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PILOT-SCALE STUDY ON ANAEROBIC DIGESTION APPLIED TO A SALINE INDUSTRIAL WASTE ACTIVATED SLUDGE

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering in

The Department of Civil and Environmental Engineering

by

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B.S., Anhui Agriculture University, 1998
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS .......................................................................................................................... ii

LIST OF TABLES ........................................................................................................................................ v

LIST OF FIGURES .................................................................................................................................. vi

ABSTRACT ........................................................................................................................................... viii

CHAPTER 1. INTRODUCTION .................................................................................................................... 1
1.1. Background ........................................................................................................................................ 1
1.2. Research Objectives ...................................................................................................................... 1
1.3. Thesis Organization ....................................................................................................................... 2

CHAPTER 2. LITERATURE REVIEW ..................................................................................................... 3
2.1. Anaerobic Digestion Reactors ....................................................................................................... 3
2.2. Important Factors Affecting Anaerobic Digestion ........................................................................ 4
  2.2.1 pH and Alkalinity .................................................................................................................... 4
  2.2.2 Organic Loading and Temperature ....................................................................................... 5
  2.2.3 Solid Retention Time ............................................................................................................ 6
  2.2.4 Toxicity of Inorganic and Organic Compounds .................................................................... 6
2.3. Anaerobic Reactor Digestion and Digestion Configurations ...................................................... 8
  2.3.1 Major Reactors .................................................................................................................... 8
  2.3.2 Digestion Configuration ..................................................................................................... 9

CHAPTER 3. PHASE 1 EXPERIMENT: BATCH OPERATION .......................................................... 13
3.1. Introduction .................................................................................................................................. 13
3.2. Materials and Methods ............................................................................................................... 13
  3.2.1 Reactors Configuration ......................................................................................................... 13
  3.2.2 Reactors Startup .................................................................................................................. 15
  3.2.3 Reactors Operation ............................................................................................................. 16
  3.2.4 Analytical Methods ........................................................................................................... 18
3.3. Results and Discussion .............................................................................................................. 20
  3.3.1 Initial Contents of Reactors at Startup ............................................................................... 20
  3.3.2 Temperature, Salinity, pH, and Alkalinity ......................................................................... 21
  3.3.3 Volatile Fatty Acids .......................................................................................................... 26
  3.3.4 Biogas Analysis ............................................................................................................... 26
  3.3.5 Solids Content .................................................................................................................... 31
3.4. Conclusions .................................................................................................................................. 32

CHAPTER 4. PHASE 2 EXPERIMENTAL TESTS ........................................................................ 33
4.1. Introduction .................................................................................................................................. 33
4.2. Materials and Methods ............................................................................................................... 33
  4.2.1 Waste Activated Sludge Characterization ......................................................................... 33
  4.2.2 Reactors Configuration ....................................................................................................... 33
4.2.3 Reactors Conditions at the Start of Period 2 ...................................................33
4.2.4 Reactors Operation ..........................................................................................34
4.2.5 Analytical Methods .........................................................................................38
4.3. Results and Discussion .........................................................................................38
  4.3.1 Initial Conditions in Pilot-Scale Digesters at Start of Period 2 ......................38
  4.3.2 Temperature, Salinity, pH, and Alkalinity .....................................................38
  4.3.3 Solids Content ................................................................................................43
  4.3.4 Biogas Analysis ..............................................................................................52
  4.3.5 Volatile Fatty Acids .......................................................................................53
  4.3.6 Chemical Oxygen Demand .............................................................................57
4.4. Conclusions .............................................................................................................61

CHAPTER 5. OVERALL CONCLUSIONS..................................................................63

REFERENCES ..............................................................................................................65

APPENDIX A. THE SOLIDS CALCULATION DURING PERIOD 1 ......................67
APPENDIX B. EVALUATION OF MIXING HR REACTOR IN PERIOD 2 ..........70
APPENDIX C. THE SOLIDS CALCULATION IN PERIOD 2 ..................................73
APPENDIX D. THE COD MASS BALANCE CALCULATION IN PERIOD 2 .......77
VITA ...............................................................................................................................80
LIST OF TABLES

Table 2-1: Toxic and inhibitory inorganic compounds for anaerobic process ............... 7
Table 3-1: The sludge comprised in the reactors at the initial of Period 1 .................. 16
Table 3-2: Analysis of sludge added to the reactors at the initial of Period 1 ........... 20
Table 3-3: Mixed sludge characteristics at the start Period 1 .............................. 21
Table 4-1: Characterization of the sludge at the beginning of Period 2 ................. 39
Table 4-2: Results of solid mass balance of Period 2 .................................................. 49
Table B-1: Statistic analysis of different mixing methods ......................................... 72
LIST OF FIGURES

Figure 2-1: Anaerobic digestion reactions. .................................................................4
Figure 2-2: Digestion reactor configurations ............................................................10
Figure 2-3: Two-stage anaerobic digestion .............................................................11
Figure 3-1: Configuration of LR Reactor (top) and HR Reactor (bottom) ..........14
Figure 3-2: Temperature of LR Reactor (top) and HR Reactor (bottom) during
Period 1 ..............................................................................................................22
Figure 3-3: Salinity in LR Reactor (top) and HR Reactor (bottom) during Period 1 .......23
Figure 3-4: pH of LR Reactor (top) and HR Reactor (bottom) during Period 1 .........24
Figure 3-5: Alkalinity of LR Reactor (top) and HR Reactor (bottom) during
Period 1 ...............................................................................................................25
Figure 3-6: Organic Acid content of LR Reactor (top) and HR Reactor (bottom)
during Period .......................................................................................................27
Figure 3-7: The ratio of propionate and acetate in LR and HR Reactors
during Period 1 ....................................................................................................28
Figure 3-8: Biogas composition of LR Reactor (top) and HR Reactor (bottom)
during Period 1 ....................................................................................................29
Figure 3-9: Biogas production rate of LR Reactor (top) and HR Reactor (bottom)
during Period 1 ....................................................................................................30
Figure 4-1: Daily sludge feeding and wasting volumes during Period 2 operation ....36
Figure 4-2: Configuration of HR Reactor mixing by gas recirculation ...............37
Figure 4-3: Temperature of LR Reactor (top) and HR Reactor (bottom) in Period 2 ....40
Figure 4-4: Salinity in the WAS supplied to the pilot-scale digesters in Period 2 .......41
Figure 4-5: Salinity in the LR Reactor (top) and HR Reactor (bottom) in Period 2 ......41
Figure 4-6: pH of LR Reactor (top) and HR Reactor (bottom) in Period 2 ...............42
Figure 4-7: Alkalinity of LR Reactor (top) and HR Reactor (bottom) in Period 2 ......44
Figure 4-8: Suspended solids concentrations in the WAS sludge fed to the two pilot-scale digesters in Period 2 .................................................................45

Figure 4-9: TSS and VSS loading rates to LR Reactor (top) and HR Reactor (bottom) in Period 2 .................................................................................................46

Figure 4-10: Suspended solids concentrations in the effluent of LR Reactor (top) and HR Reactor (bottom) in Period 2 .................................................................48

Figure 4-11: VSS mass balance of LR and HR Reactors in Period 2..............................50

Figure 4-12: Biogas production rate of LR Reactor (top) and HR Reactor (bottom) in Period 2 ........................................................................................................54

Figure 4-13: Gas composition of LR Reactor (top) and HR Reactor (bottom) in Period 2 ..............................................................................................................55

Figure 4-14: Organic acid concentrations LR Reactor (top) and HR Reactor (bottom) in Period 2 ........................................................................................................56

Figure 4-15: COD concentrations in the influent sludge in Period 2 ............................57

Figure 4-16: COD loading rate of LR and HR Reactors in Period 2 ...............................58

Figure 4-17: Effluent COD concentrations of LR Reactor (top) and HR Reactor (bottom) in Period 2 ........................................................................................................60

Figure 4-18: COD mass balance of LR and HR Reactors in Period 2 .............................61

Figure B-1: Pump recycles only for mixing HR reactor .................................................71
ABSTRACT

In the field of municipal wastewater treatment, anaerobic digestion is a well-established, effective process for stabilization of organic sludge with the attractive features of low operating costs and production of methane as a useful by-product. Application of anaerobic digestion for the treatment of saline industrial wastewater sludge, however, has not been well established. The studies described in this thesis were conducted with the overall goal of assessing the feasibility of mesophilic anaerobic digestion processes for treatment of waste activated sludge (WAS) containing moderate salinity (approximately 3% m/v). Experiments employed two 30-gallon conical-bottom HDPE reactors. In the first phase of testing, intended to produce acclimated microbial populations, both reactors were operated in batch mode without mixing for a period lasting 48 days. In the second phase of testing, two different reactor operating strategies were evaluated. One reactor was unmixed with operation at a 60-day target hydraulic residence time, while the second was a mixed system with a 30-day target hydraulic residence time. Temperature, pH, alkalinity, solids concentrations, organic acid concentrations, biogas evolution rates, and biogas methane content were measured over a period lasting more than 180 days. Results demonstrate that elevated salinity of 3% m/v does not preclude effective anaerobic digestion. Both reactors exhibited stable pH, alkalinity, and gas composition with >60% methane. The high VSS destruction efficiency, 41.3% (HR reactor) and 49% (LR reactor), showed the reactor well functioned. Both reactors exhibited a methane content of approximately 65% after 70 days (July 9, 2008) operation, which indicates that the lipid degradation was not inhibited under this digestion condition.
CHAPTER 1: INTRODUCTION

1.1 Background

Disposal of biosolids poses a challenge for wastewater treatment systems worldwide. The three major disposal methods for excess biological sludge are: 1) landfilling, 2) incineration, and 3) application in agricultural or forestland (Bela, 1991). When landfill disposal is the ultimate disposal option, it is often desirable to stabilize the solids prior to landfilling in order to minimize odors, prevent excess liquids from entering the landfill, and avoid excessive landfill settlement. When aerobic or anaerobic digestion are used for sludge stabilization, the stabilization process can have the advantages of minimizing the quantity of material placed in the landfill, thereby lowering the cost of landfill disposal, a concern where tipping fees are high, or extending landfill life, a concern where space is limited.

For treatment of primary and secondary solids derived from treatment of municipal wastewaters, anaerobic digestion is an effective sludge stabilization technique, with low operating costs and the production of a useful, combustible gas by-product that can be used as a source of energy. Although anaerobic digestion has been widely used for municipal wastewater biosolids, there are few accounts in the scientific literature of anaerobic digester performance under high salt conditions (Gebauer, 2004). Consequently, reaction kinetics, design basis, and expected reactor performance for anaerobic digesters treating high-salinity sludge is not well established.

