Performance of Acid-Gas Anaerobic Digestion for Minimization of Siloxane and Hydrogen Sulfide Produced in Biogas for Energy Recovery

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Master of Science
In
Environmental Engineering

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February 3, 2012
Blacksburg, Virginia

Keywords: multi-stage anaerobic digestion, multi-phase anaerobic digestion, acid gas anaerobic digestion, siloxane, hydrogen sulfide, sludge, biosolids
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ABSTRACT

Organosilicon compounds, which are heavily utilized in personal care products, are typically present, sometimes in high concentrations in the influent of wastewater treatment facilities. During anaerobic sludge digestion, these compounds volatilize and enter the methane gas recovery stream. As the methane is combusted for energy cogeneration, these compounds become oxidized to microcrystalline silicon dioxide and cause damage and potential failure of expensive infrastructure. Adsorption and other catchment methods are typically utilized for removal of these volatilized compounds in order to mitigate their entrance into methane combustion systems. This research investigated the effect of phased anaerobic digestion, specifically acid-gas digestion, on the behavior of the volatilization of these organosilicon compounds, particularly octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) as these are the most abundant volatile silicone compounds present in sludge. A bench scale acid reactor anaerobic digester was operated at varying solids retention times and temperatures in order to quantify biogas effects generated in the downstream gas reactor, which was operated at a constant mesophilic conditions. Results of the research indicated that the addition of an acid reactor did not cause a change in behavior of the D4 and D5 siloxane volatilization in the downstream gas reactor. However, it was observed that hydrogen sulfide gas was decreased in the gas reactor when an acid reactor was utilized, which could permit decreased corrosivity of biogas recovery. Cumulative volatile solids reduction and gas reactor methane yield data did not indicate an enhancement due to utilization of acid-gas digestion.
ACKNOWLEDGEMENTS

This research was fully funded by Hampton Roads Sanitation District (HRSD) in Virginia Beach, Virginia. I would like to express my deep appreciation to HRSD for their financial support, and selfless sharing of equipment and technical expertise throughout the course of this research. The success of this project would not have been possible without their support.

I would like to express my deepest gratitude to Dr. John Novak, my advisor throughout my tenure as a graduate student. He has provided immeasurable insight, patience, and wisdom throughout my learning experiences, in both the classroom and the lab. Although most of the public takes wastewater treatment for granted, people within our industry know that he is one of the great pioneers in our field. I have the utmost respect for him, and feel very fortunate for this experience. My academic committee members, Dr. Charles Bott and Dr. Amy Pruden, provided amazing guidance throughout my research activities. Their willingness to assist me along every rocky road was greatly appreciated. I am grateful for the opportunity to have collaborated with them.

I would like to extend my sincere thanks to Jody Smiley. Her technical expertise, and never ending willingness to aim for perfection in all laboratory analysis is certainly the reason there is any useful data presented in this thesis report. I also appreciate all the bowling tips I picked up from her during our EWR intramural matches. I am also deeply appreciative for the lab guidance provided by Julie Petruska. Her passion for science is infectious and unparalleled. I would like to thank her for pushing me to pay (almost painful) attention to detail, a skill that will certainly stick with me for the rest of my days. I’ll always remember the life lessons shared with me over our weekly burrito lunch downtown, and our time out at her farm. Special thanks are also owed to our departments Administrative Assistants, Betty Wingate and Beth Lucas. Their kindness and eagerness to help students succeed is what keeps our world-class program afloat.

Special recognition should be paid to my undergraduate research assistant, Kshitiz Uprety. He stepped up to help me out, even during his final undergraduate semester when most students would shy away from taking on new, time consuming responsibilities. I would also like to thank my lab mates Jennifer Miller, Andrew Jones, Nirupa Maharajh, Ana Maria Arango, Ritika Kacker, Renzun Zhao, Christopher Wilson, and Jongmin Kim. Without their support, kick starting and maintaining the regimen required by this research would have been impossible.

I would like to genuinely thank the staff at the Christiansburg WWTP, as they provided all the “input” material for my research. They are the kindest group of operators I have ever had the pleasure of working with. A special thanks is also owed to Jonathan Stallings at the Laboratory for Interdisciplinary Statistical Analysis (LISA) at Virginia Tech. I genuinely appreciate the time spent assisting in and generating the statistical analysis of this research, as it proved to be much more complex than anticipated.

Finally, I would like to thank my family. Without my parents pushing me to excel throughout my life, I could not have achieved any of the success I am blessed with today. I also thank my beautiful wife Allison. Her never-ending support throughout this phase of my life was certainly selfless, and everyday I’ll strive to determine a way to repay this immeasurable debt.
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CHAPTER 1 – Introduction

Due to the increase in centralized wastewater treatment facilities, energy prices, and interest in sustainable practices, anaerobic digestion of sludges generated at these facilities is becoming more attractive due to its economic viability and its ability to meet stringent government regulation. In contrast with other sludge management practices, anaerobic digestion permits a high reduction in volatile solids concentration, while producing a methane rich biogas that can be recovered for energy generation. Although full-scale energy recovery from anaerobic digestion has been occurring for decades, a significant amount of laboratory research has been executed in recent years regarding multi-phase digestion. In general, the rationale behind multi-phase digestion is that differing reactor environments, primarily involving variable temperatures and solids retention times, may enable more optimal environments for an overall higher operational efficiency. This study specifically attempts to characterize the behavior of an “acid-gas” digestion series, with specific regard to volatile solids reduction, as well as methane, hydrogen sulfide, and volatile methyl siloxane production. There is limited published literature regarding the behavior of this type of multi-phase anaerobic digestion system, specifically quantifying the above listed parameters.

The original impetus for this research is an outgrowth of the recent construction of an acid-gas system at Hampton Roads Sanitation District’s Atlantic Treatment Plant in Virginia Beach, Virginia. The utility funded this research in order to quantify the effect of differing acid reactor solid retention times and temperatures on both hydrogen sulfide and volatile methyl siloxane production since the plant captures biogas for energy recovery. This report summarizes these laboratory findings.
CHAPTER 2 – Literature Review

2.1  Generation of sludge at treatment facilities

Since its discovery in the early twentieth century, the activated sludge (AS) process has become the conventional mechanism for wastewater treatment in most developed countries. In this process, wastewater is collected, conveyed to a centralized point of treatment, and then subsequently discharged back into the environment. As the influent carbon substrate is utilized for bacterial respiration in the secondary biological treatment of the wastewaters, the concentration of the biomass inherently increases as a product of single and multicellular reproduction. The two primary control variables that are used to achieve the desired level of treatment and plant optimization are mixed liquor volatile suspended solids (MLVSS) concentrations, and solids retention time (SRT) of the MLVSS. The strategy for control of MLVSS and SRT pivots around the volume of waste activated sludge (WAS) removed from the secondary treatment process. This solids wastage, along with removal of solids from upstream primary sedimentation processes, chemical precipitation, and various external municipal solids acceptance, generates voluminous amounts of solids that must be disposed in an economically and environmentally viable manner. Approximately 6.5 billion dry kilograms of sludge are generated annually in the U.S., creating a substantial source of carbon for potential energy recovery and nutrients for agricultural fertilization (NEBRA, 2007).

2.2  Single-stage anaerobic sludge digestion

Although there are many options for sludge stabilization, aerobic and anaerobic digestion are the primary modes of stabilization utilized for volatile solids reduction in most wastewater treatment facilities. Given its lower capital costs, flexibility, and ease of operation, aerobic digestion is a
viable stabilization technique for plants with a treatment capacity less than 20,000 m$^3$ d$^{-1}$ (WEF, 2009). Due to the high costs associated with aeration, anaerobic digestion (AD) is a more viable stabilization technique for high capacity treatment facilities, particularly due to the attractive potential of energy recovery considering a methane (CH$_4$) byproduct production rate of 0.75 – 1.12 m$^3$kg$^{-1}$ volatile solids (VS) destroyed (Metcalf & Eddy, 2003).

Although single vessel AD provides substantial VS reduction (VSR) and methane generation (Parkin and Owen, 1986), research and field operation has indicated a prevalence of operational upsets. These issues may be attributed to inhibitions caused by conflicting bacterial environmental requirements and by-product imbalances in the contrasting microbial communities associated with the overall digestion process (EPA, 2006). Figure 2.2.A illustrates the general multi-step process of AD, each step distinguishing microbial requirements. Five primary communities of microbes are responsible for the digestion process: hydrolytic (hydrolysis) and non-hydrolytic acidogens (acidogenesis), syntrophic acetogens (acetogenesis), and aceticlastic and hydrogenotrophic methanogens (methanogenesis) (Lv et al., 2010; Grady et al., 1999).

