Micro-Aeration for Sulfide Removal in Anaerobic Treatment of High Solid Wastewater: A Pilot-Scale Study

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Introduction

- Biogas – Biorenewable energy source
- Methane 50-70%, Carbon dioxide 30-50%, trace gases (nitrogen, ammonia, and hydrogen sulfide)
- Hydrogen Sulfide—the most notorious
  - Corrosion to concrete and metal pipes
  - Odorous (recognition at 4.5 ppb)
  - Heath concerns (10 ppmV and death at 600 ppmV)
  - Combustion → SO_x (or SO_2) → acid rain
  - Total sulfide at 90-250mg-S/L, inhibit methanogenesis
  - Removing of H_2S is recommended as soon as possible to protect downstream equipments

Introduction

- Requirement of H_2S reduction in several processes (Zicari, 2003)
  - Microturbines: up to 70,000 ppmV
  - Boilers and Stirling engine: < 1000 ppmV
  - Internal combustion engines: < 100 ppmV
  - Kitchen stoves and Fuel cells: < 10 ppmV
  - Pipeline-grade high-BTU gas: < 4 ppmV
  - Thermo-catalytic conversion steam reforming: nothing
  - Require to prevent fouling siloxane removal media

Introduction

Where are the sulfides come from ?

- Wastewater containing: sulfate, sulfite, thiosulfate, proteins (cysteine and methionine)
- Sulfate in most city water: up to 40 mg/L (Ames: 70-90 mg/L)
- Reduction of sulfate by Sulfate reducing bacteria (*Desulfovibrio, Desulfobacter, Desulfuromonas*, many Archaea etc.)

SO_4^{2-} + organic matter → HS^{2-} + H_2O + HCO_3^-

Objectives

A Sulfide Removal System: Sulfide Oxidizing Unit (SOU) Coupled with Anaerobic Digester

- **Micro-aeration:** selective sulfide oxidation to elemental sulfur
- Sulfide-free biogas (< 4 ppmV) with minimal oxygen (< 1%) in biogas and sulfide-free effluent
- **No media:** possible to treat high solids wastewater (2-6% TS), such as those from agricultural residues and WAS
- **Condition in SOU:** controlled separately
- No additional nutrients
- No pH adjustment

Micro-aeration

- Oxidation of sulfides: < 0.1 mg/L of O_2 , selective oxidation to S^0
- Control O_2/S^{2-} ratio (2, 1, and 0.5 mole/mole)

