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Viability for oxidation of H2S gas using low concentration solutions of H2O2 peroxide in applications for biogas purification.

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VIABILITY FOR OXIDATION OF H_2S GAS USING LOW CONCENTRATION SOLUTIONS OF H_2O_2 IN APPLICATIONS FOR BIOGAS PURIFICATION

By

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Thesis Approved on

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DEDICATION

This thesis is dedicated to my parents

Mr. Walter D. McCollam

and

Mrs. Susan P. Stewart

who have given me invaluable educational opportunities

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I would like to thank my thesis advisor, Dr. Willing, for his guidance and patience throughout the last three years. I would also like to thank the other committee members, Dr. Watters and Dr. Hagerty, for their comments and assistance in the development of this thesis. Additionally, I would like to express my thanks to Charlie Staff and Mike Funk for their support and permission to write this thesis on confidential research conducted for JAF Enterprises. Finally, I would like to thank the faculty members at the University of Louisville Speed School of Engineering for their diligent educational instruction which has given me an excellent foundation on which to build as I enter my career.

ABSTRACT

VIABILITY FOR OXIDATION OF H_2S GAS USING LOW CONCENTRATION SOLUTIONS OF H_2O_2 IN APPLICATIONS FOR BIOGAS PURIFICATION

Stewart W. McCollam

This thesis is an examination of the viability of a low pH hydrogen peroxide scrubbing process for removing H_2S acid gas present in typical biogas streams generated from dairy farm anaerobic digesters. Biogas ranges in composition based on the feedstock manure used in the anaerobic digestion process but typically consists of methane (50-60%), carbon dioxide (40-50%), and trace amounts of hydrogen sulfide and ammonia.

Hydrogen sulfide is of prime concern because it is an odorous, poisonous, and highly corrosive gas which can impede use in power generation applications for biogas such as boilers, internal combustion engines, microturbines, fuel cells, and stirling engines. Thus, removal of hydrogen sulfide is highly recommended. Desirable attributes for a gas purification system include low capital cost, low operational costs, minimal preventative maintenance, minimum energy inputs, and ease of use.

H_2O_2 is a highly selective oxidant that does not produce toxic and corrosive by-products and has been shown to be a convenient way of eliminating oxidizable pollutants such as hydrogen sulfide gas from air or other gas streams. Based on these criteria, an

experimental approach was used to investigate the feasibility of using an acidic H_2O_2 scrubber for the removal of H_2S from synthetic biogas. Two test reactors were constructed, each setup with multiple configurations of packing volume, H_2O_2 concentration, and liquid volume. Synthetic biogas was introduced into the reactors and data was collected including liquid pH, liquid oxidation reduction potential, and H_2S concentration of exit gas during experiments. In total there were over twenty separate experiments conducted between the bench scale experiments, 1st scrubber trials, and 2nd scrubber trials. The results of these experiments demonstrate that a low pH H_2O_2 scrubbing system shows commercial viability for the removal of H_2S from biogas.

Functional oxidation of H_2S was achieved with removal efficiencies of 99% in certain reactor configurations. Bench scale experiments indicate that highest oxidation reduction potential of hydrogen peroxide solutions occurs in the acidic pH range between pH 3-5. Key operating parameters observed for functional oxidation of H_2S gas were the bubble diameter of inlet biogas and gas residence time. Increased residence times and smaller mean inlet bubble diameters led to maximum removal efficiencies.

The research was conducted in the University of Louisville Food Processing Laboratory and used as proof-of-concept for claims made in United States Patent Application 20090130008. These initial results indicate that future work is warranted for examining suitability of using a commercial scale acidic hydrogen peroxide scrubbing vessel as an H_2S removal technology in biogas purification.

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NOMENCLATURE

AD – Anaerobic Digestion

CNG – compressed natural gas

GAC – Granular Activated Carbon

K_p – Equilibrium Constant

LCA – Life Cycle Assessment

LPG – Liquid propane gas

ORP – Oxidation Reduction Potential

P_{H_2O} - Partial Pressure of water

P_{H_2S} - Partial Pressure of H_2S gas

VOC – Volatile Organic Compounds

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INTRODUCTION

In May of 2008, the University of Louisville Food Processing lab was retained by Michael Funk of JAF enterprises to test the viability of a hydrogen sulfide (H_2S) gas removal process utilizing low concentration hydrogen peroxide (H_2O_2) solutions to remove/oxidize H_2S acid gas from a typical biogas stream generated by a dairy farm anaerobic digester. The work of the University of Louisville Food Processing Laboratory was conducted as proof of concept for claims made in United States Patent Application 20090130008. Specifically, the Food Processing Lab was asked to:

1. Determine the efficiency of a process in which very low concentrations of hydrogen peroxide in water oxidize very low concentrations of saturated hydrogen sulfide gas to sulfur when introduced into the oxidizing solution through a distributor and then allowed to migrate through a non-pressurized oxidation vessel containing less than 1% hydrogen peroxide. The oxidation efficiency will be determined by measuring the concentration of hydrogen sulfide gas in the expelled gas.

2. Determine the efficiency of a process in which very low concentrations of hydrogen peroxide in water oxidize very low concentrations of saturated hydrogen sulfide gas to sulfur when introduced through a distributor into an oxidizing tank full of oxidizing solution and random packing. The gas will be allowed to migrate through the non-pressurized oxidation vessel containing less than 1% hydrogen peroxide.

3. Determine the efficiency of a process in which very low levels of hydrogen peroxide in water oxidize saturated hydrogen sulfide gas to sulfur when introduced into a counter-current flow scrubbing vessel where the gas enters at the bottom of the scrubbing vessel and the oxidizing agent enters through the top. The scrubbing vessel will contain random packing that will encompass 60% of the volume of the vessel. The gas and the oxidizing solution will be introduced into the vessel through distributors that will allow for the even distribution of both the gas and the oxidizing solution. Volumes of both gas and oxidizing solution introduced into the vessel will be based upon proportional volumes of less than 1% of oxidizing solution to less than 1% of hydrogen sulfide. The oxidation efficiency will be determined by measuring the concentration of hydrogen sulfide gas in the expelled gas.

The author conducted experiments based on the above listed criteria set forth by the retaining company and presented the results to JAF enterprises for use on the aforementioned patent application. The methods, procedures, results, and conclusions of the confidential research conducted by the University of Louisville Food Processing Lab are documented in this thesis with permission given by JAF enterprises.

BACKGROUND AND THEORY

A. ANAEROBIC DIGESTION

Anaerobic digestion of agricultural waste has been practiced for many years and provides a waste treatment solution, improved nutrient recovery, and energy generation potential. (Zicari 2003) Anaerobic digestion is a preferential treatment process for biomass because it produces, rather than consumes, energy and can be carried out in relatively small, enclosed tanks. (Burke 2001) Furthermore, the products of anaerobic digestion have value and can be sold to offset treatment costs. (Burke 2001) The primary product of value is biogas. Biogas is the gas produced as a by-product of the anaerobic decomposition of livestock manure and consists of approximately 60-80% methane, 30-40% carbon dioxide, and trace amounts of other gases namely hydrogen sulfide. (Kramer 2002) It has been found that the manures from dairy and swine operations tend to be more suitable for farm-based energy conversion. (Lusk 1998) Lastly, during digestion, over 80% of the pathogens and solids are eliminated creating a useful liquid fertilizer suitable for other farming operations. (Lansing 2008)

There are multiple factors that determine the biogas output of an anaerobic digester such as digester type and operational temperature. There is a vast array of reactors that can be utilized including a covered lagoon system, plug flow reactor,

anaerobic sequencing batch reactor, or a continuously mixed digester. Additionally, there are two temperature ranges which are considered optimum for anaerobic digestion, the mesophilic range (25–40 ˚C) and the thermophilic range (50–65 ˚C). (Lansing 2008) Table I below describes the different characteristics of three typical farm digesters.

TABLE I

CHARACTERISTICS OF TYPICAL ANAEROBIC DIGESTERS

	Covered Lagoon	**Complete Mix**	**Plug Flow**
Vessel	Deep lagoon	Round/Square In/Above ground Tank	In ground rectangular tank
Level of Technology	Low	Medium	Low
Additional Heat	No	Yes	Yes
Total Solids	0.5-1.5%	3-11%	<11%
HRT (days)	40-60	15+	15+
Farm Type	Dairy/Hog	Dairy/Hog	Dairy only
Optimum Climate	Temperate/Warm	All	All

Source: Roos, (2000), pg 1-2.

The microbial process of anaerobic digestion and methane production occurs through the complex action of interdependent microbial communities. (Zicari 2003) The first step involves the hydrolysis of organic compounds, including carbohydrates, proteins, and lipids via hydrolytic bacteria. (Chynoweth 1987) In this step, the substrate is broken down into organic acids, alcohols, neutral compounds, hydrogen, and carbon dioxide. The second stage consists of transitional bacteria converting soluble organic matter into methanogenic substrates such as hydrogen, carbon dioxide, and acetate. (Chynoweth 1987) In the final step, methanogenic bacteria utilize these intermediates for conversion to methane and carbon dioxide. (Chynoweth 1987) There are a number of factors which influence the digestion process, including temperature, bacterial

consortium, nutrient composition, moisture content, pH, and residence time. (Zicari 2003) In Figure 1, the anaerobic digestion process is illustrated.

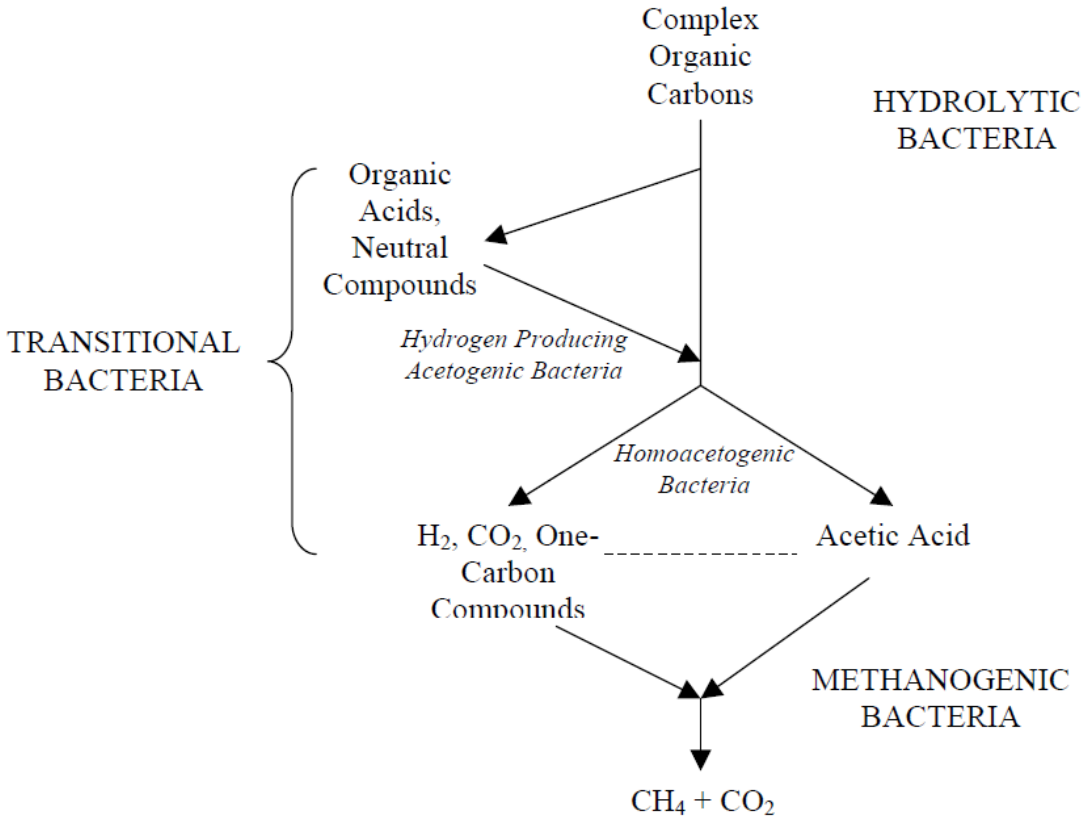

FIGURE 1 – Anaerobic Digestion Process

Source: Chynoweth (1987) pg. 3

Sulfur is an essential nutrient for methanogenesis during the anaerobic digestion process, but excessive sulfur levels too high may limit biogas production. (Chynoweth 1987) Sulfur can enter the digester in several pathways. Often chemicals such as copper and zinc sulfate solutions, used for dairy cow hoof treatment, get washed into the digester when diluting the feedstock to the digester total solids requirement. Additionally, farm animals excrete sulfur that is not digested for nutrition in the manure, which is then fed to

the digester. Farm animals consume sulfur in their food source, mostly in the form of sulfur containing amino acids such as cystine and methionine, or from their drinking water source, which may contain sulfates. (Zicari 2003)

Sulfate-reducing bacteria can out-compete methanogens during the anaerobic digestion process. (Madigan 2002) Therefore, sulfide production proceeds to completion before methanogenesis begins. The energetic reduction of sulfate with H_2 is favorable to the reduction of CO_2 with H_2, forming either CH_4 or acetate. (Madigan 2002) The toxicity level of total dissolved sulfide in anaerobic digestion is reported as 200-300 mg/l. (Chynoweth 1987) Also, a head gas concentration of 6% H_2S is the upper limit for methanogenesis, while 0.5% H_2S (11.5 mg/l) is optimum. (Chynoweth 1987)

B. BIOGAS COMPOSITION

Biogas ranges in composition based on the feedstock manure used in the anaerobic digestion process but typically consists of methane, carbon dioxide, and trace amounts of hydrogen sulfide and ammonia. Additionally, trace amounts of organic sulfur compounds, halogenated hydrocarbons, hydrogen, nitrogen, carbon monoxide, and oxygen are also occasionally present. (Zicari 2003) Moreover, the biogas is saturated with water vapor and may contain dust particles. (Wellinger 2000) Approximately 55 pounds of water is present in 49,500 cubic feet of saturated natural gas at 70˚F and atmospheric pressure. (Kohl 1997) Water-saturated biogas from dairy manure digesters consists primarily of 50-60% methane, 40-50% carbon dioxide, and less than 1% other

trace gases, the majority of which exists as hydrogen sulfide. (Pellerin 1987) In Figure 2, typical biogas components are listed.

Typical Bulk Biogas Components	**Trace Components**
Methane 50-60%	Hydrogen
Carbon Dioxide 38-48%	Hydrogen Sulfide
Trace Components	Non-methane Volatile Organic Carbons (NMVOC)
	Halocarbons

FIGURE 2 – Biogas Composition

Source: Fiesinger, Roloson et al. (2006) pg 1-1

Hydrogen sulfide is of prime concern because it is an odorous, poisonous, and highly corrosive gas. Some physical and chemical properties of hydrogen sulfide gas are listed in Table 2. Because of the characteristics listed in Table 2, removal of hydrogen sulfide is highly recommended, especially if the biogas is to be used for power generation. (Fiesinger 2006)

TABLE II

PHYSICAL, CHEMICAL, AND SAFETY DATA FOR HYDROGEN SULFIDE

Source: OSHA (2009), Ocupational Safety and Health Administration, www.OSHA.gov

Molecular Weight	34.08
Specific Gravity (relative to air)	1.192
Auto Ignition Temperature	250° C
Explosive Range in Air	4.5 to 45.5%
Odor Threshold	0.47 ppb
8-hour time weighted average (TWA) (OSHA)	10 ppm
15-minute short term exposure limit (STEL) (OSHA)	15 ppm
Immediately Dangerous to Life of Health (IDLH) (OSHA)	300 ppm

C. QUALITY REQUIREMENTS FOR BIOGAS UTILIZATION

Biogas can be used for most applications designed for natural gas assuming the biogas is purified. Gas processing is necessary to ensure proper functioning of cogeneration units, extending the life of biogas processing equipment, and increasing energy potential of the gas. (Fiesinger 2006) The gas processing cost factor detracts from the profitability and sustainability of anaerobic digester system operations. (Fiesinger 2006) Gas purification methods typically used in the natural gas processing industry are designed for higher gas flow rates and different chemical gas compositions than found at agricultural biogas production facilities. (Foral 1994) Accordingly, studies of alternative gas processing techniques in the context of small biogas production facilities are needed.

On-site, stationary biogas applications typically have few gas processing requirements. (Zicari 2003) The degree of purification for biogas utilization will depend on the end use of the gas and the technology that utilizes the biogas as a process input. Technologies that can utilize biogas include boilers, internal combustion engines, microturbines, fuel cells, and stirling engines. Biogas can also be injected into natural gas pipelines. Technologies such as boilers and stirling engines have the least stringent gas processing requirements because of their external combustion configurations. Internal combustion engines and microturbines are the next most tolerant to gas impurities. Fuel cell technology is less tolerant to contaminants due to the potential for catalytic poisoning.

Purification of biogas to natural-gas quality requires expensive and complex processing and must be done when injection into a natural-gas pipeline or production of vehicle fuel is desired. Integrated units with facilities for scrubbing, compressing and

storing have been developed in the Netherlands, UK, Australia, New Zealand and the USA. (Kapdi 2005) All these results indicate that biogas is one of the potential substitutes for present day fuels including CNG, gasoline, diesel and LPG. (Kapdi 2005)

Removal of CO_2 may also simultaneously reduce H_2S levels; however, this topic is not covered in this thesis. Many facilities in Europe have utilized water scrubbing, polyethylene glycol scrubbing, carbon molecular-sieves or membranes for upgrading of biogas to natural gas or vehicle fuel. (Zicari 2003)

D. HYDROGEN SULFIDE REMOVAL TECHNOLOGIES

Since biogas is similar in composition to raw natural gas, purification techniques developed and used in the natural-gas processing industry can be evaluated for their suitability (or lack thereof) with biogas systems. (Zicari 2003) The process chosen is dependent on several factors, including gas end use, composition, physical characteristics, available resources, byproducts generated, cost, and the volume of gas to be treated. In Table III the principal gas phase impurities that may be present are listed; additional compounds that can be problematic are water condensate and particulate matter.

TABLE III
GAS PHASE IMPURITIES IN BIOGAS

Source: Kohl (1997) pg. 3

1. Hydrogen Sulfide
2. Carbon dioxide
3. Water vapor
4. Sulfur dioxide
5. Nitrogen oxides
6. Volatile organic compounds (VOC's)
7. Volatile chlorine compounds (e.g., HCl, Cl_1)
8. Volatile fluorine compounds (e.g., HF, SiF_4)
9. Basic nitrogen compounds
10. Carbon monoxide
11. Carbonyl sulfide
12. Carbon disulfide
13. Organic sulfur compounds
14. Hydrogen cyanide

Gas purification processes typically are categorized by one of the following methods: 1) Absorption into a liquid; 2) Adsorption on a solid; 3) Permeation through a membrane; 4) Chemical conversion to another compound; or 5) Condensation. (Kohl 1997) For gas purification process comparison purposes, gas characteristics typical for a farm digester treating waste from around 500 dairy cows will be used; the summarized data is shown in Table IV below.

TABLE IV

BIOGAS CHARACTERISTICS FOR PROCESS COMPARISON

Biogas Composition	60.00 % CH_4, 39.75 % CO_2, 2500 ppm H_2S
Gas Flow Rate	~35,000 ft^3/Day
Gas Pressure	~ 17 psia
Gas Temperature	75-80 ˚F
Water Saturated	Yes

Desirable attributes for a gas purification system include low capital cost, low operational costs, minimal preventative maintenance, minimum energy inputs, and ease of use. H_2S removal processes will be divided into dry-based, membrane, physical-solvent, alternative, and liquid-based processes for the purposes of comparison. Media and media disposal costs are not mentioned for all processes within this section; however, these costs might be a significant cost of purification system.

D-I. DRY-BASED H_2S REMOVAL PROCESSES

Dry removal techniques for H_2S have historically been used at facilities with less than 500 lb S/day in the U.S. (Zicari 2003) Since the dry-sorption media eventually becomes saturated with contaminants, it is common practice to have vessels operating in parallel so one vessel can remain operational as media replacement takes place in the offline vessel.

(D-I-A) IRON OXIDES.

Iron oxides remove sulfur compounds (H_2S) by forming insoluble iron sulfides. Most iron oxides can be regenerated with exposure to air thus forming elemental sulfur; however, over time the media will become clogged with elemental sulfur and must be replaced. One of the most common iron oxide products is "iron sponge". More recently, other iron-oxide media such as Sulfa Treat® and Sulfur-Rite® have been offered as improved alternatives to iron sponge.

(D-I-A-1) IRON SPONGE.

Iron sponge consists of iron-oxide impregnated wood-chips used to selectively interact with H_2S and mercaptans. The primary active ingredients are hydrated iron-oxides (Fe_2O_3) of alpha and gamma crystalline structures. (Anerousis 1985) Lesser amounts of Fe_3O_4 ($Fe_2O_3 \cdot FeO$) also contribute to the activity.

(Anerousis 1985) Grades of iron sponge with 8, 12, 15, 20, and 25 lb Fe_2O_3/bushel are typically available with the 15 lb Fe_2O_3/bushel being the most common. Table V illustrates typical specifications for iron sponge. Equations 1 and 2 (Crynes 1978) illustrate the chemical reactions involved in removal of H_2S by Fe_2O_3 and the subsequent regeneration in the presence of oxygen.

TABLE V

SPECIFICATION FOR IRON SPONGE (15 lb/bushel)

Source: Kohl (1997) pg. 1302

Water Content (Loss on Drying, wt%)	
Iron Sponge Product	30.60
Iron Oxide Particulates	17.70
Size Distribution of Iron Oxide Particulates, wt%	
Retained on Mesh	
16	4.22
30	54.62
60	32.72
100	4.49
140	1.58
200	0.79
325	1.06
400	0.26
Smaller than 400 mesh	0.26
Chemical Analysis of Dried Iron Oxide Particulates, wt%	
Iron as Fe_2O_3	58.67
Iron as Fe_3O_4	20.40
Sulfur as S	0.49
Copper as Cu	0.11
Zinc as Zn	0.01
Lead as Pb	0.01
Silicon as Si	1.02
Aluminum as Al	0.02
Phosphorus as P	0.02
Balance primarily wood substrate material	
Flooded pH (1)	10.2
Leachable pH (2)	7.88
Weight of Iron Oxide, lb/bushel	17.61

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \qquad \Delta H = -20.9 \frac{btu}{g-mol} H_2S \tag{1}$$

$$2Fe_2S_3 + O_2 \rightarrow 2Fe_2O_3 + 3S_2 \qquad \Delta H = -188 \frac{btu}{g-mol} H_2S \tag{2}$$

Iron sponge can be operated in batch mode with separate regeneration, or with a small flow of air in the gas stream for continuous revivification. (Crynes 1978) In batch mode, operational experience indicates that only about 85% of the theoretical efficiency can be achieved. (Taylor 1956)

Spent iron sponge can be regenerated in place by recirculation of the gas in the vessel adjusted to 8% O_2 concentration and 10-20 ft^3/ft^3 bed/min space velocity. (Taylor 1956) Alternatively, the sponge can be removed, spread out into a layer approximately 6 in thick, and kept continually wetted for 10 days. (Zicari 2003) Regeneration of iron sponge is only practical once or twice because the regeneration process can reduce the iron sponge activity by roughly 33%. (Zicari 2003)

Removal rates as high as 5 lb H_2S / lb Fe_2O_3 have been reported in continuous-revivification mode with a feed-gas stream containing only a few tenths of a percent of oxygen. (Taylor 1956) At Huntington's farm in Cooperstown, NY, a removal rate of 4 lb H_2S/lb Fe_2O_3 was reported using 12 lb Fe_2O_3/bushel grade sponge and continuous revivification with 2.29% air recirculation. (Vetter 1990) Vetter et al (1990) also reported that H_2S levels at one farm digester were consistently reduced from levels as high as 3600 ppm (1350 ppm average) to below 1 ppm using a 5 ft diameter x 8 ft deep iron sponge reactor.

While the benefits of using iron sponge include simple and effective operation, there are critical drawbacks to this technology that have lead to decreased usage in recent years. (Zicari 2003) The process operating costs can be high (especially shipment of the media to the farm) and the waste stream of spent media is substantial. The estimated cost for media needed for a digester described in Table IV would be approximately $2700-3500 annually not including the cost of shipping. Moreover, the change-out process is labor intensive and can be burdensome. Lastly, safe disposal of spent iron sponge has become problematic, and in some instances, spent media may be considered hazardous waste and require special disposal procedures. (Zicari 2003)

(D-I-A-2) SULFA TREAT®. Sulfa Treat® is a proprietary sulfur scavenger, consisting mainly of Fe_2O_3 or Fe_3O_4 compounds coated onto a proprietary granulated support and marketed by the Sulfa Treat® Company of St. Louis, MO. Sulfa Treat® is used in the same manner as iron sponge in a low-pressure vessel with down-flow of gas and is effective with partially or fully hydrated gas streams.