1.2 Research Objectives

The research reported in this thesis was conducted in support of an effort to assess the potential of mesophilic anaerobic digestion to achieve solids destruction and methane gas production for a moderately saline (≈3% m/v salinity) waste activated sludge (WAS) produced
from treatment of industrial wastewater at a petrochemical plant located near Baton Rouge, LA. Specific objectives were to.

- Validate results from previously conducted lab-scale research using more controlled conditions.
- Conduct additional pilot-scale studies to evaluate options for optimizing anaerobic digester systems to maximize solids destruction efficiency.
- Evaluate potential benefits of lowering the salt concentration in the WAS fed to the anaerobic digester.
- Explore ways to increase the methane percentage in the biogas.
- Characterize expected digester supernatant in order to allow assessment of the impact of returning supernatant to existing on-site wastewater treatment units.
- Evaluate approaches for minimizing the required retention time (and associated capital cost) while achieving maximum VSS destruction efficiency.

1.3 Thesis Organization

Chapter 2 of this thesis presents a literature review regarding anaerobic digestion in general and treatment of wastes containing inhibitory compounds in particular. Chapter 3 describes experimental methods and results from initial start-up of two-pilot scale anaerobic digesters that were operated in batch mode. Chapter 4 presents experimental methods and results from subsequent experiments in which two-pilot scale anaerobic digesters were operated with different operating strategies with daily feeding/wasting over a period lasting more than 120 days. Chapter 5 contains a summary of overall conclusions from this research. References cited throughout the thesis can be found in Chapter 6.
CHAPTER 2: LITERATURE REVIEW

Stabilizing organic materials is an important step necessary to eliminate nuisance conditions to a reuse or disposal level. The process of anaerobic digestion is the most common technique employed for stabilization of municipal wastewater sludge biosolids. It may be defined as the biological oxidation of degradable sludge components by specialized groups of anaerobic microbes that ultimately convert the starting materials to stable solid and biogas under a conditions lacking molecular oxygen. The attractiveness of anaerobic digestion comes from it being a relatively stable process if properly controlled, low operating costs, and the production of combustible gas, which can be used as a source of energy. The following sections provide an overview of the microbial processes involved in anaerobic digestion and the reactor configurations and operating strategies that are commonly employed.

2.1 Anaerobic Digestion Reactions

Anaerobic digestion involves a series of biochemical reactions (Reynolds, 1982) in which complex organic materials are decomposed by two primary groups of microorganisms, organic-acid-forming heterotrophs and the methane-producing archaea in an oxygen depleted environment. The reactions and microbes involved in anaerobic digestion are discussed in this section. Conceptually, the breakdown of complex organics involves a series of sequentially microbial catalyzed reactions as depicted in Figure 2-1. Steps in the process include the following. (1) Hydrolysis reactions catalyzed by enzymes such as cellulase, protease, and lipase, during which complex organic substrates such as carbohydrates, proteins, fats, or oils are broken down into their constituent parts by hydrolytic bacteria. (2) Acidogenesis is a process which immediately follows hydrolysis and turns hydrolysis products into short chain organic acids, ketones, and alcohols. (3) Acetogenesis, which refers to another acid-producing reaction,
involves production of acetate, propionate, CO₂, and H₂ from compounds such as glucose, ethanol, bicarbonate, long chain fatty acids. The production of volatile acids from organic substrates in unbuffered or poorly buffered environments can result in pH levels in the range of 4.5-5.5 which is beneficial for the growth of acidogenic and acetagenic bacteria, but which can inhibit methanogenesis. (4) Methanogenesis is the final step of anaerobic digestion, during which short chain acids and H₂ are converted into methane by methanogens.

![Figure 2-1: Anaerobic digestion reactions (Reynolds, 1982)](image)

2.2 Important Factors Affecting Anaerobic Digestion

2.2.1 pH and Alkalinity

pH plays an important role in maintaining a healthy and stable digester and an equilibrium condition for biological conversions. Excess accumulation of organic acids has appreciable potential to decreasing the reactor pH, especially if a large amount of organics are loaded into the system over a short time period. Specifically, high organic loadings may result in the acidogenic bacteria producing high volumes of organic acids. This could decrease pH to a low level (e.g., pH of 5.0), which is lethal to methanogens because most of them tolerate a
relatively narrow pH range and grow best between 7.0 and 7.2. Therefore it is necessary to control the pH sufficiently to facilitate the growth of methanogens which consume organic acids. If, on the other hand, the growth of methanogenesis overwhelms the growth of acidogenic bacterial, prolific methanogenesis may result in a high concentration of ammonia, increasing the pH above 8.0, where it will inhibit the growth of acidogenesis (Lusk, 1999). Therefore it is important to maintain pH in a proper range, generally between 6.8 and 7.2, especially during start-up stages. In full scale operations, pH control may be achieved by adding a buffer such as bicarbonate.

2.2.2 Organic Loading and Temperature

Anaerobic digestion processes are generally characterized by high organic loading, 3.2 to 32 kg COD/m³·d, compared to 0.5 to 3.2 kg COD/m³·d for aerobic process (Speece, 1996). However, it should be noted that one potential challenge of increasing the organic load is the great possibility to disturb the pH equilibrium for the following reason. Acidogenic bacteria may produce organic acids rapidly when organic load is increased while the methanogens grow more slowly and need longer time to increase in populations. As a result, acid accumulation may occur and lead to a positive feedback loop, eventually halting effective digestion.

Temperature is another critical parameter that determines the rate of digestion reactions, particularly the rate of hydrolysis and methane formation. Mesophilic digestion with a temperature range from to 30°C to 35°C and thermophilic with a range of 50-65°C are both commonly used in anaerobic digestion process (United Tech, 2003). Though thermophilic digestion has the advantage of allowing higher loading rates, a higher efficiency of pathogen destruction, and a shorter retention time, it has the disadvantages of being more sensitive to toxins and changes in the organic loading (United Tech, 2003). Compared with thermophilic
digestion, mesophilic process is presently more popular in current anaerobic digestion applications.

### 2.2.3 Solid Retention Time

A sufficient residence time is required to allow significant destruction of volatile suspended solid to occur because hydrolysis, fermentation, and methanogenesis are directly related to Solid Retention Time (SRT). An increase or decrease in SRT could result in an increase or decrease in the extent of each reaction. In general, a SRT greater than 20 days is needed for anaerobic process at 30°C for effective treatment performance. Much longer SRTs may be required at lower temperatures. As further described in later sections, significant solids destruction at shorter retention times may be achieved using mixing by mechanical stirring, pumping, or re-circulating biogas.

### 2.2.4 Toxicity of Inorganic and Organic Compounds

Free ammonia (NH₃) with a high enough concentration is considered toxic to methanogenesis (Metcalf & Eddy, 2003). Additionally, some volatile acids, metal ions (which may come from addition of base to control pH), and sulfides (from protein degradation) have reportedly shown inhibition effects on anaerobic methanogenic reaction rates (Parkin and Owen, 1986). The presence of an inhibitory compound, however, does not necessarily result in a complete stop of the digestion process. Each ion has its own threshold level, which varies with digestion temperature, acclimatization time, and solid components. For an example, the toxicity threshold for ammonia has been reported to be 100 mg/L as NH₃-N (McCarty and McKinney, 1961), but with acclimatization time, higher concentrations (500 mg/L) may be tolerated (Lay et al. 1998). Toxic and inhibitory inorganic compounds for anaerobic processes are summarized in Table 2-1. Besides the toxic effect caused by presence of certain chemical constituents, process
upsets could also occur as a result of a sudden change in digester operation, such as a shock loading of chemical materials in the plant influent.

Table 2-1. Toxic and inhibitory inorganic compounds of concern for anaerobic process (Metcalf & Eddy, 2003)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Moderately inhibitory concentration, mg/L</th>
<th>Strongly inhibitory concentration, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>3500-5500</td>
<td>8,000</td>
</tr>
<tr>
<td>K⁺</td>
<td>2500-4500</td>
<td>12,000</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2500-4500</td>
<td>8,000</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1000-1500</td>
<td>3,000</td>
</tr>
<tr>
<td>Ammonia-nitrogen NH₄⁺</td>
<td>1500-3000</td>
<td>3,000</td>
</tr>
<tr>
<td>Sulfide, S²⁻</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Copper, Cu²⁺</td>
<td>-</td>
<td>0.5 (soluble); 50-70 (total)</td>
</tr>
<tr>
<td>Chromium, Cr(VI)</td>
<td>-</td>
<td>3.0 (soluble); 200-250 (total)</td>
</tr>
<tr>
<td>Chromium, Cr(III)</td>
<td>-</td>
<td>2.0 (soluble); 180-420 (total)</td>
</tr>
<tr>
<td>Nickel, Ni²⁺</td>
<td>-</td>
<td>30.0 (total)</td>
</tr>
<tr>
<td>Zinc, Zn²⁺</td>
<td>-</td>
<td>1.0 (soluble)</td>
</tr>
</tbody>
</table>

The effect of high salinity on anaerobic sludge digestion was first studied quite some time ago; however, the scientific literature on this subject remains relatively sparse and there are somewhat conflicting reports. The threshold concentration above which inhibition occurs has varied with experiment conditions. In an early study, Kugelman and McCarty (1965) reported that a strong inhibition effect on anaerobic digestion was observed when the sodium concentration is higher than 10 g/L. However, Omil et al. (1995) found that there is no significant inhibition effect at sodium concentrations as high as 5 g/L if the methanogenic biomass had been adaptive to the salinity environment. At the same time, Feijoo et al. (1995) point out there are some additional factors that also could influence the inhibition effect such as the type of methanogenic substrate used, the antagonistic effects of other ions at adequate concentrations, the nature and the progressive adaptation of sludge to high salinity.

Toxicity is one of the most important factors for industry waste sludge and it could cause unstable digester performance. Several methods can be used to evaluate the stability of a
digestion reactor, (1) pH level is a simple gauge of digester health, which changes in response to biological conversions and system equilibrium. Acid accumulation in anaerobic digester could cause falling pH and prolific methanogenesis may result in a higher concentration of ammonia, increasing the pH above 8.0 (Lusk, 1999). Therefore adding a buffer to the digester may be necessary to maintain a stable pH level when organic loading is changed and digester is start-up at which acid forming stages was undergo earlier than methane forming can begin (Gebauer, 2004). (2) A 60 % methane criterion was commonly used to test biogas and anaerobic digester by many researchers (Gebauer, 2004). (3) In a properly operated digester, the organic acids are utilized as rapidly as they are produced and the measured concentration should not be more than 1000 mg/L (Loll and Moller, 1984). (4) In addition, the propionate/ acetate ratio was reported as one of the indicators to inhibition and instability of anaerobic digester. A propionic to acetic acid ratio greater than 1.4 indicate impending digester failure (Hill et al., 1987).

