Process rate
Sulfide production		1			Equation 1
Sulfide precipitation*	1	-1			
Water phase sulfide oxidation, chemical		-1	-1.2		Equation 2
Water phase sulfide oxidation, biological		-1	-0.5		Equation 3
Biofilm sulfide oxidation		-1	-0.5		Equation 4
Reaeration			1		Equation 5
Sulfide emission		-1		1	Equation 6
Adsorption on moist sewer walls				-1	Equation 7

\* Sulfide precipitation is assumed instantaneous

#### Process rate equations are described as follows (Nielsen et al., 2005):

Equation 1:  $k_{S(-II), p}(S_F + S_A + X_{S1})^{0.5}(K_O/(S_O + K_O))(A/V)1.03^{(T-20)}$ 

Equation 2: k<sub>S(-II). o.c</sub>S<sub>S(-II)</sub>S<sub>O</sub><sup>0.1</sup>1.07<sup>(T-20)</sup>

Equation 3: 
$$k_{S(-II)} = b_{S(-II)} S_0^{0.1} 1.07^{(T-20)}$$

Equation 4: k<sub>S(-II), o,f</sub>S<sub>S(-II)</sub><sup>0.5</sup>S<sub>O</sub><sup>0.5</sup>(A/V)1.03<sup>(T-20)</sup>

Equation 5:  $K_L a_{So} 24(S_{OS} - S_O)$ 

Equation 6:  $K_L a_{S(-II)} 24(\gamma S_{S(-II)} S_{S(-II),eq})$ 

Equation 7: k<sub>s(-II)gas,o,w</sub> ((pH<sub>2</sub>S)/(K<sub>pH2S</sub> + pH<sub>2</sub>S))(A<sub>c</sub>/V<sub>g</sub>)1.03<sup>(T-20)</sup>

#### WATS in Peterson Matrix Notation

Source: Nielsen et al. (2003)



#### Mechanistic Modeling Tells Us That Hydraulics Matter Intensely When Predicting Corrosion Potential

- Assumed That Sulfate and Organics Exist in Sufficient Quantities to be a Potential Problem
- Mass Transfer is Critical:

S

Т

$$K_L a_{\rm H_2S} = (1.736 - 0.196 \,\mathrm{pH}) K_L a_{\rm O_2}$$
 (4.5 pH 8.0, at 20°C) (1)

$$K_L a_{O_2} = 0.86(1 + 0.2F^2)(su)^{3/8} d_m^{-1} \alpha$$

where 
$$u = \text{mean flow velocity } (\text{m s}^{-1})$$

= slope of sewers  $(m m^{-1})$ 

 $d_m$  = mean hydraulic depth, i.e., the water cross-sectional area divided by the width of the water surface (m)

$$F$$
 = Froude number =  $u(gd_m)^{-0.5}$ 

$$g = \text{gravitational acceleration } (\text{m s}^{-2})$$

$$\alpha_r$$
 = temperature coefficient for reaeration = 1.024

= temperature (°C).

Source: Nielsen et al. (2005)

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# Case Study Areas and Sulfide Modeling



- Anacostia Trunk Sewer (102")
- Horsepen Trunk Sewer (18", 24" and 27")
- Known corrosion problems
- How can we model these corrosion locations using the Mechanistic model?
- Data collected on H2S (liquid/gas), wastewater characteristics (ph, temp...)



# Anacostia Trunk Sewer (102")





# Anacostia Trunk Sewer (102")



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# Anacostia Trunk Sewer (102")

Well at Elevation of 1.5 Feet Headspace Sulfide Concentrations







# Model Results – 102" Sewer



Most significant concrete
loss has occurred at the
location where crown has
becomes submerged
upstream of the siphon
and the corresponding
whitewater locations



#### Positives and Negatives Of Mechanistic Sewer Sulfide Modeling

- Applicability of Mechanistic Modeling
  - No Limitations on Size of System
  - Can be Calibrated to Specific System
    - Ongoing headspace sulfide monitoring
  - Broad Tool Across Collection System
  - May be Deployed to Predict Corrosion Rates



#### Positives and Negatives Of Mechanistic Sewer Sulfide Modeling

# Limitations

- Requires More Data Inputs than Other Approaches
  - Hydraulic modeling: Froude number, hydraulic mean depth, pipe geometry
  - Chemical parameters: BOD<sub>5</sub>, pH, temperature
- Requires Computational or Programming Expertise to Solve Multiple Simultaneous Differentials
- Application is a Blend of Experience and Science
  - Venting is not included in model, nor is gas transport
  - Understanding of system needed to pair sulfide emission with local hydraulics



#### There Are Reasonable Ways To Simplify This Approach And Retain The Benefits Of Mechanistic Vs. Qualitative Prediction

- Some Processes are Important for Predicting Aqueous Sulfide Concentration
  - Important to Calculate Headspace Concentrations
  - The Good News is We Can Measure This Directly and it is Reasonably Predictable for a Point in a Sewer!!!