Conversion efficiency in commercial systems is in the range 1.2 – 1.6 lbs H_2S/lb iron oxide, which is similar to values reported for batch operation of iron sponge. (Kohl 1997) Particles range in size from 4 to 30 mesh with a bulk density of 70 lb/ft^3 in place. The price of Sulfa Treat® is approximately $0.50/lb at the desired quantity needed for a dairy farm with a herd of 500 cows.

Multiple benefits of using Sulfa Treat® over iron sponge are claimed. Sulfa Treat® is reportedly easier to handle than iron sponge, thus reducing operating costs, labor time for change-out, and pressure drop in reactor. Additionally, Sulfa Treat® claims

to be non-pyrophoric when exposed to air and thus does not pose a safety hazard during change-out.

Drawbacks associated with Sulfa Treat® include non-regenerative media, chemically intensive, and problematic/expensive disposal of spent media. Estimated cost for Sulfa Treat® is approximately $9,500 annually. The manufacturer suggests that the spent product may be used as a soil amendment or as a raw material in road or brick making. However, they also state that every customer must devise a plan for their spent media that is in accordance with local and state regulations.

(D-I-A-3) SULFUR-RITE®. Sulfur-Rite® is a dry-based iron-oxide product manufactured by GTP-Merichem. Sulfur-Rite® claims that insoluble iron pyrite is the final end product once the media is spent. Systems come in prepackaged cylindrical units that are recommended for installations in processes with less than 400 lb sulfur/day in the gas and flow rates below 2500 ft^3/min. Company claims spent product is non-pyrophoric and ladfillable and has 3-5 times the effectiveness of iron sponge. Many disadvantages exist when using Sulfur-Rite® as the product is very expensive (estimated annual cost 15,000 $/yr) and requires the use of proprietary reaction vessels sold or leased by the Merichem company.

(D-I-B) ZINC OXIDES. Zinc oxides are preferred for removal of trace amounts of hydrogen sulfide from gases at elevated temperatures due to their increase in selectivity over iron oxide. (Chiang 1987) Typically, zinc oxides are used in dry-boxed or fluidized-bed configurations in the form of cylindrical pellets approximately 0.10 inches in diameter by 0.25 inches in length. Hydrogen sulfide reacts with zinc oxide to form an

insoluble zinc sulfide as seen in Equation 3. (Kohl 1997) The equilibrium constant for this reaction is given in Equation 4. (Kohl 1997)

$$ZnO + H_2S = ZnS + H_2O \quad (3)$$

$$K_p = \frac{P_{H_2O}}{P_{H_2S}} \quad (4)$$

The equilibrium constant for the above mentioned chemical reaction decreases rapidly with temperature as shown in Figure 3. At very high temperatures equilibrium is approached, but at gas temperatures typical of AD, reaction kinetics are drastically reduced to unfavorable conditions.

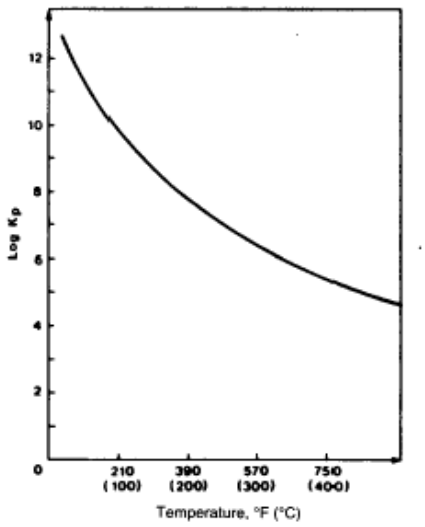

Figure 3 – Equilibrium Constant for the Reaction: ZnO + H_2S = ZnS + H_2O

Source: Kohl, (1997), pg. 1307

Maximum sulfur loading is typically in the range of 30-40 lb sulfur/100 lb sorbent for most high temperature processes (300-750 ˚F). (Zicari 2003) Formation of zinc

sulfide is irreversible and zinc oxide is not very reactive with organic sulfur compounds. To remove mercaptans, initial catalytic hydrodesulphurization to convert mercaptan compounds to the more reactive hydrogen sulfide is needed. (Kohl 1997)

(D-I-C) ALKALINE SOLIDS. Alkaline substances, such as hydrated lime, react with acid gases like H_2S, SO_2, CO_2, carbonyl sulfides, and mercaptans in neutralization reactions. (Zicari 2003) Usually liquid-based scrubbers are used, but fixed-beds of alkaline granular solid can also be used in a standard dry box arrangement with up-flow of gas. (Zicari 2003) Primary reactions are shown in Equations 5 and 6. (Kohl 1997)

$$2NaOH + H_2S \rightarrow Na_2S + 2H_2O \quad (5)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (6)$$

To achieve significant removal of H_2S, CO_2 must also be concurrently reduced at the cost of extremely high product utilization. (Zicari 2003) Given that the typical biogas stream for an anaerobic digester is 40% CO_2 by volume, the cost of CO_2 reduction is significantly greater than savings opportunities from power generation utilizing methane from the biogas stream.

(D-I-D) ADSORBENTS. Adsorbents rely on physical adsorption of a gas-phase particle onto a solid surface. High porosity and large surface areas are highly desirable physical characteristics for adsorption media. Adsorbent media will eventually become saturated and must be replaced or regenerated. If regeneration is economical and

feasible, it can be achieved by using one of the processes shown in Table VI. During the regeneration process, H_2S laden gas is released and must be exhausted appropriately or subjected to another process for sulfur recovery. (Yang 1987)

TABLE VI

Adsorbent Regeneration Processes

Regeneration Process	**Description**
Temperature Swing Adsorption (TSA)	Regeneration takes place primarily through heating. The differences between the equilibrium loadings at the two temperatures represent net removal capacity. Considerable energy and time are required to heat and cool the bed. TSA is often achieved by preheating a purge gas.
Pressure Swing Adsorption (PSA)	Regeneration is achieved by lowering the pressure of the bed and allowing the adsorbate to desorb. Typically adsorption takes place at elevated pressures to allow for regeneration at atmospheric pressure or under slight vacuum. PSA is relatively fast compared to TSA
Inert Purge	A non-adsorbing gas containing very little of the impurity is passed through the bed, reducing the partial pressure of adsorbate in the gas-phase so that desorption occurs.
Displacement Purge	A purge gas that is more strongly adsorbed than the impurity is used to desorb the original contaminant. Steam regeneration, while mostly a thermal process, also regenerates through displacing some of the original adsorbate.

Source: Zicarri (2003) pg 25

(D-I-D-1) ZEOLITES. (molecular sieves) are naturally occurring or synthetic silicates with extremely uniform pore sizes and dimensions and are especially useful for gas purification. Polar compounds, such as water, H_2S, SO_2, NH_3, carbonyl sulfide, and mercaptans, are very strongly adsorbed and can be removed from non-polar compounds such as methane. (Zicari 2003) Many different zeolite structures have been discovered and subsequently studied; properties of the four most common ones are listed by molecular sieve number (column 1) in Table VII.

TABLE VII

Commercial Zeolite Properties by Molecular Sieve Size

Basic type	Nominal pore diameter, Angstroms	Bulk density of pellets, lb/cu ft (1)	H_2O capacity, (%/wt) (2)	Molecules adsorbed (typical) (3)	Molecules excluded	Typical applications
3A	3	47	20	H_2O, NH_3	Ethane and larger	Dehydration of unsaturated hydrocarbons
4A	4	45	22	H_2S, CO_2, SO_2, C_2H_4, C_2H_6, C_3H_6	Propane and larger	Static desiccant in refrigeration systems, etc. Drying saturated hydrocarbons
5A	5	43	21.5	n-C_4H_9OH,	Iso compounds, 4 carbons rings and larger	Separates n-paraffins from branched and cyclic hydro-carbons
13X	10	38	28.5	Di-n-propyl-amine	$(C_4F_9)_3N$ and larger	Coadsorption of H_2O, H_2S, and CO_2

Notes:
1) Bulk density for ⅛" pellets.
2) Pounds H_2O/100 lb activated adsorbent at 17.5 mm Hg partial pressure and 25°C, adsorbent in pellet form.
3) Each type adsorbs listed compounds plus those of all preceding types.
Data from UOP (1990)

Source: Kohl, (1997), pg. 1043.

Adsorption processes via hydrophilic, ion-rich zeolites show promise for biogas purification. (Cosoli 2008) From research it has been shown that hydrophilic zeolites are more desirable for H_2S adsorption. (Cosoli 2008)

Zeolites do not come without drawbacks; the contaminants (CO_2, H_2S, H_2O) within the gas stream essentially compete for adsorption sites. Within a packed bed reactor multiple adsorption zones may occur as illustrated in Figure 4. Additionally, without a regeneration process, the zeolite consumption required to purify a gas stream would not be economically feasible.

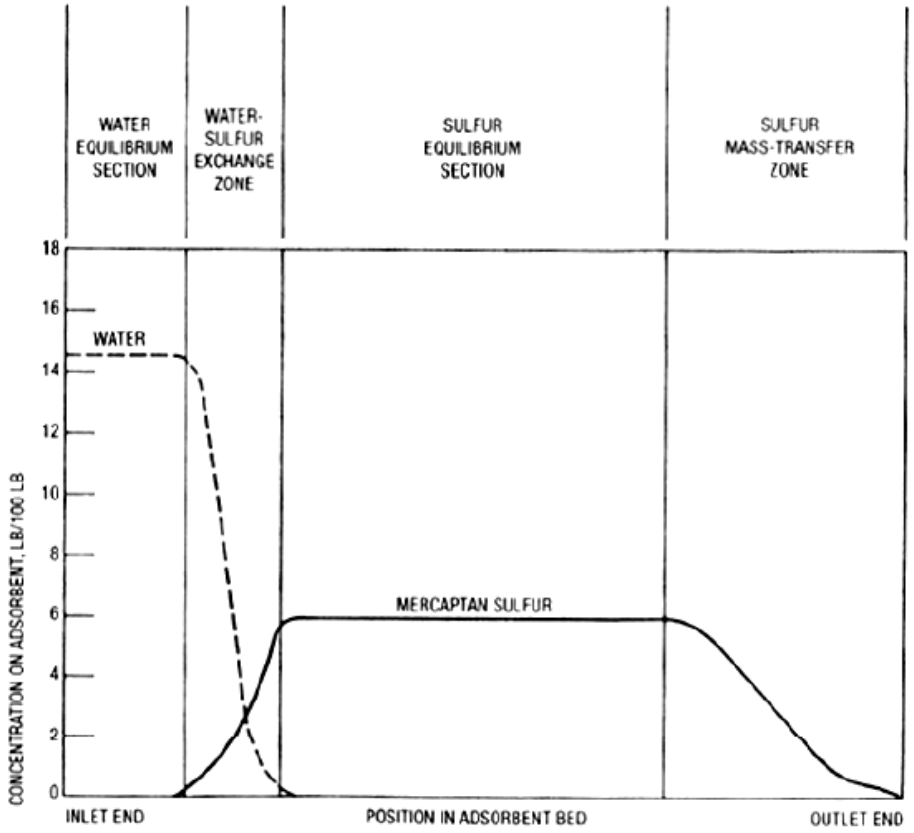

Figure 4 – Zeolite Packed Bed Reactor Adsorption Zones

Source: Kohl, (1997), pg. 1071

(D-I-D-2) ACTIVATED CARBON COMPOUNDS. Granular activated carbon (GAC) is a preferred method for removal of volatile organic compounds (VOC) from industrial gas streams. (Zicari 2003) Utilization of GAC for removal of H_2S has been limited to removing lower concentrations mostly in water treatment processes. (Zicari 2003) If H_2S is in higher concentrations, GAC coated with alkaline or oxide coatings are preferred for their enhanced physical adsorptive characteristics. Sodium hydroxide, sodium carbonate, potassium hydroxide (KOH), potassium iodide, and metal oxides are commonly employed coatings.

An example of a gas pretreatment unit using a non-regenerable KOH-impregnated activated carbon bed for removal of H_2S from an anaerobic digester and landfill gas for use in a fuel cell was documented by Spiegel (1997, 2000). Oxygen (0.3-0.5% by volume) was added to facilitate conversion of H_2S to elemental sulfur. (Spiegel 1997) Two beds, 2 ft in diameter by 4.5 ft in height, were piped in series and run with space velocities of 5300 ft^3/hr. (Spiegel 1997) Inlet H_2S concentration ranged from 0.7-50 ppm, averaging 24.1 ppm, and 98% removal was demonstrated. (Spiegel 2000) A loading capacity of 0.51 g sulfur/g carbon was reported by Spiegel and Preston (2000); this value is considerably higher than typical loading values 0.15-0.35 g sulfur/g carbon issued by manufacturers of material. For the GPU, capital costs (including sulfur removal, blowers, and coalescing filters) were estimated to be $500/kW. (Spiegel 1997)

A primary drawback to the systems studied by Spiegel and Preston (2003) was its system complexity which utilized extra equipment (gas chiller, compressor, coalescing filters, and a moisture separator) to reduce other contaminant levels (organic halides) to California mandated emission levels to power a fuel cell. In fact, a system with main features consisting of a non-regenerable KOH-impregnated activated carbon bed for H_2S removal, followed by a coalescing filter to remove liquids and a blower to deliver the gas to the fuel cell at the required pressure, has operated successfully at a commercial venture on a landfill in Braintree, MA. (Spiegel 2003) Moreover, other power generation technologies (synchronous, induction, and microturbine generators) do not require ultra purified gas and are a more common option for biogas power generation.

D-II. MEMBRANE PROCESSES

Many processes for separation of gaseous mixtures use semi-permeable membranes that allow one or more constituents of the mixture to pass through more readily than others. (McCabe 2005) Membranes are often made of flexible films or synthetic polymers prepared to have high permeability for a specific type of molecule. (McCabe 2005) Separation of gaseous mixtures through membranes can be achieved using porous or non-porous membranes by diffusing a gas stream at high pressure through the membrane into a region of lower pressure. (McCabe 2005) Porous membranes utilize Knudsen diffusion, capillary condensation, surface diffusion, and molecular sieving as transport mechanisms for the selective diffusion of components within the gaseous mixture. The transport of gases through nonporous membranes occurs by a solution-diffusion mechanism. (McCabe 2005) Membranes are generally not used for selective removal of H_2S from biogas but are becoming more attractive for upgrading biogas to natural gas standards. (Zicari 2003) Attributes such as reduced capital investment, ease of operation, low environmental impact, gas dehydration capability, and high reliability are several reasons for this interest. (Zicari 2003)

High pressure cellulose acetate membranes specifically designed for purification of anaerobic digester gas were found to reduce H_2S levels from 1000 ppm to 430 ppm. (Kayhanian 1988) Three-stage units treating landfill gas have achieved product gases with over 96% CH_4 but utilize separate H_2S removal systems to extend the membrane life, which typically ranges from three to five years. (Wellinger 2000)

Even though there are a large number of other potential applications for gas separation using polymeric membranes, only few of them have been adopted in practice. (Sridhar 2007) In Table VIII, companies and the commercial membrane technologies they produce are listed. Among the membranes commercialized for treating natural gas, cellulose acetate derivatives and polyimides were found to be the best materials for CO_2/CH_4 separation, while poly(ether-block-amide) was the bench-mark for H_2S/CH_4 mixtures. (Sridhar 2007) For most polymer membranes, separation factors for H_2O/CH_4 and H_2S/CH_4 were generally greater than those for CO_2/CH_4, which means that high selectivity for the latter system is critical for purification of natural gas in totality. (Sridhar 2007)

TABLE VIII

Commercial Scale Gas Membrane Suppliers

Company	CO_2	H_2S	H_2	Air	NO_2	N_2
A/G Technology (AVIR)	X	—	—	X		X
Air products (Separex)	X	—	X	—		—
Asahi Glass (HISEP)	—	—	—	X		X
Cynara (Dow)	X	—	—	—		—
Dow (Generon)	—	—	—	X		X
Dupont	—	—	X	—		—
Grace Membrane Systems	X	—	X	—		—
International Permeation	X	—	—	—		—
Monsanto	X	—	X	X		X
Osaka Gas	—	—	—	X		—
Oxygen Enrichment Co.	—	—	—	X		—
Techmash export	—	—	—	X		—
Toyobo	—	—	—	X		—
Ube Industries	—	—	X	—		—
Union Carbide (Linde)	—	—	X	X		X
UOP / Union Carbide	—	—	X	—		—
Delta Projects Ltd.	X	—	—	—		—
Envirogenics System Co.	X	—	—	—		—
ENSTAR Engineering Inc.	X	X	—	—		—

Source: Sridhar (2007), pg. 147.

D-III. PHYSICAL SOLVENT PROCESSES

When acid gases represent a large proportion of the total gas stream, the cost of removing them with heat-regenerative amine processes may be more costly than the value of the purified gas. (Zicari 2003) Physical solvent systems, where acid gases are dissolved in a liquid and flashed off elsewhere utilizing reduced pressure, have seldom been used. If utilizing higher pressures, the product gas may be lost due to the partial pressure driving forces utilized.

(D-III-A) WATER WASHING. Water is a low cost highly available liquid absorbent; however, other liquids contain high solubility parameters for acid gases H_2S and CO_2. Absorption of acid gases into water produces corrosive solutions that can be damaging to equipment if not treated. Table IX displays Henry's law constants for the major constituents in biogas. Since both CO_2 and H_2S have similar solubility parameters in water a system will remove both gases rather than H_2S gas selectively.

TABLE IX

Henry's Law Constants of Biogas Compounds at 77˚F and 1atm

CH_4	$1.5 \times 10^{-4} \frac{M}{atm}$
CO_2	$3.6 \times 10^{-2} \frac{M}{atm}$
H_2S	$8.7 \times 10^{-2} \frac{M}{atm}$

(D-III-B) ALTERNATIVE PHYSICAL SOLVENTS. Solvents such as methanol, propylene carbonate, and ethers of polyethylene glycol offer better absorption capacity than water alone. (Zicari 2003) Criteria for solvent selection include high absorption capacity, low reactivity with equipment and gas constituents, and low viscosity. (Zicari 2003) Thermal regeneration techniques are typically needed to achieve pipeline-quality gas. Additionally, loss of product gases as high as 10% have been reported. (Kohl 1997)

The SELEXOL® process utilizes a mixture of dimethyl ethers of polyethylene glycol (DMPEG), and has the formulation of $CH_3(CH_2CH_20)_nCH_3$, where n is between 3 and 9. (Breckenridge 2000) Like water scrubbing, the cost for selective H_2S removal has not yet shown to be competitive. This process will most likely only be considered for applications in which upgrading to relatively pure methane is desired. (Wellinger 2000)

The SULFINOL® process is a mixed solvent process that removes H_2S, CO_2, carbonyl sulfide, and organic sulfur compounds from natural gas by scrubbing with diisopropanolamine dissolved in a mixture of sulfolane and water. (Maxwell 2004) As a mixed solvent system, the sovent formation can be tailored to obtain good treating economy, single-step treating for sweetening and organic sulfur removal, high acid gas loading or selective treating. (Maxwell 2004) While this method is highly effective, it has yet to demonstrate economic feasibility at the scale of a single anaerobic digester.

D-IV. ALTERNATIVE H_2S ABATEMENT TECHNOLOGIES

(D-IV-A) DIGESTER SULFIDE ABATEMENT. Iron chlorides, phosphates, and oxides can be added directly to the digester to bind with H_2S and form insoluble iron sulfides. (Zicari 2003) Lab studies have shown that the addition of iron phosphate and phosphate buffers (increases pH range from 6.7 to 8.2) reduced gaseous sulfide emissions from 2900 to 100 ppm, while increasing soluble sulfide concentrations from 18 to 61 mg/l. (McFarland 1989) Soluble sulfide levels around 120 mg/l begin to inhibit CH_4 production. Addition of insoluble iron^{3+} phosphate up to $FePO_4$-Fe:SO_4^{2-}-S ratios of 3.5 reduced gaseous sulfide levels from 2400 to 100 ppm. (McFarland 1989) Ferric phosphate ($FePO_4$) and ferric oxide (Fe_2O_3) can lower HS^- concentration inside digester from reactions shown in Equations 7 and 8. (Jewell 1993) While this method shows potential, concern exists that accumulation of insoluble iron sulfides might cause premature buildup in a digester. (Jewell 1993)

$$2\ FePO_4H_2O + 3\ H_2S \rightarrow Fe_2S_3 + 2\ H_3PO_4 + 2\ H_2O \quad (7)$$

$$Fe_2O_3H_2O + 3\ H_2S \rightarrow Fe_2S_3 + 4\ H_2O \quad (8)$$

(D-IV-B) LIVESTOCK DIETARY ADJUSTMENT. Diet composition influences sulfur content in animal wastes, which directly impact sulfur compounds emitted from an anaerobic digester. Since sulfur is a required nutrient for animal health, it cannot be completely eliminated from a diet. Studies have shown that by carefully selecting low sulfur feed ingredients and using them to formulate nutritionally adequate,

low sulfur starter diets, total sulfur and sulfate excretion can be reduced by approximately 30%, without compromising energy and nitrogen digestibility or pig performance. (Shurson 1998) Dietary adjustment is not generally used for sulfide reduction, because diets are typically optimized for product yields and animal health, rather than sulfur levels present in manure. (Zicari 2003) Additionally, limiting sulfur containing chemicals (copper sulfate hoof baths commonly used in milk parlors) from entering digester is another recommended step for limiting sulfur input to digester.

(D-IV-C) AERATION. A simple technique for H_2S reduction, now practiced in Europe, includes air/oxygen dosing into the biogas. (Zicari 2003) Air is carefully admitted to the digester or biogas storage tank at levels corresponding to 2-6% air in biogas. It is believed effectiveness is based on biological aerobic oxidation of H_2S to elemental sulfur and sulfates. Inoculation is not required, as Thiobacillus species are naturally occurring at aerobic liquid-manure-wetted surfaces. (Zicari 2003) The result of this process leaves deposits of yellow sulfur clusters on the surfaces of digester equipment. Utilizing this method can create explosive gas mixtures and care must be taken to avoid these situations with careful monitoring.

(D-IV-D) BIOLOGICAL PROCESSES. Biologically active agents have been used in a variety of process arrangements, such as biofilters, fixed-film bioscrubbers, and suspended-growth bioscrubbers. (Dawson 1993) These processes may also have added benefit of removing multiple contaminants from a gas stream thus increasing functionality. While not covered in this thesis, there are many microorganisms that can be utilized in the selective removal of H_2S in a biogas stream. Readers are directed to the

references listed in Table X for further information of biological processes and technologies associated with anaerobic digestion.

TABLE X

Microorganisms Utilized for Selective Removal of H_2S from Biogas Streams

MICROORGANISM	REFERENCE
Thiobacillus species	Degorce-Dumas, et al. (1997), Nishimura and Yoda (1997), Koe and Yang (2000), Oh, et al. (1998)
Thiobacillus thioxidans	Cho, et al. (2000), Cadenhead and Sublette (1990)
Thiobacillus denitrificans	Sublette, et al. (1994), Sublette and Sylvester (1987a, 1987b)
Thiobacillus thioparus	Cho, et al. (1992), Cadenhead and Sublette (1990)
Thiobacillus ferrooxidans	Jensen and Webb (1995)
Thiobacillus novellas	Chung, et al. (1998)
Thiobacillus versutus	Cadenhead and Sublette (1990)
Thiobacillus neopolitanus	Cadenhead and Sublette (1990)
Pseudomonas putida	Chung, et al. (1996, 2001)
Hyphomicrobium	Zhang, et al. (1991)
Xanthamonas species DY44	Cho, et al. (1992)

Source: Zicari, (2003), pg 49.

D-V. LQUID-BASED H_2S REMOVAL PROCESSES

Liquid-based H_2S removal processes have replaced many dry-based technologies for natural gas purification because of reduced ground space requirements, reduced labor costs, and increased potential for elemental sulfur recovery. (Zicari 2003) Technologies include amine systems, alkaline salts processes, and oxidation/reduction techniques.

(D-V-A) AMINE SYSTEMS. Amine processes are commonly used in large scale natural gas purification processes and the petrochemical industry. These systems are attractive because the regenerative media and high removal efficiencies of H_2S and/or

CO_2. Complications of using an amine system include complex flow diagrams, foaming problems, chemical losses, and the air treatment needed for regeneration process.