2.3 Anaerobic Reactor Design and Digestion Configurations

2.3.1 Major Reactors

During early applications of anaerobic digester technology, anaerobic digestion experienced relative low solid destruction efficiency with the possible reason that great numbers of bacteria are washed out with the effluent and interior conditions are altered, by pH fluctuations caused by organic loading change (Ndon and Dague, 1997). To achieve efficient anaerobic treatment of liquid wastes, researchers investigate new methods to maintain a higher population of bacteria inside the digester. Stander (1950) found that separating the bacteria from the effluent stream and returning them in the reactor was helpful to maintain high bacterial population (Stander, 1950). The first well-known high-rate anaerobic reactor was developed by using the concept of capturing solid to be recycled back to reactor (Fullen, 1953). These
Attachment concepts were then extended by Switzenbaum and Jewell to build the anaerobic attached film expanded bed reactor in 1980, and the upflow anaerobic sludge blanket reactor (UASB) was developed by using a gas circulation mixing system (Letting and Vinken, 1980). Basically, influent is distributed at the bottom of the UASB reactor and travels in an upflow mode through the sludge blanket (Metcalf & Eddy, 2003). Another high-rate methanogenic reactor process, Anaerobic Sequencing Batch Reactor (ASBR) operated in a batch mode, with solids separation occurring within the reactor prior to withdrawal of supernatant as effluent, depending on the development of a good settling granulated sludge (Hill et al., 1987).

2.3.2 Digester Configuration

The common configurations used for anaerobic digestion are low-rate digestion, high-rate digestion and two-stage digestion. The first two of these processes are shown in Figure 2-2. In addition, anaerobic digestion can also be operated in mesophilic and thermophilic conditions.

- Low-rate Digestion

A low-rate or conventional digester is a cylindrically shaped tank with a sloping bottom and a floating or fixed cover. Sludge addition and withdrawal in such systems are both generally intermittent. Because no mixing other than that caused by rising gas bubbles is provided in this system, the digester contents become stratified. For a floating cover digester, when sludge is being added, recycle is needed to seed the incoming fresh sludge. After the fresh sludge addition, recycle is stopped to allow mixture stratification. Stabilized solids settle to the tank bottom, where they can be drawn off intermittently (e.g., every two weeks) for removal and further processing. Biogas accumulates in the headspace of the tank and is drawn off for storage or use. Supernatant is generally drawn off from the mid-to-upper portion of the digester on an
intermittent basis (e.g., every several days) and is recycled either to the primary clarifier or the secondary treatment process.

![Diagram of digestion reactor configurations](image)

**Figure 2-2: Digestion reactor configurations (Reynolds, 1982)**

Though low-rate digestion has the advantage of easy operation, scum layers and grit can accumulate in the top and bottom of the tank, respectively, thereby decreasing the effective volume available for sludge stabilization and increasing the need for large tank sizes. Also low-rate digesters have a long detention time and low organic loading. It was reported that the common retention times of low rate digestion ranged from 30-60 days with an organic loading rate between 0.48 and 1.6 kg TVS/m³/day (Davis and Cornwell, 1998). Therefore, low-rate digesters are generally considered only for small plants.

- **High-rate Digestion**

  High-rate digesters have a continuous mixing system which provides better contact between the seeded and fresh sludge. This allows a high-rate digester to operate at a high organic loading of 0.15-0.4 lb VSS/d·ft³ (2.4-6.4 kg VSS/m³·day) and a short detention time of 10-20 days (Reynolds, 1982). Two common methods are used to separate sludge from supernatant. One is to displace digested solids to a holding tank where the supernatant liquor is separated when fresh sludge is added; the other is to stop the mixing and allow the contents to stratify. High-rate digestion could be operated under mesophilic and thermophilic conditions and the
heating methods include steam injection, internal heat exchangers, and external heat exchangers. For the advantage of flexibility and ease of maintaining the heat surface, external heat exchangers are the most commonly used approach (Reynolds, 1982). Auxiliary mixing could be provided by the following: (1) recycling gas to a draft tube which mounts in the center of the digester; (2) diffuse recycling gas to the bottom of the tank; or (3) mechanical pumping (Metcalf &Eddy, 2003). Besides providing a good contact for sludge and seeds, mixing also is helpful to dilute inhibitory substances (Vesilind. et al).

- **Two-stage Anaerobic Digestion**

Two-stage digestion is modification of the high-rate digestion technology that divides the fermentation operation and the solid-liquid separation process into two stages that are carried out in separate tanks. The first stage is usually a high-rate digester with a fixed cover and continuous mixing where hydrolysis of organic solids, digestion, and gas production occur.

![Figure 2-3: Two-stage anaerobic digestion (Reynolds, 1982)](image)

The second stage is an unmixed, low-rate digester with a floating cover and the main use is to separate supernatant and digested sludge. From a microbiological perspective, two stage anaerobic digestions take advantage of the fact that the biochemical pathways of digestion occur in phases. The first tank allows hydrolysis and acidogenesis to occur while the second optimizes...
methanogenesis. The first tank can be mixed and heated to a uniform temperature and fed continuously and operated at lower pH and the second tank must maintain a higher pH and provide capacity for gas collection or storage.
CHAPTER 3: PHASE 1 EXPERIMENTS: BATCH OPERATION

3.1 Introduction

As discussed in Chapter 2, although anaerobic digestion has been widely applied with great success for treatment of municipal wastewater sludge, it has not been widely applied for treatment of high-salt content sludge. In support of an overall effort to evaluate anaerobic digestion for management of a moderately saline waste activated sludge (WAS) produced by a petrochemical industry, a pilot-scale treatability study was carried out. The experimental testing was carried out in multiple phases, the first of which is described in this chapter. The goal of the initial period of testing, hereafter referred to as Period, was to acclimate methanogenic biomass to elevated salinity levels while treating WAS representative of the industrial facility. Results from the first period of testing served as the driving mechanism for decision-making regarding subsequent research described in Chapter 4.

3.2 Materials and Methods

3.2.1 Reactors Configuration

The pilot-scale experiments were carried out in two conical-bottoms, high density polyethylene (HDPE) tanks, each with a working liquid volume of 30 gallons (113.6 L). When filled with 30 gallons liquid, the gas headspace in each reactor vessel was 3.7 gallons (14.1 L). Stainless steel compression fittings (¼ inch, Swagelock SS-436S4,) with rubber gaskets were installed at various locations at the top, bottom, and side-walls of the tanks as shown in Figure 3-1. Two-way stainless steel ball on/ off valves were attached to the compression fittings, terminating with stainless-steel hose-barb connections (1/4 inch, Swagelok). As shown in the figure, one of the reactors, designated as the “LR Reactor” had five liquid injection/withdrawal
ports (numbered as 1 though 5 in Figure 3-1). The other, designated as the “HR Reactor” had four liquid injection/withdrawal ports (numbered as 1 though 4 in Figure 3-1).

Figure 3-1: Configuration of LR Reactor (top) and HR Reactor (bottom)
Variable voltage controllers (Variac) attached to two 8-ft lengths of electrical heating tapes affixed to the outside surfaces of each tank below the liquid level provided temperature control. Peristaltic pumps (Masterflex L/S) were used for sludge filling and withdrawal. Biogas exited through Tygon tubing attached to a port located at the top of each reactor and after passing through water trap (used to prevent back-flow of oxygen from the surrounding air to the digester), was collected in 25 L Tedlar bags (Supelco). A glass tube with a septum-filled monitoring port was located between the reactor and the water trap to allow sampling of the reactors’ gas headspace.

3.2.2 Reactor Startup

The WAS biosolids treated in this study consisted of mixture of two sludge produced in separate aerobic activated sludge treatment processes within a single petrochemical facility located in Plaquemine, LA. The two kinds of sludge are hereafter referred to as “UNOX” and “BHR”. On Tuesday, April 29, 2008, a volume of 19.5 gallons of unthickened BHR sludge was poured into each of the two pilot-scale reactors. Then, 6.5 gallons of thickened UNOX sludge was poured into each of the reactors. After stirring to mix the contents of the reactors, aliquots were removed, and salinity was measured using a refractometer. The reactors were left open to the ambient laboratory atmosphere at ambient temperature overnight. On April 30, 2008, the contents were manually stirred to mix, and samples were removed for measurement of solids, alkalinity, and pH. Then, 4.0 gallons of municipal anaerobic digester sludge from the Central Wastewater Treatment Plant in Baton Rouge, LA, was added to each reactor. Table 3-1 summarizes the volumes of sludge combined in the reactors at startup.

After manually mixing the reactor contents, lids were placed on the reactor vessels, and they were sealed using a combination of epoxy and silicone caulking. Then, ultra-high-purity
nitrogen (N$_2$) gas was sparged through each reactor to remove O$_2$ from the headspace. Sealing of the reactors was completed at 12:00 p.m. on April 30, 2008. Time was measured in days from that point onward.

Table 3-1: The sludge comprised in the reactors at the initial of Period 1

<table>
<thead>
<tr>
<th>Reactor ID</th>
<th>BHR (gallon)</th>
<th>UNOX (gallon)</th>
<th>Inoculation Sludge (gallon)</th>
<th>Total Volume (gallon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR Reactor</td>
<td>19.5</td>
<td>6.5</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>HR Reactor</td>
<td>19.5</td>
<td>6.5</td>
<td>4</td>
<td>30</td>
</tr>
</tbody>
</table>

3.2.3 Reactor Operation

- **Reactor Start-up and pH Adjustment**

  During Period 1 operation, the two reactors were operated in batch mode. Aside from occasional mixing during pH adjustment intervals, neither of the reactors was mixed. The target temperature for both reactors was 35ºC. Temperature was controlled by manually adjusting the voltage supplied to the electrical heating tapes affixed to the outside surfaces of the reactors.