Although the growth rate of acetogens and methanogens is lower than that of the hydrolytic acidogens, hydrolysis is typically considered the rate-limiting step. This is due to the complex kinetic operations associated with the complex, slowly degradable influent materials. Therefore, this complexity decreases overall AD efficiency (de Bok et al., 2004). Fortunately, elevated temperatures have been shown to accelerate the kinetic activity of hydrolytic and non-hydrolytic acidogens, thereby decreasing the bottleneck of this rate-limiting kinetic process of hydrolysis.
(Lv et al. 2010). Unfortunately, this desired increase in acidogenic kinetics can generate volatile fatty acids (VFA) at a rate which can overcome the acetogens ability to convert them to acetate, causing a decrease in reactor pH, and therefore inhibition of acetogenesis and methanogenesis (EPA 2006). Due to these contrasting microbial requirements, the optimal conditions for each community of bacteria cannot be available in one common reactor volume due to the varying physiology, kinetics, and metabolic requirements, thereby permitting subpar performance of the overall AD process.
2.3 Multi-stage anaerobic sludge digestion

Stated in publications as early as the 1950’s, Babbit and Baumann (1958) suggested that inhibitory effects of products generated in early processes of AD could be minimized by separating the contrasting digestion process steps into separate physical reactors. Two-phase AD consists of two separate completely mixed anaerobic biological reactors in series. The first reactor is operated to permit acid fermentation, and the following for methane generation. The operating conditions of the initial reactor are tightly controlled to encourage the optimal conditions for acid forming bacteria, while the second downstream reactor receives the effluent of the first reactor and is operated to provide maximum CH$_4$ production and VSR. The suggested advantages of such an operation included the capability of providing an optimal environment for each type of organism, a cumulative overall decrease in required reactor volume and heating requirements, a higher VSR and CH$_4$ production rate, and ease for retrofit of existing digester field installations (Ghosh et al., 1975). Utilization of multi-phase AD has also proven to mitigate foaming problems associated with single-stage AD, minimize odors, and permit the ability to meet Class A pathogen reduction when thermophilic temperatures are utilized in at least one of the AD reactors (Ghosh et al., 1995; EPA, 2006).

Although Pohland and Ghosh (1971) demonstrated the feasibility of phase separation utilizing glucose as the soluble substrate, in 1975 they executed research regarding the potential operational advantages utilizing wastewater sludge as throughput. Utilizing 100% WAS feed, mesophilic temperatures for both reactors, acid phase SRT’s ranging from 11 – 28 hours, and a constant gas phase SRT of 6.46 days (155 hours), it was observed that acidogenic organisms were enriched in the first reactor, while the second reactor contained dominant cultures of
methane formers. Results also indicated that VFA production was directly proportional to VSR in the acid reactor, inferring that the volatile fraction of sludge serves as substrate for the acidogenic organisms. Also, there was no reduction, and often an increase, in chemical oxygen demand (COD) in the acid reactor, indicating that acidogens were unable to use these substances as substrates. It was suggested that the increase in COD could be attributed to the addition of degradation products from the organic solids. The overarching engineering significance of this landmark research was the determination that phase separation enabled an increase in VSR and CH₄ production. When compared to the single-reactor AD control, which was operated at a mesophilic temperature and an SRT equal to 21 days, the two-reactor set-up operated by Ghosh et al. (1975), which employed a cumulative SRT of 7.0 - 7.5 days, yielded a VSR increase of 33 - 40% and a methane yield increase of 0.48 - 0.66 m³kg⁻¹ VS reduced.

Later research by Ghosh (1987) on two-phase AD built upon his earlier research to further explore the effect of varying SRTs, temperatures, solids loading rates (SLR), and pH on process performance. Compared to single-reactor AD (executed at both mesophilic and thermophilic temperatures), the results of this study indicated a superior performance of the two-phase systems, which included the following reactor series temperature configurations: mesophilic → mesophilic, mesophilic → thermophilic, and thermophilic → thermophilic. The highest methane yield occurred with a temperature configuration of mesophilic → mesophilic, with acid and gas phase SRT’s of 2 and 13 days, respectively. The results of this study also revealed that thermophilic acid phase temperatures enhanced hydrolysis, but retarded acetogenesis, particularly as the SRT decreased. Also, in all scenarios, VFA accumulation in the gas reactor was significantly diminished, indicating that the two-phase system experienced enhanced
acetogenic and methanogenic activity relative to that of the single-stage system. Results also indicated that process stability increased with the two-phase system as significantly higher ammonium bicarbonate alkalinity was produced in the gas phase reactor, particularly at shorter SRT (Ghosh 1987).

The first documented study of both pilot and full-scale acid-gas AD fed by 100% WAS indicated an enhanced performance compared to the single-stage AD, as published by Ghosh et al. (1995). This mesophilic mesophilic series digestion was operated with SRT’s equal to 3 and 9 days, respectively. Compared to the single-stage AD, this multi-stage system experienced an increased VSR, even at 50% of the single-stage’s SRT, as well as satisfactory operation at approximately double the SLR. Also, the gas reactor alkalinity was 90% higher than the maximum value reported in the single-stage AD, indicating enhanced kinetic stability of the sensitive acetogenic and methanogenic bacteria due to the upstream acid phase operation. It was also suggested that this ability to increase of the SLR to the acid-gas system, in contrast to the single-stage operation, permitted a significant increase in the biogas production rate of the gas reactor (approximately 500% increase). Additional benefits of this installation were indicated by a complete mitigation of foaming that was experienced with operation of the earlier single-stage AD at the full-scale wastewater treatment facility.

Recent research has taken this principle of enhanced, high-stability operation of multi-stage AD, and attempted to optimize it by varying controlled parameters such as individual reactor SRT and temperatures, SLR, and number of reactors in series. Roberts et al. (1999) suggests that a thermophilic acid reactor can operate at very short SRTs, as low as 4 hours, and provide
performance comparable to a 2-3 day SRT at mesophilic temperatures. This configuration, as well as configurations with thermophilic acid reactor SRTs up to 12 hours, generated methane yields that were generally higher than the single-stage mesophilic control. Bhattacharya et al. (1996) studied the VSR potential with different feed sludge ratios (100% WAS, and 50% primary + 50% WAS) and determined that the maximum VSR increases were 8.7% and 6.0%, respectively, compared to single-stage mesophilic AD. Given this minimal increase in VSR, the author suggested that the increased cost of capital and operations and maintenance (O&M) may not be cost effective at full-scale. This opinion is certainly subject to specific conditions at individual wastewater treatment facilities. Later studies of Kraft-mill sludges indicated that performance of mesophilic → mesophilic series acid-gas AD performed comparably to single-stage thermophilic AD, with approximately equivalent methane yield and VSR (0.17 m$^3$kg$^{-1}$ VS added and 43%, respectively) (Ghosh and Taylor, 1999). Given the variance in performance results, it is apparent that optimal operation of acid-gas AD is highly contingent upon sludge feed type and other controlled parameters including SRT, SLR, temperature, mixing efficiencies, recycling, and the presence of inhibitory constituents. Given the sheer number of influent and control variables, an optimal operation of multi-stage AD has not been fully realized, and is in need of comprehensive future study.

2.4 Generation and consequences of siloxanes in biogas

Volatile methyl siloxanes (VMS) are low viscosity silicone fluids with a low water solubility and relatively high vapor pressure. Due to their low solubility and hydrophobicity, they tend to easily sorb to solids. Since VMS are somewhat volatile, they’re characterized by moderate Henry’s constant values (Kochetov et al., 2001). It is suggested by Watts et al. (1995) that any
unvolatilized VMS compounds ultimately partition to the sludge floc in the AS treatment process.

These compounds are released into the environment as a function of industrial processes and domestic disposal practices. Within the last 20 years, the use of VMS has increased because these solvents are aroma free, widely available, and they’re not included in volatile organic compound (VOC) regulations and therefore not considered a health risk to humans (Rasi et al., 2010). They are primarily utilized for personal care products such as skin creams, stick deodorants, shampoos, and pharmaceuticals, as well as other consumer grade products (e.g. inks, lubricants, adhesives) (McBean, 2008). Based on their behavior of volatility, approximately 90% of disposed VMS are volatilized into the atmosphere (Mueller et al., 1995), while the remaining fraction is ultimately disposed into landfills and wastewater treatment facilities. Recent industry and regulatory attention has been focused toward siloxanes with claims that bioaccumulation is occurring in marine environments. However, disputes regarding disparity between field samples and model predictions have permitted continued usage of these siloxane compounds as a primary carrier compound for many consumer grade personal care products (Genualdi et al., 2011; Reisch, 2011). Properties of D4 and D5 siloxanes are shown in Table 2.4.A, and chemical structures illustrated in Figure 2.4.A.

Table 2.4.A – Relevant siloxane physical properties (McBean, 2008; Oshita et al., 2004)

<table>
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<tr>
<th>Siloxane Abbrev.</th>
<th>Molec. Wt. (g mol⁻¹)</th>
<th>Boiling Pt. (°C)</th>
<th>Melting Pt. (°C)</th>
<th>Vapor Press. (kPa) @ 25°C</th>
<th>Solubility (μg L⁻¹) @ 25°C</th>
<th>Henry's Constant (unitless) @ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D4</td>
<td>296.61</td>
<td>175</td>
<td>17.4</td>
<td>0.13</td>
<td>56.3</td>
<td>259</td>
</tr>
<tr>
<td>D5</td>
<td>370.77</td>
<td>210</td>
<td>-44</td>
<td>0.05</td>
<td>17.2</td>
<td>185</td>
</tr>
</tbody>
</table>
Watts et al. (1995) determined that the majority of VMS that does not partition into the atmosphere ultimately sorbs to the extrapolymeric substances (EPS) present on biofloc utilized in the AS treatment process. Given the sludge management practices employed at AS treatment facilities, sludge is either digested (aerobically or anaerobically), or stabilized by other methods (e.g. lime conditioning, incineration), which ultimately disposes VMS compounds in the atmosphere (volatilization or flare combustion), landfills, or other environmental destinations via sludge land application.