Alkanolamine molecules generally contain a hydroxyl group on one end and amine group on the opposite. The hydroxyl group lowers the vapor pressure and increases water solubility, while the amine group provides alkalinity necessary for absorption of acid gases. (Zicari 2003) The primary chemical reactions occurring in systems are outlined in Equations 9 through 13. (Kohl 1997)

$$H_2O = H^+ + OH^- \quad (9)$$

$$H_2S = H^+ + HS^- \quad (10)$$

$$CO_2 + H_2O = HCO_3^- + H^+ \quad (11)$$

$$RNH_2 + H^+ = RNH_3^+ \quad (12)$$

$$RNH_2 + CO_2 = RNHCOO^- + H^+ \quad (13)$$

Amines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and diisopropanolamine (DIPA) are commonly used in processes. Absorption is typically conducted at high pressures with heat regeneration in the stripper. A basic flow diagram for an alkanolamines acid-gas removal process is shown in Figure 5.

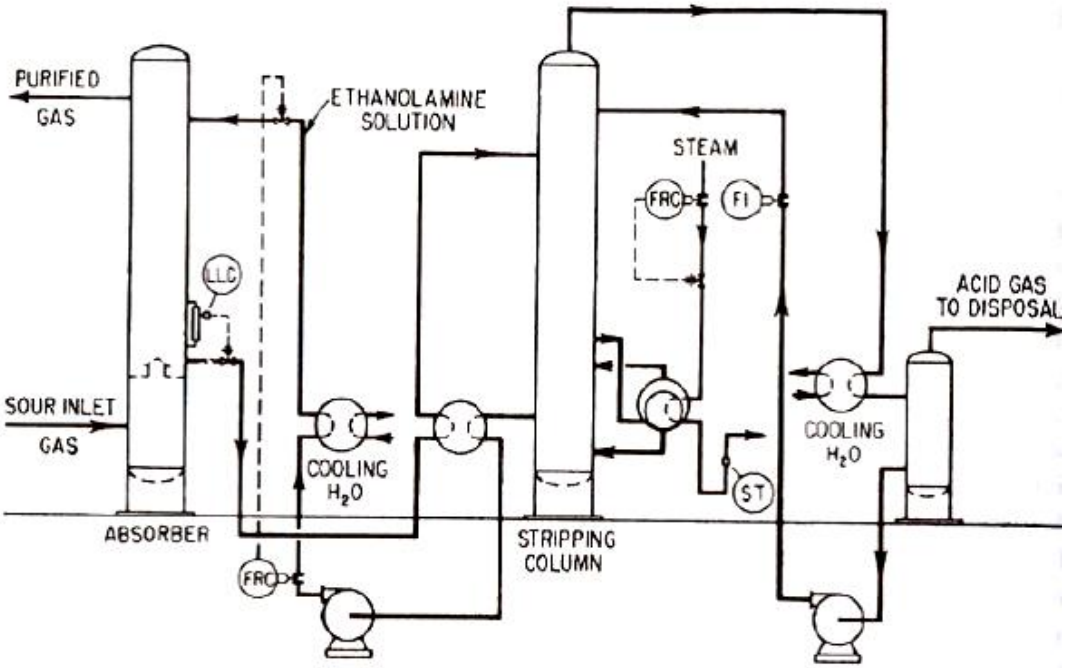

Figure 5 – Flow Diagram for Alkanolamine Process

Source: Kohl, (1997), pg. 58

(D-V-B) ALKALINE SALT PROCESSES. Alkaline salts such as sodium carbonate, potassium carbonate, phosphate, borate, arsenite, phenolate, and salts of weak organic acids can be used for acid gas removal. Since H_2S is absorbed more rapidly than CO_2 by aqueous alkaline solutions, some partial selectivity can be attained by using short contact times and low temperatures when both gases are present. (Kohl 1997)

(D-V-B-1) CAUSTIC SCRUBBING. Hydroxide solutions are effective at removing CO_2 and H_2S, but are non-regenerable. Commercial caustic plants, such as those used by Dow Chemical Company have developed low-residence-time absorbers for the selective removal of H_2S. Test results from Dow indicate a reduction of 1000 ppm H_2S to less than 100 ppm (in the presence of 3.5% CO_2 at 50,000 ft^3/day), with a gas residence time of 0.02 sec. (Zicari 2003)

(D-V-B-2) SEABOARD PROCESS. ICF Kaiser was the first company to commercially employ a liquid process for H_2S removal using a sodium carbonate absorbing solution with air regeneration. The chemical reaction utilized in process is shown in Equation 14. (Kohl 1997)

$$Na_2CO_3 + H_2S = NaHCO_3 + NaHS \quad (14)$$

Removal efficiencies of 85%-95% were realized, but the occurrence of side reactions and problems with disposal of regeneration air, containing H_2S, has restricted the use of this process. (Kohl 1997) Variations on the Seaboard process including vacuum capture of the stripping gas and the use of alternative alkaline solutions have replaced this simplistic process.

Other processes using alkaline-salt solutions for the removal of H_2S and CO_2 from gas streams are currently available. However, the complexity of these alternative processes makes them unattractive for H_2S removal from small biogas streams.

(D-V-C) LIQUID OXIDATION/REDUCTION SYSTEMS. Many liquid phase oxidation/reduction processes exist which have the capacity to remove acid gases from biogas streams. Systems utilizing iron oxide slurries, zinc oxide slurries, quinones with vanadium salts, and chelated-iron solutions have been employed. Additionally, hydrogen peroxide has been utilized for acid gas removal, but is has not been commercially employed for the treatment of biogas purification.

(D-V-C-1) IRON OXIDE PROCESSES. Iron oxide slurry process historically mark the transistion between dry-box technologies and modern liquid-redox processes. (Zicari 2003) The basic chemistry is similar to dry-box iron oxide processes. H_2S is reacted with an alkaline compound in solution and then iron oxide to iron sulfide as seen in Equation 15 and 16. (Kohl 1997) Equation 17 shows regeneration process achieved by aeration in which the sulfide is converted to elemental sulfur. (Kohl 1997)

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3 \quad (15)$$

$$Fe_2O_3 \cdot 3H_2O + 3NaHS + 3NaHCO_3 = Fe_2S_2 \cdot 3H_2O + 3Na_2CO_3 + 3H_2O \quad (16)$$

$$2Fe_2S_2 \cdot 3H_2O + 3O_2 = 2Fe_2O_3 \cdot 3H_2O + 6S \quad (17)$$

Side reactions can occur; these reactions form thiosulfates and thiocynates, which continually deplete the active iron oxide supply. Commercial processes that were available in the past include the Ferrox (1926), Gludd (1927), Burkheiser (1953), Manchester (1953), and Slurrisweet (1982) processes. (Kohl 1997)

(D-V-C-2) ZINC OXIDE PROCESSES. A zinc-oxide process, known as Chemsweet® (Natco, INC) can be used for acid gas removal. The proprietary powder, consisting of a zinc oxide, zinc acetate, and a dispersant, is mixed with water and used in a simple bubble column. The reaction equations for the chemical process are presented in Equations 18, 19, and 20. (Kohl 1997)

$$ZnAc_2 + H_2S = ZnS + 2HAc \quad (18)$$

$$ZnO + 2HAc = ZnAc_2 + H_2O \quad (19)$$

$$ZnO + H_2S = ZnS + H_2O \quad (20)$$

Low pH is maintained to avoid CO_2 absorption and vessel corrosion while encouraging RSH and COS removal. (Kohl 1997) Pipeline-gas specifications are easily met, but the high cost of non-regenerable reactant usually limits use of this process to removing trace amounts of sulfur. (Zicari 2003)

(D-V-C-3) QUINONES AND VANADIUM PROCESSES. Processes using quinones with vanadium salts, such as the Stretford process, account for a large portion of the liquid-based natural-gas purification market today. (Kohl 1997) Because of the high capital and operating costs and significant thiosulfate byproduct formation, quinone-based H_2S technologies are generally used for smaller gas streams. Figure 6 depicts the reduction-oxidation cycle of quinones. (Kohl 1997)

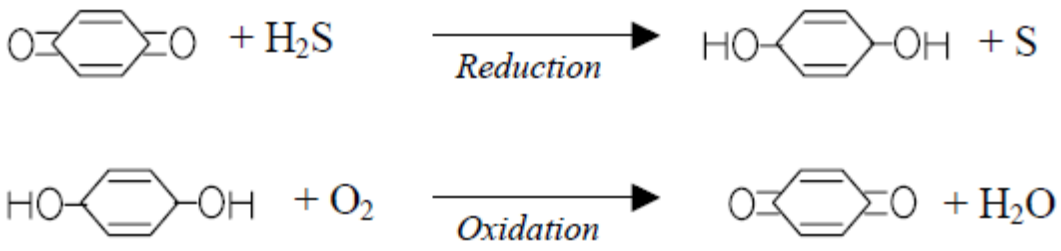

Figure 6 – Quinone Reduction-Oxidation Cycle

(D-V-C-4) CHELATED-IRON SYSTEMS. Chelated-iron solutions utilize iron ions bound to a chelating agent for acid gas removal. LO-CAT® (US Filter/Merichem) and SulFerox® (Shell) are the prominent systems utilizing chelated-iron for H_2S removal. Basic redox reactions for adsorption and regeneration are as shown in Equations 21 and 22. (Kohl 1997)

$$2Fe^{3+} + H_2S = 2Fe^{2+} + S + 2H^+ \quad (21)$$

$$2Fe^{2+} + \frac{1}{2}O_2 + H_2O = 2Fe^{3+} + 2OH^- \quad (22)$$

The LO-CAT® process is potentially attractive for biogas applications because it is 99+% effective, the catalyst solution is nontoxic, and it operates at ambient temperatures. (Zicari 2003) Systems are currently only recommended and economical for facilities that generate 500+ lb S/day. The principal operating costs for system include powering pumps and blowers, and catalyst replacement due to losses via thiosulfate and bicarbonate production. (Kohl 1997) Figure 7 illustrates a typical LO-CAT® process.

The SulFerox® process is targeted for gas streams with 250-45,000 lb S/day and high CO_2/H_2S ratios. CO_2 will not be removed significantly and up to 99% H_2S removal can be achieved. Proper operation of the SulFerox® process requires good solution maintenance procedures including maintaining proper iron and pH levels. (Kohl 1997) The main disadvantage of the SulFerox® to the LO-CAT® is that the SulFerox® process iron concentration is approximately 2% while the LO-CAT® is usually about 0.1-0.05%.

(Merichem 2008) The more dilute catalyst system of the LO-CAT® has system stability benefits, ease of operation and catalyst consumption with approximately one half to one third the chemical cost of a SulFerox® unit. (Merichem 2008)

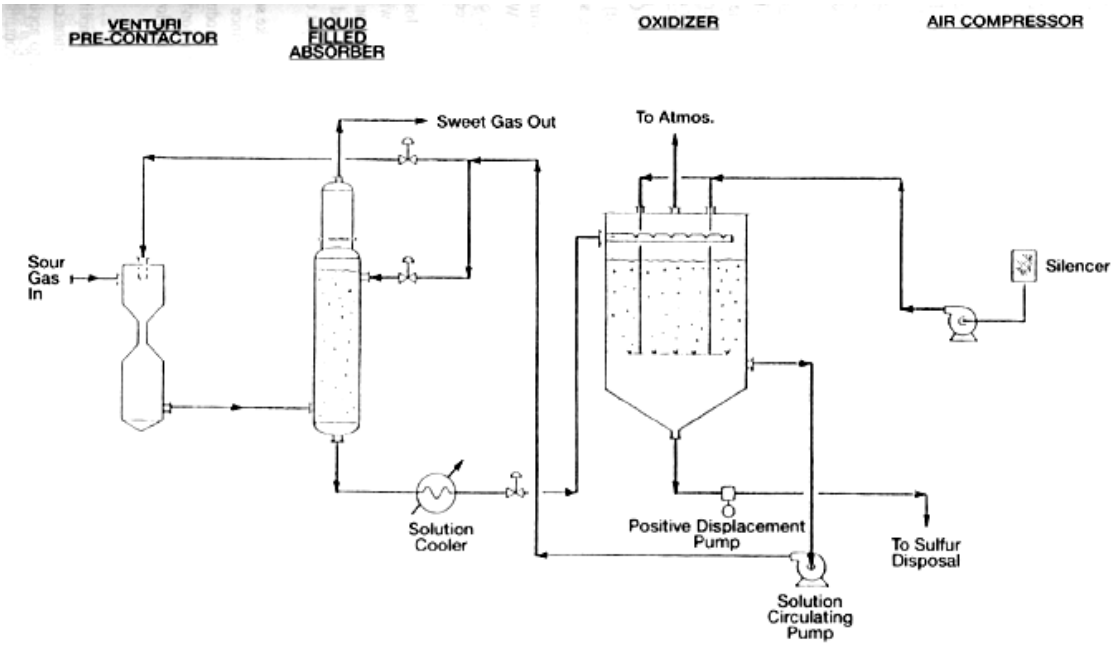

Figure 7 – Flow Diagram for LO-CAT® System

Source: Kohl (1997), pg. 809.

(D-V-D) HYDROGEN PEROXIDE TECHNOLOGIES. Hydrogen peroxide has been shown to be a convenient way of eliminating oxidizable pollutants such as hydrogen sulfide gas from air or other gases. (FMC 2003) The most widely applied oxidant in the scrubbing solutions for the control of odorous compounds has been the various forms of chlorine. However, the use of chlorine has the major drawback of producing chlorinated byproducts such as halomethanes, which are known toxics. (Moussavi 2008) To avoid forming these toxic byproducts, research has been focused on finding an efficient surrogate oxidant; hydrogen peroxide (H_2O_2), which is the strongest oxidant after O_3, has

been considered a suitable replacement for chlorine compounds. (Moussavi 2008) H_2O_2 is a highly selective oxidant that does not produce toxic and corrosive by-products. The Oxidation of hydrogen peroxide is illustrated by Equation 23. (FMC 2002)

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E = 1.77 \tag{23}$$

Depending on the pH of a H_2O_2 solution, H_2S is oxidized to molecular sulfur or sulfate by either Equation 24 or Equation 25.

$$H_2O_2 + H_2S \rightarrow S + 2H_2O \qquad pH < 8.5 \tag{24}$$

$$4H_2O_2 + H_2S \rightarrow H_2SO_4 + 4H_2O \qquad pH > 8.5 \tag{25}$$

Couvert et al studied the feasibility of using hydrogen peroxide for treatment of odorous sulfur compounds (hydrogen sulfide and methylmercaptan) for the replacement of chlorine in chemical scrubbing towers. Using hydrogen peroxide in conjunction with sodium hydroxide (NaOH) in a scrubbing tower gave quite satisfactory results for the removal of hydrogen sulfide, and encouraging ones for methylmercaptan. (Couvert 2006) The observed hydrogen peroxide decomposition was economically acceptable, even if compared with the chlorine process. However, sodium hydroxide consumption was found important because of the carbon dioxide competitive absorption in water. (Couvert 2006)

To better understand the kinetics of the reactions taking place in the scrubbing vessel Couvert et al looked at several key reactions occurring within the system. Based on Equation 25, absorption is limited by pollutant solubility in the liquid phase where

Henry's constant for H_2S is 9.83 $\frac{atm \cdot L}{mol}$ at 292 K. (Couvert 2006) However, acid-base and oxidizing reactions shown in Equations 26 and Equation 27 directly increase mass transfer by promoting the dissociation of the pollutants into HS^-, while Equation 28 shows the oxidation reaction of HS^- in the liquid phase. (Couvert 2006)

$$H_2S_{(G)} \leftrightarrow H_2S_{(aq)} \tag{26}$$

$$H_2S_{(aq)} + OH^- \leftrightarrow HS^- + H_2O \tag{27}$$

$$HS^- + 4H_2O_2 \rightarrow SO_4^{2-} + 4H_2O + H^+ \tag{28}$$

The Hatta number is a dimensionless parameter that compares the rate of absorption of a solute, A, in a reactive system to the rate of absorption of the same solute in the case of physical absorption. The Hatta number calculated for H_2S in chemical systems shown in Equations 26 and 27 is greater than 3. This result implies that mass transfer is enhanced by these reaction in the liquid phase; H_2S mass transfer is also enhanced by increased concentrations of both H_2O_2 and NaOH. (Couvert 2006) The Hatta number calculation for H_2S is shown in Equations 29, 30, and 31. (Couvert 2006)

$$Ha_1 = \frac{\sqrt{\gamma_{H_2S_{(G)}} k D_{P/L} [H_2S_{(G)}]}}{k_L} \tag{29}$$

$$Ha_2 = \frac{\sqrt{\gamma_{OH^-_{(aq)}} k D_{P/L} [OH^-]}}{k_L} \tag{30}$$

$$Ha = \sqrt{Ha_1^2 + Ha_2^2} \quad (31)$$

Where:

Ha_1 = Hatta number for disassociation reaction (Equation 26)

Ha_2 = Hatta number for oxidation reaction (Equation 27)

Ha = Hatta number for H_2S in system

γ = Stoichiometric coefficient of reagent in corresponding reaction

k = Kinetic constant of corresponding reaction, $\frac{L}{mol \cdot sec}$

$D_{P/L}$ = Diffusion coefficient of pollutant in liquid phase, $\frac{m^2}{sec}$

k_L = Mass transfer coefficient in the liquid phase, $\frac{m}{sec}$

[ ] = Concentration of reagent, $\frac{mol}{L}$

This mechanism reduces H_2S accumulation in the liquid phase, and allows for an efficient scrubbing process. Thus, H_2S removal by H_2O_2 alkaline scrubbing becomes conceivable despite the low solubility of the pollutants. (Couvert 2006)

Statistical analysis of the results presented by Moussavi et al reveals that with a confidence limit of 95 %, superficial gas velocity (contact time) and inlet fraction (ppm H_2S) had no significant effect on performance of the scrubber under the operational conditions (pH = 10) investigated. This implies that the overall system will attain high removal efficiencies even if there are large fluctuations in biogas output and/or composition.

One major economical concern about using a H_2O_2/NaOH scrubbing system for biogas purification is the chemical consumption of NaOH. The primary consumption mechanism of NaOH is the absorption of CO_2 from the biogas stream into liquid phase. The CO_2 then reacts with NaOH to form either sodium carbonate ($NaHCO_3$) or sodium bicarbonate (Na_2CO_3) which will consume NaOH at a very high rate. Equations 32 through 36 show CO_2 and NaOH reactions within system. (Couvert 2006)

$$CO_{2_{(G)}} \rightarrow CO_{2_{(aq)}} \quad (32)$$

$$CO_{2_{(aq)}} + OH^- \rightarrow HCO_3^- \quad (33)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad (34)$$

$$CO_3^{2-} + Na^+ + H^+ \rightarrow NaHCO_3 \quad (35)$$

$$2NaHCO_3 \leftrightarrow Na_2CO_3 + H_2O + CO_2 \quad (36)$$

The primary reason for using sodium hydroxide in a liquid scrubbing system designed to remove H_2S is to shift system pH to alkaline conditions allowing for easier oxidation of sulfur compounds. Additionally, the solubility of HS^- ions in liquid phase is increased at higher pH ranges which is important in applications such as wastewater treatment. (CWT 2002) However, with high CO_2 concentrations in biogas, NaOH consumption will be further increased due to the presence of H_2O_2. Couvert, Charron et al reported high consumption rates of NaOH (above theoretically calculated values) at alkaline pH ranges with no sulfur compounds present in the gas stream. This phenomenon is believed to occur due to increased mass transfer of CO_2 with the presence

of H_2O_2 in system. Figure 8 shows the overconsumption rates of NaOH in alkaline pH ranges due to CO_2 absorption. Figure 9 illustrates the higher absorption rates of CO_2 into liquid oxidant systems utilizing H_2O_2 at alkaline pH levels.

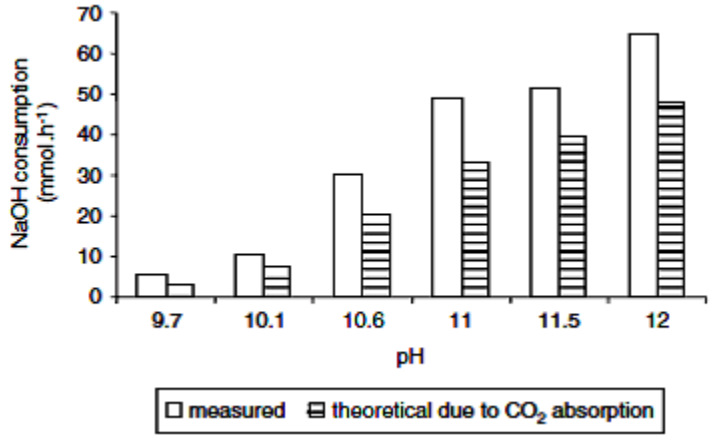

Figure 8 – Comparison Between Measured NaOH Consumption and Theoretical NaOH Consumption due CO_2 Absorption

Source: Couvert, (2006), pg 7245

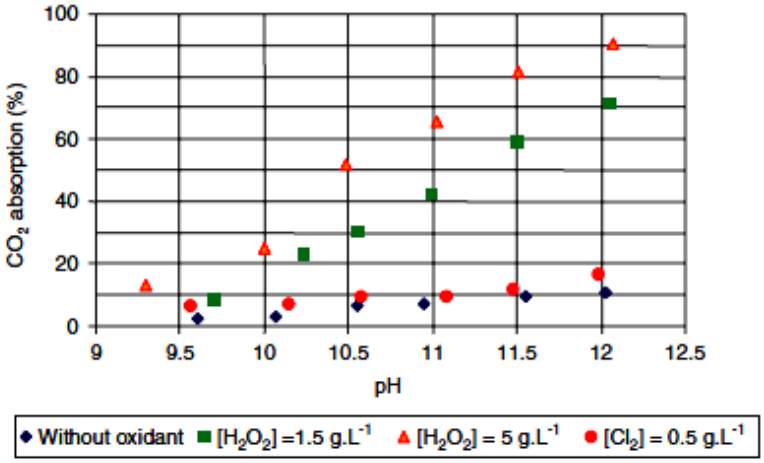

Figure 9 – Influence of pH and Oxidant Type on CO_2 Absorption

Source: Couvert (2006), pg 7245

Additional research has been conducted for the use of hydrogen peroxide to effectively remove other gas pollutants such as sulfur dioxide (SO_2), nitrogen oxides

(NO_x), and phenols. Catalytic abatement of water pollutants utilizing hydrogen peroxide has also been studied. While these systems do not directly address the removal of H_2S from biogas streams, readers are directed to the following sources for more information on the design and uses of hydrogen peroxide in pollutant remediation technologies: Deo (1988), Gohara and Johnson (1997), Thomas and Vanderschuren (1996), Thomas and Vanderschuren (1998), Al Hyek and Dore (1990), Borup and Ashcroft (1992), Basu (2007), de Paiva and Kachan (1998), Zamansky, Ho, et al (1996), Martin and Damschen (1981), and Matatov-Meytal and Sheintuch (1998).

While there is a wealth of operational and research knowledge on utilizing hydrogen peroxide in alkaline scrubbing systems, flue gas desulferization, and waste water treatment, there is limited information about acidic scrubbing systems utilizing hydrogen peroxide to remove H_2S from biogas. No studies, to this author's knowledge, exist where an acidic hydrogen peroxide scrubbing system has been tested for its feasibility to remove H_2S from laboratory gas similar in composition to biogas. The following research directly addresses this opportunity.

INSTRUMENTATION AND EQUIPMENT

An experimental approach was used to investigate the feasibility of using an acidic H_2O_2 scrubber for the removal of H_2S from synthetic biogas. Two test reactors were constructed, each setup with multiple configurations of packing volume, H_2O_2 concentration, and liquid volume. The experimental setup was located in the Food Processing Laboratory at the University of Louisville.

A. REACTION VESSEL COMPONENTS

Two separate reaction vessels were used for experiments; each reactor utilized various reactor configurations. One reaction vessel was a 105 gallon plastic agricultural tank and is shown in Figure 10. Another vessel used was a 60 gallon conical bottom tank shown in Figure 11. Both vessels utilized random packing at varying levels through the experimental trials. Koch-Glitsch IMTP® (25 mm nominal size) packing was used for multiple experimental trials (trials 6-9 and 12-20); Koch-Glitsch plastic INTALOX® SNOWFLAKE® mixed with FLEXIRING® (1 inch nominal size) packing was also utilized in the 105 gallon reaction vessel for trials 21 and 22. Each vessel was fitted with a gas distributor to bubble sour gas stream through the oxidant liquid. In the 60 gallon tank, two different types of gas distributors were used. The first gas distributor used was

a hand-made pvc pipe gas distributor utilizing tiny drilled holes to allow gas to diffuse, as can be seen in Figure 12. The second gas distribution system, used in both the 60 gallon and 105 gallon vessel, was a set of two ceramic dome diffusers, model FBS-775, made by Diffused Gas Technologies, INC. A picture of a FBS-775 ceramic dome diffuser can be seen in Figure 13. When configuring inlet and outlet gas streams for both reaction vessels, ½ inch PVC pipe was used to feed the gas stream into the distributors. For exit gas, ½ inch PVC compression fittings were used to attach PVC piping to a drilled hole placed approximately two inches from the lid in the top of the reaction vessel. In the ½ inch PVC exit line, a tap was inserted so exit gas composition could be monitored.