  After 1.4 days of operation (i.e., on May 1, 2008), 341 g of sodium bicarbonate (corresponding to a sodium bicarbonate dose of 3.0 g per L reactor liquid volume) was added to each reactor. This was accomplished by withdrawing approximately 0.8 L of sludge from each reactor using a peristaltic pump, mixing it with the sodium bicarbonate, and then pumping back into the reactor. A peristaltic pump was then connected to the reactor, withdrawing from one side of the reactor and re-introducing into the opposite side. The pH did not markedly increase. To further increase the pH, 160 mL of 0.2 M NaOH was added to the LR Reactor, but the pH did not markedly increase. Finally, 650 mL of 1.0 M NaOH was added to the LR Reactor by injecting 10 mL aliquots into the tubing connected to a peristaltic withdrawing sludge from one
side of the reactor and returning it to another at a rate of 300 mL/min. A total 550 mL of 1.0 M NaOH was added to the HR Reactor in identical manner. One to three hours was applied to mix the reactor contents by using a peristaltic pump at a rate of 300 mL/min.

Additional pH adjustments were performed for the LR Reactor following the procedure described above with addition of 650 mL of 1.0 M NaOH in volumes of 450 mL, 370 mL and 250 mL on days 3, 5, and 9, respectively (May 3, 5, and 9, 2008). In similar fashion, pH adjustments were performed for the HR Reactor with addition of 1.0 M NaOH in volumes of 550 mL and 1000 mL on days 3 and 5 (May 3 and 5, 2008), respectively.

The pH of the LR Reactor was adjusted via addition of 250 mL, 1000 mL, and 700 mL of 1.0 M HCl on days 9, 42, and 47 (May 09, June 11, and June 16, 2008). The pH of the HR Reactor was adjusted via addition of 1.0 M HCl in volumes of 1300 mL, 1500 mL, 300 mL, and 900 mL on days 27, 42, 43, and 47, respectively (May 27, June 11, June 12, and June 16, 2008).

Period 1 operation continued with operation in batch mode for a total of 48 days (i.e., until June 18, 2008). As discussed in section 3.3, some differences were observed in performance of the two reactors during the startup period. In an attempt to homogenize the contents of the two reactors, on day 48 (June 17, 2008) two peristaltic pumps were used in an attempt to fully mix the contents of the two reactors. One pump was intended to pump sludge from the HR Reactor to the LR Reactor at a rate of 300 mL/min. A second pump was intended to pump sludge from the LR Reactor to the HR Reactor at a rate of 300 mL/min. Due to a mechanical failure, one of the pumps overfilled the HR Reactor, partially emptying the LR Reactor, and spilling approximately 20 gallons of the reactor contents.
• **Sampling and Parameter Measurements**

After filling the reactors at the beginning of the study on April 30, 2008, no additional sludge was supplied to the reactors for the remainder of Period 1 operation. On a daily basis, samples were withdrawn from sample ports located on the side walls of reactors. Temperature, total suspended solid (TSS), volatile suspended solid (VSS), biogas production volume, and biogas composition were measured daily. Concentrations of salinity, alkalinity, and volatile fatty acids (VFA) were measured on a regular but less frequent basis (every 2-3 days). Analysis of alkalinity, pH, and temperature were carried out with two samples which were collected from port 1 and port 4, and the results were averaged. Solids concentrations were determined based on sludge sampled from port 1, and the test was conducted in duplicate with the average value reported.

### 3.2.4 Analytical Methods

- **pH and ORP**

  pH was measured using a pH electrode with internal temperature compensation (-Denver Instruments) into sample and the pH value was recorded. Oxidation-reduction potential (ORP) was measured according to Standard Method 2580 (APHA, 1998) by using ORP electrode (Cole-Parmer Instrument Co.).

- **Solids Concentrations**

  Total solids (TS) concentrations were measured according to Standard Method 2540B (APHA, 1998). Total suspended solids (TSS) and volatile suspended solids (VSS) concentrations were measured according to Standard Method 2540D and 2540E (APHA, 1998), respectively.
• **Salinity Concentration**

  For salinity measurements, 2 mL aliquots were centrifuged at 13,000×g for 2 minutes. Then, 0.3 mL aliquots of the clarified supernatant were transferred to the prism surface of a refractometer (Atago 4403 PAL-03S) for measurement of salinity concentration (expressed as % m/v).

• **Alkalinity**

  Alkalinity was measured according to Standard Method 2320B (APHA, 1998). Because the alkalinity concentrations were generally in the range of 1000-6000 mg/L as CaCO₃, 10 mL sample volumes collected from each reactor were diluted 10 fold prior to titration with by 1.6 N sulfuric acid (H₂SO₄) using a digital titrator (HACH Model 16900).

• **Gas Analysis**

  Gas produced in the digesters was collected in 25 L Tedlar bags (Supelco). The volume of gas collected was measured by determining the volume of water displaced in a water-filled bucket. Gas production rate was calculated by dividing the gas volume collected by the duration of time (in hours) that the gas collection bag was connected to the reactor.

  Methane and carbon dioxide concentrations in the biogas were measured via a gas chromatograph (SRI 310C) equipped with a thermal conductivity detector and an Alltech Poropak Q 80/100 column (6’×1/8”×0.085”). 100 µL samples collected in gas-tight glass syringes (Valco) equipped with luer-lok valve assemblies were introduced to the GC via direct, splitless injection. The carrier gas was helium at a constant pressure of 15 psi. Temperature was isothermal at 50 °C and for the duration of the 2.1 minute run times.
• **Volatile Organic Acids (VFA)**

Volatile organic acids were measured using an ion chromatograph (Dionex ICS-2000, Sunnyvale, CA) equipped with an IonPac ICE-AS6 column, AMS-ICE II suppressor, and conductivity detector. Sample injection volume was 100 mL, with isocratic elution performed with 0.4 mM heptafluorobutyric acid at a flow rate of 1.0 mL min\(^{-1}\). Tetrabutylammonium hydroxide (5 mM) was used as regenerant. Retention times and peak areas of fermentation products were compared to those of standards which included acetate, citrate, formate, fumarate, lactate, malate, propionate, pyruvate, and succinate.

### 3.3 Results and Discussion

#### 3.3.1 Initial Contents of the Reactors at Startup

After filling the mixture of unthickened BHR sludge and thickened UNOX sludge in the reactors on April 29, 2008, salinity was measured (via refractometer) to be 2.1\% (m/v) in the HR Reactor and 2.2\% in the LR Reactor. Parameters measured in the two reactors containing the UNOX plus BHR mixture prior to addition of anaerobic digester sludge on day 0, as well as the municipal anaerobic sludge, is shown below in Table 3-2.

The concentrations of various constituents within the two reactors after mixing the anaerobic digester sludge with the UNOX + BHR sludge are shown in Table 3-3.

<table>
<thead>
<tr>
<th>Sludge</th>
<th>pH</th>
<th>Alkalinity (mg/L)</th>
<th>TS (g/L)</th>
<th>TSS (g/L)</th>
<th>VSS (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR UNOX + BHR</td>
<td>7.06</td>
<td>2240</td>
<td>44.4</td>
<td>16.57</td>
<td>14.81</td>
</tr>
<tr>
<td>HR UNOX + BHR</td>
<td>6.97</td>
<td>2200</td>
<td>44.6</td>
<td>15.23</td>
<td>13.15</td>
</tr>
<tr>
<td>Anaerobic sludge(only)</td>
<td>6.97</td>
<td>1500</td>
<td>4.85</td>
<td>5.65</td>
<td>2.51</td>
</tr>
</tbody>
</table>
Table 3-3: Mixed sludge characteristics at the start of Period 1

<table>
<thead>
<tr>
<th>Sludge</th>
<th>Alkalinity (mg/L)</th>
<th>TS (g/L)</th>
<th>TSS (g/L)</th>
<th>VSS (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR Reactor</td>
<td>2140</td>
<td>39.1</td>
<td>15.1</td>
<td>13.2</td>
</tr>
<tr>
<td>HR Reactor</td>
<td>2110</td>
<td>39.3</td>
<td>14.0</td>
<td>11.7</td>
</tr>
</tbody>
</table>

3.3.2 Temperature, Salinity, pH, and Alkalinity

As shown in Figure 3-2, following startup, the temperatures in both reactors were relatively stable near the target level of 35°C. The temperature in the LR Reactor ranged from 31 to 38°C during Period 1, averaging 34.2°C. The temperature in the HR Reactor ranged from 31 to 38°C during Period 1, averaging 34.2°C. Thus, both reactors were operated within the mesophilic temperature range of 29.4 to 35 ºC (Reynolds, 1982).

Figure 3-3 depicts the salinity measured in the two reactors during Period 1 operation. As shown in the figure, both of the pilot-scale digester systems had moderate salinity. The salinity in the LR Reactor ranged from 3.1 to 3.3% m/v during Period 1, averaging 3.2%. The salinity in the HR Reactor ranged from 3.05 to 3.3% during Period 1, averaging 3.25%. The average salinity of two reactors was higher than original salinity, 2.8%. At least a portion of the variation in salinity measurements likely resulted from the fact that there were some inconsistencies in processing of sludge samples (some samples were centrifuged prior to analysis while others were not, and the time allowed for temperature equilibration was variable) during early stages of operation.

Figure 3-4 presents the pH values measured in both reactors during Period 1 operation. As noted in Section 3.2.3, the pH of was adjusted several times through addition of base (NaOH)
or acid (HCl) in an attempt to maintain the reactors within the range of 7 and 7.3. During the first 10 days of operation, pH had large variability in both LR and HR Reactors.

![LR Reactor: Temperature](image1)

![HR Reactor: Temperature](image2)

**Figure 3-2:** Temperature of LR Reactor (top) and HR Reactor (bottom) during Period 1
Figure 3-3: Salinity in LR Reactor (top) and HR Reactor (bottom) during Period 1

The pH had a tendency to rapidly decrease over time, reaching levels in the range of 6.5 to 7.0 before the pH temporarily increasing following addition of NaOH on days 1, 3, 5, and 9 in the LR Reactor and days 1, 3, and 5 in the HR Reactor. After each pH adjustment, the reactors were mixed (via pumping to recirculate sludge) for 1-2 hours before returning to the base-line condition of no mixing.
After the first 10 days, the pH was more stable but with an overall increase over time. The pH of both reactors eventually increased above 7.6, and HCl was added to decrease the pH in the LR Reactor on days 42 and 47 and the HR Reactor on days 27, 42, 43, and 47.
Figure 3-5: Alkalinity of LR Reactor (top) and HR Reactor (bottom) during Period 1

The results of alkalinity measurements are presented in Figure 3-5. As shown in the figure, alkalinity increased rapidly in both reactors during first 10 days, followed by a more gradual increase over time. As expected, the alkalinity decreased somewhat following addition of HCl to control pH. In both reactors, however, the alkalinity levels remained higher than 6000 mg/L as CaCO₃.
3.3.3 Volatile Fatty Acids

According to previous research, in a properly operated digester, volatile fatty acids (VFAs) are utilized as rapidly as they are produced and the measured concentration should not be more than 1000 mg/L (Loll and Moller, 1984). In order to assess the stabilization process in the two pilot-scale reactors, the VFAs including formate, lactate, acetate, succinate, propionate, were monitored over time during Period 1 operation. Results are presented in Figure 3-6.