As energy costs rise, it is becoming more economically viable to recover these methane rich landfill and AD biogases for power generation. Even at very low concentrations in solution, the relatively high vapor pressures VMS exhibit at temperatures typically present in landfills and AD readily encourage volatilization in these concentrated gas volumes (McBean, 2008). During combustion of these collected biogases, VMS are oxidized to silicon dioxide ($\text{SiO}_2$) microcrystalline deposits of which lead to catastrophic abrasion of engine parts, or simply accumulate in layers that inhibit critical heat transfer or proper operation of lubrication systems (Ajhar et al., 2010). According to past research by Schweigkofler and Niessner (2001), the primary cyclic siloxane compounds found in AD biogas are in the form of D4 and D5, which has
been further verified by AD biogas testing in the following decade (Oshita et al., 2010; Rasi et al., 2010). The proliferation of these compounds in AD biogas correlates well with the heavy consumption and usage in developed countries (Reisch, 2011).

2.4.1 Control of siloxanes in biogas

While a few methods of biogas VMS abatement are currently employed on a wide scale, many have been, and are currently, under laboratory study in order to attempt an optimal, economically viable capture rate. Non-regenerative adsorption on fixed beds of granular activated carbon (GAC) and/or silica gel resins are the most common field methods, in which primary adsorption beds are replaced with fresh beds, then reversing the sequence, thereby utilizing the lead/lag concept. In this operation, the exhausted sorption bed must be replaced at regular intervals. VMS field removal is also achieved by utilization of fluidized adsorption beds. In this method, a portion of the GAC is continuously transported to a desorber where VMS is removed from the media by hot gas, then permitted to cool before being returned to the fluidized adsorption bed, thereby permitting continuous media regeneration. This mitigates downtime and minimizes operational costs. This method is typically followed by non-regenerative fixed-bed adsorption for biogas polishing (Ajhar et al., 2010). Many studies have indicated that VMS adsorption capacities vary greatly with the class of GAC utilized for abatement. This distinction of GAC can be based upon vendor source, BET surface adsorption, impregnation type, and microporous volume (Boulinguez and Le Clorirec, 2009; Finocchio et al., 2009; Matsui and Immamura, 2009). Unfortunately, as biogas contains a contrasting range of constituents, often present at varying orders of magnitude, competitive adsorption can occur. The presence of hydrogen sulfide (H₂S) has been shown to greatly reduce the adsorption capacity of VMS on GAC (Urban
et al., 2009). In order to mitigate this preferential, yet detrimental adsorption mechanism, an impregnated GAC, biological, or physical-chemical abatement method may be used as a first adsorbent for \( \text{H}_2\text{S} \), while a downstream non-impregnated GAC can be utilized for VMS removal due to uninhibited performance. “Iron sponge” removal technologies, which are further discussed in section 2.5 of this literature review, as well as other iron based media products, are the most common initial absorption technologies utilized in these types of series adsorption operations.

Alternate absorbents, such as silica gel, have also exhibited promise, which specifically has shown a 50% increase in VMS capture capacity compared to GAC in laboratory studies (Wheless and Pierce, 2004). Alumina has also shown promise as another absorbent media, indicating a regeneration capability at 90% of its initial capture potency (Lee et al., 2001). Chemical absorption methods, such as acid absorption, are capable of destroying the siloxane compounds with low pH acids such as nitric or sulfuric, up to levels of 95% removal (Schweigkofler and Niessner, 2001). Unfortunately, safety, corrosion potential, and high operating costs typically make this method unattractive (Urban et al., 2009). Although physical absorption of VMS in pH neutral water has proven unsuccessful (Rasi et al., 2008), absorption utilizing common and proprietary organic solvents has indicated desirable performance (Wheless and Pierce, 2004). Physical absorption does, however, pose the potential of desorption. Due to fluctuating concentrations of VMS within the treated biogas (McBean, 2008), it is possible that these compounds could desorb due to their high volatility during periods of low VMS concentrations or elevated production of biogas (Schweigkofler and Niessner, 2001).
Deep chilling, or cryogenic freezing of biogas flow has gained in popularity in recent years as a viable method for VMS abatement. Schweigkofler and Niessner (2001) chilled AD biogas to a temperature to 5°C, and was only able to achieve a VMS reduction of 18%. When utilizing an increase in pressure at a comparable temperature (25 bar and 4°C, respectively), elimination rates of 50% were observed (Wheless and Pierce, 2004). When temperature was decreased to -30°C at atmospheric pressure, VMS removal rates of 80-90% were observed (Rossol and Schmelz, 2005). Unfortunately, due to high capital and operating costs, this method of VMS abatement is typically only economically attractive at high biogas production or VMS concentrations (Urban et al., 2009). VMS removal via membrane separation has shown promise, suggesting removal rates of up to 80%. Due to high capital and operational costs, this removal technology is not currently viable, although ongoing research is being executed to determine optimal membrane materials for an increase in potential economic viability (Ajhar et al., 2010).

Recent studies have investigated the removal of siloxanes by biological means. Popat and Deshusses (2008) utilized synthetic gas, composed of only humid air and D4, and tested the usage of an aerobic biotrickling filter for removal of D4. The D4 removal in the filter was maximized at 43% at an empty bed residence time (EBRT) of 19.5 minutes. An anaerobic biotrickling filter removed 15% at an EBRT of 4 minutes; but unfortunately, no other EBRT’s were simulated as part of the study. It is suggested that the necessity for high EBRT’s can be explained by poor degradability of D4, or limited mass transfer from the gas phase into the biofilm.
While the majority of VMS abatement practices are achieved in the gas phase, attempts of removal in the liquid phase prior to AD have been investigated in various studies. Research into the effect of peroxidation has shown potential. Appels et al. (2008b) added multiple forms of peroxide into solution prior to AD where this strong oxidant was capable of oxidizing a variety of organic and inorganic pollutants. All peroxides utilized in this research were reported to remove 40-50\% of D4 and D5 concentrations from the sludge volume. One tested peroxide, dimethyldioxiranes, was capable of 85\% removal of D4. The author suggested that the decrease in D4 and D5 siloxane concentration was a function of two primary, simultaneously occurring mechanisms: breakdown into lower molecular weight siloxanes and partial oxidation to silicones and silica, and volatilization into the atmosphere due to destruction of the EPS in which the siloxanes are sorbed (Appels et al., 2008b). Research by Klingel et al. (2002) has also shown promising results for stripping, utilizing both mesophilic and thermophilic temperatures. The results suggest that pH had little effect on stripping efficiency; rather, an increase in temperature and water content of the sludge led to faster outgassing of hexamethyldisiloxane (L2). The authors concluded that stripping appears to be feasible for VMS reduction in the liquid phase, particularly in an intermediate process step between sludge heating and digestion.

2.5 Generation and consequences of hydrogen sulfide in biogas

Hydrogen sulfide is a colorless, flammable, poisonous gas, and is highly soluble in water (2,650 mg L\(^{-1}\) at 35°C) compared to the low solubility of CH\(_4\). Sulfide (S\(^{-2}\)) is a byproduct of both the degradation of sulfur containing organics and the reduction of oxidized sulfur compounds during AD. Due to typical operating pH ranges of AD reactors, S\(^{-2}\) becomes protonated to bisulfide (HS\(^{-}\)) and H\(_2\)S where it acts as a weak acid. The generalized reaction is as follows:
Organic Matter + SO$_4^{2-}$ ---> S$^{2-}$ + H$_2$O + CO$_2$; S$^{2-}$ + 2H$^+$ ---> H$_2$S

Consequently, a pKa value of 7 defines the following relationship H$_2$S $<$---> HS$^-$ + H$, indicating that comparable values of both H$_2$S and HS$^-$ exist at near neutral pH operating conditions of conventional AD (Metcalf & Eddy, 2003). As H$_2$S reaches saturation in the liquid phase, methanogens present in AD sludges produce low solubility CH$_4$ and CO$_2$, thus facilitating H$_2$S to come out of solution into the gas phase. H$_2$S concentrations in reactor headspace are then further oxidized by sulfur oxidizing bacteria present upon moist surfaces on tankage and equipment surfaces, thereby forming sulfuric acid (H$_2$SO$_4$). The production of this strong acid, and the presence of trace amounts of headspace molecular oxygen (O$_2$) that can be introduced by poorly sealed reactors or dissolution from the influent sludge, creates a corrosive environment for these equipment surfaces.

The presence of proteins has been confirmed to be readily abundant in the organic matter of AS treatment facilities (Dignac et al., 2000), and their degradation contributes heavily to the generation of H$_2$S during AD. This is a major contributor to H$_2$S production considering that the carbohydrate, lipid, and protein content constitute approximately 90% of the organic load of biosolids processed in AD (Batstone et al., 2002). In general, the formation of H$_2$S is due to the enzymatic hydrolysis of proteins into cysteine, a sulfur containing amino acid, which is then further degraded into H$_2$S as shown by the following equation (Higgins et al., 2004):

Proteins ---> Polypeptides ---> Cysteine [C$_3$H$_6$O$_2$NSCH$_3$] ---> H$_2$S
The presence of sulfate (SO$_4^{2-}$) in AD influent sludges also readily contributes to the production of H$_2$S. During AD, SO$_4^{2-}$ is reduced by two primary communities of sulfate reducing bacteria (SRB): incomplete oxidizers (e.g. reduction of lactate to acetate and CO$_2$), and complete oxidizers (e.g. completely convert acetate to CO$_2$ and HCO$_3^-$) (Chen et al., 2008). As a function of this mechanistic reduction of SO$_4^{2-}$, two general types of inhibition can occur in the AD sludge volume: S$^2$ toxicity to the communities of anaerobic microorganisms present in the AD reactor volume, and SRB competition for organic and inorganic substrate (Colleran et al., 1998).