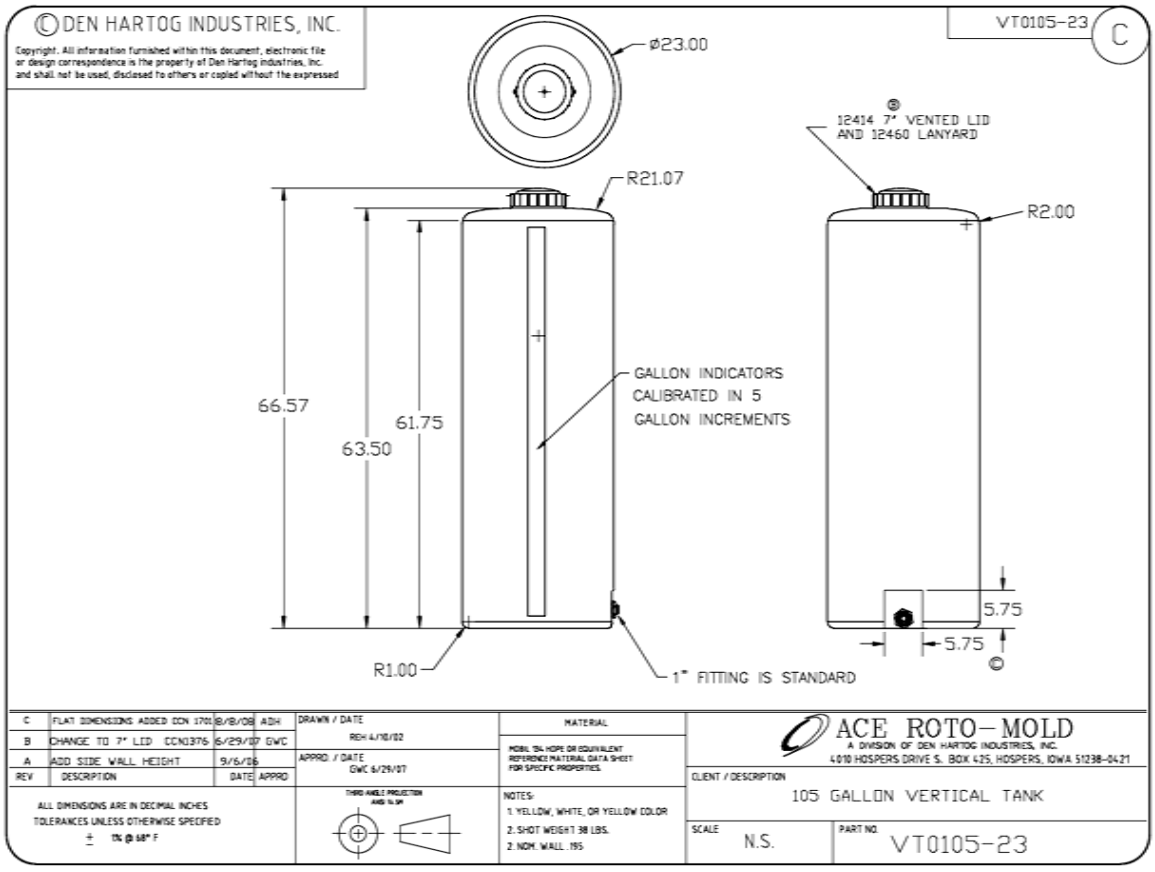

Figure 10 – 105 Gallon Reaction Vessel

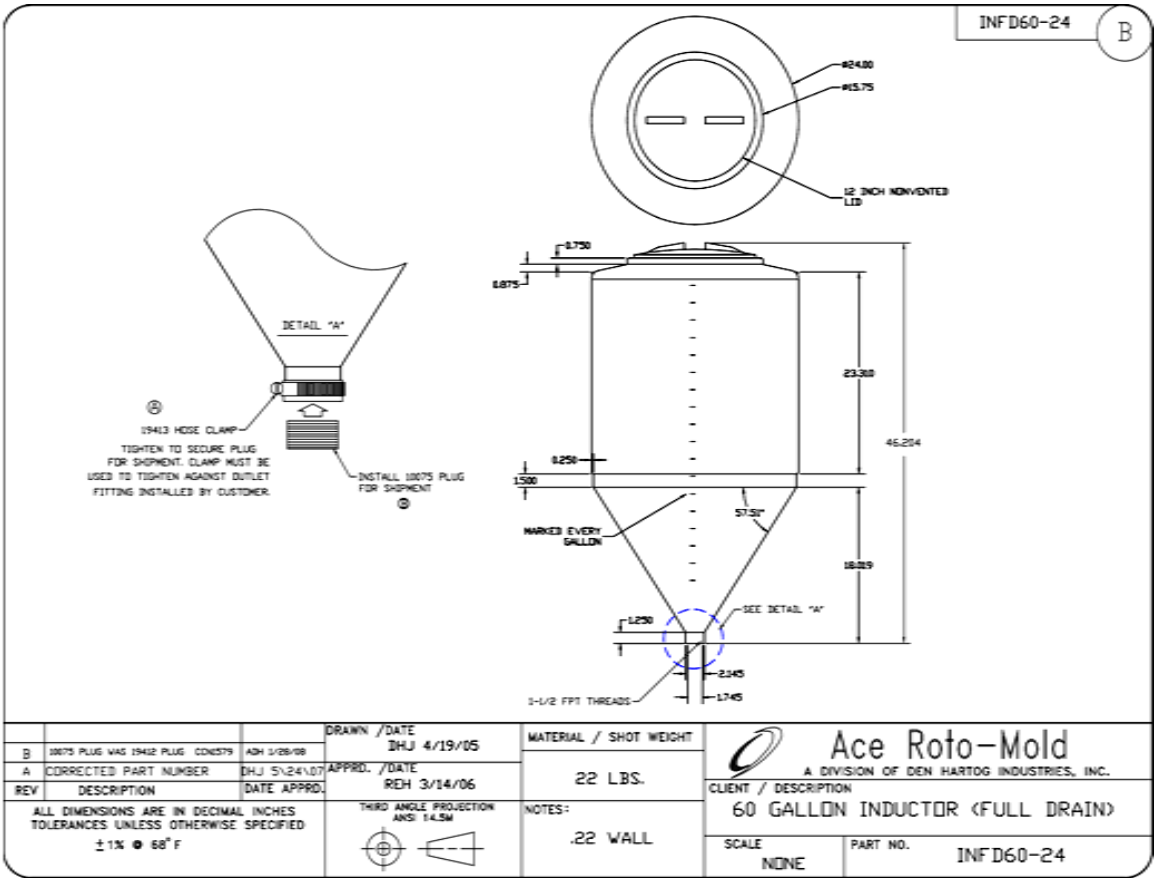

Figure 11 – 60 Gallon Conical Bottom Reaction Vessel

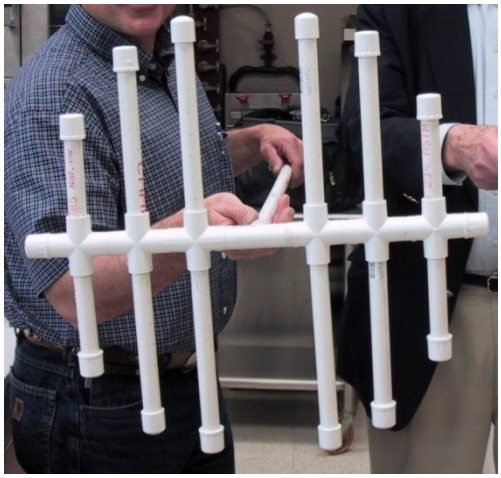

Figure 12 – PVC Gas Distributor

Figure 13 – FBS-775 Ceramic Dome Diffuser

B. EXPERIMENTAL SETUP

In order to test the viability of a low pH hydrogen peroxide scrubber for biogas purification, a gas cylinder full of synthetic biogas was used to simulate a typical biogas stream from an anaerobic digester. The synthetic biogas was composed of a lab certified mixed gas produced by Matheson Tri-Gas gas containing 60% methane, 39.75% CO_2, and 0.25% (2500 ppm) H_2S gas. This gas was metered to the reactor using a regulator followed in series by a variable area flow meter as shown in Figure 14. The gas exiting the variable area flow meter flowed through 3/8 inch flexible pvc tubing to a 1/2 PVC pipe which fed gas to one of the two gas distributing systems previously mentioned inside the reaction vessels. The entire experimental setup utilizing the 60 gallon conical bottom tank and PVC gas distributor is illustrated in Figure 15. An overall experimental schematic utilizing the ceramic dome gas distributors in the 105 gallon reaction vessel is shown in Figure 16.

Figure 14 – Gas Regulator and Variable Area Flow Meter

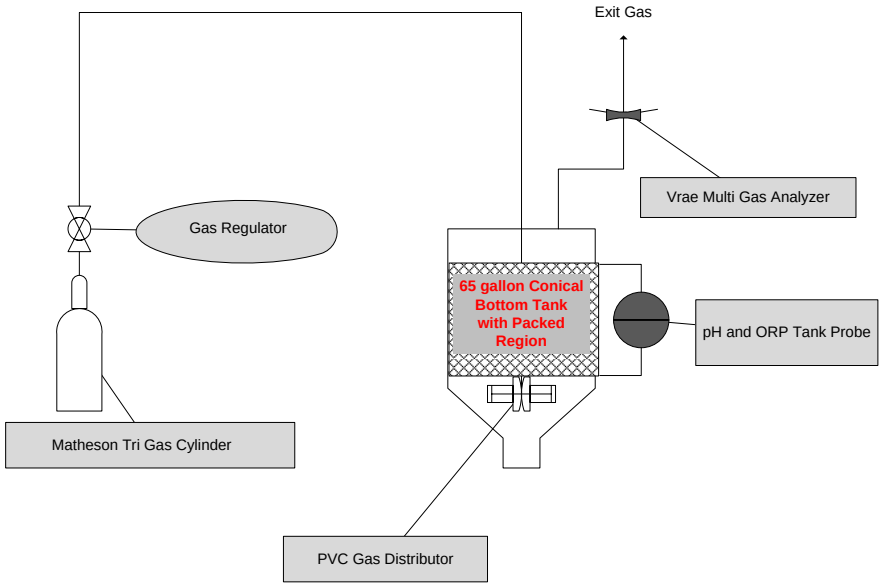

Figure 15 – Experimental Setup 1: 60 Gallon Vessel with PVC Gas Distributor

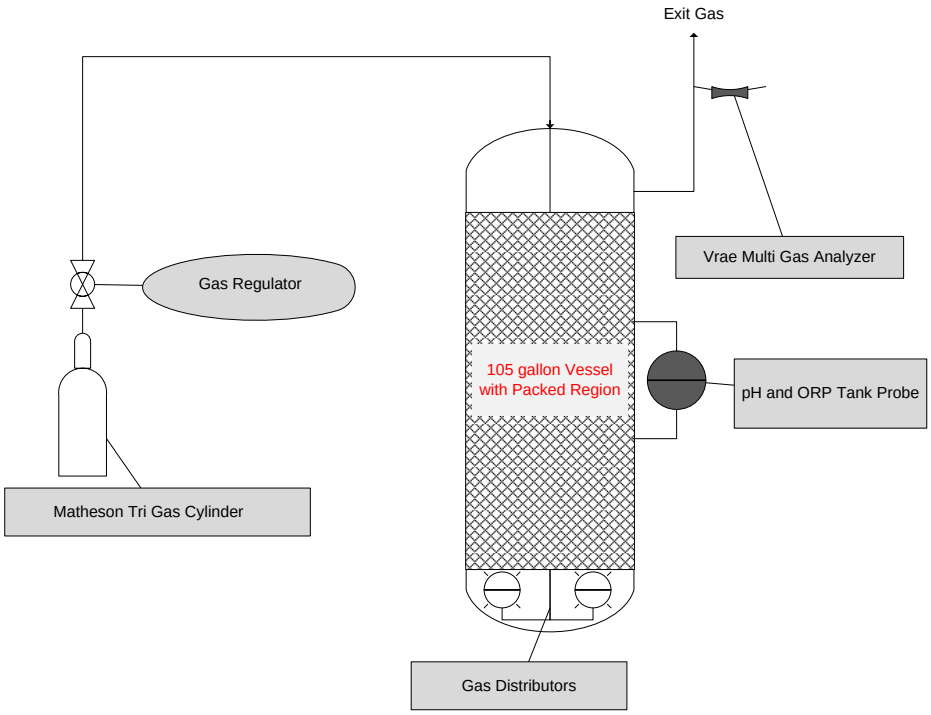

Figure 16 - Experimental Setup 2: 105 Gallon Vessel with FBS-775 Gas Distributor

Gas flow rates were controlled with a FM-1100 variable area flow meter (Matheson Company). Rates are measured by visually correlating the center of the float with a graduated scale, calibrated for standard cubic feet per minute (scfm) of air at standard temperature and pressure. A correction equation supplied by Matheson determined that the air equivalent flow rate of biogas through the FM-1100 shown in Equation 35. (Matheson 2009) The air equivalent flow rate was calculated using the mole fraction of each gas constituent where X was 0.60, 0.3975, and 0.0025 for CH_4, CO_2, and H_2S respectively; and the gas flow rate factor F was 0.75, 1.23, and 1.08 for CH_4, CO_2, and H_2S respectively. (flow rate factor values supplied in technical literature by Matheson) The air equivalent factor was then determined by the summation of the products of the mole fractions (X_i) and flow rate factor (F_i). The air equivalent flow rate for biogas was calculated at 0.942 where air at STP is 1.00. Given the low gas flow rates

tested, the direct reading FM-1100 flow meter was used with no correction factor needed as instructed by Matheson Tri-gas due to high similarity of the gas mixture's air equivalent factor.

$$Q_{air} = Q_{mix} \cdot \sum F_i \cdot \chi_i \quad (35)$$

Where:

Q_{air} = Air equivalent volumetric flow rate

Q_{mix} = Desired gas mixture volumertic flow rate

F_i = Gas flow rate factor i^{th} component

X_i = Mole Fraction of i^{th} component

C. GAS SAMPLING AND MEASUREMENT

To confirm that H_2S gas was being oxidized inside the reaction vessel, a PGM 7800 - VRAE Multi Gas Monitor, shown in figure 17, measured H_2S gas concentrations in the exit stream. Taps were placed inline on the exit 1/2 inch PVC pipe which allowed the VRAE meter to measure H_2S concentrations directly through 1/4 inch tygon tubing attached to the tap. The meter contains an integrated diaphragm sampling pump providing 400 cm^3/minute flow which can pull in air samples from 200 feet away horizontally or 90 feet vertically. Additionally, the PGM 7800 meter contains data logging capabilities allowing for easy compilation of readings made during experimental

trials which can be collected at intervals from one second to 60 minutes. The PGM 7800 meter uses a thermal conductivity sensor in conjunction with an electrochemical sensor to detect H_2S concentrations at levels ranging from 0 to 428 (±2) ppm of H_2S. (All readings above 428 ppm will register at max detectable level of 428 ppm)

Figure 17 – PGM 7800 VRAE Multi Gas Monitor

D. TEMPERATURE, pH, HUMIDITY, AND ORP MEASUREMENT

Temperatures measurements in the reaction vessel liquid solution and ORP measurements were made with an Oakton® pH 300/310 meter. Calibration of the ORP sensor utilized a YSI 3682 Zobell Solution to establish a reference ORP reading ensuring the sensor was functioning properly before any experimental readings were made.

Measurements of oxidant solution pH were made using an Oakton® Acorn™ pH 6 meter. The meter was calibrated on a daily basis with the recommended pH buffer solutions of 4,7, and 10 to ensure accurate sample collection.

Relative Humidity of the exit gas stream was measured with a DeltaTRAK Thermo-Hygrometer. Measurements in all trials showed the gas was 99.99% saturated with water vapor which was expected given the reaction vessel setup.

E. SULFUR DEPOSITION

Based on reaction chemistry, elemental sulfur deposits from the reaction of H_2S gas with H_2O_2 were expected on surfaces inside reaction vessel. Visual examination including low magnification microscopy techniques were used to observe the elemental form of sulfur formed (crystalline or amorphous) as a product of reactions within the vessel.

E. OPERATIONAL NOTES

The first experimental setup consisting of the 60 gallon conical bottom tank and PVC gas distributor was used for 9 experimental trials with various configurations. A summary of the varied parameters is listed in Table X. The second experimental setup utilizing the ceramic dome gas diffusers and the 105 gallon tank was used for 13 trials and the summary of operational parameters is shown in Table XI. For all experiments, 35% food grade hydrogen peroxide from FMC Corporation was diluted to achieve reaction vessel concentrations listed.

TABLE X

Summary of Trial Conditions Using Experimental Setup 1

Trial	*Liquid Volume (gal)*	*Packing , Volume*	*H_2O_2 Concentration*	*Biogas Flow rate* $\frac{ft^3}{min}$
1	50	None	0.01%	2.00
2	50	None	0.10%	2.00
3	50	None	1.00%	2.25
4	50	None	1.00%	1.00
5	50	None	1.00%	0.50
6	50	Metal, 4 ft^3	1.00%	1.00
7	50	Metal, 4 ft^3	1.00%	0.50
8	50	Metal, 6 ft^3	1.00%	1.00
9	50	Metal, 6 ft^3	1.00%	1.00

TABLE XI

Summary of Trial Conditions Using Experimental Setup 2

Trial	*Liquid Volume (gal)*	*Packing , Volume*	*H_2O_2 Concentration*	*Biogas Flow rate* $\frac{ft^3}{min}$
10	50	None	1.00%	2.00
11	100	None	0.10%	2.00
12	100	Metal, 6 ft^3	1.00%	2.00
13	100	Metal, 6 ft^3	0.50%	2.00
14	100	Metal, 6 ft^3	0.25%	2.00
15	100	Metal, 6 ft^3	0.125%	2.00
16	50	Metal, 6 ft^3	0.10%	2.00
17	100	Metal, 6 ft^3	0.10%	2.00
18	100	Metal, 11 ft^3	0.125%	2.00
19	100	Metal, 11 ft^3	0.25%	2.00
20	100	Metal, 11 ft^3	1.00%	2.00
21	100	Plastic, 6 ft^3	0.50%	2.00
22	100	Plastic, 6 ft^3	0.50%	2.00

RESULTS AND DICUSSION OF RESULTS

In total twenty-four separate experiments were conducted in bench scale experiments, 1st scrubber trials, and 2nd scrubber trials. In order to maintain flow and readability of this section, data tables and plots from many scrubber experiments are placed in Appendix A and Appendix B of this thesis because a number of trials were terminated due to poor results or equipment deficiencies, and several others are not needed for evaluation in this section. Section A presents the operational summary and includes analysis of results for the twenty-two scrubber trials conducted using the different reaction vessel configurations. In section B, results of the bench scale experiments are presented, and finally in section C the overall results of all experiments are evaluated.

A. OPERATIONAL SUMMARY

Using the initial scrubber setup (60 gallon tank, PVC gas distributor) 9 successful trials were conducted. After approximately one minute into trials 1, 2, and 3 the H_2S detector peaked at 425 ppm (highest operational reading for gas analyzer). These trials were conducted as breakthrough experiments to gather preliminary data about the process. With data collected, lower flow rates of biogas were utilized for trials 4 and 5 to

see if increased residence time due to decreased superficial velocity of inlet gas would increase breakthrough time. Breakthrough time was increased from approximately 1 minute to 2.5 minutes with a lower inlet superficial velocity.

Trials 6 and 7 were the first trials to utilize metal packing placed above the gas distributor in the oxidizing solution. Four cubic feet of packing was used in each trial with biogas flow rates of 1.0 ft^3/min for trial 6 and 0.5 ft^3/min for trial 7. The addition of packing did not achieve higher H_2S removal efficiencies. The packing was intended to promote turbidity in the system, increase residence time, and breakup larger gas bubbles. While the changes in reactor configuration were intended to increase H_2S removal efficiencies, this was not observed.

In trial 8 and trial 9, the tank was agitated using compressed air bubbled through the gas distributor prior to introduction of biogas into the reaction vessel, to more thoroughly mix the oxidizing solution. Mixing via air agitation showed an increased oxidation reduction potential (ORP) reading of the solution. Additionally, six cubic feet of metal packing was used in the reaction vessel. With the addition of extra metal packing and mixing of oxidant solution, breakthrough did not occur until 7.5 minutes at an inlet biogas rate of 1 ft^3/min. In Figure 18, the results from trial 8 can be seen. The plot of removal efficiency for trial 8 can be seen in Figure 19.

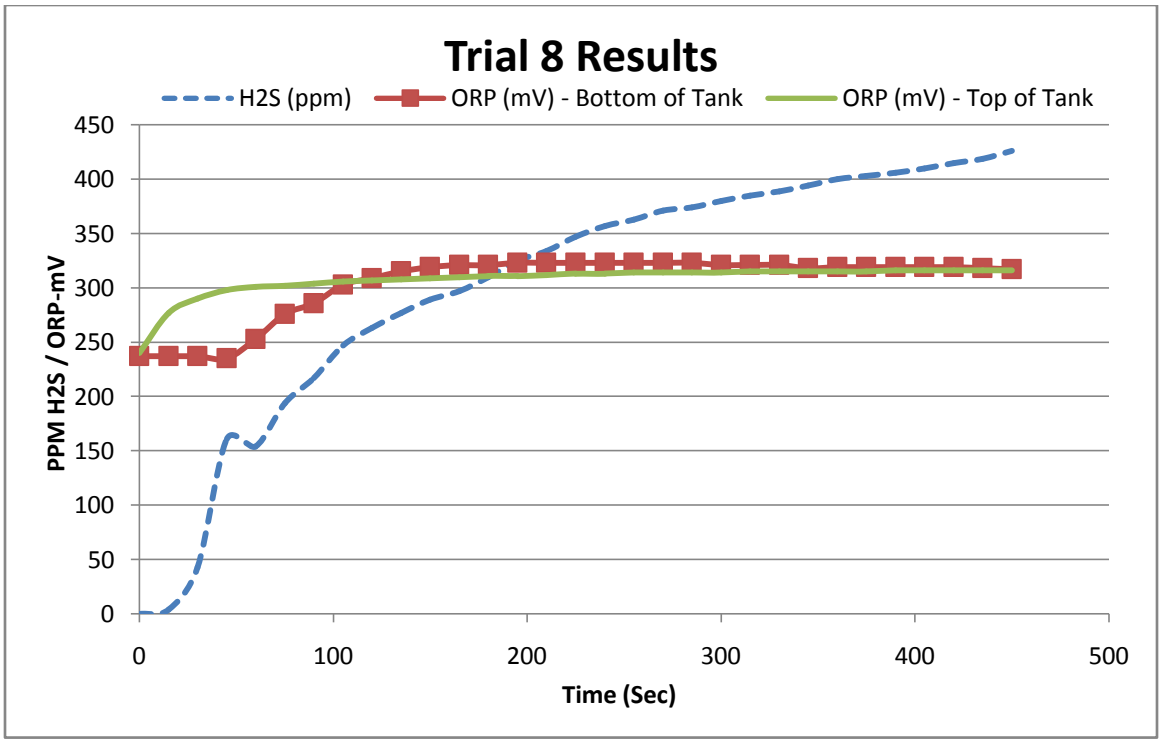

Figure 18 – Trial 8 H_2S Concentration and ORP Plot

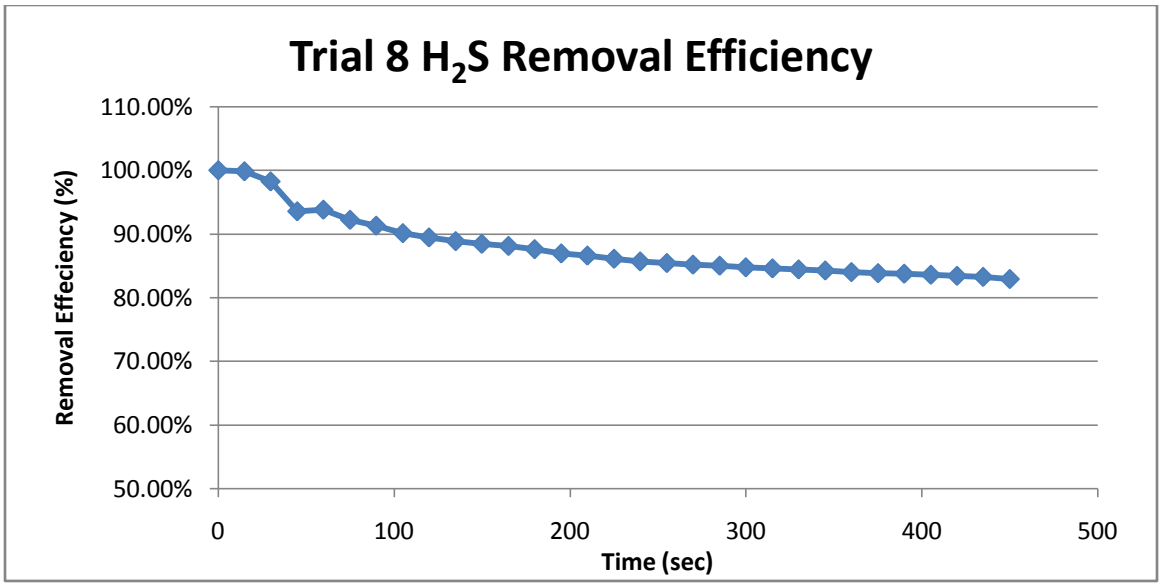

Figure 19 – Trial 8 H_2S Removal Efficiency

After trial 9, two additional trials were conducted utilizing a two-tank counter-current scrubbing unit. In theory, the addition of another vessel would increase reaction area and residency time; however, it was impossible to form a seal between the two tanks, thus it was not possible to obtain desired operational status. Because of this failure, the results from these two trials are omitted in this summary.