For both reactors, VFA concentrations rapidly increased during the first two weeks of operation, reaching peak concentrations as high as 1808 mg/L in the LR Reactor and 1936 mg/L in the HR Reactor, which was far higher than the recommended 1000 mg/L criterion (Loll, Moller, 1984). In addition, the propionate/acetate ratio was reported as an indicator of inhibition and instability of anaerobic digester performance (as shown in Figure 3-7). The propionate/acetate ratios observed in the HR Reactor were far beyond the proposed threshold value of 1.4 (Hill et al, 1987), indicating poor stability. The ratio, however, rapidly decreased from days 40 to 47. In the LR Reactor, the propionate/acetate ratio increased during first 20 days of operation and then decrease below 1.4 after 27 days.

The total VFA concentration in the LR Reactor began to gradually decrease after day 21, reaching a level below 1000 mg/L by day 42 and a level of approximately 400 mg/L by day 47. In the HR Reactor, the total VFA concentrations also decreased over time, but to a somewhat lesser extent, reaching a level of 990 mg/L on day 47.

3.3.4 Biogas Analysis

The two reactors were operated for a total of 50 days under the conditions described in section 3.2. Gas and methane production (Figure 3-9) started on day 2 (May 2, 2008) and steadily increased from day 10 to day 20, in accordance with the trend of VFA concentrations.
Figure 3-6: Organic Acid content of LR Reactor (top) and HR Reactor (bottom) during Period 1
Overall gas and methane production rates increased during the first 20 days of operation, when organic acid concentrations were increasing. Gas production subsequently decreased over time, corresponding to intervals when organic acid concentrations were also decreasing. In the gas production rate figures, there were two extra large values for gas production rates in both HR and LR Reactors, corresponding to days when HCl was added to adjust pH. Much of the gas produced during and immediately after the HCl addition was comprised of CO₂, evolved from abiotic reactions. The high gas production rates shown in Figure 3-9 correspond to intervals when the reactor headspace gas contained high CO₂ concentrations (Figure 3-9).

A 60% methane criterion has been commonly used to assess biogas and anaerobic digester by many researchers (Gebauer, 2004). In this study the gas compositions of both
Figure 3-8: Biogas composition of LR Reactor (top) and HR Reactor (bottom) during Period 1
Figure 3-9: Biogas production rate of LR Reactor (top) and HR Reactor (bottom) during Period 1

Reactors is shown in Figure 3-8. For both the LR and HR Reactors, the methane content in the biogas increased to greater than 60% (by volume) after 20 days operation. In both reactors, there was a marked decrease in methane content and increase in CO₂ content following addition of
HCl for pH adjustment. The methane content of gas emitted by the reactors, however, increased over time following these sharp decreases.

Considering all of Period 1 operation (days 0 to 47), the total gas volume produced by the LR Reactor was 642.7 L, of which 65 % (v/v) was methane. The total gas volume produced by the HR Reactor was 577.6 L, of which 62.4% (v/v) was methane.

3.3.5 Solids Content

At the end of Period 1, unexpected spilling happened on the night of June 17, 2008 during mixing. On the following day, June 18, samples from the remaining sludge were collected after mixing. The VSS of HR and LR initial sludge were 13.15 g/L and 14.81g/L. The VSS of HR and LR final sludge were 9.75g/L and 9.7g/L.

Because it is not known how thoroughly the reactors’ contents were mixed prior to the accidental spill (it is possible that the sludge overflowing the reactor contained higher or lower solids content than the sludge remaining in the reactors), a rigorous mass balance on solids in the reactors over the first 47 days of reactor operation is not possible. Nevertheless, the fraction of solids destroyed was estimated based on a mass balance calculation based on the starting suspended solids concentration on day 0 minus the average suspended solids concentration in the reactors after mixing the sludge that remained times the reactor liquid volume of 30 gallons.

As a secondary estimate, solids destruction was also estimated based on typical gas production in anaerobic digesters treating solids from municipal wastewater, where gas production is typically 0.75 to 1.12 m³/kg volatile solids destroyed (Metcalf & Eddy, 2003). Based on this range, an estimate of the mass of volatile solids destroyed in the two pilot-scale digesters was calculated from the total gas production measured in the systems.
Calculations regarding the VSS destruction based on both of the calculation approaches are shown in Appendix A. According to the calculation (See Appendix A), the VSS destruction efficiency in the LR Reactor calculated from mass balance on solids concentrations measured at the start of operation and after the spill was 29%. The VSS destruction efficiency calculated based on gas production in the LR Reactor was in the range of 27%-41%. Thus, for the LR Reactor, both approaches for estimation of VSS destruction efficiency are in good agreement. For the HR Reactor, the VSS destruction efficiency calculated based on solids concentrations was 21%. The VSS destruction efficiency based on gas production was in the range of 28%-41%. Thus, while a rigorous mass balance is not possible, it appears as if the pilot-scale anaerobic digesters destroyed an appreciable fraction of the suspended solids.

3.4 Conclusions

Collectively, data collected during Period 1 operation suggested that anaerobic digestion of the saline WAS generated by the industrial facility is feasible in spite of the elevated salinity levels. Methane production was detected shortly after startup of the two pilot-scale reactors, and continued throughout the course of the initial operating period. Although VFA concentrations increased to high levels initially, they subsequently decreased to less than 1000 mg/L in both reactors. Taken together, the VFA and methane data demonstrate that a methanogenic population was able to acclimate to the elevated salinity conditions. Although a complete mass balance on solids destruction efficiency was not possible due to the accidental spilling of sludge, estimates of solids destruction based on gas production rates suggest that an appreciable fraction of the volatile suspended solids were destroyed in the process.
CHAPTER 4: PHASE 2 EXPERIMENTAL TESTS

4.1 Introduction

During Period 1 of reactor operation described in Chapter 3, it was established that an anaerobic microbial community could be successfully acclimated to treat the moderately saline WAS mixture from the industrial wastewater treatment plants under investigation. Research described in this chapter was conducted to evaluate anaerobic digester performance under two different mixing and loading regimes. One of the pilot-scale anaerobic digesters, designated as the LR Reactor, was operated with a longer hydraulic residence time, low organic loading rate, and no mixing. The second pilot-scale anaerobic digester, designated as the HR Reactor, was operated with a shorter hydraulic residence time, higher organic loading rate, and intermittent mixing.

4.2 Materials and Methods

4.2.1 Waste Activated Sludge Characterization

A mixture of UNOX and BHR waste activated sludge was delivered to LSU from the industrial facility approximately twice per week. The combined sludge was stored at 4ºC until use. Salinity, TS, TSS, VSS, and COD concentrations were measured for each separate batch of sludge received.

4.2.2 Reactors Configuration

The basic configuration of both pilot-scale anaerobic digesters was same as in Period 1 operation described in Chapter 3.

4.2.3 Reactors Conditions at the Start of Period 2

As noted in Section 3.3.3, there was an unintentional spill of a sizeable volume of the reactors’ contents on day 48 (June 17, 2008) at the end of Period 1 operation. To recover the
reactors, the remaining 47 gallons of digested sludge was mixed by sparging with ultra high purity nitrogen gas (N₂) for one hour and divided evenly into the two reactors with 23.5 gallons sludge of each. On day 49 (June 18, 2008), samples were removed for measurement of solids, alkalinity, and pH. Then, ultra-high-purity nitrogen (N₂) gas was sparged through each reactor to remove O₂ from the headspace. The epoxy and silicone seals on the reactor lids were compromised, requiring that they be replaced. Following the re-sealing, leaks in the new seals were repaired on day 50. Gas production and composition were not measured from day 49 to day 53.

During this same time interval, the pH in reactors was adjusted on several occasions via addition of a total of 2200 mL and 2100 mL of 1.0 M HCl in the LR and HR Reactors, respectively, in an attempt to maintain pH in the range of 7-7.1. The pH of the LR and HR Reactors was 7.08 and 6.95, respectively on day 54 (June 23, 2008). The time interval hereafter referred to as Period 2 of Reactor operation began on day 54.

4.2.4 Reactors Operation

- Feeding and Wasting

For Period 2 operation, the target operating conditions were to have HRT of 60 days and 30 days in the LR and HR Reactors, respectively, with a liquid volume of 30 gallons in each reactor. As noted in the preceding section, however, both reactors were at less than full liquid capacity at the beginning of Period 2 operation. The sludge volume in the digesters was increased gradually, by withdrawing only one half of the sludge volume fed on a daily basis until the full liquid volume of 30 gallons was reached. This was achieved by feeding 1.0 gallon of mixed WAS to the HR reactor from port 1 and pumping out 0.5 gal sludge from port 4, which resulted in a net increase of 0.5 gallon/day. For the LR reactor, 0.5 gal of mixed WAS was added
to port 1, and 0.25 gal sludge was pumped out from port 4, which resulted in an increase in reactor liquid volume of 0.25 gal/day. Sludge addition and removal was accomplished by means of peristaltic pumps (Masterflex).

The duration of the interval during which only one half of the fed WAS volume was removed each day lasted for a period of 29 days in the LR Reactor (June 23 through July 21, 2008) and 14 days for the HR reactor (June 23 through July 6, 2008). Thus, full 30-gallon liquid volume was achieved in the LR and HR Reactors on days 66 and 81, respectively. Thereafter, the volume of sludge removed from each reactor was the same as the volume fed to each reactor on a daily basis. The mixed WAS was fed once per day to the reactors from port 1 by peristaltic pump with a flow rate of 150 ml/min (62 rpm). Simultaneous withdrawal was conducted from port 4 by another pump with same flow rate. The feeding and withdraw lasted 25 minutes and mixing was temporarily turned off in the HR Reactor during the feeding interval.

After reaching a liquid volume of 30 gallons, in general, 0.5 gallons was fed and wasted from the LR Reactor on a daily basis and 1.0 gallon was fed and wasted from the HR Reactor on a daily basis to target operation with HRTs of 60 days and 30 days, respectively.