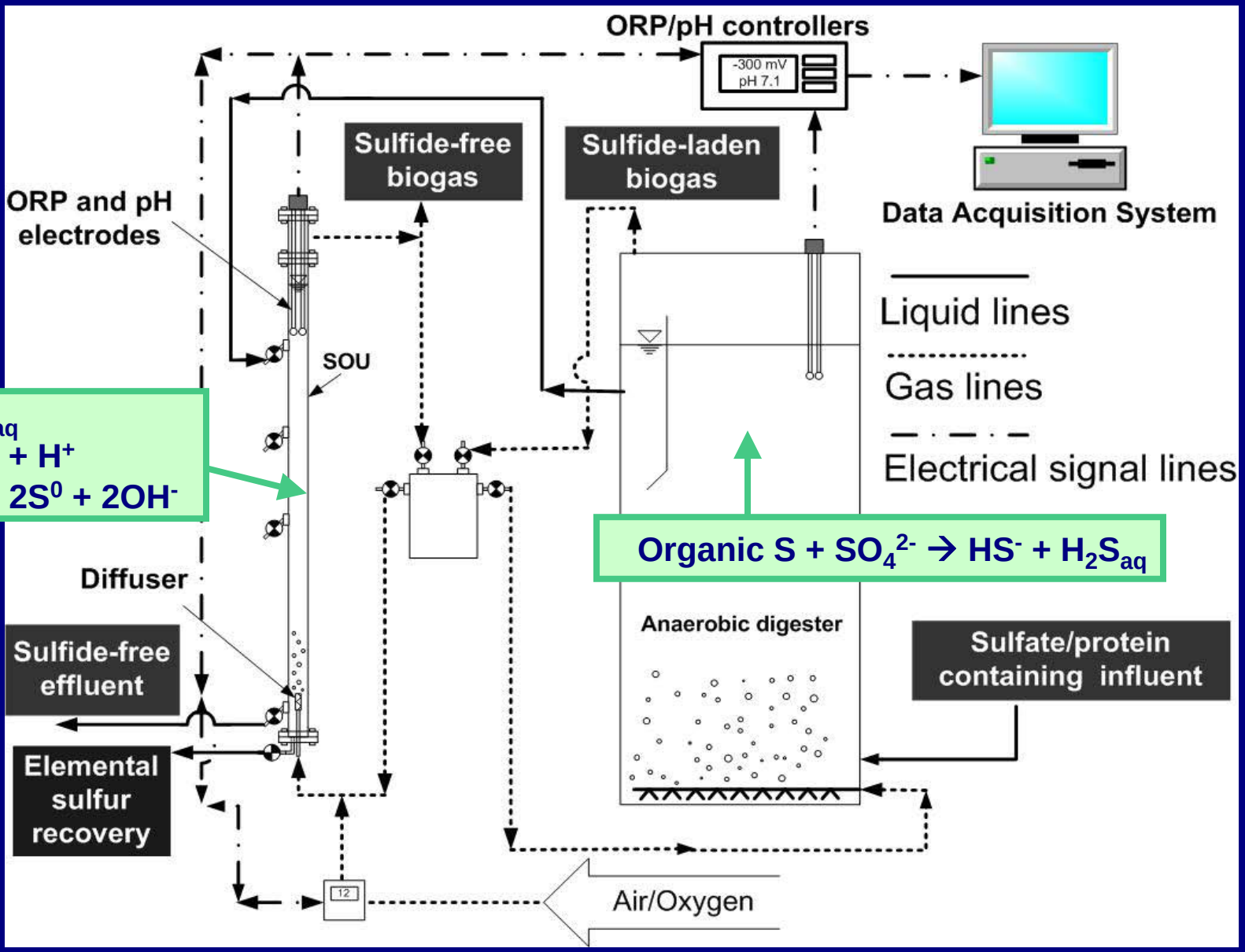
$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \quad \Delta G° = -772.43$ kJ/mol HS^-

$2HS^- + 2O_2 \rightarrow H_2O + S_2O_3^{2-}$ (auto-oxidation)