With slightly promising results from the initial experimental trials, it was decided to conduct additional pilot scale trials with an improved scrubbing vessel. To improve efficiency, a tank with increased height and volume was used to help increase volume of oxidant solution and increase residency time for inlet biogas. Additionally, two ceramic dome gas diffusers were used to achieve smaller more uniform bubbles, further increasing reaction efficiency and mixing. The addition of new gas distributors allowed for greater inlet synthetic biogas flow rates as the new distributor generated a lower pressure drop and promoted mixing of solution inside the reaction vessel. Finally, additional packing was added to determine if higher oxidation efficiency could be achieved.

Using the 2nd scrubber setup (105 gallon tank, 2 ceramic dome gas distributors) a series of 11 trials was conducted. Two additional trials utilizing plastic packing and the aforementioned experimental setup were conducted at a later date. Additional data tables and plots for each individual trial can be found in Appendix B of this report. The focus of the following analysis is trials 12, 13, and 14.

Trial 10 utilized approximately 50 gallons of 1.0% H_2O_2 solution and Trial 11 utilized 100 gallons of 1.0% H_2O_2 solution, each trial contained no packing inside the

reaction vessel, and both trials had an inlet biogas flow rate of 2.0 ft^3/minute. The results of trials 10 and 11 were similar to the poor results of trials utilizing the 1st scrubbing system. H_2S removal efficiency was low and breakthrough occurred quickly. These results were most likely attributed to the observed coalescing/channeling of biogas bubbles inside the reaction vessel. Because of this observed phenomenon, packing was implemented in subsequent trials.

The trial 12 experimental conditions utilized approximately 100 gallons of 1.0% H_2O_2 solution with six cubic feet of packing above the distributor, and an inlet biogas flow rate of 2.0 ft^3/minute. This trial showed the most promising results of all tests conducted in the 2nd scrubbing vessel. After 17 minutes, the H_2S sensor was only detecting 32 ppm while the ORP reading remained high (353 mV average) and relatively constant throughout the trial. Packing substantially improved efficiency in the 105 gallon vessel. Figure 20 shows the H_2S Concentration and ORP Plot for trial 12 while Figure 21 shows the H_2S removal efficiency is shown. The result of this trial indicates that sustained operation has feasibility and additional scale-up testing should be conducted. Additionally, the ORP readings indicate that the system has a high sustained reaction potential in the oxidizing solution.

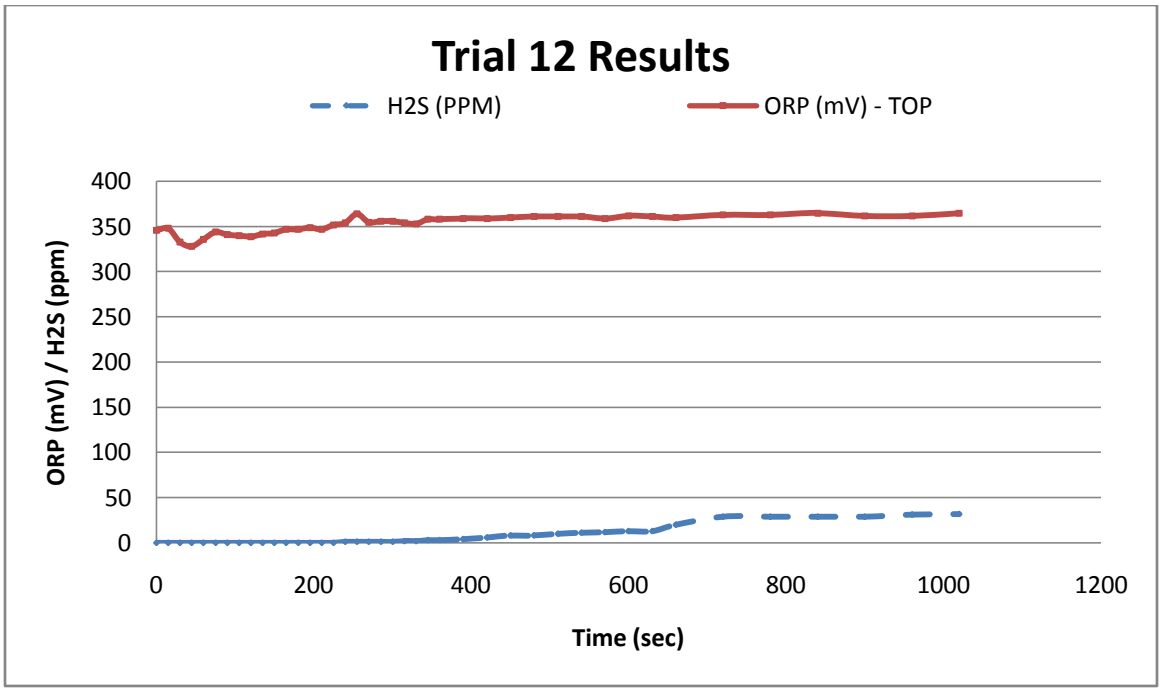

Figure 20 – Trial 12 H_2S Concentration and ORP Plot

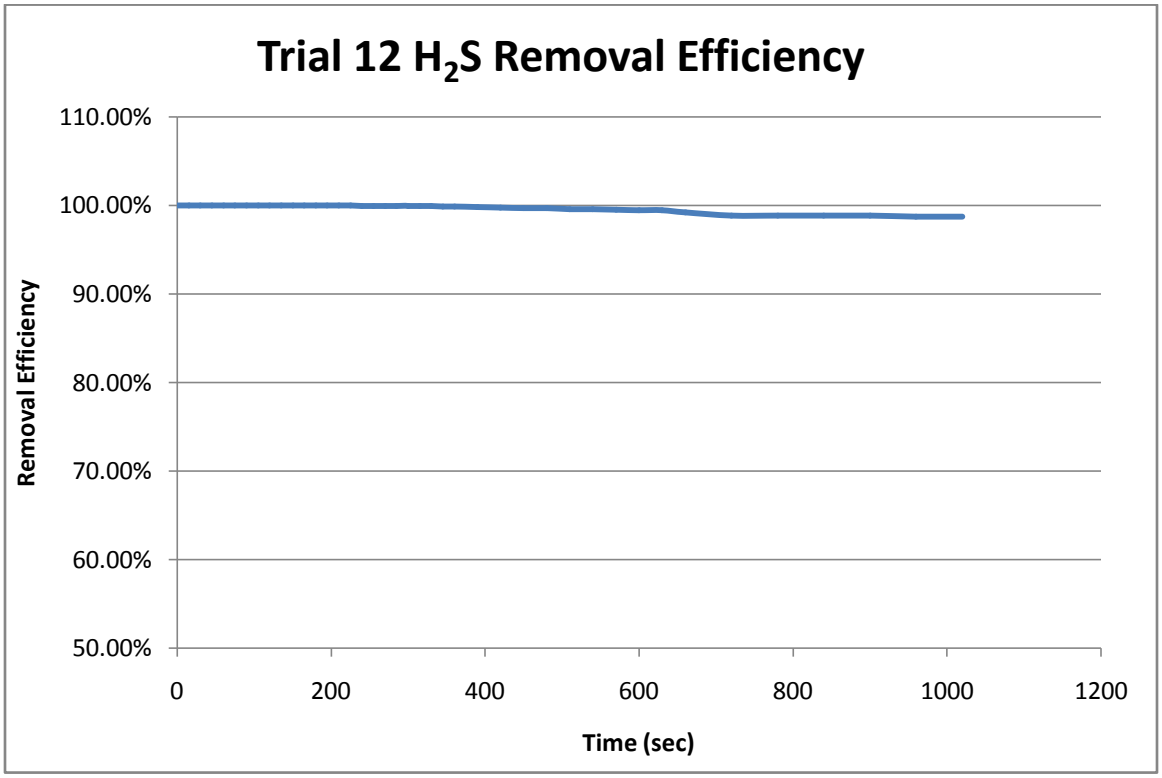

Figure 21 – Trial 12 H_2S Removal Efficiency

Experimental conditions for trial 13 were similar to those for trial 12, but the reactor utilized approximately 100 gallons of 0.50% H_2O_2 solution and six cubic feet of packing above the distributor, and an inlet synthetic biogas flow rate of 2.0 ft^3 per minute. After 17 minutes, the H_2S sensor detected 32 ppm while the ORP reading remained high with almost identical numbers as observed in trial 12. This result indicates that the oxidation reduction potential is not highly dependent on hydrogen peroxide concentration in solution. Figure 22 shows the H_2S Concentration and ORP Plot for trial 13 and Figure 23 shows the H_2S removal efficiency.

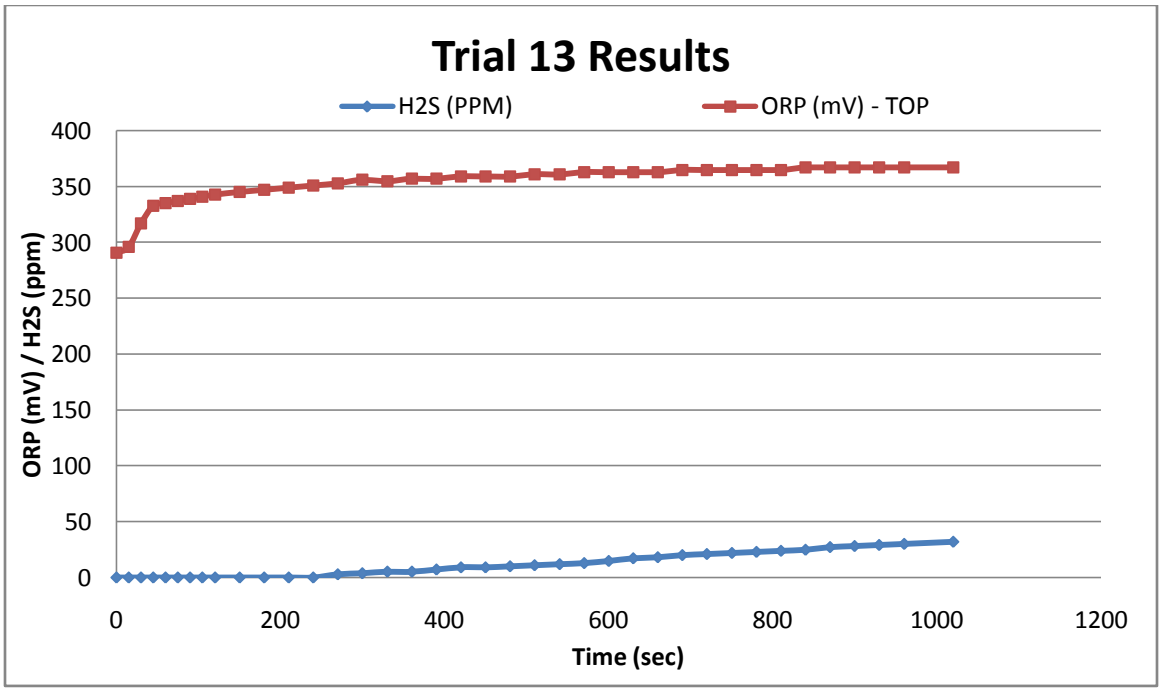

Figure 22 – Trial 13 H_2S Concentration and ORP Plot

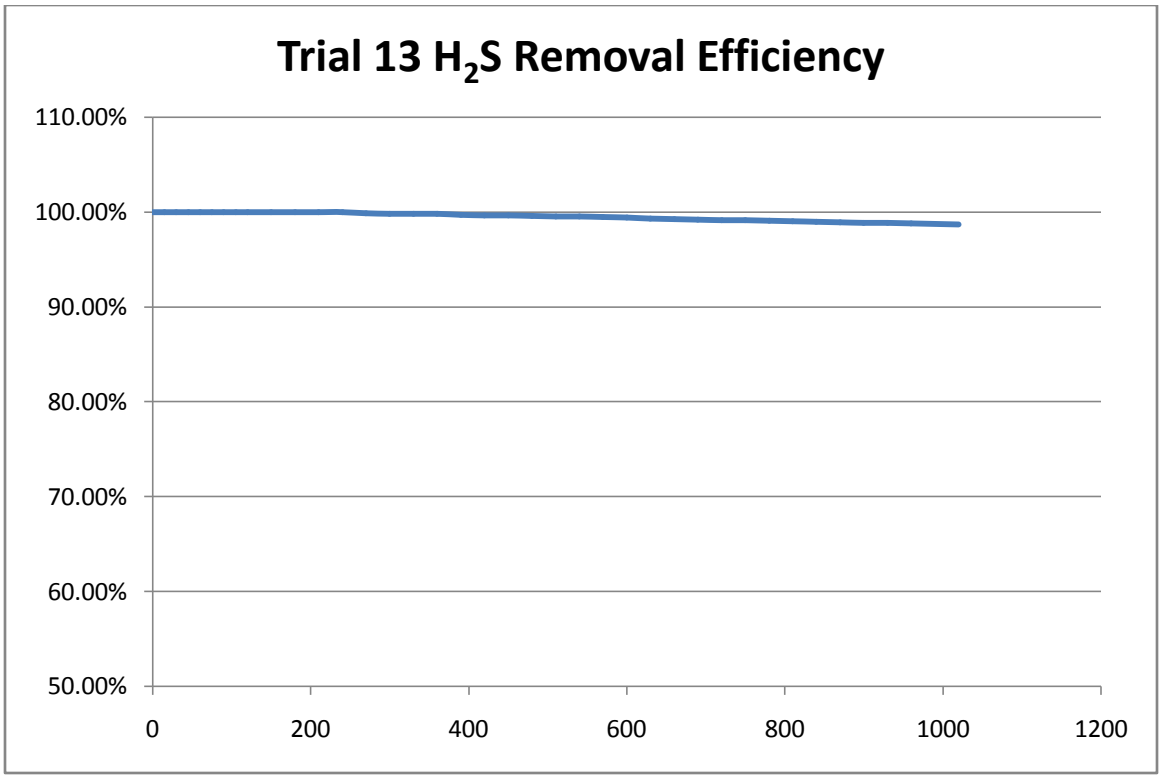

Figure 23– Trial 13 H_2S Removal Efficiency

Trial 14 utilized approximately 100 gallons of 0.25% H_2O_2 solution, 6 ft^3 of metal packing above distributor, and an inlet biogas flow rate of 2.0 ft^3 per minute. Similar results from the previous two trials were obtained as the H_2S reading was only 8 ppm after 8 minutes. Because the results were very similar to both previous trials the trial was stopped after 8 minutes in the interest of saving biogas for future trials. The results of trial 14 further confirm that oxidation reduction potential is not highly dependent on hydrogen peroxide concentration in solution.

Experimental conditions utilized for trial 15 included 100 gallons of 0.12 % H_2O_2 solution, six cubic feet of metal packing above distributor, and an inlet synthetic biogas flow rate of 2.0 ft^3/minute. When the concentration of H_2O_2 was reduced to this low level, oxidation efficiency was lowered; however, the H_2S removal rate was acceptable.

The trial concluded after 9 minutes with a H_2S concentration at an acceptable level of 110 ppm. Lastly, ORP readings were relatively high, similar to the readings of the previous three trials.

Trial 16 utilized 50 gallons of oxidant solution with a 0.10% concentration of H_2O_2. The setup still utilized six cubic feet of packing above distributor along with an inlet synthetic biogas flow rate of 2.0 ft^3/minute. The experiment setup for trial 17 utilized 100 gallons of 0.10 % H_2O_2, six cubic feet of metal packing above the distributor, and an inlet synthetic biogas flow rate of 2.0 ft^3 per minute. Both trials had poor results due to the very low concentrations of H_2O_2 and both trials incurred H_2S breakthrough around 8 minutes after start of trial.

The experiment setup utilized for trial 18 included 100 gallons of 0.125% H_2O_2, 11 ft^3 of metal packing, and an inlet synthetic biogas flow rate of 2.0 ft^3 per minute. The additional packing did not show an improvement in efficiency as expected. The additional packing appeared to hinder the mixing/turbulence of the system inside the reaction vessel that was observed when the packing height/liquid height was lower. Additionally, the ORP readings were relatively low (220 avg) compared to the trials with the most successful results (353 avg). Trial 19 utilized 100 gallons of 0.25% H_2O_2, 11 ft^3 of metal packing, and an inlet synthetic biogas flow rate of 2.0 ft^3 per minute. The additional H_2O_2 in this experiment did not significantly increase oxidation of H_2S as levels reached 400 ppm in only 6 minutes. Again, the additional packing appeared to hinder the mixing/turbulence of liquid inside the reaction vessel that was observed when the packing height/liquid height was lower. Lastly, the ORP readings were relatively low compared to trials with most successful results.

Trial 20 utilized 100 gallons of 0.25% H_2O_2 heated to 110 °F, 11 ft^3 of metal packing, and an inlet synthetic biogas flow rate of 2.0 ft^3 per minute. Heating of the solution was done to simulate hot summer conditions of a system located on a farm. H_2S removal efficiencies were lower than previous trials, but still acceptable with H_2S readings below 250 ppm after 17 minutes. This difference in removal efficiencies observed in trial 20 may be attributed to a two-way interaction of low pH and high solution temperature which was not tested at the bench scale. Further investigation is needed to better understand this phenomenon was the only pilot scale trial conducted with heated solution. It is important to note that one of the primary factors contributing to H_2O_2 decomposition is increasing temperature (2.2 factor increase for each 10°C). (FMC 2002) This phenomenon might lead to overconsumption of H_2O_2 in a commercial unit.

After trial 20, two additional trials were conducted with a system of baffles in the tank to help promote mixing of the oxidizing solution and further increase residency time of the inlet gas. Unfortunately, the baffles used did not seal properly along the inside wall of the vessel, allowing gas channeling. Results of these trials were worse than previous trials conducted in the 105 gallon vessel and thus were omitted from this analysis. However, this is an area of interest to pursue for future testing as baffling could promote better oxidation efficiency through increased mixing without the need of mechanical agitation.

The final two pilot scale experiments (trials 23 and 24) were conducted using plastic packing inside the reaction vessel. The conditions for these trials included 100 gallons of 0.25% H_2O_2 solution (trial 23) and 0.50% H_2O_2 solution (trial 24) in the 105

gallon reaction vessel with the ceramic dome diffusers. Both trials utilized six cubic feet of plastic packing above gas distributor and an inlet biogas flow rate of 2 ft^3/min. Results of both trials were similar to trials 12 and 13 and can be seen in Appendix B.

From all the collected data and observations made during the pilot scale trials, it was shown that using a low pH H_2O_2 scrubbing system shows potential for removing H_2S from biogas streams. A highly turbulent system showed higher and more consistent removal efficiencies of H_2S. The addition of packing is desirable to increase surface area of reaction by breaking-up bubbles from the diffusers and increasing the residence time of inlet biogas. The optimal level of packing is yet to be determined as trials were conducted using two different vessels (60 gallon and 105 gallon), three levels of packing volume (4 ft^3, 6 ft^3, and 11 ft^3), various H_2O_2 concentrations (0.10% to 1.00%), and different time scales. Given the large extent of change in experiment variables, statistical analysis of trials to determine the most significant factors for achieving high removal efficiencies is not possible. Given these factors, bench scale experiments were conducted to elucidate system dynamics.

B. BENCH SCALE EXPERIMENTS

Bench scale experiments were conducted to elucidate the effects on oxidation reduction potential (ORP) of oxidizing solution when varying pH and H_2O_2 concentration. It was found that ORP increases as pH decreases. This phenomenon helps to explain the general trend observed during scrubber trials, showing an initial increase in ORP reading when biogas was introduced into system, followed by steady state values as

each trial continued. This phenomenon is attributed to acidification of the oxidizing solution by absorption of carbon dioxide from inlet biogas. Additionally, it was shown that as temperature increased, ORP decreased, attributed to decomposition of H_2O_2 at higher temperatures. Figure 24 shows relationship of ORP and temperature in varying concentrations of H_2O_2 solutions, while figure 25 shows the relationship of ORP and pH at various H_2O_2 solution concentrations. The results of these bench scale experiments indicate that a low pH (3.0-4.0) is the most important factor for maintaining a high ORP in solution. Interesting to note is that the H_2O_2 concentration has little effect on the ORP of solution indicating that high concentrations will not be needed to effectively remove H_2S assuming there are sufficient total moles of H_2O_2 in solution to react with moles of H_2S present in inlet biogas.

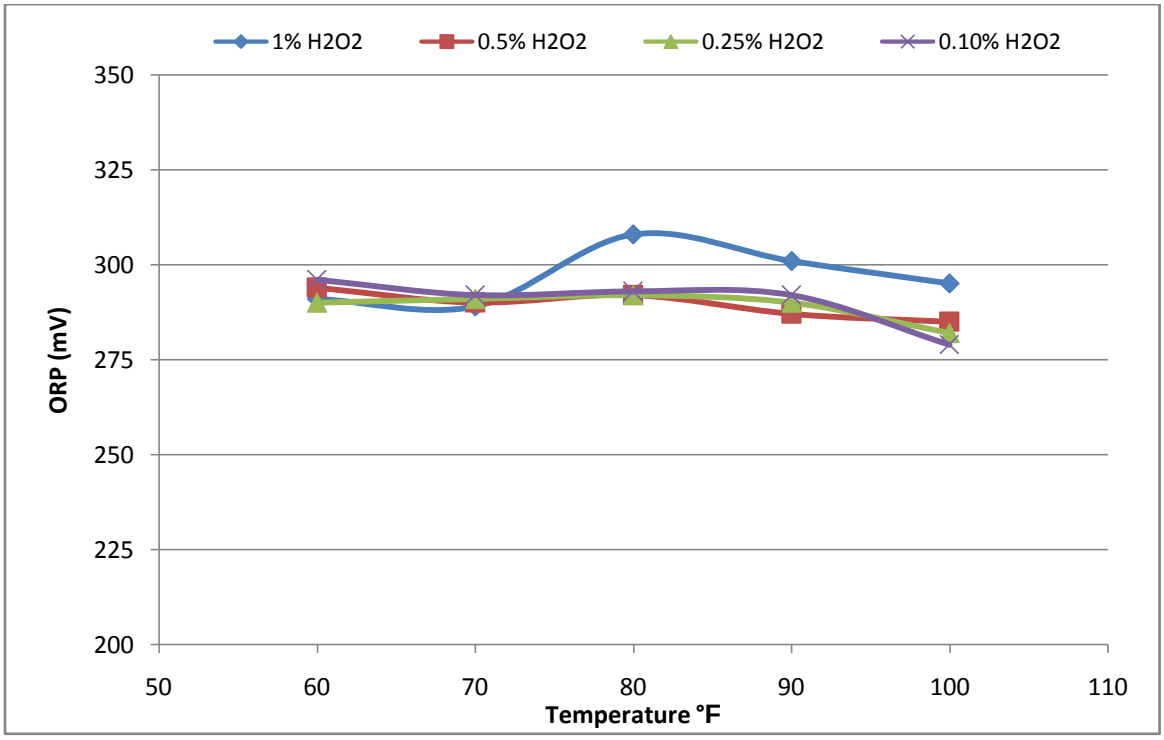

Figure 24 – Oxidation Reduction Potential of Oxidant Solution at Varying Temperatures

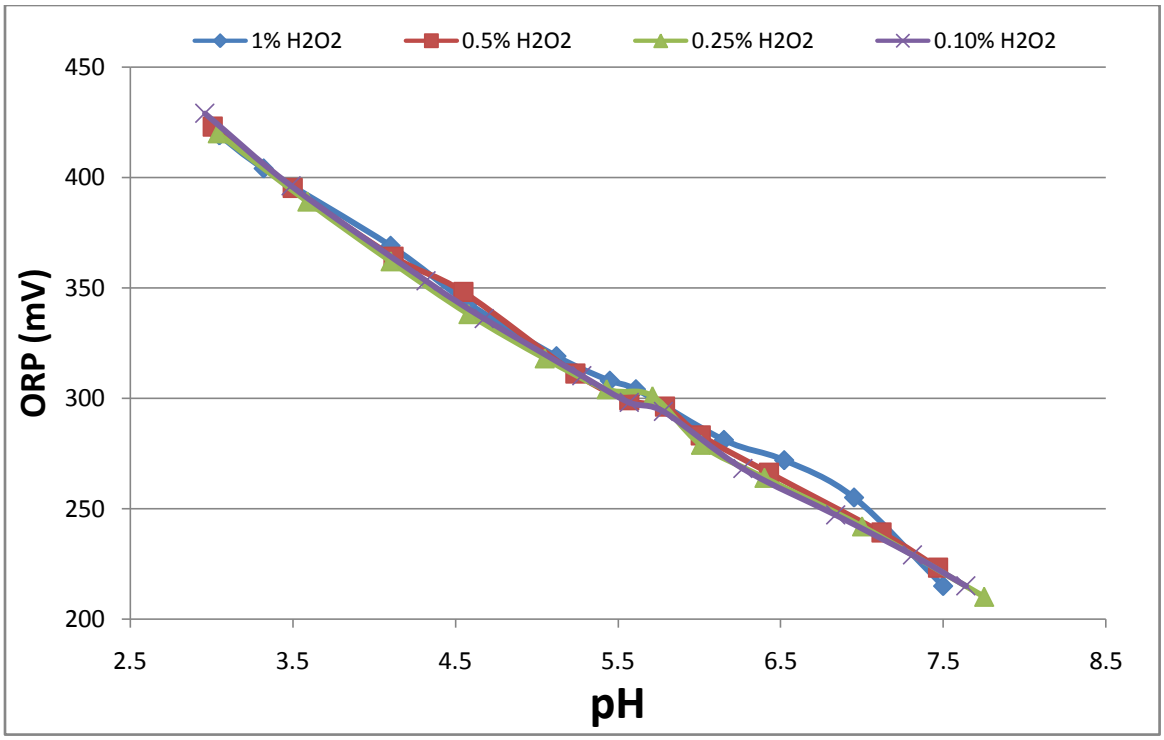

Figure 25 – Oxidation Reduction Potential of Oxidant Solution at Varying pH Ranges

C. OVERALL RESULTS

After all bench scale and pilot scale experiments were concluded, the information obtained by the research was used to submit a patent application to the U.S. patent office. U.S. Patent Application 20090130008 was successfully submitted by Michael Funk on May 21, 2009.