Although the target HRTs were 60 and 30 days in the LR and HR Reactors, respectively. There were multiple occasions, however, in which the daily feed/withdrawal volumes were not at the target levels. For example, on days 70, 81, 88, 103, and 166 (July 10, July 21, July 28, Aug. 11, and Oct. 13, 2008) the feeding/withdraw volumes in the HR Reactor were 3.25L, 2.25L, 1.5 L, 2.3 L, and 3 L, respectively, due to lack of available WAS sludge from the industrial facility. Additionally, there was no feed or withdraw from either of the reactors during the interval from day 124 to 131 (September 1, 2008 through September 8) due to a disruption caused by
Hurricane Gustav. Graphs showing the volumes of sludge fed to and removed from the two reactors during Period 2 are presented in Figure 4-1.

![Figure 4-1: Daily sludge feeding and wasting volumes during Period 2 operation](image)

- **Mixing Procedure**

  Throughout Period 2 operation, the LR Reactor was operated without any externally supplied mixing. The goal was for the HR Reactor to be completely mixed. In practice, mixing was accomplished using different approaches at different times during Period 2. During the time interval from days 53 to 123, mixing was provided by withdrawing sludge from port 2 and pumping back to port 3 using a peristaltic pump with a flow rate of 2000 mL/min. This was continued for 6-9 hours per day. Daily reactor feeding/wasting was conducted immediately after the end of this daily mixing procedure. The recycling pump was turned off during night time to minimize the potential for leaks or mechanical failures. A short-term test to evaluate the effectiveness of this mixing approach is presented in Appendix B.
Because of disruptions associated with Hurricane Gustav, no sludge was fed to either reactor and no mixing was performed in the HR Reactor from days 123 to 131. From days 131 to 149, the HR Reactor was mixed for approximately two hours per day by recirculating headspace gas withdrawn from a port located at the top of the reactor and reintroducing it into port 2 located at the bottom of the reactor (see Figure 4-2) using a peristaltic pump (2 L/min). Daily reactor feeding/wasting was conducted immediately after the end of this daily mixing procedure.

From day 131 onward, the HR Reactor was mixed via recirculation of headspace gas as described above but with duration of four hours per day. Results from short-term tests to evaluate the effectiveness of the gas recirculation mixing approach are presented in Appendix A.

- **Temperature and pH control**

  As in Period 1 operation, the target temperature in both of the pilot-scale reactors was 35°C. Temperature was controlled by manually adjusting the voltage controller attached to the electrical heating tape attached to the external surfaces of the two reactors. Temperature was measured by submerging the probe from a (Oakton) electronic thermometer in the sludge.

![Figure 4-2: Configuration of HR Reactor mixing by gas recirculation](image)
collection container immediately upon removal from the digesters during the daily feed/wasting procedure. There was no heating for the reactors during the interval from day 124 to 131 (September 1, 2008 through September 8) due to a disruption caused by Hurricane Gustav.

No external pH control was provided during Period 2 following the initial adjustments described in Section 4.2.3 (i.e., there was no addition of acid, base or bicarbonate).

**4.2.5 Analytical Methods**

The pH, ORP, TS, TSS, VSS, salinity, alkalinity, and VFA concentrations were measured as described in Chapter 3. Total COD was measured in triplicate using HACH (High range plus COD Reagent 0-15,000ppm range). Because of the high initial salinity and COD concentrations, samples were diluted by a factor of 2 or 4 using deionized water prior to homogenizing for 30 seconds in a blender (Hamilton Beach, commercial) prior to analysis. For COD analysis, absorbance was measured at a wavelength of 620 nm using an Evolution 60 spectrophotometer (Thermo Scientific).

Gas production volumes and gas composition were monitored daily following the same procedures as described in Chapter 3.

**4.3 Results and Discussion**

**4.3.1 Initial Conditions in Pilot-Scale Digesters at Start of Period 2**

Characterization of the reactor contents at the start of Period 2 are summarized in Table 4-1.

**4.3.2 Temperature, Salinity, pH, and Alkalinity**

Temperatures in the reactors during Period 2 experiments are shown in Figure 4-3. Although some fluctuations were observed, the temperatures were maintained at a roughly constant temperature near the target of 35°C. The temperature in the LR reactor ranged from 32
to 43°C during Period 2 with an average value of 35.5°C. The temperature in the HR reactor ranged from 31 to 43°C during Period 2 with an average value of 35°C. The highest temperatures occurred on days 129 to 130 (Sep. 6-7, 2008) following the re-start of heating because power shutdown caused by Hurricane Gustav.

**Table 4-1. Characterization of the sludge at the beginning of Period 2**

<table>
<thead>
<tr>
<th>Sludge</th>
<th>pH$^a$</th>
<th>Alkalinity (mg/L)$^a$</th>
<th>TS (g/L)$^a$</th>
<th>TSS (g/L)$^b$</th>
<th>VSS (g/L)$^b$</th>
<th>COD (g/L)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR Reactor</td>
<td>6.95</td>
<td>3460</td>
<td>30.59</td>
<td>10.3</td>
<td>9.75</td>
<td>13.8</td>
</tr>
<tr>
<td>LR Reactor</td>
<td>7.08</td>
<td>3780</td>
<td>30</td>
<td>10.0</td>
<td>9.7</td>
<td>13.8</td>
</tr>
</tbody>
</table>

$^a$ Data from day 54

$^b$ Data from day 51

The salinity concentration of the WAS fed to the reactors is shown below in Figure 4-4. As shown in the figure, the salinity in the feed was relatively stable over time, ranging from 2.7 to 3.3%, averaging 2.9% (m/v).

The salinity concentrations measured in the reactors’ effluents over time are presented in Figure 4-5. As shown in the figure, both digester systems had relatively stable salinity, ranging from 2.8 to 3.3% (m/v) and averaging 3.1% during Period 2. The salinity in both reactors increased slightly over time, likely reflecting release of inorganic ions as solids were digested.

The pH levels in the two pilot-scale digesters during Period 2 are depicted Figure 4-2. For both reactors, pH was relatively stable around the initial value at the beginning of the experiment. As shown in the figure, the pH of the LR Reactor ranged from 7.04 to 7.42, averaging 7.29. The pH of the HR Reactor ranged from 6.95 to 7.43, averaging 7.25.
Alkalinity concentrations measured in the two reactors as a function of time are depicted in Figure 4-7. The LR Reactor exhibited a gradual increase in alkalinity concentration from 3400 mg/L as CaCO₃ on day 54 to a level of 5300 mg/L as CaCO₃ on day 179. A similar trend was found for the HR Reactor, where alkalinity concentration increased from 3400 to 5500 mg/L as CaCO₃ over the same time interval.

Figure 4-3: Temperatures of the LR Reactor (top) and HR Reactor (bottom) in Period 2
Figure 4-4: Salinity in the WAS supplied to the pilot-scale digesters in Period 2

Figure 4-5: Salinity in the LR Reactor (top) and HR Reactor (bottom) in Period 2
An alkalinity concentration with the range of 2500-5500 mg/L as CaCO₃ is generally considered necessary to provide enough buffer capacity to neutralize volatile acids during anaerobic digestion (Eckenfelder, 1996). Experimental results from this study demonstrated that both reactors maintained alkalinity in this range without the need for any external adjustment via chemical addition (e.g., in the form of bicarbonate). The gradual increase in alkalinity in the reactors over time may have resulted from formation of NH₄HCO₃, produced by the combination
of the NH$_3$ from the breakdown of protein and amino acids and the CO$_2$ and H$_2$O present in the system (Metcalf & Eddy, 2003).

### 4.3.3 Solids Content

The concentrations of TSS and VSS in the feed supplied to the two reactors during Period 2 are shown in Figure 4-8. As shown in the figure, the TSS and VSS concentrations in the feed varied somewhat as a function of time. The TSS concentration ranged from 11.15 to 22.7 g/L. The VSS concentration ranged from 9.05 to 19.45 g/L. The flow weighted average TSS and VSS concentrations in the WAS fed to the reactors were 16.84 and 14.18 g/L, respectively. The ratio of the VSS to TSS concentrations in the WAS fed to the two reactors average 0.84 during Period 2 operation.

The solids loading rates to each of the reactors are shown in Figure 4-9. The data depicted in the figure represent the mass of TSS or VSS loaded into the reactor per volume of reactor liquid volume per day. Calculated values depicted in the figure accounted for the fact that from day 54 to 80 in the LR Reactor and from day 54 to 67 in the HR Reactor, the reactor liquid volume was less than 30 gallons. Calculations for time intervals after day 80 in the LR Reactor and day 67 in the HR Reactor reflect the mass of solids in the daily influent divided by 30 gallon liquid volume.

Aside from the interval when no sludge was fed to the reactors (due to hurricane impacts on power supply and sludge delivery), the TSS and VSS loading rates for LR Reactor ranged from 0.74 to 1.68 g/(L-day) and 0.56 to 1.47 g/(L-day) respectively. The HR reactor was fed with a TSS and VSS loading rates ranging from 0.42 to 3.33 g TSS/(L-day) and 0.36 to 2.91 g TSS/(L-day) respectively.
Figure 4-7: Alkalinity of the LR Reactor (top) and HR Reactor (bottom) in Period 2
Neglecting interval from days 124 to 131 when no sludge was supplied to the reactors, the time-weighted average TSS loading rates for the LR and HR Reactors were 31.1 and 62.4 g/(L-day), respectively, and the time-weighted average VSS loading rates for the LR and HR Reactors were 26.1 and 52.4 g/(L-day), respectively. Including the interval from days 124 to 131 when the loading rate was zero, the time-weighted average TSS loading rates for the LR and HR Reactors were 29.1 and 58.5 g/(L-day), respectively, and the time-weighted average VSS loading rates for the LR and HR Reactors were 24.5 and 49.1 g/(L-day), respectively.

From days 54 to 180, the total mass of TSS fed to the LR and HR Reactors was 3658 and 7305 g TSS. During the same time interval, the total mass of VSS fed to the LR and HR Reactors was 3038 and 6130 g VSS.
The TSS and VSS concentrations exiting the two reactors during Period 2 operation are shown in Figure 4-10. As shown in the Figure the TSS and VSS concentrations in the effluent from the LR reactor were consistently low throughout the entire duration of Period 2. Effluent TSS concentrations ranged from 0.13 to 0.93 g/L, averaging 0.66 g/L.
Effluent VSS concentrations ranged from 0.10 to 0.73 g/L, averaging 0.48 g/L. The low suspended solids concentrations in the effluent of the LR Reactor reflect the fact that the system was unmixed, which allowed settling of solids and separation of solids and hydraulic retention times in the system.