Processes	Role in Proposed Simplified Model
1. Sulfide production	<b>Omit – Impacts dissolved sulfide concentration</b>
2. Sulfide precipitation*	Omit – Serves as sink for dissolved sulfide
3. Water phase sulfide oxidation, chemical	Omit – Serves as sink for dissolved sulfide
4. Water phase sulfide oxidation, biological	Omit – Serves as sink for dissolved sulfide
5. Biofilm sulfide oxidation	Omit – Serves as sink for dissolved sulfide
6. Reaeration	Omit – Serves as brake on sulfide production
7. Sulfide emission	RETAINED
8. Adsorption on moist sewer walls	RETAINED



#### There Are Reasonable Ways To Simplify This Approach And Retain The Benefits Of Mechanistic Vs. Qualitative Prediction

• Predictive Tool is Very Simple at Steady State:

Sulfide Emission:  $K_L a_{S(-II)} 24(\gamma S_{S(-II)} S_{S(-II),eq})$ 

Adsorption: 
$$\frac{\Delta p_{H2S}}{dt} = 0 = -1 \text{ x } \text{k}_{\text{s(-II)gas,o,w}} ((\text{pH}_2\text{S})/(\text{K}_{\text{pH2S}} + \text{pH}_2\text{S}))(\text{A}_{\text{c}}/\text{V}_{\text{g}})1.03^{(\text{T-20})}$$

- Set these Equations Equal to One Another and Solve for pH<sub>2</sub>S
  - We Know by Literature, Assumption, or Measurement Every Other Parameter in These Equations
  - Now it is a Suitable Job for a Spreadsheet  $\square$



# Horsepen Trunk Sewer





#### Hydraulics Of This Pipe Section Drive Specific Areas Of Concrete Corrosion (Horsepen Trunk Sewer)



- Hydrogen Sulfide Concentrations More or Less Track Inverse of Diurnal Flow Pattern in Pipe
- Can This be Described by Simplified Model?



#### Hydraulics Of This Pipe Section Drive Specific Areas Of Concrete Corrosion



#### Velocity Profile In Pipe Shows Maximum Corrosion Occurs Where Pipe Flattens And Water Slows Down



# What did we learn? Factors controlling headspace H<sub>2</sub>S

#### Sulfide Generation

- H<sub>2</sub>S was generated upstream of case study in both cases
- $-H_2^{-}S$  generated within the case study was not an important factor for headspace  $H_2S$
- Sulfide Transport
  - Pipe hydraulics played a significant role in headspace  $H_2S$
  - -102" headspace H<sub>2</sub>S increased with diurnal flow increase
  - Horsepen headspace H<sub>2</sub>S decreased with diurnal flow increase
- Corrosion
  - Confirmed by prior inspection results



# What did we learn? Sulfide modeling as a predictive tool

- WATS Mechanistic Model
  - Biological and H<sub>2</sub>S phase transformation
  - Model proved to be:
    - comparable to the monitored data
    - sensitive to mechanisms controlling headspace H<sub>2</sub>S
- Integrated Hydraulic/Sulfide model
  - Enables user to run sensitivity analysis on sulfide generation and emission
    - Pipe flow rate
    - ph and temperature



### Take Home: A Simplified Mechanistic Approach Can Provide Useful Prescriptive Information About Sulfide Corrosion

- Sulfide in Itself is Not Evil It is Ubiquitous
- Sulfide Acts by Volatilizing, Adsorbing, and Oxidizing on the Moist Sewer Wall
- Prior Qualitative Methods of Predicting Corrosion Ignore the Complex Hydraulics of Real Sewer Networks
- Fully Mechanistic Methods Can be Cumbersome
- Useful Information Can be Obtained From a Simplified Method Focusing on the Point of Action of Sulfide
  - Volatilization
  - Adsorption
- Simplified Approach Can be Used for Targeted Field Investigations in Areas With High Headspace Sulfide



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# THANK YOU