Other key operating parameters for functional oxidation of H_2S gas were the bubble size and gas residency time, based on observed phenomena during experimental trials. A decreasing bubble diameter increases the gas residency time as bubble rise velocity is lower for smaller bubbles, as shown in Figure 26. The ceramic dome diffusers used in the 105 gallon vessel had a average bubble diameter of 1.71 mm (based on

manufacturer literature) with little observed bubble coalescence while the PVC gas distributor had a larger bubble diameter of approximately 3.2 mm (based on diameter of drill bit used to create holes) with a higher observed rate of bubble coalescence. Moreover, the 60 gallon tank had a bubble rise distance (at 60 gallons liquid) of approximately 30 in. while the 105 gallon vessel (at 100 gallons liquid) had a rise distance of 53 in. The combination of increased tank volume and smaller mean bubble diameter showed increased efficiency in pilot scale trials. This result will be an important factor in design for commercial scale-up to best use decreased bubble diameters and increased gas residence time to ensure high H_2S removal efficiencies.

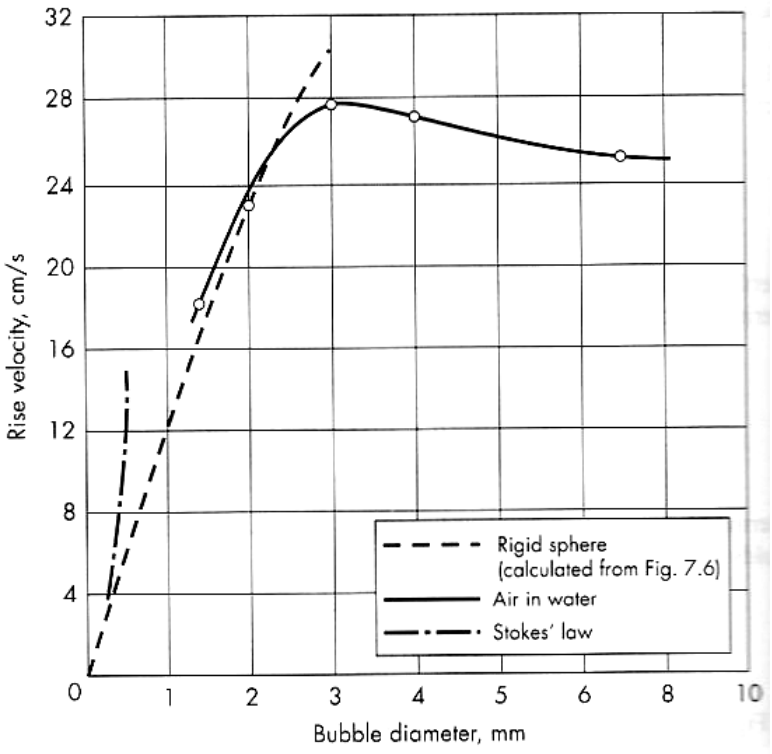

Figure 26 – Bubble Rise Velocity

Source: McCabe, Smith et al., (2005), pg 176

CONCLUSIONS

1. The process of using a low pH H_2O_2 scrubbing system shows viability for the removal of H_2S from biogas.
2. High concentration gradients (i.e. 1.0% H_2O_2) show better observed removal efficiencies of H_2S gas which is consistent with previous research for alkaline hydrogen peroxide scrubbing systems.
3. Bubble size and gas residency time are key operating parameters to achieve functional oxidation of H_2S gas in the system.
4. Removal efficiencies of 99.9% were observed, consistent with results obtained in alkaline hydrogen peroxide scrubbing systems by Moussavi et al (2008).

RECOMMENDATIONS

While the present study partially fulfills its objectives, there are limitations in the study that should be addressed with future research. The study completed in this work could be expanded to include a Life Cycle Assessment (LCA) for current process and other competitive processes. The LCA should include economic, environmental and social impacts for the most competitive H_2S removal technologies available at farm scale. Operational, maintenance, and media disposal costs also should be investigated. Moreover, LCA's for other biogas purification processes, such as CO_2 reduction, water removal, particulate filtration and removal of other gas contaminants, should be conducted. Lastly, the processing requirements for specific gas-utilization technologies should be compiled, including boilers, modified diesel engine sets, microturbines, and fuel cells.

This study was effective as a proof of concept, indicating that a low pH hydrogen peroxide scrubber can be used as an effective H_2S removal system for biogas purification. Further investigation of operational parameters is recommended before implementing a large commercial scale unit. The most important operational parameters that need additional research are control schemes, packing technology (type, quantity, and volume), and gas diffusing technologies.

From observations during the pilot scale experiments, it is recommended to generate a highly turbulent liquid system to increase oxidation efficiency. A demisting

system or gas chiller to reduce moisture content of exit gas in the reactor should be used if biogas is to be used for power generation. Lastly, a vessel with a large height to diameter ratio should be used to increase gas residence time.

During commercial scale-up, efforts should be made to collect/remove sulfur continuously from oxidant solution. Research is needed to better understand what type of recovery units (hydrocyclones, centrifuges, or sand filters) work best in conjunction with a scrubbing vessel. Investigation of a viable process for conversion of amorphous sulfur to crystalline form is highly recommended. Crystalline sulfur presents an excellent opportunity to generate revenue streams from process by-products; crystalline sulfur has a higher commercial value than amorphous sulfur and has possibility to generate copper sulfate solutions (used in cattle hoof baths).

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Appendix A

INITIAL SCRUBBER SETUP (60 GAL VESSEL, PVC GAS DISTRIBUTOR)

SPREADSHEETS, DATA, & PLOTS

Trial 1

Initial Test - 0.01% H2O2 = 100 ppm, Approx 50 gal of Solution

Gas Flow Rate = 2 ft^3/min, 5-12-08

Time	H2S (PPM)	pH	ORP (mV)
0	0	8.23	188.1
40	304		
60	425		
Final		5.7	60.7

Trial 2

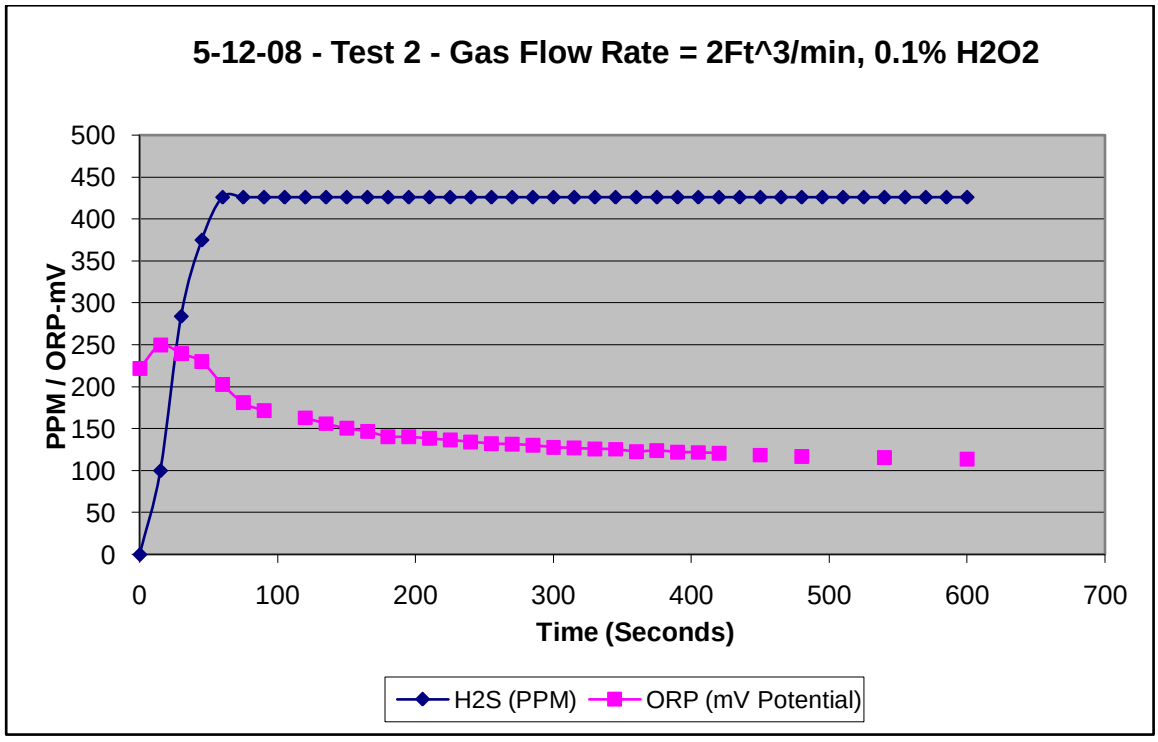
2nd Test - 0.1% H2O2 = 1000 ppm, Approx 50 gal of Soln.,

Gas Flow Rate = 2 ft^3/min , 5-12-08

Time (sec)	H2S (PPM)	pH	ORP (mV)	Temp Solution °C
0	0	7.78	222	18.8
15	100		250	18.8
30	284	6.68	240	18.8
45	375		230	18.8
60	426	6.2	203	18.8
75	426		181	18.8
90	426	6.02	171.5	18.8
105	426			18.8

120	426	5.9	163	18.8
135	426	5.84	156	18.8
150	426	5.78	150.4	18.8
165	426	5.7	146.7	18.8
180	426	5.68	140.6	18.8
195	426	5.66	140.2	18.8
210	426	5.61	138.2	18.8
225	426		136.4	18.8
240	426	5.58	134.3	18.8
255	426		132.3	18.8
270	426		131.5	18.8
285	426	5.52	130.2	18.8
300	426		127.9	18.8
315	426	5.48	126.9	18.8
330	426		125.8	18.8
345	426		125.4	18.8
360	426		122.7	18.8
375	426	5.44	123.9	18.8
390	426		122.2	18.8
405	426	5.41	121.6	18.8
420	426		120.8	18.8
435	426			18.8
450	426	5.39	118.4	18.8
465	426			18.8
480	426		117.1	18.8
495	426			18.8
510	426			18.8

525	426			18.8
540	426	5.33	115.7	18.8
555	426			18.8
570	426			18.8
585	426			18.8
600	426		113.6	18.8



Trial 3

3rd Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2

Approx 50 gal of Soln., Gas Flow Rate = 2.25 ft^3/min , 5-12-08

Time (sec)	H2S (PPM)	pH	ORP (mV)		Temp Solution °C
0	0	7.57	229		19.4
15	23	6.83	268		19.4
30	255		276		19.4
45	383	6.11	280		19.4
60	426		283		19.4
75	426	5.93	287		19.4
90	426		284		19.4
105	426		285		19.4
120	426	5.73	284		19.4
135	426		282		19.4
150	426		280		19.4
165	426		281		19.4
180	426		278		19.4
195	426		278		19.4
210	426	5.58	277		19.4
225	426	5.53	275		19.4
240	426				19.4
255	426				19.4
270	426		274		19.4
285	426	5.44	271		19.4
300	426		272		19.4
315	426		269		19.4

330	426		270		19.4
345	426	5.38	268		19.4
360	426	5.36	267		19.4
375	426		266		19.4
390	426	5.34	265		19.4
405	426		264		19.4
420	426	5.34	263		19.4
435	426	5.3	263		19.4
450	426		263		19.4
465	426		260		19.4
480	426	5.28	261		19.4
495	426		260		19.4
510	426		259		19.4
525	426		260		19.4
540	426		258		19.4
555	426				19.4
570	426				19.4
585	426				19.4
600	426		255		19.4

Trial 4

4th Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2,

Gas Flow Rate = 1.0 ft^3/min , 5-12-08

Time (sec)	H2S (PPM)	pH	ORP (mV)		Temp Solution °C

0	103	5.24	339		19.6
15	141		331		19.6
30	178	5.22	330		19.6
45	239	5.22	326		19.6
60	282		324		19.6
75	320	5.22	322		19.6
90	352		321		19.6
105	387	5.22	317		19.6
120	403		316		19.6
135	420		314		19.6
150	426		314		19.6
165	426		314		19.6
180	426		314		19.6
195	426		312		19.6
210	426		312		19.6

Trial 5

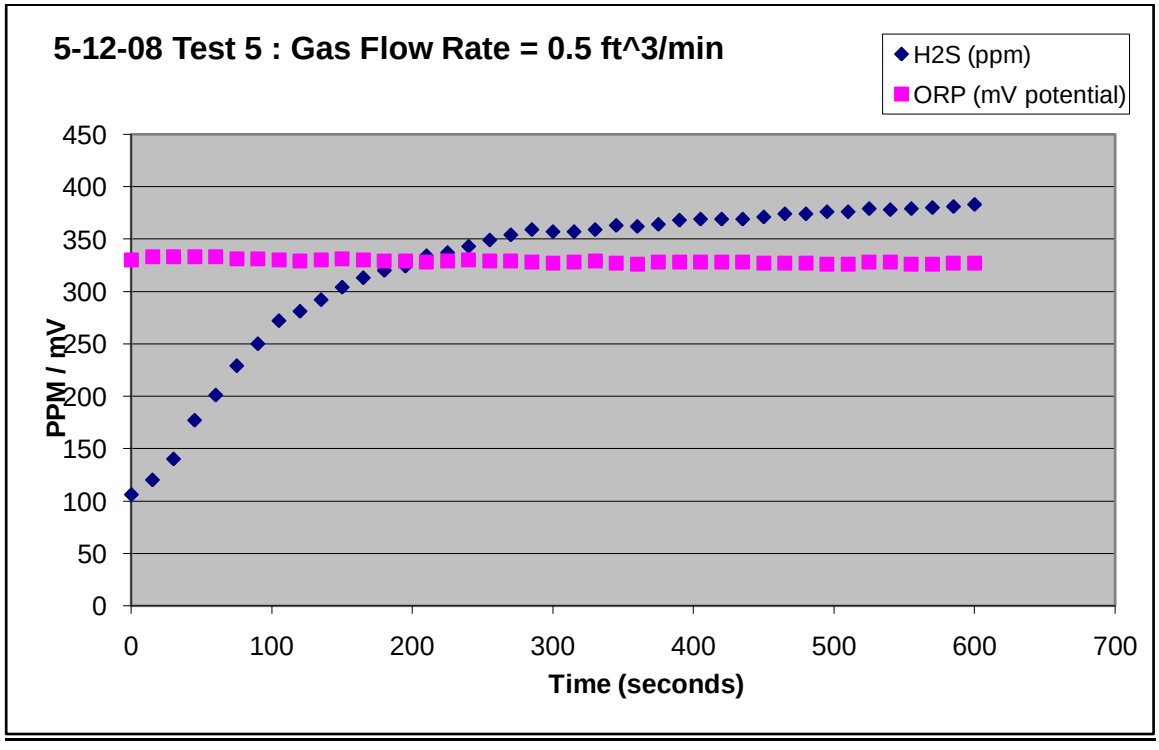
5th Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2,

Gas Flow Rate = 0.50 ft^3/min , 5-12-08

Time (sec)	H2S (PPM)	pH	ORP (mV)		Temp Solution °C
0	106	5.23	330		19.6
15	120	5.23	333		19.6
30	140		333		19.6
45	177		333		19.6

60	201		333	19.6
75	229		331	19.6
90	250	5.21	331	19.6
105	272		330	19.6
120	281		329	19.6
135	292		330	19.6
150	304		331	19.6
165	313		330	19.6
180	320	5.21	329	19.6
195	324		329	19.6
210	334		328	19.6
225	337		329	19.6
240	343		330	19.6
255	349	5.21	329	19.6
270	354		329	19.6
285	359		328	19.6
300	357		327	19.6
315	357		328	19.6
330	359		329	19.6
345	363	5.21	327	19.6
360	362		326	19.6
375	364		328	19.6
390	368		328	19.6
405	369		328	19.6
420	369		328	19.6
435	369		328	19.6
450	371		327	19.6

465	374		327		19.6
480	374		327		19.6
495	376		326		19.6
510	376		326		19.6
525	379		328		19.6
540	378		328		19.6
555	379		326		19.6
570	380	5.19	326		19.6
585	381		327		19.6
600	383		327		19.6



Trial 6

6th Test-1.0% H2O2 = 10000 ppm,5.470 Liters H2O2; Inserted 4 ft^3 of Burl Saddle Packing, Gas Flow Rate = 1.0 ft^3/min,5-13-08

Time (sec)	H2S (PPM)	pH	ORP (mV)		Temp Solution °C
0	0	5.29	337		21.7
15	33		338		21.7
30	235		342		21.7
45	371		343		21.7
60	420	5.22	342		21.7
75	426		342		21.7
90	426		341		21.7
105	426		340		21.7
120	426	5.22	337		21.7
135	426		337		21.7
150	426		336		21.7
165	426		335		21.7
180	426	5.2	335		21.7
195	426		333		21.7
210	426		335		21.7
225	426		332		21.7
240	426	5.18	331		21.7
255	426		331		21.7
270	426		330		21.7
285	426		330		21.7

300	426	5.18	330		21.7
315	426		330		21.7
330	426		329		21.7
345	426		330		21.7
360	426	5.16	328		21.7
375	426		329		21.7
390	426		329		21.7
405	426		328		21.7
420	426	5.16	329		21.7

Trial 7

7th Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2, Inserted 4 ft^3 of Burl Saddle Packing, Gas Flow Rate =0.5 ft^3/min , 5-13-08

Time (sec)	H2S (PPM)	pH	ORP (mV)		Temp Solution °C
0	38	5.2	354		21.7
15	37		353		21.7
30	51		354		21.7
45	142		354		21.7
60	187	5.16	354		21.7
75	206		354		21.7
90	236		353		21.7
105	272		353		21.7

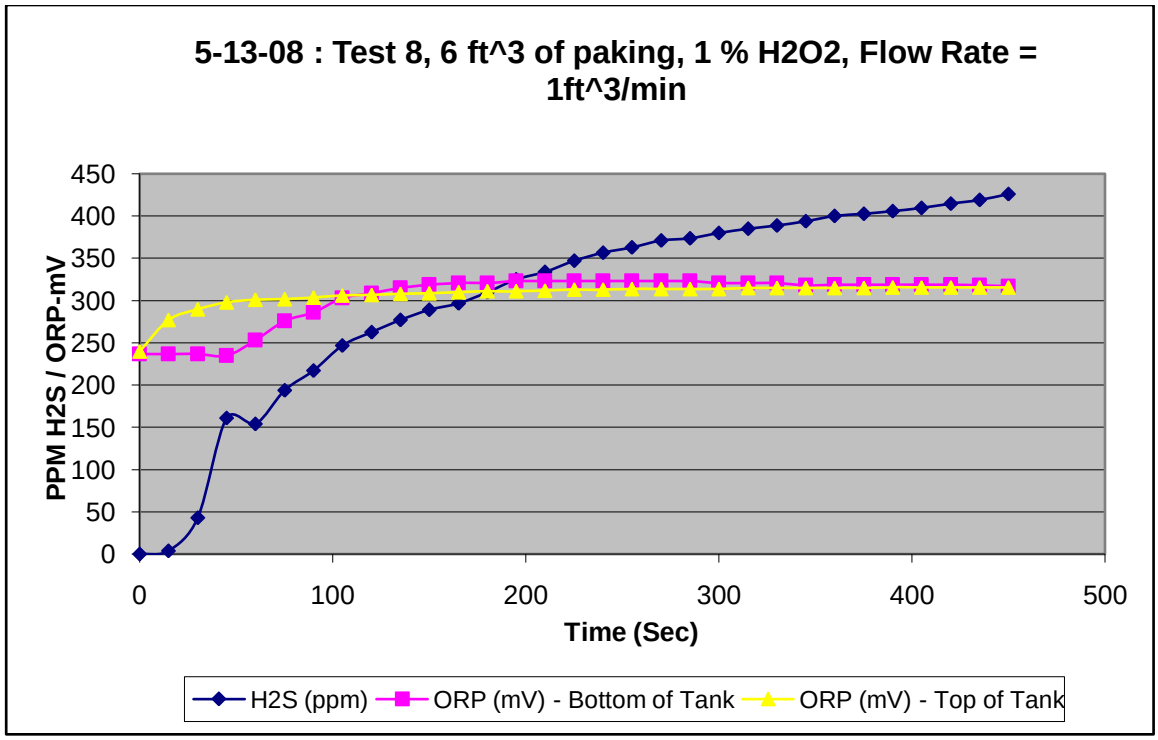
120	288	5.16	353		21.7
135	321		352		21.7
150	336		352		21.7
165	358		352		21.7
180	374	5.14	352		21.7
195	383		352		21.7
210	395		351		21.7
225	407		352		21.7
240	418	5.14	351		21.7
255	426		350		21.7
270	426		350		21.7
285	426		350		21.7
300	426	5.14	350		21.7

Trial 8

8th Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2
Total of 6 ft^3 of Burl Saddle Packing,
Tank Agitated with lab Air for greater H2O2 mixing
Gas Flow Rate =1.0 ft^3/min , 5-13-08

Time (sec)	H2S (PPM)	ORP(mV) - BTTM	ORP (mV) - TOP
0	0	237	240
15	4	237	277
30	43	237	290
45	161	235	298
60	154	253	301
75	194	276	302

90	217	286	304
105	247	303	306
120	263	309	307
135	277	315	308
150	289	319	309
165	297	321	310
180	310	321	311
195	325	323	311
210	334	323	312
225	347	323	313
240	357	323	313
255	363	323	314
270	371	323	314
285	374	323	314
300	380	321	314
315	385	321	315
330	389	321	315
345	394	318	315
360	400	319	315
375	403	319	315
390	406	319	316
405	410	319	316
420	415	319	316
435	419	318	316
450	426	317	316