Research has indicated that S$^2$ does not inhibit acidogenic activity as severely as it does methanogenic populations. Research by Maillacheruvu et al. (1993) shows that hydrolytic organisms involved in the conversion of lactate and glucose into simpler products were not adversely affected by S$^2$ toxicity. Further research by O’Flaherty et al. (1998b) indicates that acetogens were found to be less susceptible to S$^2$ inhibition than methanogens, and that toxicity levels were comparable to that of the SRB. Sulfide exhibits extreme toxicity toward methanogens, thereby permitting significant inhibition of methane production (Karhadkar et al., 1987).

SRB’s are capable of complete or partial degradation of branched and long-chain fatty acids, ethanol and other alcohols, organic acids, and aromatic compounds (Oude Elferink et al., 1994). During AD, SRB compete with methanogens, acetogens, or fermentative microorganisms for reduced substrate such as H$_2$, propionate, and other organic electron donors, preferentially in this listed order (Colleran et al. 1995; Laanbroek et al., 1984).
In general, competition for substrate does not occur in the initial hydrolysis stage of AD. Although a few species of SRB are capable of utilizing simple sugars and amino acids as substrate (Klemps et al., 1985; Min and Zinder, 1990), appreciable growth does not typically occur utilizing acidogenic substrate since SRB cannot outcompete the faster growing, monomer degrading fermentative acidogens (Postgate, 1984).

In reference to acetogenic competition, SRB’s should heartily outcompete acetogens for substrate on a thermodynamic basis; however, many confounding factors affect this performance (e.g. COD/\(\text{SO}_4^{2-}\) ratio, SRB population, \(\text{S}^{2-}\) toxicity), rendering complex and contradictory research results in published literature (Chen et al., 2008). The results of multiple studies have indicated that SRB’s play a primary role in the conversion of propionate to acetate as sulfidogenic oxidation is the key degradation pathway of this VFA substrate (Ukei et al., 1988; Qatibi et al., 1990; Heppner et al., 1992; Colleran 1994, 1998). SRB show a higher consumption and growth rate when utilizing this VFA, compared to other propionate-utilizing syntrophic species present in the AD sludge (Colleran et al., 1995). In an upflow anaerobic sludge blanket reactor (UASB), a synthetic feed with a COD/\(\text{SO}_4^{2-}\) ratio (0.5) permitted a competitive edge for SRB over methanogens, as they exclusively utilized butyrate as substrate (Visser et al., 1993a). When the COD/\(\text{SO}_4^{2-}\) ratio was increased to 3 and 5.6, both sulfidogenic and methanogenic bacteria were present, indicating competition for butyrate and ethanol (Colleran et al., 1998; O’Flaherty et al., 1998a), which can be attributed to a lower affinity of SRB to these substrates (Laanbroek et al., 1984; Overmeire et al., 1994).
Although methanogenesis appears to occur simultaneously with SO$_4^{2-}$ reduction (Oremland and Taylor, 1978), hydrogenotrophic methanogens cannot outcompete hydrogenotrophic SRB for H$_2$ oxidation in typical AD conditions with regard to thermodynamic and substrate affinities (Zinder, 1993). This theory has been confirmed by a considerable amount of research in which H$_2$ oxidation is primarily executed by hydrogenotrophic SRB’s in ADs volumes containing SO$_4^{2-}$ (Visser et al., 1993b; Alphenaar et al., 1993; Harada et al., 1994; Colleran et al., 1998; O’Flaherty et al., 1999). Later research by Colleran and Pender (2002) suggests that an increase in temperature from mesophilic (37°C) to thermophilic (55°C) permits a shift in competitive edge to hydrogenotrophic methanogens dominance over the SRB’s in H$_2$ oxidation.

A literature review of the competition between aceticlastic SRB’s and methanogens also yields contradictory conclusions. The outcome of some research has suggested that SRB can successfully compete (Rinzema et al., 1988; Alphenaar et al., 1993; Stucki et al., 1993; Gupta et al., 1994), while many studies have suggested that aceticlastic methanogens clearly dominate for acetate utilization (Rinzema et al., 1988; Isa et al., 1986, b; Visser et al., 1993b; Omil et al., 1996; Oude Elferink et al., 1994; Colleran et al., 1998; O’Flaherty et al., 1998a; Colleran and Pender, 2002). In one study, Choi and Rim (1991) determined that the COD/SO$_4^{2-}$ ratio determined the dominant utilization. The results of this study indicated that aceticlastic methanogens dominated at ratios above 2.7, SRB below 1.7, and active competition occurred at ratios between these two values. Other research by O’Flaherty et al. (1998b) suggests that contrasting performance between aceticlastic methanogens and SRB is based upon differing growth behavior at varying pH values, while Oude Elferink et al. (1994) observed that initial population values dictated competitive behavior. Studies by Colleran and Pender (2002)
indicated that aceticlastic methanogens dominated due to the SRB displaying a lower affinity to acetate, compared to other readily available substrate. Considering many of these factors, a dominant competitive edge for SRB may simply be attributed to their lowered $K_s$ values compared to the aceticlastic methanogens present in typical AD environments (Rinzema and Littinga, 1988; Gupta et al., 1994; Harada et al., 1994).

2.5.1 Control of hydrogen sulfide in biogas

Solubility and dissociation constants of $\text{H}_2\text{S}$ have been quantified in previous research, and results have confirmed that the behavior of this weak acid is highly dependent on liquid temperature. Figures 2.5.A and 2.5.B, from Sun et al. (2008), illustrate the behavior of $\text{H}_2\text{S}$ at varying liquid temperatures. In general, it may be concluded that both the gas solubility and pKa values of $\text{H}_2\text{S}$ decreases as the liquid temperature increases.

There is not a considerable amount of literature discussing the affect multi-stage digestion on the behavior of $\text{H}_2\text{S}$ production, particularly the beneficial performance of reactors utilized for gas recovery. However, promising research indicates that $\text{SO}_4^{2-}$ can be successfully reduced in the acidogenic phase of anaerobic digestion. In a study by Mizuno et al. (1998), SRB were capable of 90% reduction of $\text{SO}_4^{2-}$ in a mesophilic reactor (35°C) within an 8 hour SRT, up to a feed concentration of 1,200 mg $\text{SO}_4^{2-}$ L$^{-1}$.

There are many forms of $\text{H}_2\text{S}$ control to reduce this corrosive gas in both the liquid and gas phase. The most commonly employed method for control of reduced sulfur species present in the liquid phase of AD is the addition of ferric chloride ($\text{FeCl}_3$) for the ultimate precipitation of ferric
Figure 2.5.A – Comparison of \( \text{H}_2\text{S} \) Henry’s constants (\( K_{\text{H}_2\text{S}} \)) at varying liquid temperatures utilizing different models by Weiss (1970), Roberts (1985), Hogfeldt (1982), Carroll and Mather (1989), and Suleimenov and Krupp (1994) (Sun et al., 2008)

Figure 2.5.B – Comparison of \( \text{H}_2\text{S} \rightleftharpoons \text{HS}^- \) dissociation constant (\( K_{\text{a},1} \)) at varying liquid temperatures utilizing different models by Barbero et al. (1982), Millero (1986), Kharaka (1989), and Suleimenov and Seward (1997) (Sun et al., 2008)
sulfide (FeS). Although this is an effective and mature method for mitigation of H\textsubscript{2}S gas production, it can add sludge biosolids handling volumes (e.g. dewatering, hauling), depending on the concentrations of sulfur present in the AD sludge volume.

When energy is to be recovered from the biogas generation, “iron sponge” is the most common form of treatment for removal of reduced sulfur compounds. This technology employs an iron oxide impregnated wood chip that selectively adsorbs H\textsubscript{2}S and mercaptans from AD biogas. The primary active ingredients are hydrated iron oxides (Fe\textsubscript{2}O\textsubscript{3}). H\textsubscript{2}S removal with this technology requires either batch operation with discontinuous regeneration, or with a small flow of air in the gas stream for continuous regeneration (Abatzoglou and Bolvin 2009). Based on data available from the widespread usage of this removal technology, 85% removal efficiencies of H\textsubscript{2}S are typical (Anerousis and Whitman, 1985). Although iron sponge operation is both simple and effective, the process is chemical intensive and requires high operating costs. Additionally, a continuous stream of spent waste material is accumulated, and media change-out is labor intensive. Also, in some instances spent media can be considered hazardous, requiring special, expensive disposal requirements. Alternative adsorbents have been introduced that achieve comparable levels treatment (e.g. SulfaTreat®, Sulfur-Rite®, and Media-G2®). Utilization of these technologies is still subject to case-by-case field conditions, and continued lab trials for optimization (Abatzoglou and Bolvin 2009).