The HR Reactor had comparatively higher effluent TSS concentrations which ranged from 1.34 to 23.4 g/L and averaged 7.1 g/L. Effluent VSS concentration ranged from 1.17 to 16.8 g/L, averaging 5.28 g/L. Effluent suspended solids concentrations were relatively stable in the interval from day 54 to day 122 (June 23 to Aug. 30, 2008) when pumping mixing was applied. Effluent suspended solids concentration increased immediately following the switch to mixing via gas recirculation on day 131 (Sept. 8, 2008), indicating that gas recirculation might provide better mixing than pumping. An evaluation of the different mixing regimes is presented in Appendix B. The higher suspended solids concentrations in the HR Reactor relative to the LR Reactor reflect the fact that mixing, even if not perfect, was sufficient to prevent the degree of settling observed in the HR Reactor (See Appendix B).

From days 54 to 180, the total mass of TSS exiting the LR and HR Reactors via the treated effluent was 89.8 and 2921g TSS. During the same time interval, the total mass of VSS exiting the LR and HR Reactors via the treated effluent was 79.2 and 2150 g VSS.

The overall TSS and VSS removal efficiencies (calculated as total mass of suspended solids entering minus the mass exiting, divided by the mass entering time 100%) for the LR Reactor during Period 2 operation were 43 and 49%. The overall TSS and VSS removal efficiencies for the HR Reactor during Period 2 were 37 and 41%. It should be noted, however, that a portion of the “removal” was due to accumulation of solids within the reactors rather than solids destruction.
Figure 4-10: Suspended solids concentrations in the effluent of LR Reactor (top) and HR Reactor (bottom) in Period 2
Calculation of solids destruction efficiency required measurement of solids concentrations within the reactors at the end of Period 2 operation. On day 180 (Oct. 27, 2008), each of the reactors was mixed via recirculation of headspace gas as normally employed in the daily mixing regime for the HR Reactor. Then, ultra-high-purity N₂ was sparged into the reactors at a rate of 9 L/min for a duration of 15 minutes. Samples were then collected from each of the liquid sampling ports for measurement of TSS, VSS, TVS, TFS, total COD, and soluble COD. Average values from these measurements were used in calculating concentrations of the various constituents within the reactors.

Overall mass balance calculations for TSS and VSS in the two pilot-scale digesters during Period 2 operation can be found in Appendix C and the results were summarized in Table 4-2.

The initial mass of TSS and VSS in the reactors at the start of period 2 was similar. The mass of TSS and VSS fed to the HR reactor was roughly double the amount fed to the LR Reactor. The suspended solids withdrawal from LR Reactor was much less than that for the HR Reactor. On the basis of mass balance calculations, the LR Reactor was found to have solids destruction efficiencies of 49% for VSS and 43% for TSS. The HR Reactor was found to have somewhat lower solids destruction efficiencies of 41% for VSS and 37% for TSS.

**Table 4-2: Results of solid mass balance of Period 2**

<table>
<thead>
<tr>
<th></th>
<th>Initial in reactor (g)</th>
<th>Feed (g)</th>
<th>Withdrawal (g)</th>
<th>Final in reactor (g)</th>
<th>Destruction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LR</td>
<td>HR</td>
<td>LR</td>
<td>HR</td>
<td>LR</td>
</tr>
<tr>
<td>VSS</td>
<td>826.9</td>
<td>867.3</td>
<td>3058</td>
<td>6130.5</td>
<td>2149.9</td>
</tr>
<tr>
<td>TSS</td>
<td>892.2</td>
<td>1164</td>
<td>3643.3</td>
<td>7305.0</td>
<td>2921</td>
</tr>
</tbody>
</table>
As a means of assessing whether the solids destruction efficiencies presented in Table 4-2 appeared to be reasonable, estimates of the solids destruction were calculated based on the empirical relationship between gas production and volatile solids destruction in digesters treating municipal wastewater sludge. It has been reported that gas production is typically in the range of 0.75 to 1.12 liters of gas produced per gram of volatile solids destroyed (Metcalf & Eddy, 2003).

The mass of solids destroyed was estimated based on this empirical range and the total gas production measured in the system (see section 4.3.4) as described in Appendix C. A comparison of the solids destruction determined from the direct mass balance approach and the indirect approach based on gas production are illustrated in Figure 4-11. Columns 1 and 3 represent the VSS present in the reactors at the start of Period 2 (blue) plus the VSS input to the reactors from daily feeding (maroon). Columns 2 and 4 present the VSS exiting the reactors in period 2.
the effluent (tan), the VSS present in the reactors at the end of Period 2 (yellow) and the mass of VSS destroyed as estimated based on gas production (aqua). The error bars represents the upper and lower ends of the range calculated based on the range of gas produced per gram volatile solids destroyed. In the calculation of solids destruction based on direct mass balance (Table 4-2), the mass VSS destroyed was assumed to equal the total amount of VSS present in the reactor at the start of Period 2 plus the VSS entering minus the sum of the VSS present at the end of the period plus the VSS exiting in the effluent. This would correspond to total heights of columns 2 and 4 exactly equal to the column heights depicted in columns 1 and 2, respectively, in Figure 4-11. As shown in the figure, VSS destruction in the HR Reactor calculated from mass balance (2887 g VSS destroyed) is consistent with the range calculated based on gas production (range of 2532 to 3781 g VSS destroyed). VSS destruction in the LR Reactor calculated from mass balance (1921 g VSS destroyed) is somewhat lower than the range calculated based on gas production (range of 1008 to 1506 g VSS destroyed). The range of VSS mass destroyed estimated from the gas production volume would correspond to a VSS destruction efficiency in the range of 26 to 38%. It should be noted, however, that gas production volume from days 124 to 132 (i.e., the hurricane impacted time interval) was not measured and thus was not included in the calculation of solids destruction based on gas production. Thus, the range of calculated solids destruction calculated here based on gas production volume would likely underestimate the actual solids destruction. Nevertheless, the calculations support the notion that reasonably high solids destruction efficiencies were achieved in both reactors.

4.3.4 Biogas Analysis

The quantity and composition of gas exiting the reactors was measured on a daily basis. Biogas production rate data are presented in Figure 4-12. Gas production started immediately
after feeding was started, with total gas production rates of 0.38 L/hr and 0.22 L/hr in the LR and HR Reactors, respectively, on day 54. Gas, and perhaps more importantly, methane production, observed following the start of Period 2 operation demonstrated that the reactors’ performance was able to quickly recover following the sludge spill and potential oxygen exposure at the end of Period 1.

Gas production rates rapidly increased over the 10 days following the start of Period 2 and its associated daily feeding. Thereafter, gas production rates were somewhat variable as a function of time. Likely due to a higher daily sludge loading, the HR Reactor consistently exhibited higher biogas production rates than the LR Reactor.

On the day 109, a leak was found in the gas collecting bag of LR Reactor, and the Tedlar gas collection bags were replaced for both reactors. It is unknown how long the leak existed prior to detection. There was a dramatic increase in the measured gas production rate after the leaking problem was fixed; however, this also corresponded to a time interval when the solids loading rates to the reactors increased (see Figures 4-9 and 4-17), so drawing an unequivocal conclusion regarding the impact of the leak on the measured gas production is not possible. There was no gas measurement in the duration of days 123 to 128 (Sept. 1- 5, 2008) due to power outages associated with Hurricane Gustav.

Composition of the gas in both reactors in Period 2 is presented in Figure 4-12. For both reactors, the methane content in the biogas increased during the interval immediately after the start of Period 2 operation. Aside from a temporary decrease following resumption of feeding after the hurricane-associated period, the methane content of gas produced in both reactors was consistently greater than 60% (v/v). According to the 60 % methane criterion, (Gebauer, 2004) both reactors were well functioning during Period 2 operation.
During the interval from day 54 to day 180 (i.e., the duration of Period 2), the total volume of gas production in the LR and HR Reactors were 1412 and 2230 L. Of this, 64 and 65% was methane and 29 and 30% was CO₂ in the LR and HR Reactors, respectively.

4.3.5 Volatile Fatty Acids

Volatile fatty acids (VFA) concentrations measured in the two reactors during Period 2 are shown in Figure 4-14. During the first three weeks of Period 2 operation, the VFA concentrations of in both reactors increased, reaching peak total VFA concentrations of on 1128 mg/L in the LR Reactor on day 75 and 1601 mg/L in the HR Reactor on day 70. During this time interval, acetate, formate, succinate, and propionate were detected. The VFA concentrations subsequently decreased, with total VFA levels less than 1000 mg/L for all measurements after day 77 in both reactors. From day 99 forward, the total VFA content was comprised almost entirely of succinate.

In well-functioning digesters exhibiting stable performance, organic acids are utilized as rapidly as they are produced. For digesters treating biosolids from municipal wastewater treatment, the total VFA concentration generally should be less than 1000 mg/L (Reynolds, 1982). The VFA concentrations measured in the present study indicate good stability of the system following startup.

An additional VFA criterion sometimes used to evaluate the stability of conventional anaerobic digesters is the ratio of propionate to acetate, which was proposed to have a threshold Value of 1.4, above which unstable performance can occur (Hill et al., 1987). The ratios of propionate and acetate observed in the LR and HR Reactors are presented in Figure 4-14. Although there were some fluctuations for both reactors; the peak ratios were both lower than the
Figure 4-12: Biogas production rate of LR Reactor (top) and HR Reactor (bottom) in Period 2
Figure 4-13: Gas composition of LR Reactor (top) and HR Reactor (bottom) in Period 2
Figure 4-14: Organic acid concentrations of LR Reactor (top) and HR Reactor (bottom) in Period 2
threshold value. This generally suggests that stable conditions might have prevailed, at least according to this VFA criterion.

4.3.6 Chemical Oxygen Demand

The concentrations of COD in the feed supplied to the two reactors during Period 2 are shown in Figure 4-15.

![Influent COD (Mixed Sludge)](image)

Figure 4-15: COD concentrations in the influent sludge in Period 2

As shown in the figure, the COD concentration in the feed varied somewhat as a function of time, ranging from 15.6 g/L to 44.2 g/L. The flow weighted average COD concentration in the WAS fed to the reactors during Period 2 was 24.15 g/L.

The COD loading rates to each of the reactors are shown in Figure 4-16. The data depicted in the figure represent the mass of COD loaded into the reactors per reactor liquid volume per day. Calculated values depicted in the figure accounted for the fact that from days 54 to 80 in the LR Reactor and from days 54 to 67 in the HR Reactor, the reactor liquid volume was less than 30 gallons. Calculations for time intervals after day 80 in the LR Reactor and day
67 in the HR Reactor reflect the mass of COD in the daily influent divided by 30 gallon liquid volume. There was no feed to either of the reactors from days 124 to 131.