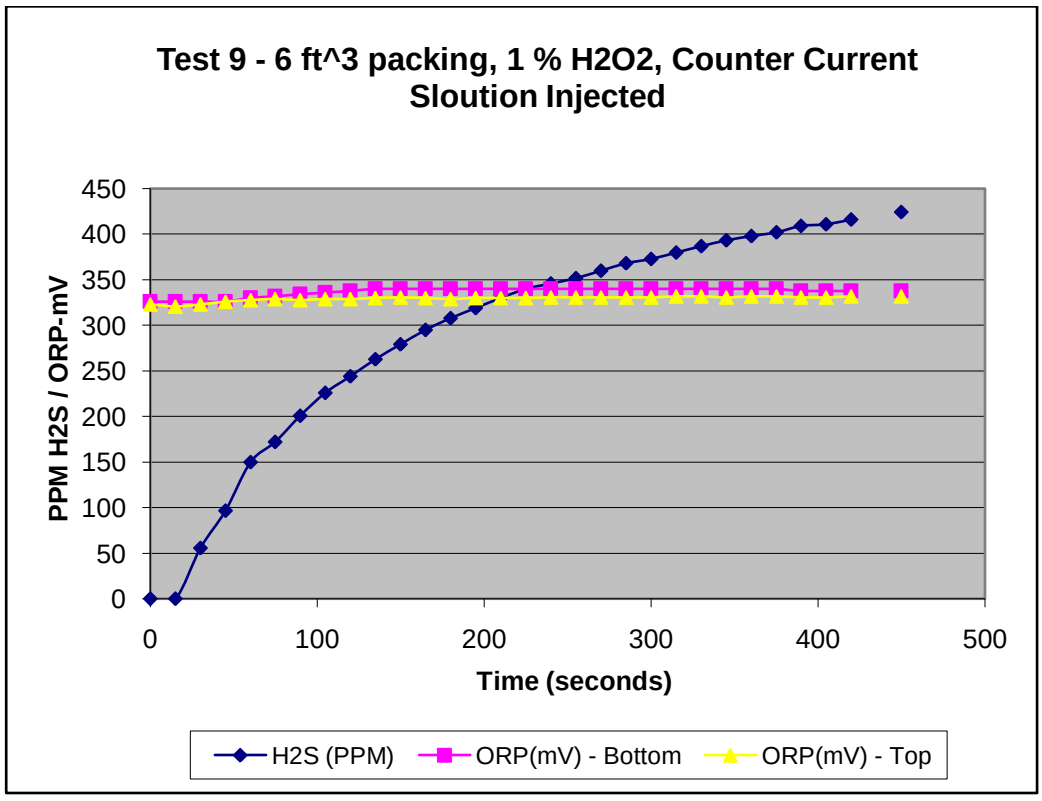


Trial 9

9th Test - 1.0% H2O2 = 10000 ppm,5.470 Liters H2O2
Total of 6 ft^3 of Burl Saddle Packing,
Tank Agitated with lab Air for greater H2O2 mixing, Counter Current H2O2 Injection
Gas Flow Rate =1.0 ft^3/min , 5-13-08

Time (sec)	H2S (PPM)	ORP(mV) - BTTM	ORP (mV) - TOP
0	0	326	323
15	0	326	321
30	56	326	323
45	97	326	326
60	150	330	328
75	172	332	329
90	201	334	328
105	226	336	329
120	244	338	329
135	263	340	330
150	279	340	331
165	295	340	330

180	308	340	329
195	319	340	330
210	330	340	330
225	340	340	330
240	346	340	331
255	352	340	331
270	360	340	331
285	368	340	331
300	373	340	331
315	380	340	332
330	387	340	332
345	393	340	331
360	398	340	332
375	402	340	332
390	409	338	331
405	411	338	331
420	416	338	332
435			
450	424	338	332



Appendix B

2nd SCRUBBER SETUP (105 GAL VESSEL, CERAMIC DOME GAS DISTRIBUTORS)

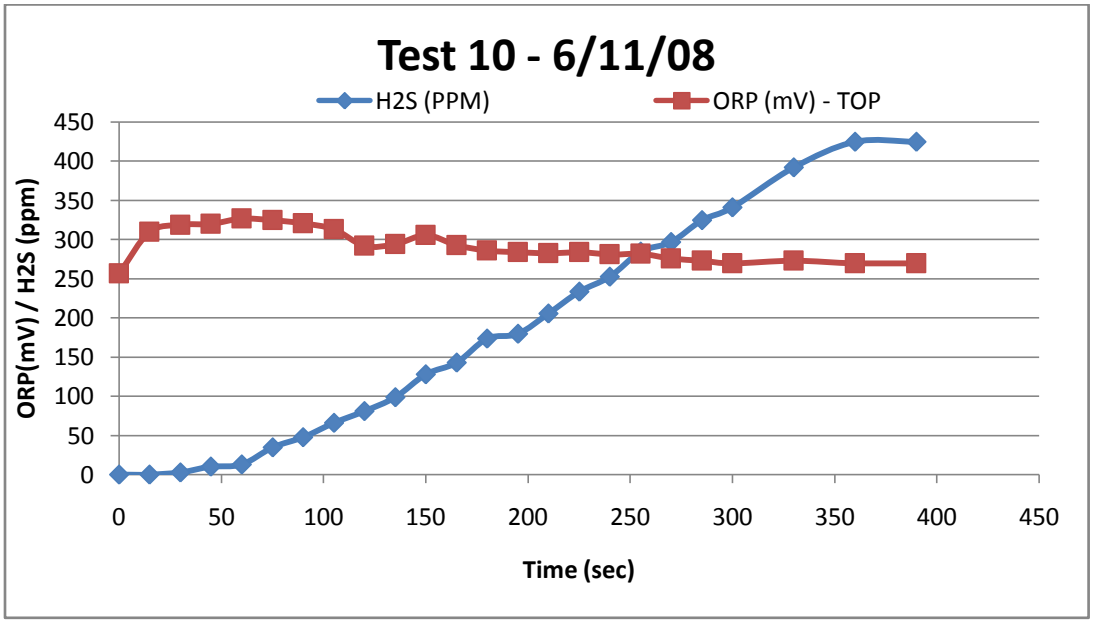
SPREADSHEETS, DATA, & PLOTS

Trial 10

105 gallon scrubbing vessel, ceramic dome gas distributors, 5470 mL 35% H202 (0.50%), no packing, 50 gallons of solution

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	257
15	0	310
30	3	319
45	10	320
60	13	327
75	35	325
90	48	321
105	66	313
120	81	292
135	99	294
150	128	306
165	143	293
180	174	286
195	180	284
210	206	283
225	234	284
240	253	281
255	285	282
270	297	276
285	325	273

300	341	270
330	392	273
360	425	270
390	425	270

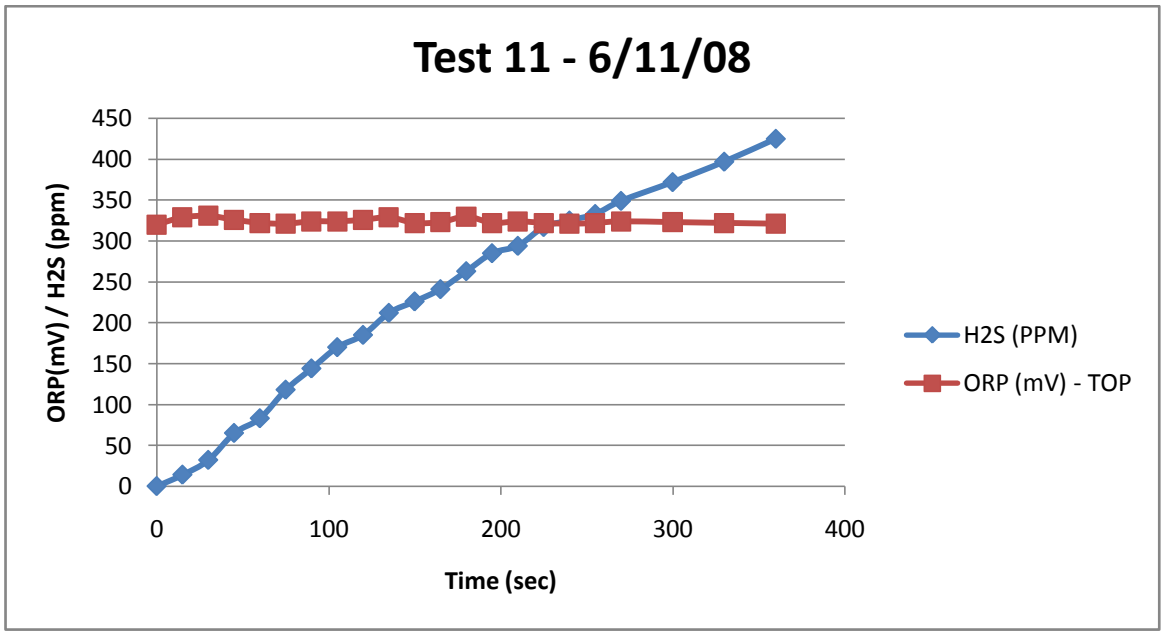


Trial 11

105 gallon scrubbing vessel, new gas distributors, no packing, 100 gallon of solution at 1.0 % H_2O_2

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	320
15	14	329
30	32	331
45	65	326

60	83	322
75	118	321
90	144	324
105	170	324
120	185	326
135	212	329
150	226	322
165	241	323
180	263	330
195	285	322
210	294	324
225	317	322
240	325	321
255	333	322
270	349	324
300	372	323
330	397	322
360	425	321



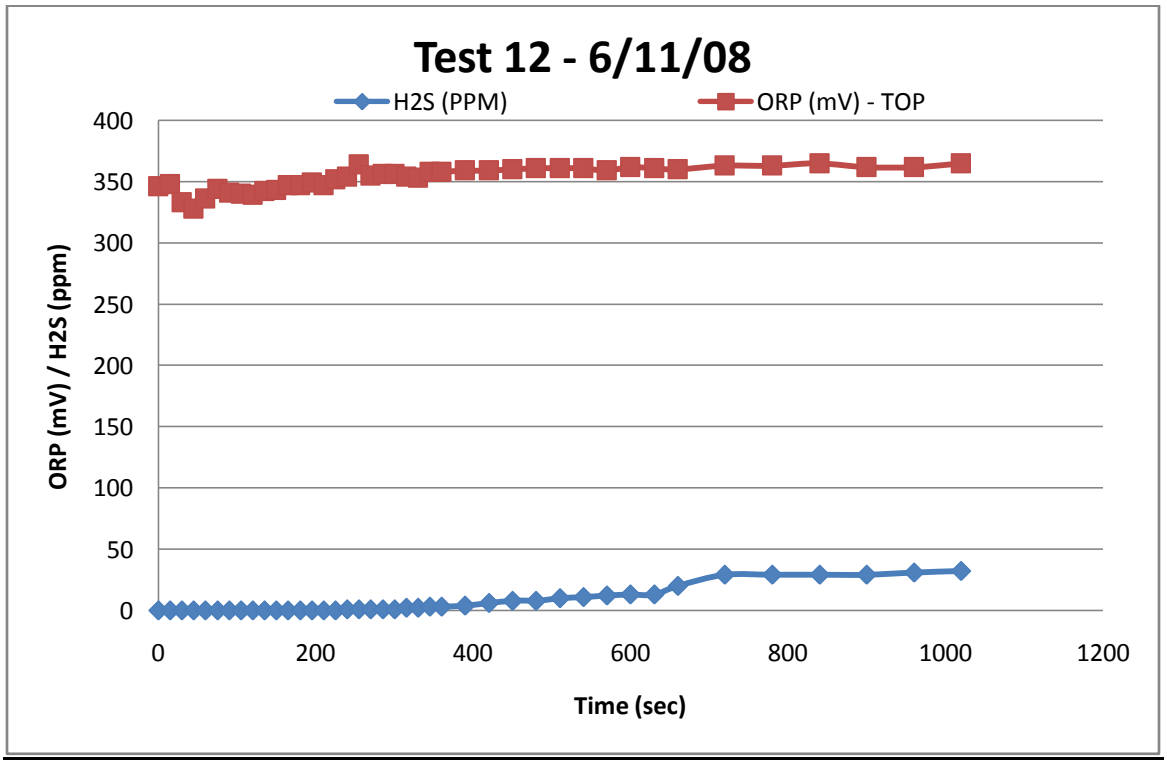
Trial 12

105 gallon scrubbing vessel, new gas distributors, 100 gallon of solution at 1.0% H_2O_2 , 6 ft^3 of packing

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	346
15	0	348
30	0	333
45	0	328
60	0	336
75	0	344
90	0	341
105	0	340

120	0	339
135	0	342
150	0	343
165	0	347
180	0	347
195	0	349
210	0	347
225	0	352
240	1	354
255	1	364
270	1	355
285	1	356
300	1	356
315	2	354
330	2	353
345	3	358
360	3	358
390	4	359
420	6	359
450	8	360
480	8	361
510	10	361
540	11	361
570	12	359
600	13	362
630	13	361

660	20	360
720	29	363
780	29	363
840	29	365
900	29	362
960	31	362
1020	32	365

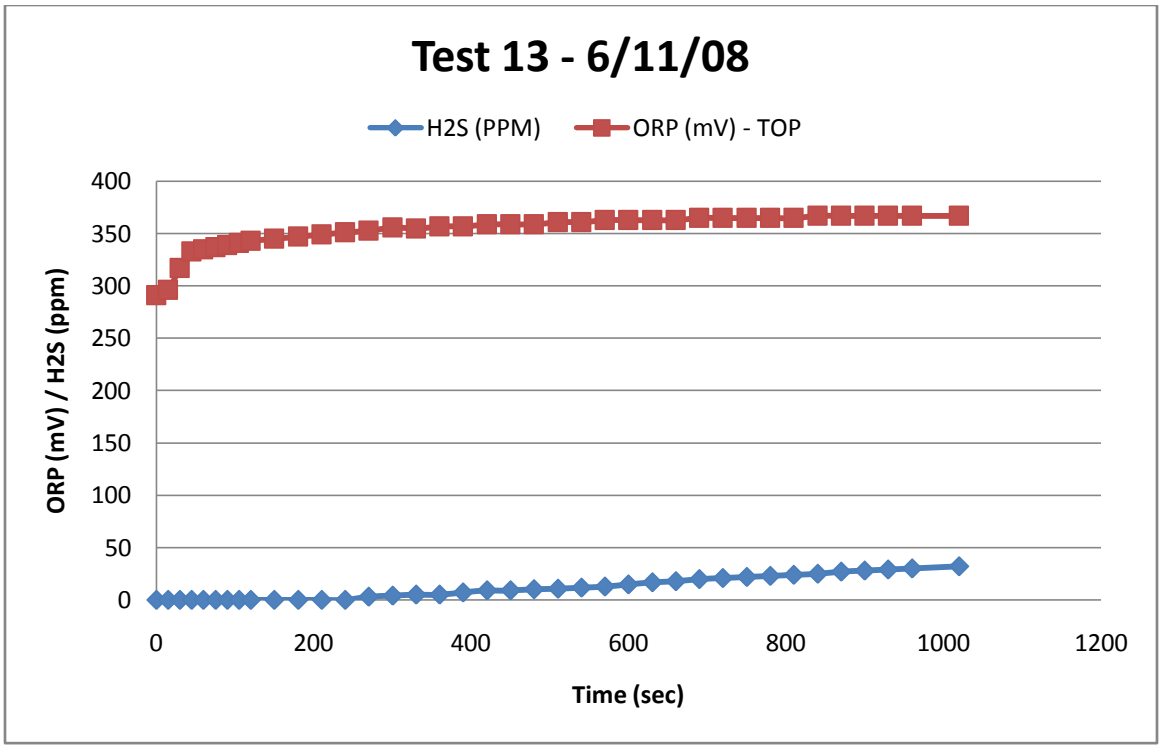


Trial 13

105 gallon scrubbing vessel, new gas distributors, 100 gallon of solution at 0.50% concentration H_2O_2 , 6 ft^3 of packing

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	291
15	0	296
30	0	317
45	0	333
60	0	335
75	0	337
90	0	339
105	0	341
120	0	343
150	0	345
180	0	347
210	0	349
240	0	351
270	3	353
300	4	356
330	5	355
360	5	357
390	7	357
420	9	359
450	9	359

480	10	359
510	11	361
540	12	361
570	13	363
600	15	363
630	17	363
660	18	363
690	20	365
720	21	365
750	22	365
780	23	365
810	24	365
840	25	367
870	27	367
900	28	367
930	29	367
960	30	367
1020	32	367

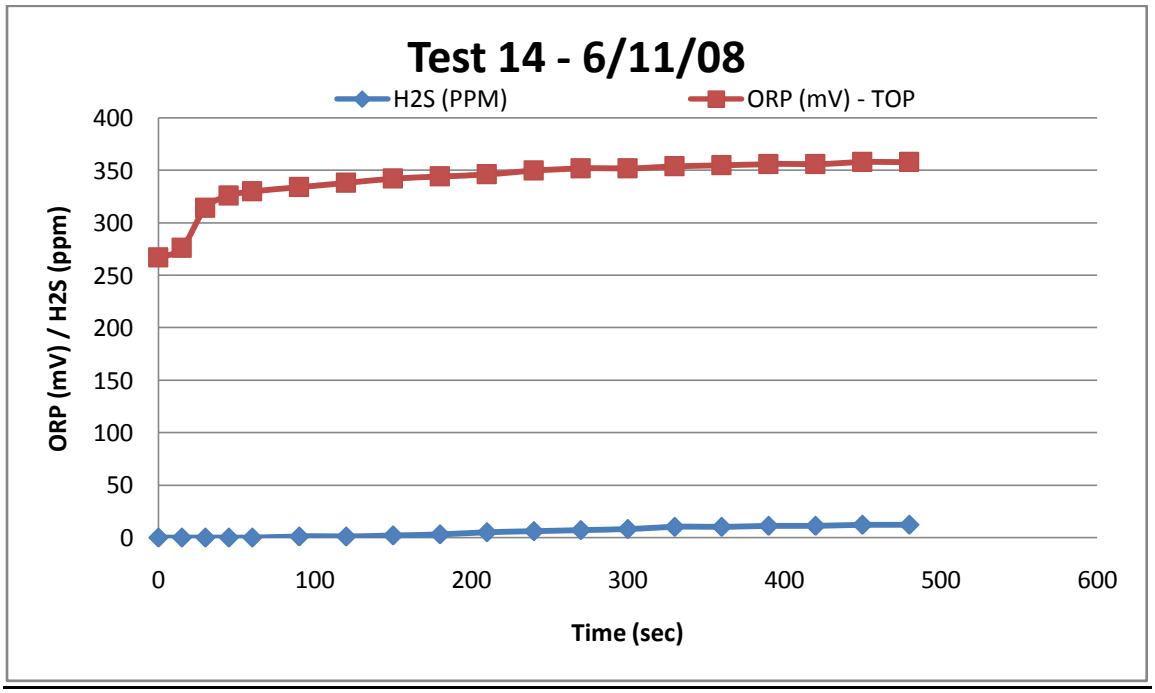


Trial 14

105 gallon scrubbing vessel, new gas distributors, 100 gallon of solution at 0.25% concentration, 6 ft^3 of packing, 2 ft3 per min gas flow

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	267
15	0	276
30	0	314
45	0	326
60	0	330
90	1	334
120	1	338
150	2	342

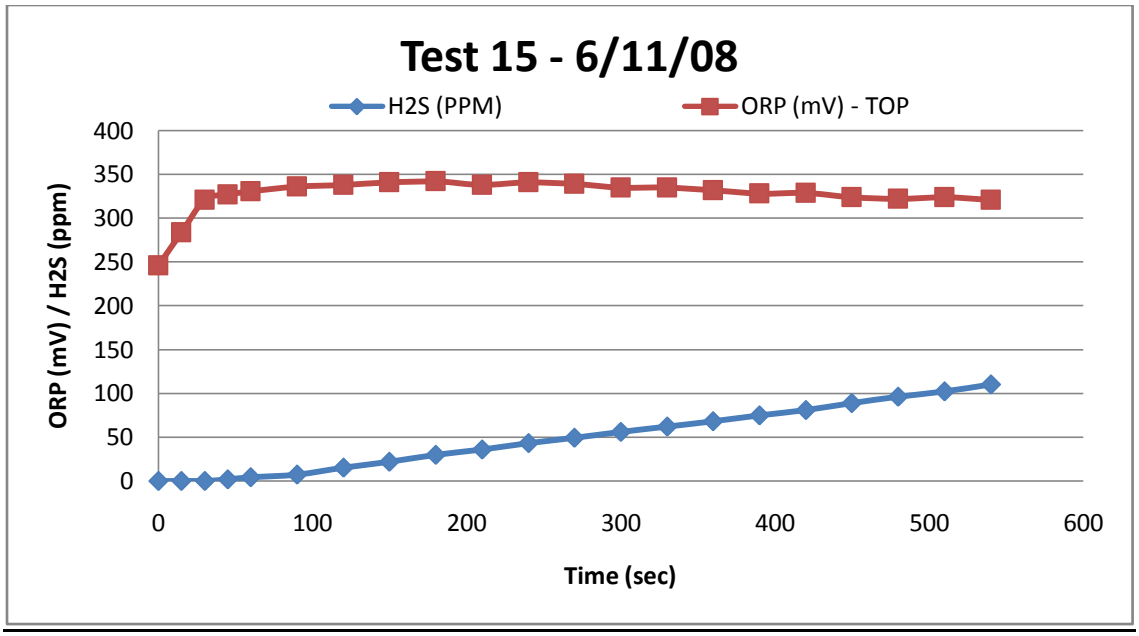
180	3	344
210	5	346
240	6	350
270	7	352
300	8	352
330	10	354
360	10	355
390	11	356
420	11	356
450	12	358
480	12	358



Trial 15

105 gallon scrubbing vessel, new gas distributors, 100 gallon of solution at 0.125% concentration H_2O_2 , 6 ft^3 of packing, 2 ft^3/min gas flow

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	246
15	0	284
30	0	321
45	2	327
60	4	331
90	7	336
120	15	338
150	22	341
180	30	342
210	36	338
240	43	341
270	49	339
300	56	335
330	62	335
360	68	332
390	75	328
420	81	329
450	89	324
480	96	322
510	102	324
540	110	321

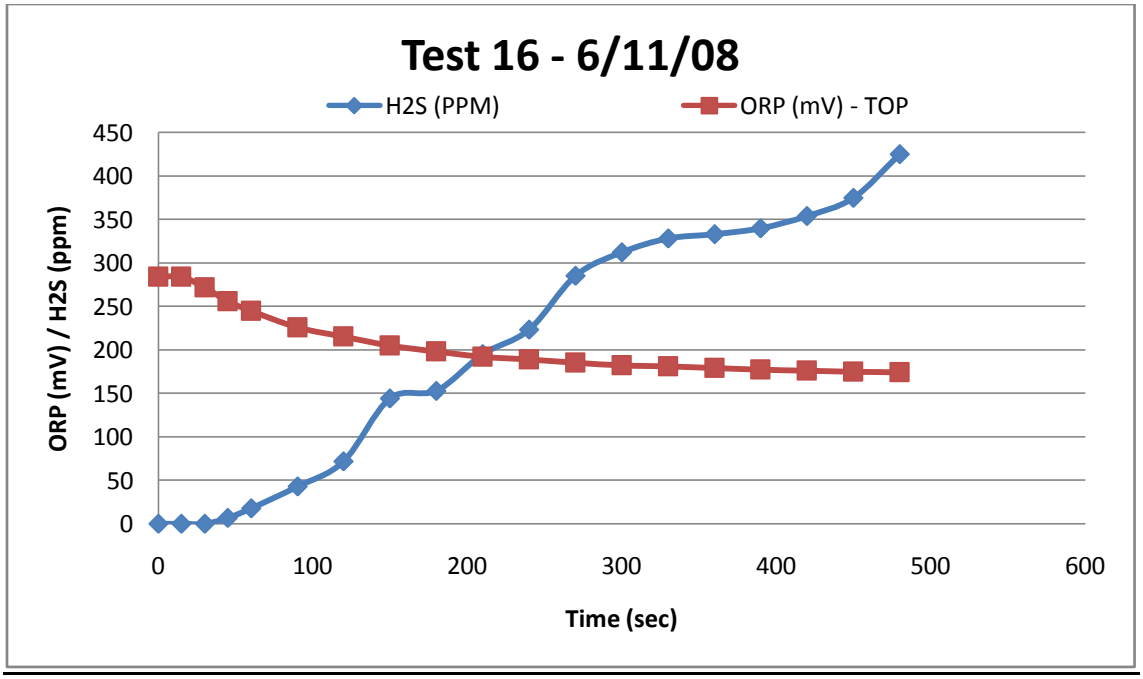


Trial 16

Tank drained and washed out with water and aerated. Filled to 50 gallon with 547 mL H2O2 (35%), gas flow = 2 ft3/min

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	284
15	0	284
30	0	272
45	7	256
60	18	245
90	43	226
120	72	215
150	144	205
180	153	198