In order to manage H\textsubscript{2}S generated by AD, a common abatement method is the utilization of GAC. This method can be used for abatement of odors associated with H\textsubscript{2}S gas discharge into the atmosphere, or as a pretreatment or coupled treatment practice for mitigation of inhibited
VMS abatement by other concurrently operating removal equipment. GAC is generally available in three forms: catalytic-impregnated (regenerable), impregnated carbons, and non-impregnated carbons. Catalytic GAC is manufactured with urea, or another nitrogen containing compound (i.e. NH₃), and these added compounds react with GAC surface sites adding nitrogen functionalities. Although catalytic GAC is said to be regenerable, the waste streams created by this activity are quite acidic and require large amounts of water. Plants that currently utilize water regeneration report diminishing efficiencies within the first two or three washes. Impregnated GAC is a carbon media to which a solid or liquid compound has been added prior, during, or after activation. The primary compounds utilized for impregnation include sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium iodide (KI), and potassium permanganate (KMnO₄). GAC impregnated with a strong base is considered regenerable by utilizing the same strong base after desorption of the H₂S and other constituents collected from the biogas (Norit Americas, Inc, 2007). Non-impregnated GAC is highly effective for removal of VOC, particularly from industrial streams. Because of its relatively lower affinity for H₂S, utilization for its removal has been somewhat limited (Abatzoglou and Bolvin 2009). Research by Adib et al. (1999) has indicated that local pH plays a significant role on both the GAC adsorption capacity and speciation of the H₂S. When the GAC surface is acidic, the sulfur is highly oxidized, thereby producing more water-soluble species and less elemental sulfur. Also, the total GAC sorption capacity significantly diminishes with increasing acidity. A slight increase in pH (~0.5) can result in an increase in adsorption capacity of approximately 1500%. Further research by Abid et al. (2000) and Bagreev et al. (2001) on different non-impregnated GAC sources (coconut shell and bituminous coal, respectively) concluded that the choice of GAC utilized for H₂S adsorption
should be made based on pH conditions in the AD environment, as their performance can vary significantly. They reported that pH values above 5 lend to considerable H₂S adsorption capacities.

Although H₂S gas scrubbing has major applications in large-scale industrial operations, this technology has not been widely accepted for use in AD biogas operations due to some major limitations (Abatzoglou and Bolvin 2009). It is generally impossible to effectively remove all desired contaminants within one stage, and undesirable byproducts may be developed when attempting to do so, thereby requiring multiple stages. Also due to poor gas-liquid transfer coefficients, large scrubbing volumes are required (Couvert et al., 2008).

Biological methods for the abatement of H₂S in the gas phase have grown in popularity, and are becoming more common in full-scale practice as a viable alternative to media adsorption technologies. Since biogas typically contains ~30% CO₂, this provides a suitable source of inorganic carbon for effective utilization of chemotrophic *Thiobacillus* bacteria to oxidize HS⁻ (dissociated from H₂S) in a redox reaction to elemental sulfur (S⁰) in limited oxygen conditions. The overall reaction occurs as follows (Abatzoglou and Bolvin 2009):

\[
\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^- \quad \text{(dissociation)}
\]

\[
\text{HS}^- + 0.5\text{O}_2 \rightarrow \text{S}^0 + \text{OH}^-
\]

There are three general categories of biological H₂S desulfurization technologies: bioscrubber, biofilter, and biotrickling filter. The last two listed technologies are very similar, the primary difference being that a nutrient solution is trickled in the latter type. The primary performance
attributes for both biofiltration, trickling and non-trickling, include porosity, alkalinity, pressure drop, fluid behavior, nutrient concentration, and accumulation of solids. One commonly utilized propriety technology, THIOPAQ®, is a viable technology for large biogas operations. An initial scrubber, operating at a pH range of 8-9, dissociates H₂S to HS⁻ in solution. This solution is then delivered to a bioreactor where the chemotrophic bacteria oxidize the HS⁻ to S⁰, simultaneously generating OH⁻ for use in the first stage (dissociation). This technology touts a guaranteed outlet concentration of 4 ppmv or less, even at a 100% H₂S inlet concentration (Abatzoglou and Bolvin 2009). Since biological H₂S abatement in biogas is an emerging technology, many new proprietary technologies are beginning to enter the municipal market, including Biorem and BioGasclean. Unfortunately, literature and product information describing the treatment mechanisms or performance were not readily available for inclusion in this literature review.

2.6 Summary

Although sludge generation and management comprise a significant portion of capital and O&M expenditures at wastewater treatment facilities, energy recovery from biogas capture is becoming a more viable, economically attractive practice for offsetting these costs. Research activities with respect to both single-stage and multi-stage AD have attempted to identify the responsible biological mechanisms, and quantify optimal AD conditions in order to maximize non-detrimental energy recovery practices for full-scale implementation. Ongoing research into multi-stage, temperature-phased, and pressure treated AD have indicated promising results; however, additional research is warranted due to the plethora of potential field conditions at full scale treatment facilities, each with contrasting feed sludge conditions, and operational constraints. Although a few pioneering utilities have implemented these AD schemes in full-
scale, widespread acceptance of these laboratory research studies is unlikely to occur until practical tankage configurations, temperature requirements, and ease of operation have been fully realized.

In order to enhance the cost-effectiveness of AD energy recovery, the minimization, or potential abatement of H$_2$S and VMS concentrations in the biogas also needs to occur. In current full-scale operations, the presence of these two compounds is not simply a nuisance; rather, they inflict significant, and often catastrophic damages to expensive tankage and cogeneration equipment. Many general and proprietary technologies exist for management of these compounds, with varying degrees of success and cost-effectiveness. While H$_2$S can be successfully controlled in both the liquid and gas phases, current technologies for control of VMS are only capable of management in the gas phase. Based on this literature review and current field practices, there are no viable biological means, which are already utilized as part of typical AD, for management of these two detrimental compounds.

2.7 References


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CHAPTER 3 – Performance of Acid-Gas Anaerobic Digestion for Minimization of Siloxane and Hydrogen Sulfide Produced in Biogas for Energy Recovery

3.1 Introduction

3.1.1 Background

Since its discovery in the early 20th century, the utilization of activated sludge (AS) for the treatment of municipal and moderate-strength industrial wastewaters has been an extremely viable and effective practice and is the primary mechanism for wastewater treatment in most developed countries. As a function of cell metabolism and reproduction, excess microbial cell mass (sludge) is generated from the AS treatment process and must be wasted from the process since an uncontrolled increase in its concentration may lead to operational failure of a wastewater treatment plant (WWTP). In order to minimize both the hauling and disposal costs associated with the removal of sludge and the influent solids accumulated from primary treatment steps, solids reduction can be achieved by either aerobic or anaerobic digestion. Although either method of digestion may be employed by a treatment facility, anaerobic digestion (AD) is typically more attractive for larger facilities due to the production of methane (CH$_4$) as a recoverable energy source (0.35 m$^3$/kg COD removed) (Hall, 1992) and a nutrient rich biosolid byproduct that may be utilized as an agricultural, commercial, or domestic fertilizer. However, in order to achieve these beneficial end products, a significant amount of operational cost, ranging from 25-65% of the WWTP’s total operational cost, must be expended to effectively operate these digestion facilities (Perez-Elvira et al., 2006).

Multiple methods of AD have been tested in both bench and full scale in order to quantify the production of CH$_4$ and reduction of pathogens in biosolids. In general, AD can be conceptualized
within four generalized steps. The first step is the hydrolysis of complex particulate organic matter to soluble substrates (amino acids, simple sugars, and long chain fatty acids). Secondly, the sugars are converted into volatile fatty acids & alcohols (Batstone and Jensen, 2011) and amino acids are converted to ammonium, volatile fatty acids, and alcohols by acidogenic bacteria (acidogenesis). Thirdly, acidogenesis products are converted to acetate and hydrogen by acetogenic bacteria (acetogenesis). Lastly, CH₄ is generated (methanogenesis) by aceticlastic methanogens that convert acetate into CH₄ and carbon dioxide and hydrogenotrophic methanogens reduce carbon dioxide and hydrogen into CH₄. There has been a recent focus on multi-stage AD in order to isolate these steps for optimization of digestion and to maximize the beneficial by-products of the process. AD is a complex, multi-step process involving many types of bacteria, some of which require distinct conditions that cannot be met in a single AD reactor. The multi-stage AD process studied within the scope of this research is a two-stage acid-gas system in which the process of methanogenesis is physically separated from the processes of hydrolysis, acidogenesis, and acetogenesis in optimal environments. Previous results of acid-gas anaerobic digestion research and field operation have indicated mixed results for VS reduction (VSR), CH₄ production, and COD removal, all of which were dependent on the type of waste digested, and operational scheme of the digestion series (Demirel and Yenigün, 2002).