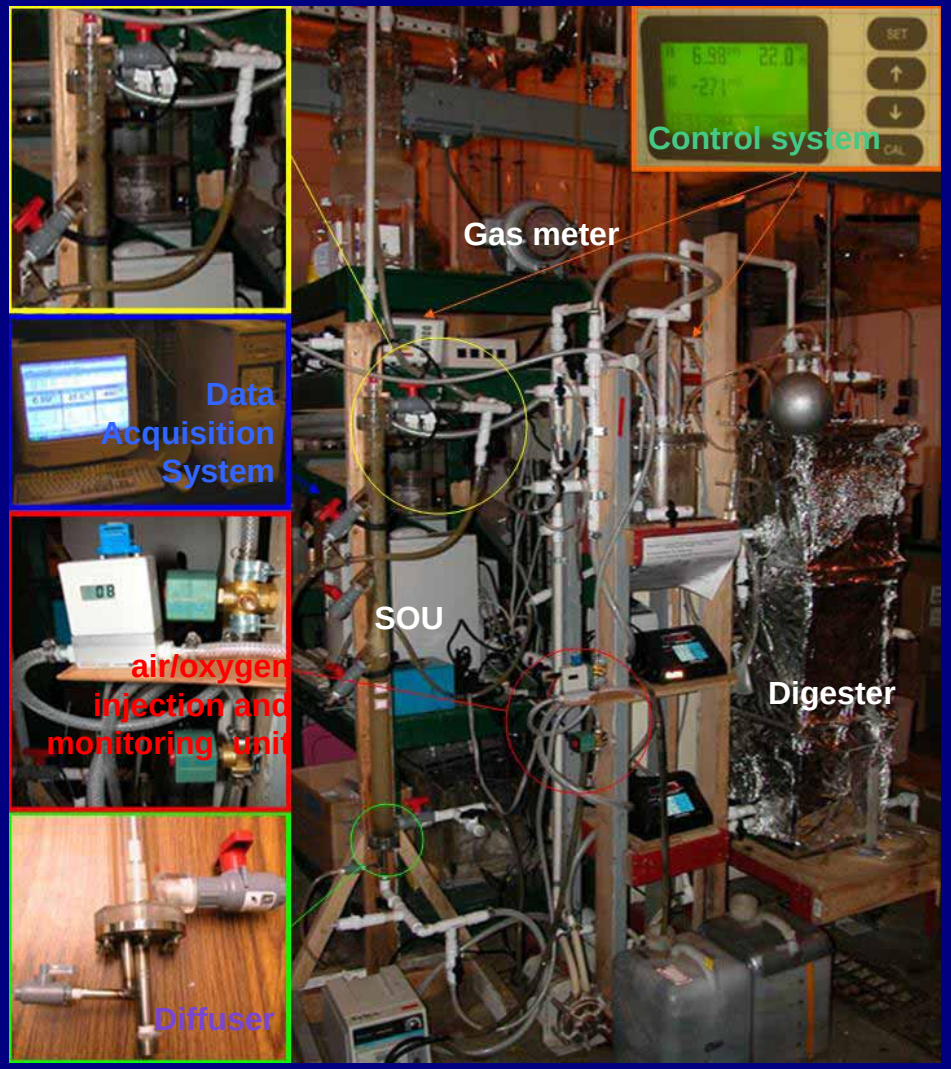
$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad \Delta G° = -129.50$ kJ/mol HS^-

- Oxidation of sulfide to sulfur is faster than the oxidation to sulfate (Janssen et al., 1995)
- Tough to control <0.1 mg/L O_2
- ORP used as controlling parameter
- Sulfide and Oxygen concentration affect the ORP

Procedures – Reactor schematic



Procedures



Digester, 92 L (HRT = 20 day)

SOU, 1 L (HRT = 4 hrs)

Digester, Biogas recirculation (mixing) = 1.5 L/min

SOU, Biogas recirculation = 0.5 L/min

pH = not controlled

Air flow rate = 1-10 ml/min

Temp = ambient (~25 °C)