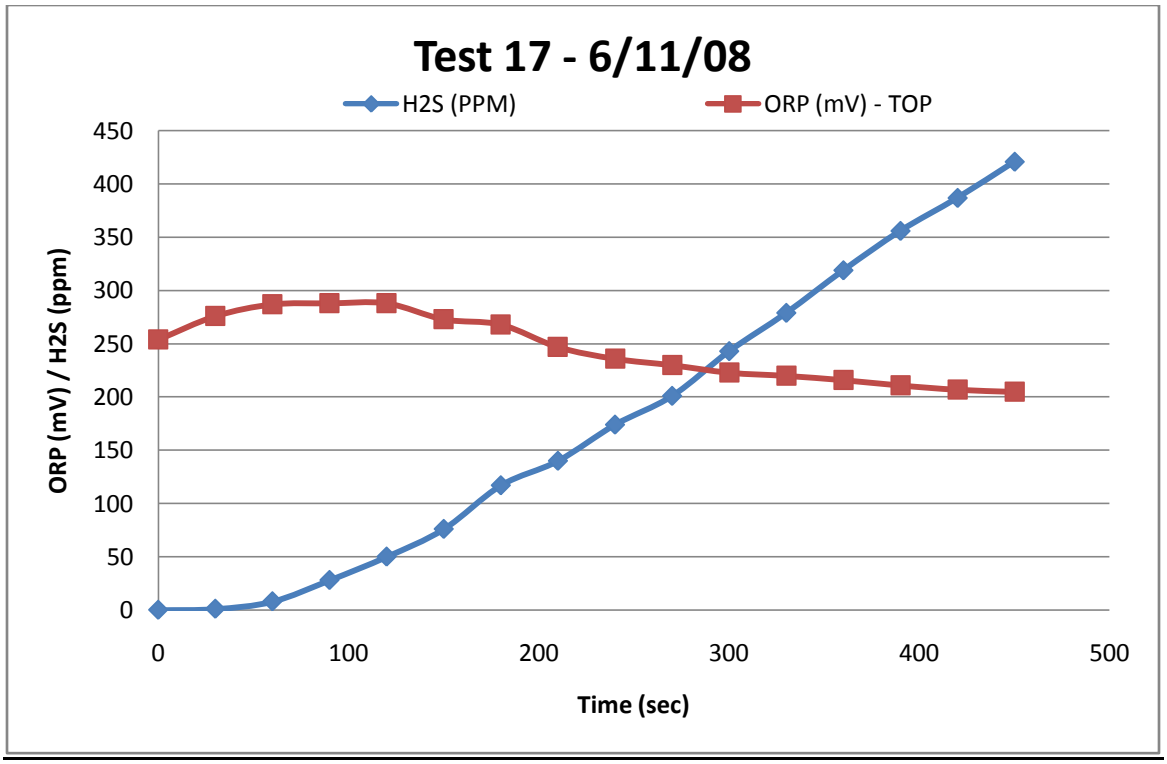
210	195	192
240	223	189
270	285	185
300	312	182
330	328	181
360	333	179
390	340	177
420	354	176
450	375	175
480	425	174



Trial 17

100 gallons with 6 ft^3 packing, approx 0.10% H2O2, gas flow = 2 ft3/min

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	254
30	1	276
60	8	287
90	28	288
120	50	288
150	76	273
180	117	268
210	140	247
240	174	236
270	201	230
300	243	223
330	279	220
360	319	216
390	356	211
420	387	207
450	421	205



Trial 18

100 gallons with 11 ft^3 packing, approx 0.125% H2O2, gas flow = 2 ft3/min

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	254
30	5	256
60	86	250
90	141	250
120	189	249
150	218	247
180	248	243
210	278	240
240	308	237

270	343	233
300	375	231
330	400	229
360	416	227
390	415	225
420	415	223
450	415	221
480	414	221
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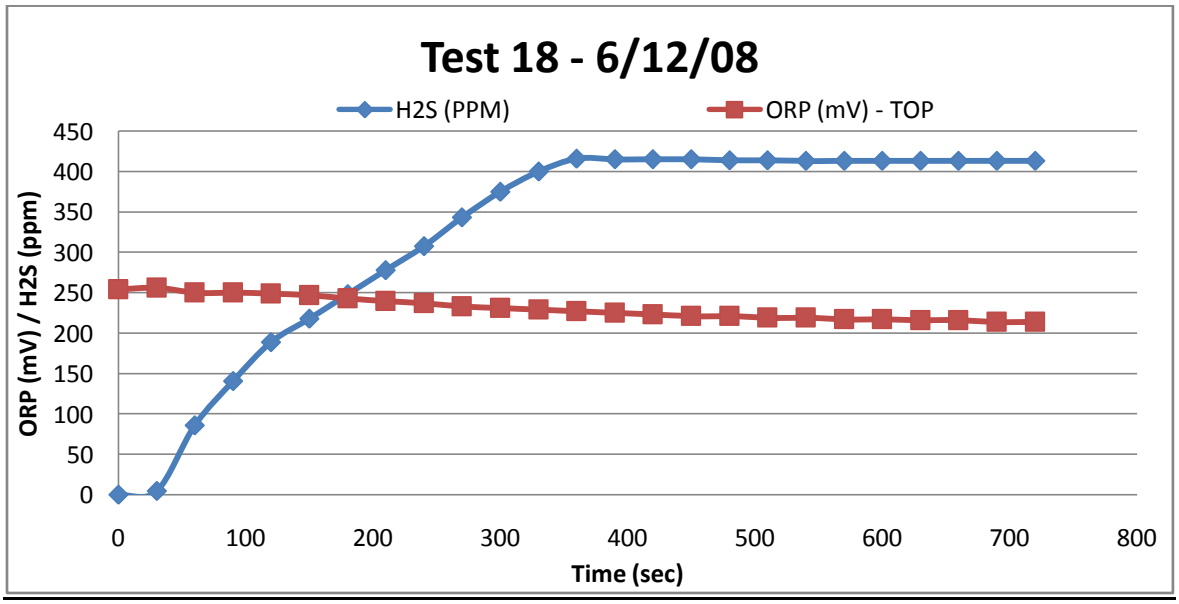
630	413	216
660	413	216
690	413	214
720	413	214



Trial 19

100 gallons with 11 ft^3 packing, approx 0.25% H2O2, gas flow = 2 ft3/min

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	349
30	16	292
60	98	287
90	154	279
120	202	276
150	237	272
180	270	270
210	298	268
240	325	268
270	349	266
300	370	264
330	390	264
360	416	262
390	416	262
420	416	260
450	415	260
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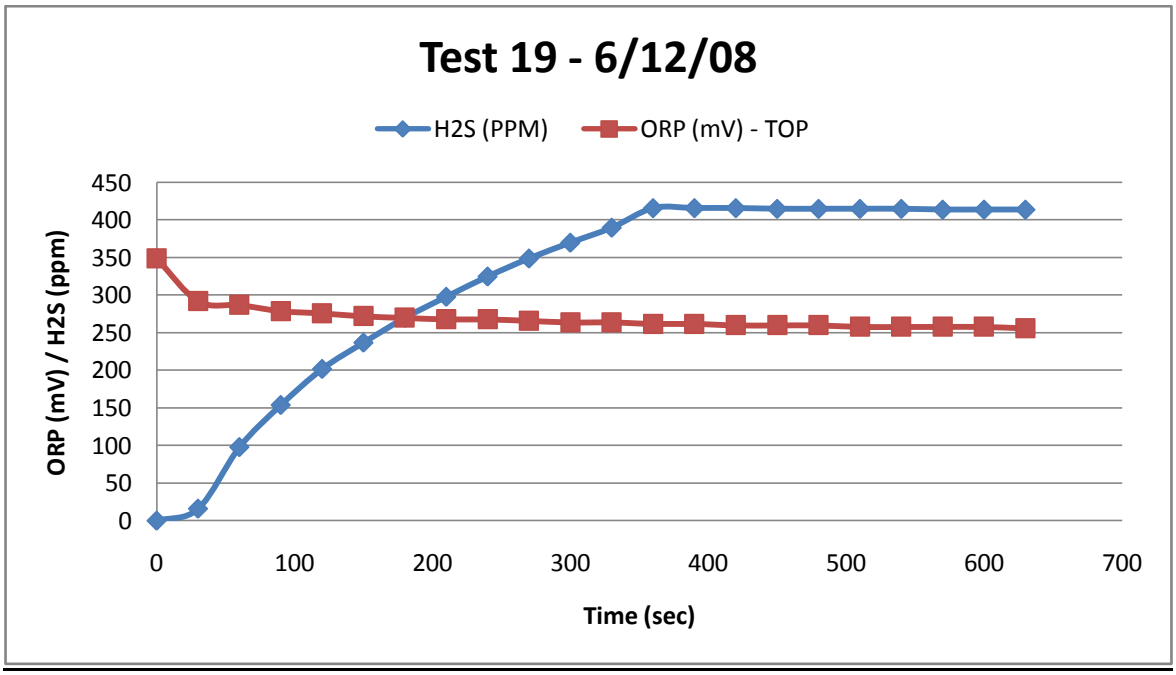
540	415	258
570	414	258
600	414	258
630	414	256



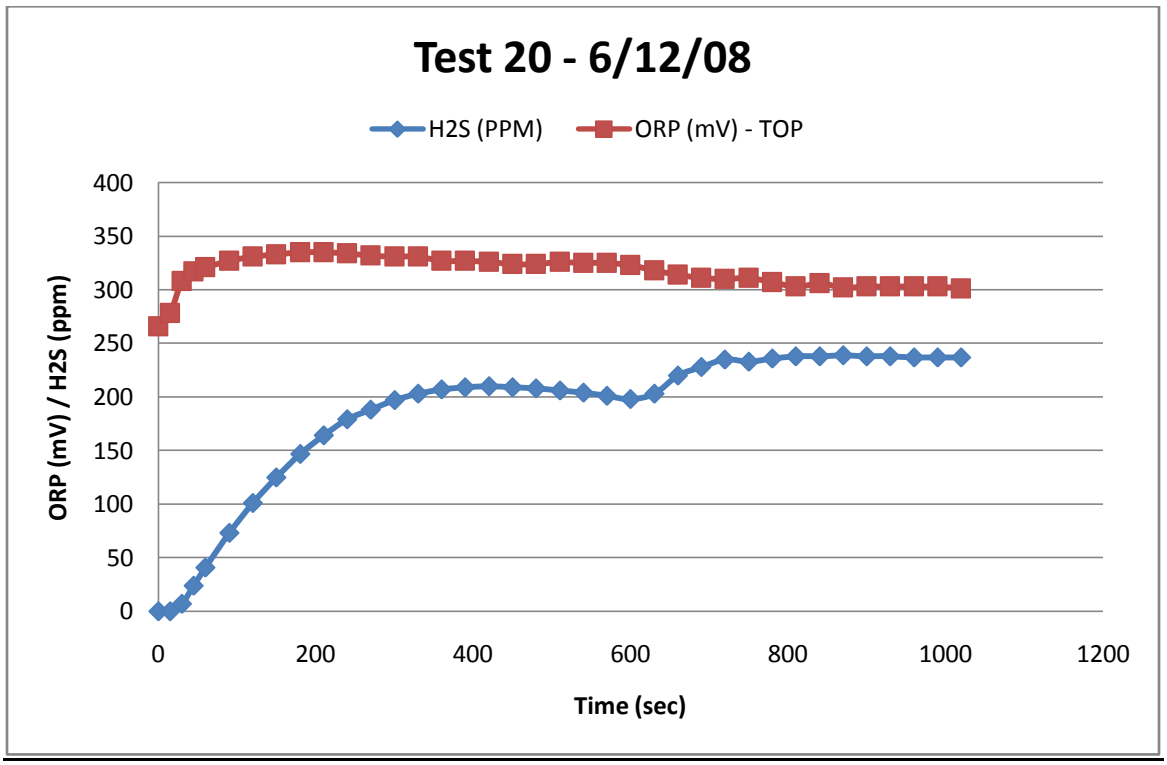
Trial 20

100 gallons with 11 ft^3 packing, approx 0.25% H2O2, gas flow = 2 ft3/min, used heated water, temp 110-115 F

Time (sec)	H2S (PPM)	ORP (mV) - TOP
0	0	266
15	0	278
30	7	308
45	24	317
60	41	321
90	73	327
120	101	331

150	125	333
180	147	335
210	164	335
240	179	334
270	188	332
300	197	331
330	203	331
360	207	327
390	209	327
420	210	326
450	209	324
480	208	324
510	206	326
540	204	325
570	201	325
600	198	323
630	203	318
660	220	314
690	228	311
720	235	310
750	233	311
780	236	307
810	238	303
840	238	306
870	239	302
900	238	303

930	238	303
960	237	303
990	237	303
1020	237	301



Appendix C

UNITED STATES PATENT APPLICATION 20090130008

PROCESS FOR REMOVING HYDROGEN DISULFIDE FROM GAS

United States Patent Application **20090130008**
Kind Code **A1**
Funk; Michael N. **May 21, 2009**

Process for Removing Hydrogen Disulfide from Gas

Abstract

A reactor and process for removing ***hydrogen sulfide from gas***. The reactor vessel contains an oxidizing solution and packing, where the packing fill about 25% to about 75% of the liquid volume of the vessel.

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Intern'l Class: B01D 53/52 20060101 B01D053/52; B01D 53/22 20060101 B01D053/22

Claims

1. A process for removing ***hydrogen sulfide from gas*** comprising the steps of:diffusing the gas; and passing the diffused gas through a vessel containing packing and a solution comprising an oxidant and water, where the packing fills about 25% to about 75% of the liquid volume of the vessel.

2. The process of claim 1, where the temperature of the solution is from about 55.degree. F. to about 200.degree. F.

3. The process of claim 1, where the pH of the solution is from about 3 to about 8.

4. The process of claim 1, where the packing has a void fraction from about 93% to about 98%.

5. The process of claim 1, where the oxidant is ***hydrogen peroxide***.

6. The process of claim 1, where the diffused gas is formed by passing the gas through a diffuser with a pore size of from about 0.2 to about 100 microns.

7. The process of claim 1, where the ORP of the solution is above about 300 mV.

8. The process of claim 1, where the packing fills about half of the liquid volume of the vessel.

9. The process of claim 1, where the packing is random packing.

10. A reactor for removing ***hydrogen sulfide from gas*** comprising:a vessel containing packing and a solution comprising an oxidant and water; anda diffuser for the gas;where the packing fills about 25% to about 75% of the vessel.

11. The reactor of claim 10, where the packing has a void fraction from about 93% to about 98%.

12. The reactor of claim 10, where the diffuser has a porosity of from about 0.2 to about 100 microns.

13. The reactor of claim 10, where the packing fills about half of the vessel.

14. The reactor of claim 10, where the packing is random packing.

Description

CROSS REFERENCE TO RELATED APPLICATIONS

[0001]The present application hereby claims the benefit of the provisional patent application of the same title, Ser. No. 61/003,621, filed on Nov. 19, 2007, the disclosure of which is hereby incorporated by reference in its entirety.

BACKGROUND

[0002]Biogas is a potential renewable energy source that may be produced from anaerobic digestion. It may occur naturally in landfills or in controlled environments that enhance the biological degradation of sewage waste, foodstuff waste, or animal waste.

[0003]Biogas and other sour gases are often not useful as an energy source because they are a low btu gas often containing hydrogen sulfide (H.sub.2S), carbon dioxide, and water. Hydrogen sulfide has a

foul odor, is toxic, and corrosive. Biogas containing hydrogen sulfide is very corrosive to equipment that burns it for fuel. Combustion of hydrogen sulfide oxidizes it to sulfur dioxide which contributes to acid rain.

[0004]Hydrogen sulfide may be removed from a gas through a number of different methods such as chemical or biological oxidation. However the expense of removing the hydrogen sulfide may make the use of the gas uneconomical. Consequently, a significant need exists for an efficient method for removal of ***hydrogen sulfide from a gas***.

BRIEF SUMMARY

[0005]The above-noted and other deficiencies may be overcome by providing a reactor for removing ***hydrogen sulfide from gas*** comprising: a vessel containing packing and a solution comprising an oxidant and water; and a diffuser for the gas; where the random packing fills about 25% to about 75% liquid volume of the vessel.

[0006]Hydrogen sulfide may be removed from a gas by a process comprising the steps of: diffusing the gas; and passing the diffused gas through a vessel containing packing and a solution comprising an oxidant and water; where the packing fills about 25% to about 75% of the liquid volume of the vessel.

[0007]These and other objects and advantages shall be made apparent from the accompanying drawings and the description thereof

BRIEF DESCRIPTION OF THE FIGURES

[0008]The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments, and together with the general description given above, and the

detailed description of the embodiments given below, serve to explain the principles of the present disclosure.

[0009]FIG. 1 is a process flow diagram of an embodiment of the overall process for removing ***hydrogen sulfide from gas***.

DETAILED DESCRIPTION

[0010]An embodiment depicted in FIG. 1 will be described below in further detail by reviewing each of the individual parts. Hand valves are labeled HV, and check valves are labeled CV.

[0011]The blower (1), which may be driven by a variable frequency drive (VFD) motor, may be used to elevate the pressure of the gas (sour gas or biogas) from the source to allow proper flow through the gas diffuser (2). The blower's VFD motor's throughput may be controlled by a pressure sensor at the gas source, the hydrogen sulfide monitor (5), and the demand for clean gas. If the pressure becomes too high, it may be released through the pressure release valve (15).

[0012]The gas diffuser (2) is used to evenly diffuse the gas through the oxidizing solution (3) and the packing (4). The gas diffuser creates smaller bubbles. Smaller bubbles have a higher surface to volume ratio which allows more interaction between the hydrogen sulfide and the oxidant. In general smaller bubbles oxidize the hydrogen sulfide more rapidly. The bubble size is determined in part by the pore size of the gas diffuser. The mean pore size of the gas diffuser may be from about 0.2 to about 100 microns. The mean pore size may be from about 1 to about 75 microns, from about 5 to about 50 microns, from about 10 to about 40 microns, about 20, about 25, about 30, about 35, or about 37 microns. There may be a single gas diffuser or there may be multiple gas diffusers.

[0013]The packing (4) is used to maximize surface contact between the gas and the oxidizing solution.

The packing may be any type of material that could be used to decrease bubble coalescence, including random packing, structured packing, conventional trays, and high performance trays. Structural packing material could be a manufactured to fit inside the vessel. Random packing may be made from plastic or metal, it may be any shape. Examples of random packing are INTALOX SNOWFLAKE, FLEXIRING, and IMTP. The packing may have a void fraction from about 93% to about 98%, or about 95% to about 97%. The packing may be all of one type of material, or it may be a mixture. It may be a mixture of random packing and structural packing.

[0014]The packing (4) fills about 25% to about 75% of the liquid volume of the oxidizing vessel (6). The packing may fill from about 35% to about 65%, from about 40% to about 60%, about 40%, about 50%, or about 60% of the liquid volume of the oxidizing vessel (6). The vessel may be filled to the top with oxidizing solution, in which case, packing that fills about 50% of the liquid volume also fills about 50% of the vessel volume. Typically the vessel will be more than 50% full of oxidizing solution, more than 70% full, more than 80% full, or more than 90% full.

[0015]Oxidation reduction/pH Probes (7) measure the oxidation potential and the pH of the oxidizing solution (3). The ORP/pH Probes (7) along with the hydrogen sulfide monitor (5) may control the chemical injection pump (8). If the oxidation potential of the oxidizing solution (3) falls below the required level to remove the hydrogen sulfide or the hydrogen sulfide monitor (5) detects hydrogen sulfide in the departing scrubbed gas, then the chemical injection pump (8) injects oxidant from the bulk storage tank (9) through the oxidizing solution distributor (10) until the system removes more hydrogen sulfide.

[0016]The pH of the oxidizing solution may be adjusted by adding acid or base to the solution. It may fluctuate during the removal of hydrogen sulfide. Typically the pH is from about 3 to about 8, it may be from about 5 to 7.5.

[0017]The temperature of the oxidizing solution is measured by the temperature probe (14). The temperature may be adjusted by heating or cooling it. Typically the rate of oxidation of hydrogen sulfide will be faster at a higher temperature. However, the temperature should not be too high as it may increase the rate at which the oxidant decomposes. The temperature of the solution may be from about 55.degree. F. to about 200.degree. F., from about 65.degree. F. to about 150.degree. F., or from about 75.degree. F. to about 120.degree. F.

[0018]The oxidizing solution is a solution that contains one or more dissolved or suspended oxidants. Examples of an oxidant are ***hydrogen peroxide,*** other peroxides, ozone, permanganates, hypochlorite, perchlorate, ammonium cerium nitrate, hexavalent chromium compounds, iodine, and sulfoxides. The solution may be water, an organic solvent such as toluene; an alcohol, such as methanol, ethanol, isopropanol; acetone; dioxane; tetrahydrofuran; acetonitrile; dimethylformamide; dimethyl sulfoxide; esters, such as ethyl acetate; chlorinated solvents, such as chloroform, methylene chloride, carbon tetrachloride; hydrocarbons, such as pentane, hexane, heptane, and heavier hydrocarbons; or combinations of solvents.

[0019]The concentration of oxidant in the oxidizing solution may be not more than about 1%, not more than about 0.5%, or not more than about 0.25% when the concentration of hydrogen sulfide is about 0.25%. The ratio of the oxidizing solution percent concentration to the hydrogen sulfide percent concentration may be about 4:1, about 2:1, or about 1:1.

[0020]As the chemical injection pump (8) introduces additional oxidizing solution into the system the level indicator (13) on the oxidizing solution tank may cause the flow valve (32) to open. The spent oxidizing solution which contains elemental sulfur may then go through the sulfur recovery system (11). After removing the sulfur, the spent oxidizing solution can be recirculated through circulation pump (12) and mixed with oxidant to be used as oxidizing solution (3) which is delivered through the oxidizing solution distributor (10), or discharged as waste water. Flow valve (33) and flow valve (34)

control the direction of the waste water, which is dependent upon the system's demand for additional mixing solution. The flow valve (35) is used to introduce additional water (make up water) when the level indicator (13) indicates a need for additional solution and the ORP/pH probes (7) do not indicate a need for additional oxidant.

[0021]During optimal system performance where the oxidizing solution (3) is removing all or substantially all of the ***hydrogen sulfide, the gas*** may be delivered to the point of demand. The hydrogen sulfide concentration in the scrubbed gas may be less than 400 ppm, 300 ppm, 200 ppm, 100 ppm, or less than 1 ppm.

[0022]While the present disclosure has illustrated by description several embodiments and while the illustrative embodiments have been described in considerable detail, it is not the intention of the applicant to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications may readily appear to those skilled in the art.

EXAMPLES

[0023]Several experiments were performed using an oxidizing vessel with a capacity of 105 gallons (14 cubic feet). Gas containing 65% methane, 39.75% carbon dioxide, and 2500 ppm hydrogen sulfide was bubbled into the oxidizing vessel through a ceramic dome gas diffuser that produced fine bubbles. The gas flow rate was 2 cubic feet per minute. The oxidizing solution was 0.5% ***hydrogen peroxide***.

Example 1

[0024]In this experiment about 6 cubic feet of plastic packing was used in the vessel (approximately 50% of the liquid volume of the vessel) with enough oxidizing solution to fill the vessel to about 12 cubic feet. The temperature of the oxidizing solution was 78.degree. F. The initial ORP was 220 mV

and the pH was 8.1. After 12 minutes, the ORP was 326, the pH was 5.3, and the hydrogen sulfide concentration of the scrubbed gas was 138 ppm. After 25 minutes, the ORP was 338 mV, the pH was 5.2, and the hydrogen sulfide concentration was 96 ppm.

Example 2

[0025]In this experiment about 12 cubic feet of plastic packing was used in the vessel (approximately 100% of the liquid volume of the vessel) with enough oxidizing solution to fill the vessel to about 12 cubic feet. The temperature of the oxidizing solution was 78.degree. F. After 25 minutes, the hydrogen sulfide concentration was 400 ppm.

Example 3

[0026]In this experiment about 12 cubic feet of plastic packing was used in the vessel (approximately 100% of the liquid volume of the vessel) with enough oxidizing solution to fill the vessel to about 12 cubic feet. The temperature of the oxidizing solution was 115.degree. F. After 12 minutes, the ORP was 310 mV, the pH was 5.4, the hydrogen sulfide concentration was 239 ppm.

VITA

Stewart McCollam, the son of Walter D. McCollam and Susan P. Stewart, was born in Baton Rouge, Louisiana on March 12, 1985. After spending his childhood in Baton Rouge, LA and Henderson, NV, Stewart attended high school in Floyds Knobs, IN where he graduated from Floyd Central Jr/Sr High School in June 2003. After graduation, he enrolled at the University of Louisville Speed School of Engineering where he received his B.S. in Chemical Engineering in May of 2008 and his Masters of Engineering with specialization in Chemical Engineering in December 2009. He currently works as the Laboratory Manager at the University of Louisville Food Processing Lab.