Siloxanes are a group of silicones that contain Si-O bonds with radicals primarily comprised of methyl groups. Widely utilized in personal care products, their properties include low flammability, water repelling, and resistance to detrimental temperature effect, all while exhibiting low toxicity, biodegradability in the atmosphere, and are compliant with volatile organic compound (VOC) regulations. Most siloxane compounds are considered highly volatile
(high vapor pressure and low solubility) and will dissipate into the atmosphere where they decompose into silanols (Si-OH) (Dewil et al., 2006). However, due to their heavy industrial and domestic usage, high volumes are ultimately discharged as influent to wastewater treatment facilities, and it is estimated that 17,000 tons/year is discharged into wastewater in the United States (Hagman et al., 1999). Although the majority of detrimental siloxanes are removed from the bulk solution in the activated sludge treatment process (Mueller et al., 1995), they are preferentially absorbed onto the extracellular polymeric substances (EPS) of sludge floc (Neyens et al., 2004) thereby increasing the concentration of siloxanes when this sludge is wasted and diverted to the digestion facility. When anaerobically digested, siloxanes may be released from the floc and EPS structures, and ultimately volatilize into the biogas along with a portion of the concentration already present in the bulk solution. The primary siloxane compounds present in the biogas are octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) due to their high vapor pressure and overall abundance in the digested sludge (Schweigkofler and Niessner, 2001). Depending on the sludge feed characteristics and digestion operation efficiency, the biogas produced can be comprised of 60-70% (by volume) CH₄ (Appels et al., 2008); therefore, the energy recovery can be very attractive for large facilities. Combustion of this D4 and D5 siloxane containing biogas for energy recovery activities produces SiO₂, a microcrystalline silica, having chemical and physical properties very similar to that of glass. This damage to the energy recovery systems can cause a decrease in efficiency, higher maintenance costs, and potential overall engine failure, and causation occurs on multiple fronts: abrasion and overheating to engine and motor parts, and coating of spark plugs, pistons, cylinder heads, valve faces, and catalytic exhaust gas treatment systems (Dewil et al., 2006). All methods currently utilized for siloxane abatement involve removal from the gas phase, with the most
common method being adsorption to activated carbon. Although effective, adsorption capacities must be considered since biogas contains a broad range of other compounds, primarily hydrogen sulfide (H\textsubscript{2}S) and other organics, often in concentrations ranging over several orders of magnitude. Therefore, large adsorption capacities for these targeted siloxane compounds are required for adequate biogas pre-treatment performance (Schweigkofler and Niessner, 2001). Other adsorbents used for pre-treatment include molecular sieves and polymer beads. Other less common forms of siloxane gas abatement include absorption using high boiling organic solvents, cryogenic condensation, and chemical catalysis by use of caustic or acidic solutions in which the silicon-oxygen bonds are hydrolyzed (Dewil et al., 2006).

An undesirable effect associated with anaerobic digestion is the generation of H\textsubscript{2}S, which is generally created by the degradation of sulfur containing organic matter and the reduction of sulfite and sulfate. As the maximum hydrogen sulfide solubility is reached in the bulk sludge, it enters the gas phase and is highly corrosive to digestion and energy recovery systems. Because this is a costly issue, it is typically controlled in the liquid phase by the addition of iron compounds, such as ferric chloride (FeCl\textsubscript{3}), in order to precipitate sulfur as FeS for ultimate discharge with the digested sludge. It can also be controlled in the gas phase upstream of the energy recovery systems by adsorption, which is typically achieved by usage of KI impregnated activated carbon where H\textsubscript{2}S is converted to elemental sulfur.

To date, there is no published literature regarding the effect of multi-stage AD, specifically acid-gas, on the behavior of siloxane and H\textsubscript{2}S biogas concentrations in the second stage reactor, which is typically utilized for biogas recovery. The results of such a study could provide merit to the
addition of acid phase digesters to not only enhance the overall VSR and CH₄ production efficiency, but minimization of siloxane and H₂S produced in the gas reactor’s recovered biogas.

### 3.1.2 Research Objectives

1. To characterize performance of acid-gas anaerobic digestion at acid reactor operating temperatures of 37, 42 and 55°C, and SRT’s of 2, 3, and 5 days.

2. To determine optimal conditions, if any, for minimization of D4 and D5 siloxanes in biogas from the gas phase reactor.

3. To determine optimal conditions, if any, for minimization of H₂S in biogas production from the gas phase reactor.

### 3.2 Materials and Methods

#### 3.2.1 Research Approach

Bench-scale anaerobic sludge reactors (digesters) were set up in a thermostat-controlled constant temperature room at 37°C. Two reactors were utilized for acid-gas digestion studies, while one independent reactor was used as a control, or conventional single-stage, digester. A raw feed sludge mixture was fed into the acid reactor, and effluent from this reactor was subsequently fed into the gas reactor. Independent of the acid-gas digestion series, a raw feed sludge mixture was fed into the control reactor. In the interest of time and available materials, the control reactor was only utilized concurrently with sampling campaigns 2 and 3. The SRT and temperature of the acid reactor were operated in varying combinations to determine the effect this operation would have on the downstream gas reactor. Table 3.2.1.A indicates the acid reactor operational
parameters used in this study. Both the gas and control reactors were held at a constant SRT of 15 days and a temperature of 37°C (mesophilic).

<table>
<thead>
<tr>
<th>Sampling Campaign</th>
<th>Acid Reactor SRT (Days)</th>
<th>Acid Reactor Temp. (°C)</th>
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<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>37</td>
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<td>2*</td>
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<td>37</td>
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<td>6</td>
<td>2</td>
<td>55</td>
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*Control reactor was also operated during these campaigns

The acid reactor was comprised of a 4 L HDPE cylindrical container manufactured by Nalgene (model 2125-4000). The gas and control reactors were comprised of a 25 L HDPE cylindrical fermenting vessel, with a conical bottom, manufactured by Hobby Beverage Equipment Company (model f6.5). Mixing of the reactor contents was achieved by recirculation of the reactors’ headspace gas from its top to the reactor bottom utilizing 6.4 mm diameter PVC tubing and a peristaltic pump manufactured by Cole Parmer (model 7553-70). The mixing intensity was set at 50% of the pump motor capacity. In order to encourage homogeneity, 100% of the motor capacity was utilized for a ten-minute period prior to reactor sampling (wasting), and after each subsequent reactor feeding. Heating tape, manufactured by Thermolyne (model BSAT101-100), was used to increase the temperature of the acid reactor. Utilization of fiberglass insulation wrapping around the reactor, coupled with adequate gas mixing ensured uniform, reliable heating of the complete reactor sludge volume. Figure 3.2.1.A illustrates the reactor set-up and flow scheme.
Figure 3.2.1.A – Laboratory reactor set-up and flow scheme
Headspace biogas from each reactor was collected utilizing 4.8 mm diameter PVC tubing and 1 L and 25 L Tedlar® bags manufactured by Restek (model 22050 and 22044, respectively). During each sampling event, 1 L bags were connected to each reactor for 1 to 3 hours, depending on the biogas production rate, in order to obtain discrete samples. The 25 L bags were connected during periods of non-discrete sampling in order to quantify the average daily biogas production volume.

The anaerobic reactors were seeded with anaerobically digested sludge obtained from the Town of Christiansburg Wastewater Treatment Plant in Christiansburg, Virginia, USA. The pH and VS reduction of each reactor was monitored prior to any sampling to ensure the reactors were at steady state. When the results of these tests showed a variation of 5% or less for five consecutive days, it was determined that the reactor had reached steady state. After steady state was achieved, a sampling period was executed to gather data for the analysis.

The feed for the acid and control reactors was a blend of primary and thickened waste activated sludge (tWAS) collected from the Town of Christiansburg Wastewater Treatment Plant. This plant was chosen for this research because it did not have significant industrial dischargers contributing to the plants influent, did not employ any control measures for the production of hydrogen sulfide in the anaerobic digesters, and was located in close proximity to the laboratory in which the bench scale reactors were operated. The primary sludge was withdrawn from the plant’s rectangular primary clarifiers, and the waste activated sludge was withdrawn from the plant’s circular secondary clarifiers, then thickened by a gravity belt thickener into tWAS. After collection from the treatment facility, the primary sludge was screened through a 4.8 mm wire
screen to remove large inert material and prevent clogging within the reactors. After screening, this primary sludge was mixed with the tWAS, 70% and 30% by volume, respectively. This sludge mixture was either decanted or diluted with Town of Blacksburg potable tap water in order to achieve approximate TS and VS concentrations of 2.7% and 2.2%, respectively. Sodium sulfate was then added to this sludge mixture in order to achieve an approximate sulfate concentration of 65 mg/L. Addition of sulfate to the sludge feed ensured adequate hydrogen sulfide production in the reactors in order to achieve research objectives. The sulfate concentration was also representative of wastewater quality found within the research funding agency’s wastewater treatment facilities due to saltwater intrusion. This sludge feed mixture was stored at 4°C until fed to the acid and control reactors. The acid reactor was manually slug fed 3 or 4 times per SRT (1 or 2 times daily), depending on its SRT. The gas and control reactors were manually slug fed once per day. In order to ensure more ideal SRT’s, waste sludge was typically withdrawn from each reactor, and then reactor feeding followed. During sampling, the SRT’s of each reactor were held constant by maintaining a consistent reactor volume, as well as a uniform feeding and wasting volumes.

3.2.2 Analytical Methods

Feed and reactor liquid samples were analyzed for TS, VS, and COD in accordance with Standard Methods (APHA, 1998). Measurements for pH were taken with an Accumet meter and probe (model 910 and 13-620-287A, respectively). Liquid temperature measurements were taken with a mercury thermometer. All CO₂, CH₄, and H₂S reactor headspace biogas measurements were taken with a BioGas-CDM instrument, as manufactured by Landtec. Reactor headspace gas production was measured with a peristaltic pump (Cole Parmer model 7553-70), which
withdrew reactor biogas collected in a 25 L Tedlar® bag. The peristaltic pump was calibrated daily with a known gas volume.