Feed: Commercial dog food with trace elements

TS = 2-3%

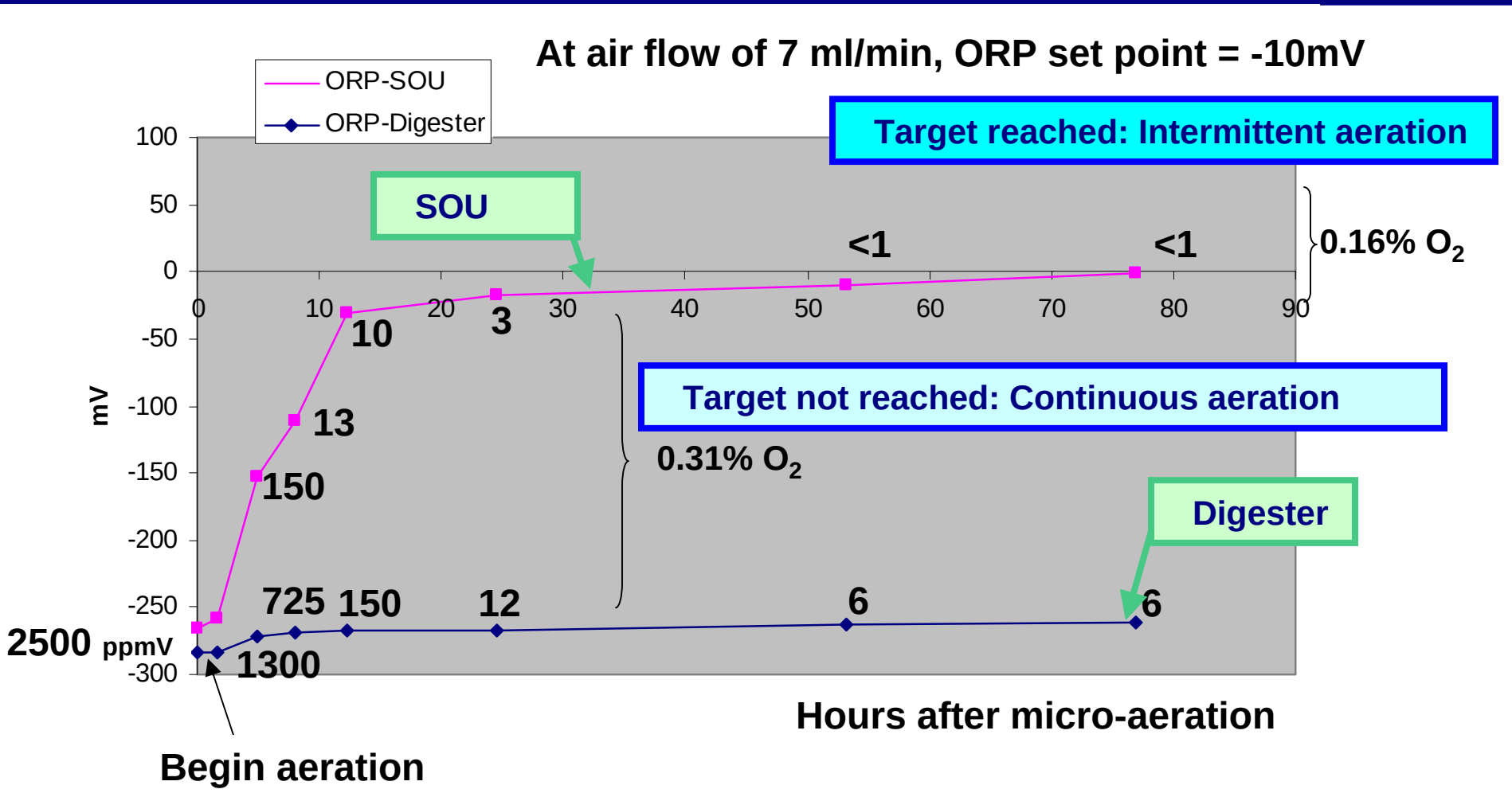
Loading rate: 1.2 g-COD/L-day

$H_2S_{(g)}$ = 1,800 – 2,600 ppmV

S^{2-} = 16 - 25 mg/L-S

Results

- ORP and $H_2S_{(g)}$ profile after starting micro-aeration at SOU



Results – Continuous air flow

Flow rate = 5.1 ml/min	Before aeration		After aeration	
	Reactor	SOU	Reactor	SOU
Biogas				
N_2, %	0.5 ± 0.1	N/A	5.8 ± 0.8	6.8 ± 1.0
CH_4, %	65.6 ± 0.6	N/A	63.3 ± 2.2	62.6 ± 2.4
CO_2, %	33.6 ± 1.1	N/A	30.2 ± 1.3	29.8 ± 1.1
O_2, %	N/A	N/A	0.4 ± 0.2	0.7 ± 0.1
H_2S, ppmV	2450 ± 150	2420 ± 170	29.0 ± 5.8	1.7 ± 1.7
Biogas production, L/d	54.2 ± 4.5		59.8 ± 2.6	
Methane production, L/d	35.0 ± 0.6		37.8 ± 2.1	
Liquid				
Sulfide, mg/L	17.7 ± 1.7	17.4 ± 1.7	1.1 ± 1.1	ND
Sulfate, mg/L	ND	ND	0.1 ± 0.2	12.5 ± 8.3
Thiosulfate, mg/L	ND	ND	ND	ND
ORP, mV	-277 ± 8	-261 ± 7	-265 ± 12	-246 ± 3
pH	7.17 ± 0.01	7.20 ± 0.01	7.24 ± 0.03	7.23 ± 0.01

Note: 98% S^{2-} conversion to S^0, O_2/S^{2-} = 5.6, not 0.5

Procedures - Disconnect SOU from Digester

- SOU as a standalone unit
- Perfect for digester without sulfide toxicity
- No requirement for mixing by biogas
- No requirement for removal of elemental sulfur deposit on digester headspace

Results – Disconnect SOU from Digester

Flow rate = 5.2 ml/min	Before aeration		After aeration	
	Reactor	SOU	Reactor	SOU
Biogas				
N_2, %	0.5 ± 0.1	N/A	0.2 ± 0.2	5.1 ± 1.8
CH_4, %	65.6 ± 0.6	N/A	66.2 ± 1.1	62.3 ± 2.1
CO_2, %	33.6 ± 1.1	N/A	32.8 ± 0.7	30.9 ± 1.1
O_2, %	N/A	N/A	ND	0.3 ± 0.2
H_2S, ppmV	2450 ± 150	2420 ± 170	2550 ± 170	2.1 ± 0.4
Biogas production, L/d	54.2 ± 4.5		60.2 ± 3.0	
Methane production, L/d	35.0 ± 0.6		37.5 ± 2.1	
Liquid				
Sulfide, mg/L	17.7 ± 1.7	17.4 ± 1.7	22.8 ± 2.3	ND
Sulfate, mg/L	ND	ND	ND	42.2 ± 16
Thiosulfate, mg/L	ND	ND	ND	0.3 ± 0.2
ORP, mV	-277 ± 8	-261 ± 7	-270 ± 3	-245 ± 5
pH	7.17 ± 0.01	7.20 ± 0.01	7.24 ± 0.03	7.20 ± 0.01

Note: 94% S^{2-} conversion to S^0, O_2/S^{2-} = 5.8

Important findings

- Possible to use the integrated or disconnected system to remove H_2S from biogas to be < 4 ppmV with O_2 < 1% at 0.24 kg-S/m^3/day
- The activities of methanogens were not affected during micro-aeration
- Conversion of sulfide to S^0 of 98% with minimal sulfate production
- O_2/S^{2-} = 5.6, instead of 0.5, resulted from facultative bacteria activity and reduction/oxidation of accumulated sulfur in SOU
- Recommend ORP monitoring for high oxygen dosing alarm

Equipments required

1. **SOU:** 10-ft tall cylindrical container (PVC, HDPE, or concrete with liners)
2. **Biogas recirculation:** one centrifugal blower, compressor, or peristaltic pumps
3. **Medium flow:** one peristaltic pump
4. **Air flow:** air compressor, solenoid valves, and a flow meter
5. **ORP, pH probes, and controller**

Pilot-scale at WPCF of Ames (Dec 07)

- **Background**
  - Primary and WAS digesters and storage (1 Mgal)
  - Biogas production 50,000 ft^3/day
  - Hydrogen sulfide 1000 ppmV (1.7 kg-S/day)
- **Suggested full-scale installation**
  - Based on Sulfide removal rate of 0.24 kg-S/m^3/day (expected to be higher)
  - 7 m^3 SOU (6 ft-Ø and 10 ft-tall)
- **Pilot-scale unit installation**
  - 0.2 m^3 (52 gal,1 ft-Ø and 10 ft-tall) made by PVC
  - Treat biogas 1400 ft^3/day
  - Use final effluent as medium

Farm Digesters

- **Swine farm**
  - 3,000-head finishing farm
  - Biogas production 18,000 ft^3/day
  - Hydrogen sulfide 2000 ppmV (1.3 kg-S/day)
  - 5 m^3 SOU (5 ft-Ø and 10 ft-tall)
- **Daily farm**
  - 500-head dairy farm
  - Biogas production 25,000 ft^3/day
  - Hydrogen sulfide 2000 ppmV (1.7 kg-S/day)
  - 7 m^3 SOU (6 ft-Ø and 10 ft-tall)

Thank you

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