Feed and reactor sludge samples were preserved at -48°C, then thawed for SO₄ analysis. Samples were filtered through a 0.45 μm nitrocellulose membrane filter (Millipore model SA1J791H5) before analysis. Sulfate was analyzed using an ion chromatograph (model DX120, Dionex) equipped with an AG9-HC guard column (model 051791, IonPac) and an AS9-HC analytical column (model 051786, IonPac). The eluent was 9:0 mM Na₂CO₃, and the flow rate was 1:0 mL= min.

Feed and reactor sludge samples were preserved at -48°C, then thawed for VFA analysis. Samples were filtered through a 0.45 μm nitrocellulose membrane filter before analysis. The samples were acidified by adding 85% phosphoric acid at a rate of 1% v/v, then analyzed using gas chromatography with flame ionization detector (model HP-5890) equipped with a Supelco Nukol column utilizing the following gas flow rates: N₂ = 14 mL/min, Air = 450 mL/min, H₂ = 44 mL/min, He = 16 mL/min. The initial oven temperature was set to 80°C and ran isothermally for 3 minutes, then increased at 6°C/min for the next 10 minutes.

D4 and D5 siloxane compounds within the reactor headspace biogases were analyzed using Thermo Scientific gas chromatography and mass spectrometry (models Focus and DSQ II, respectively). One-hundred μL of headspace biogas was injected into the injection inlet (250°C), utilizing helium as a carrier gas (1.2 mL/ min at 250°C), into a Restek GC column (model Rxi®-5Sil MS, 30 m x 0.25 mm x 0.25 μm). The initial oven temperature held constant at 40°C for 1
minute, was increased to 100°C at a rate of 15°C/min and held constant for 1 minute, then finally increased to 200°C at a rate of 20°C/min and held constant for 1 minute. The transfer line between the GC and MS was heated to 300°C. The MS scanned in full range mode, from 50-450 amu. Peak areas of each of the D4 and D5 siloxane compounds were integrated using Thermo Scientific Xcalibur software, with molecular weights of 281 and 73 g/mol, respectively, used to identify each compound. The concentrations in each sample were quantified by comparing the sample peak area with the area of a standard curve, which was comprised of five data points reflective of varying stock solutions of D4 and D5 siloxanes prepared in a methanol solution.

3.3 Results and Discussion

3.3.1 Acid-Gas Digestion Performance

As a function of the operational environment, efficient acidification of soluble complex influent solids is permitted and desired in the acid reactor prior to transfer to the downstream gas reactor. The first two steps of AD, hydrolysis and acidogenesis, are encouraged to occur in this initial reactor to increase overall efficiency, particularly since hydrolysis is considered the rate-limiting step of the overall digestion process (Eastman and Ferguson, 1981). Table 3.3.1.A indicates the average pH and total VFA concentrations from the laboratory analysis. The total VFA concentration is a sum of acetic, propionic, isobutyric, butyric, isovaleric, and valeric acids.

The acid reactor data in Table 3.3.1.A shows that pH is significantly lower at 37°C for SRTs of two and three days. The high acid reactor VFA concentrations in these two conditions indicate that hydrolysis and acidogenesis are occurring, as suggested by Ghosh et al. (1975), who determined that effective acidogenesis of raw sludge occurs at SRTs as low as 20-24 hours at
Table 3.3.1.A – Summary of average pH and total VFA concentrations

<table>
<thead>
<tr>
<th>Acid Reactor Condition</th>
<th>Acid Reactor</th>
<th>Gas Reactor</th>
<th>Control Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Std. Dev.</td>
<td>VFA Conc. (mg/L)</td>
</tr>
<tr>
<td>2 d SRT @ 37°C</td>
<td>5.05</td>
<td>0.02</td>
<td>4,230</td>
</tr>
<tr>
<td>2 d SRT @ 42°C</td>
<td>6.51</td>
<td>0.03</td>
<td>2,506</td>
</tr>
<tr>
<td>2 d SRT @ 55°C</td>
<td>6.05</td>
<td>0.02</td>
<td>4,497</td>
</tr>
<tr>
<td>3 d SRT @ 37°C</td>
<td>5.01</td>
<td>0.05</td>
<td>6,559</td>
</tr>
<tr>
<td>3 d SRT @ 42°C</td>
<td>6.19</td>
<td>0.20</td>
<td>3,152</td>
</tr>
<tr>
<td>5 d SRT @ 37°C</td>
<td>6.58</td>
<td>0.11</td>
<td>2,565</td>
</tr>
</tbody>
</table>

Mesophilic temperatures. This rate of hydrolyzation is reflective of the high growth rate of acidogenic bacteria. Considering that the wash-out value for methanogenic bacteria is approximately three days at mesophilic temperatures (Grady et al., 1999), data indicates that two and three day acid reactor SRTs at 37°C may be preferable for minimization of methanogenesis in the acid reactor. Maximization of acetogenic and methanogenic activity in the downstream gas reactor may enable higher CH₄ production yields.

The pH values of the two acid reactor conditions at 42°C (SRTs equal to 2 and 3 days) are both higher relative to the pH values of the equivalent SRTs at the lower 37°C operating temperature. Considering the increased pH values coupled with the decreased total VFA concentrations (relative to concentrations at the 2 day SRTs), it may be suggested that the temperature increase from 37°C to 42°C permits accelerated acetogenesis, as well as methanogenesis. This may provide elevated concentrations of acetate available for aceticlastic methanogen utilization in the
acidi reactor, thereby permitting undesirable methane gas production in this “throw-away” (flared) biogas volume. This was apparent as this 5°C acid reactor temperature increased the acid reactor CH₄ biogas percentage from 29% to 49% at the two day SRT, and 24% to 40% at the three day SRT.

The pH values of both the gas and control reactors are comparable and consistent. This minimal pH variability was indicated by the low values of standard deviation in Table 3.3.1.A. Ghosh (1987) determined that significantly higher ammonium bicarbonate alkalinity is produced in the gas reactor compared to single stage control. The minimal pH fluctuation present in this data may be reflective of the relatively brief sampling campaigns executed as part of this research. Should the sampling periods be extended for additional time, it is speculated that pH swings in the gas reactor could potentially be minimized due to the buffer capacity of this reactor. This realistic pH variability is apparent in the two different control reactor sampling periods where average pH values between the two campaigns are 7.31 and 7.18. Buffer, and subsequently control, of the pH in the gas reactor could ensure consistent and high efficiency methane production.

Enhanced VSR is one of the attractive characteristics of AD; however, previous research has indicated inconsistent results for multi-phased acid-gas AD. Utilizing a mesophilic → mesophilic acid-gas AD scheme with SRTs of 2 and 13 days, respectively, Ghosh (1987) saw comparable performance to that of the single-stage AD, which operated at a 15 day SRT, and obtained a 38.2% VSR. A study of a full-scale acid-gas AD system by Ghosh et al. (1995) showed that the addition of a mesophilic acid reactor with a 3 day SRT upstream of an existing mesophilic
reactor, operating at an SRT of 9 days, indicated an increase in VSR in the range of 17-70%.

Figure 3.3.1.A shows the VSR results of this acid-gas research. Due to the standard deviation and limited control reactor data, it is difficult to draw rigid conclusions regarding statistical disparity in the different acid-gas configurations. This may also be attributed to the brief sampling periods, and variability in sludge feed as evidenced by the range of reported control reactor VSR values in Figure 3.3.1.A (59.6 and 52.8%). Also, comparisons to existing literature are difficult due to the differences in sludge feed characteristics; however, in general, VSR results of this study are generally higher than published literature. This may be attributed to differences in feeding and wasting patterns, reactor mixing efficiency, or sludge feed primary:tWAS mix ratio. In each of the two campaigns in which the control reactor was operated parallel to the acid-gas system, there was no significant statistical difference in VSR.

![Volatile solids reduction (VSR) for each acid-gas condition]

Figure 3.3.1.A – Volatile solids reduction (VSR) for each acid-gas condition
On par with the VSR evaluation, analysis of CH₄ yield in the gas reactor also proves difficult due to the reasons previously discussed. Also, there does not appear to be any correlation to H₂S gas concentration or VSR in the gas phase. These results are shown in Figure 3.3.1.B.

Figure 3.3.1.B – Gas reactor methane gas (CH₄) yield for each acid-gas condition

3.3.2 Siloxanes in Gas Phase Reactor Biogas

As discussed previously, to date there is no published literature regarding the effect of multi-phased AD on the volatilization of siloxanes in the biogas recovery (gas) reactor. However, an ongoing Water Environment Research Foundation (WERF) study suggests that single-stage AD thermophilic operating temperatures yield higher D5 biogas concentrations than reactors operated in the mesophilic temperature range (WERF, 2012). Currently, the only viable method for siloxane abatement is control in the gas phase. A primarily objective of this research was to
determine the feasibility of utilizing acid-gas AD for minimization of D4 and D5 siloxanes biogas concentrations by capitalizing on biological conditions occurring as a function of the acid-gas system performance. In this sense, this research and approach to D4 and D5 siloxane abatement is novel.

The results of the data collected in this study are shown in Figure 3.3.2.A. As discussed previously in section 3.3.1, it is difficult to draw firm conclusions regarding desirable performance differences between the different acid-gas configurations due to the considerable standard deviation values and limited control reactor data. This is specifically true due to the colloidal, non-uniform dispersion of siloxane concentrations in solution and adsorbed to sludge floc EPS in the sludge influent. Therefore, “slug” concentrations within reactor sludge influent can adversely affect statistically reflective performance, particularly during short sampling periods. As shown in Figure 3.3.2.A, the control reactors siloxane biogas concentration was highly variable between the two sampling periods. However, in both sampling periods, the control reactors siloxane concentrations in the biogas are comparable to those of the gas reactor, which were run in parallel. As the control and acid-gas reactors were sampled simultaneously, and both fed with the same influent sludge feed composition, it is reasonable to conclude that an upstream acid reactor at an SRT equal to 3 days, at both 37°C and 42°C, does not have an affect on siloxane volatilization in the gas reactors biogas.
These results provide insight into the steadfast nature of D4 and D5 siloxane compounds in the acid-gas AD biological process. Based on the variable operating conditions of the acid reactor at both 37°C and 42°C at the 3 day SRT, it is apparent that the lower pH values (5) and a slight increase in temperature (+5°C) do not encourage enhanced volatilization in the acid reactor biogas. Due to the lack of control reactor data during the campaign in which the acid reactor was operated at an SRT of 2 days at 55°C, the effect of thermophilic temperatures on enhanced D4 and D5 siloxane volatilization in the acid reactor is not readily determinable.

### 3.3.3 Hydrogen Sulfide in Gas Phase Reactor Biogas

As mentioned in the previous section, to date there is no published literature regarding the effect
of multi-phased AD on the H$_2$S gas production in the biogas recovery (gas) reactor. A primarily objective of this research is to determine the feasibility of utilizing acid-gas AD for minimization of H$_2$S biogas concentrations by capitalizing on biological conditions occurring as a function of the AD system performance in lieu of implementation of H$_2$S control and abatement measures. In this sense, this research and approach to H$_2$S abatement is also novel.

The results of the data collected in this study are shown in Figure 3.3.3.A. As discussed previously, a parallel control reactor was only utilized in two sampling campaigns, therefore conclusions may only be drawn from these systems. Based on this premise, it may be suggested that utilization of acid-gas AD decreases the amount of H$_2$S in the biogas generated in the gas reactor for an acid reactor SRT equal to 3 days, at both 37°C and 42°C. Due to the limited control reactor information, it is statistically impossible to apply this conclusion to the other acid-gas scenarios shown on Figure 3.3.3.A. This may be a more probable comparison by conjecture if the two control reactor sampling events yielded more similar concentrations; however, this is not the case, and further verifies the uncontrollable variability of the feed sludge characteristics.

In the case that conjecture between all acid-gas AD scenarios and the two control reactor sample sets were possible, it would appear that all tested acid-gas scenarios provided a decreased H$_2$S concentration in the gas reactor’s biogas volume. If probable, this may be attributed to a number of findings described in previous research. Findings by Mizuno et al. (1998) demonstrated that SRB are capable of effective reduction of high concentrations of SO$_4^{2-}$ at low SRTs. Although SO$_4^{2-}$ reduction was more effective when present at lower concentrations, a 90% removal was
possible at a concentration as high as 1,200 mg SO$_4^{2-}$ L$^{-1}$ at an SRT as low as 8 hours at a mesophilic temperature.

Given that protein degradation contributes heavily to the production of H$_2$S, the fact that 90% of the organic load of biosolids processed in AD is comprised of carbohydrates, lipids, and proteins (Batstone et al., 2002) it is evident that the general digestion of VS will generate H$_2$S. As evidenced by the presence of acidogenic products in the acid phase reactor configurations as part of this research, the degradation of amino acids is occurring. Higgins et al. (2004) determined that the primary mechanism for H$_2$S production from organic matter in sludge is a function of degradation of cysteine, a sulfur containing amino acid that is a product of the enzymatic
hydrolysis of proteins present in the sludge. By permitting acidogenic activity in the acid phase reactor of each tested laboratory configuration, it is suggested that this degradation will allow H₂S generation in this reactor, thereby reducing the H₂S generated in the downstream gas reactor. Therefore, it may be suggested that the addition of an acid phase reactor that permits acidogenesis will decrease the H₂S concentrations in the biogas recovered from the gas reactor. This reactor could aid in minimizing any additional H₂S control or abatement measures that would need to be implemented for mitigation of catastrophic corrosion effects on biogas energy generation processes, as well as the detrimental effects of the H₂S on any siloxane removal media.

3.4 Conclusions

1. Congruent with previous research on acid-gas AD, resultant data from this laboratory research indicates mixed results for VSR and methane yield. There are no apparent trends or ideal configurations for optimization of these parameters from the limited data sets.

2. It may be reasonably concluded that utilization of acid-gas AD does not cease or attenuate the volatilization of D4 and D5 siloxanes in biogas generated in the gas phase reactor, specifically for an acid reactor SRT equal to 3 days, at both 37°C and 42°C. The resultant data collected from two of the laboratory campaigns indicates that the biogas in both the gas and control reactors contained comparable concentrations of these two most abundant siloxane compounds.
3. Based on the data from this laboratory study, it may be suggested that an acid phase reactor aids in the decrease of \( \text{H}_2\text{S} \) generation in the gas reactor biogas. This may be primarily attributed to the effective reduction of \( \text{SO}_4^{2-} \) and degradation of the amino acid cysteine in the acid reactor, thereby minimizing this occurrence in the gas reactor sludge volume. Although a breadth of statistically comparable acid-gas SRT and temperature scenarios are not available due to the limited data collected in this research, the disparity of \( \text{H}_2\text{S} \) concentrations between the control reactor and the scenarios in which the acid reactor was operated at 37°C and 42°C at a 3 day SRT indicates the overall possibility of downstream \( \text{H}_2\text{S} \) generation minimization due to utilization of acid-gas AD.

3.5 References


Chapter 4 – Summary and Conclusions

As stated in Section 3.1.2 of this report, the three primary objectives of this laboratory research were as follows:

1. To characterize performance of acid-gas anaerobic digestion at acid reactor operating temperatures of 37, 42 and 55°C, and SRT’s of 2, 3, and 5 days.
2. To determine optimal conditions, if any, for minimization of D4 and D5 siloxanes in biogas production of gas phase reactor.
3. To determine optimal conditions, if any, for minimization of H₂S in biogas production of gas phase reactor.

In regards to research objective number 1, it can be concluded that hydrolysis and acidogenesis occurred in the acid reactor at SRTs as low as 2 days. This was readily apparent by the low pH values and high VFA concentrations present at these temperatures and SRTs. It appears that the lowest average acid reactor pH values of 5.05 and 5.01 occurred at a mesophilic operating temperature of 37°C at SRTs of 2 and 3 days, respectively. Although operating conditions of low pH may inhibit methanogenesis, which is a desirable behavior in the acid reactor, laboratory results supporting an enhanced methane yield in the downstream gas reactor were inconclusive. It also appears that VSR may potentially be increased when an upstream acid reactor is utilized due to higher average VSR values (in comparison to the control reactor). However, due to the small data set and high standard deviation values, it is not possible to draw a statistical conclusion regarding this suggested claim.
In discussion of research objective number 2, we are able to conclude that acid-gas AD does not enable the minimization of D4 and D5 siloxane volatilization in the downstream gas reactor. Since the gas reactor is the digester in which biogas would be captured for energy recovery, it is apparent that a decrease in siloxane volatilization is not an advantage of an acid-gas configuration, specifically at an acid reactor SRT equal to 3 days, at both 37°C and 42°C. It was hypothesized that an increase in reactor operating temperature (i.e. high acid reactor operating temperatures) may facilitate an enhanced volatilization in that reactor, thereby decreasing the concentration in biogas produced in the gas reactor. The mechanism of this enhanced volatilization was based on an assumed vehicle of physical-chemical reaction, and not due to microbiological degradation. Also, although the data did not support this hypothesis, the small sample set may unfortunately lend to doubt of the final data reporting. Future research should include work toward developing Henry’s constants for D4 and D5 siloxanes at mesophilic and thermophilic temperatures, as this could permit the prediction of concentrations in biogas to enable more effective measures of abatement.

In summary of the findings for research objective number 3, it does appear that the use of the acid-gas AD configuration does permit a decrease in H₂S gas produced in the gas reactor, which is a desirable outcome due to the decreased corrosivity to the AD infrastructure and energy recovery systems. It may be concluded that this gas reactor decrease occurs at an acid reactor SRT equal to 3 days, at both 37°C and 42°C. Although comparative control reactors were not utilized for the remaining acid reactor operational condition scenarios, and the effect is statistically indeterminable, it may be suggested that utilization of an acid reactor may also permit a decrease in gas reactor H₂S production, particularly at an acid reactor SRT equal to 2
days at 37°C, 42°C, and 55°C. Since SO$_4^{2-}$ reduction is possible at very low acid reactor SRTs, this, coupled with upstream cysteine degradation in the acid reactor, may permit the decrease in H$_2$S production in the downstream gas reactor.