**Figure 4-16: COD loading rate of LR and HR Reactors in Period 2**

Neglecting the interval of days 124 to 131 when no sludge was fed to the reactors, the COD loading rate to the LR Reactor ranged from 1.23 to 2.79 g COD/(L·day) with an average of 1.59 g COD/(L·day). During the same time interval, the COD loading rate to the HR Reactor ranged from 1.23 to 5.57 g COD/(L·day) with an average of 3.1 g COD/(L·day). For comparison purposes, loading of anaerobic process is 3.2 to 32 kg COD/m³·d.

The loading rates were highest for both reactors during the interval from days 115-117 due to higher than normal COD concentrations in the mixed sludge obtained from the industrial facility. While sudden increases in organic load have the potential to cause increases in organic acid concentrations and therefore decrease in pH, there were no large spikes in organic acid
concentrations (see Figure 4-14) or pH (Figure 4-6) in either reactor following this interval of elevated COD loading.

From day 54 to day 180 (i.e., the duration of Period 2), the total mass of COD loaded to the LR and HR Reactors via the daily feed was 5478 and 10753 g, respectively.

The total COD concentrations (i.e., those measured using unfiltered samples) exiting the two reactors during Period 2 operation are shown in Figure 4-17. As shown in the figure the COD concentrations in the effluent from the LR Reactor were consistently low throughout the entire duration of Period 2, ranging from 0.95-3.58 g/L and averaging 2.33 g/L. Effluent COD concentrations from the HR Reactor were somewhat higher, ranging from 2.31 to 26.57 g/L, averaging 9.9 g/L. Similar to what was described previously with respect to suspended solids concentrations (see Section 4.3.3) the effluent COD in the HR Reactor increased immediately after the gas recirculation process was applied starting on day 131 (Sept. 8, 2008).

From day 54 to day 180 (i.e., the duration of Period 2), the total mass of COD exiting the LR and HR Reactors via the liquid effluent withdrawn on a daily basis was 441.2 and 4133 g, respectively.

Overall mass balance calculations for COD in the two pilot-scale digesters during Period 2 operation can be found in Appendix D. Results are summarized in Figure 4-18.

Theoretically the percentage of COD removed calculated by mass balance should be equal to the fraction of COD methanized. In this study, for HR Reactor, the results calculated from the two methods were close, 38.9% for the former and 32.2% for the latter. There was slight difference for LR Reactor, 48.3% for the mass balance result and the 36.1% for methanized. Figure 4-17 presents a graphical representation of total influent COD and effluent COD for both reactors.
Figure 4-17: Effluent COD concentrations of LR Reactor (top) and HR Reactor (bottom) in Period 2
The overall mass balance closure was 87.9% for the LR Reactor and 93.3% for the HR Reactor. One possible explanation for the lack of complete mass balance closure is that leaks in the gas collection bags resulted in less methane accounted for in the mass balance calculation than was actually produced. Another reason is that gas production volume and gas composition was not measured during the interval of disruption associated with Hurricane Gustav and was not accounted for in the COD equivalent of methane exiting the system in the mass balance calculation. Regardless, there was reasonable closure on the COD mass balance for both reactors.

4.4 Conclusions

Collectively, data collected during Period 2 operation demonstrated that anaerobic digestion of the saline WAS generated by the industrial facility is feasible in spite of the elevated salinity levels. Two reactor operating strategies were experimentally tested. One of the pilot-scale anaerobic digesters, designated as the LR Reactor, was operated with a longer hydraulic residence time, lower organic loading rate, and no mixing. The second pilot-scale anaerobic
digester, designated as the HR Reactor, was operated with a shorter hydraulic residence time, higher organic loading rate, and intermittent mixing. Both reactors exhibited stable pH levels in the range from 6.95 to 7.43 without the need for external pH adjustment. Although VFA concentrations initially accumulated to high levels near the beginning of the operating period, VFA concentrations subsequently decreased to below 1000 mg/L.

Because multiple variables were different between the two reactors (they differed in both HRT and mixing), it is not possible to conclusively assess the impact of either HRT or mixing on digester performance based on the data collected. Nevertheless, results demonstrated that both reactor configurations could be effectively used to digest the WAS from this facility. Both reactors produced gas high in methane content (>60% v/v) and achieved appreciable solids destruction. The average methane production rate, however, was higher in the HR Reactor than the LR Reactor. On the other hand, solids destruction efficiency was higher in the LR Reactor than in the HR Reactor (49% vs. 41%).

Selection of either of the reactor operating strategies as being more optimal for a full-scale implementation would depend on whether it is more desirable to achieve high solids destruction efficiency or whether it is more desirable to maximize methane production per unit volume of reactor capacity. Selection would also depend on a number of other complex factors including capital and operating costs, so it cannot be determined from the data collected in this study which system would be best for use at the industrial facility generating the WAS that was treated.
CHAPTER 5: OVERALL CONCLUSIONS

The research reported in this thesis was conducted in support of an effort to assess the potential of mesophilic anaerobic digestion. There are several conclusions that can be derived from the study:

In the first phase of batch operation, the goal of acclimation of methanogenic biomass to elevated salinity was realized during 50 days operation. The mixed biosolid of BHR and UNOX sludge with 2-3 g/L salinity showed some anaerobic digestion activity with the proof of medium VSS removal efficiency for both reactors. The temperatures in both reactors were relatively stable near the target level of 35°C. pH of both reactor could be maintained within the range of 7 and 7.3 by addition of base (NaOH) or acid (HCl) at beginning and then self adjustment after start up, which predicted growth equilibrium of acid acetagenic bacteria and methanogens. VFA concentrations increased after the reactors were started up and then tended to decrease because the VFA was consumed by menthanogens. Only one reactor was believed to reach stability while the other on did not because the VFA of the later was far higher than the criterion of 1000 mg/L.

In phase 2, both reactors had reached stability with the two proofs, (1) exhibition of stable pH levels without external pH adjustment (2) low VFA concentrations. The overall anaerobic digestion of the mixed sludge of BHR and UNOX sludge in this phase showed generally good performance with the high VSS destruction efficiency, 41.26% (HR reactor) and 49% (LR reactor) and high methane content of approximately 65% after 70 days (July 9, 2008) operation.

Both reactors exhibited stable pH levels in the range from 6.95 to 7.43 without the need for external pH adjustment. Although VFA concentrations initially accumulated to high levels near the beginning of the operating period, VFA concentrations subsequently decreased to below
1000 mg/L. Both reactors produced gas high in methane content (>60% v/v) and achieved appreciable solids destruction.

Future work could focus on the cost assessment and improvement in methane production rate.
REFERENCES


Anaerobic Digestion of Biomass, 1987, David P. Chynoweth, Ron Isaacson, Contributor David P. Chynoweth, Published by Springer


APPENDIX A: THE SOLIDS CALCULATION DURING PERIOD 1

- LR VSS Destruction:

Calculation based on mass balance:

Initial VSS values at the start of Period 1

\[ VSS_{\text{initial}} = 14.81\text{g/L} \times 3.7854\text{L/gal} \times 30\text{gal} = 1681.85\text{g} \]

The total VSS taken out due to sampling

\[ VSS_{\text{out}} = 92.657\text{g} \]

The final VSS measured after mixing sludge following spill

\[ VSS_{\text{final}} = 9.7\frac{\text{g}}{\text{L}} \times 3.7854\frac{\text{L}}{\text{gal}} \times 30\text{gal} = 1101.55\text{g} \]

The mass balance for the LR VSS destroyed

\[ VSS_{\text{reduced}} = VSS_{\text{initial}} - VSS_{\text{out}} - VSS_{\text{final}} = 487.64\text{g} \]

% Reduction

\[ \text{LR VSS reduction(\%)} = \frac{VSS_{\text{reduced}}}{VSS_{\text{initial}}} \times 100\% = 29\% \]

- Estimation of the VSS destruction based on biogas back-calculation method:

Min. VS reduction = \[ \frac{642.7 \text{ L gas}}{1.12 \text{ g VS destroyed}} = 573.8\text{g VS destroyed} \]

Max. VS reduction = \[ \frac{642.7 \text{ L gas}}{0.75 \text{ g VS destroyed}} = 856.9\text{g VS} \]
Typically, volatile solid (VS) includes volatile suspended solid and volatile dissolved solid. An assumption was made that the ratio of VSS to VS is 0.8 to calculate the equivalent of VSS destruction.

Min. VSS reduction = 573.8g VS × 0.8 = 459g VSS

Max. VSS reduction = 856.9g VS × 0.8 = 686g VSS

A range of percentage of VSS reduction could be calculated as:

\[
\frac{459g}{1681.9g} \times 100% \approx \frac{686g}{1681.9g} \times 100% = 27\% \sim 41\%
\]

- **HR VSS Destruction:**

Calculation of the VSS destruction (HR reactor) based on mass balance:

Initial VSS values at the start of Period 1

Initial VSS = 13.15g/L × 3.7854L/gal × 30gal = 1493.34g

The total VSS taken out due to sampling

\[ VSS_{out} = 71.825g \]

The final VSS measured after mixing sludge following spill

\[ VSS_{final} = 9.75 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 30gal = 1107.23g \]

The mass balance for the HR VSS destroyed

\[ VSS_{reduced} = VSS_{initial} - VSS_{out} - VSS_{final} = 314.28g \]

% Reduction

\[ HR \ VSS \ reduction(\%) = \frac{VSS_{reduced}}{VSS_{initial}} \times 100\% = 21\% \]
• **Estimation of the VSS destruction based on biogas back-calculation method:**

Min. VS reduction = \( \frac{577.6 \text{ L gas}}{1.12 \text{ L gas per g VS destroyed}} = 515.7 \text{ g VS destroyed} \approx 421.56 \text{ g VSS destroyed} \)

Max. VS reduction = \( \frac{577.6 \text{ L gas}}{0.75 \text{ L gas per g VS}} = 770.1 \text{ g VS destroyed} \approx 616.08 \text{ g VSS destroyed} \)

Percentage of VSS reduction = \( \frac{421.56 \text{ g}}{1493.3 \text{ g}} \times 100\% \approx \frac{616.08 \text{ g}}{1493.3 \text{ g}} \times 100\% = 28\% \sim 41\% \)
APPENDIX B: EVALUATION OF MIXING IN THE HR REACTOR IN PERIOD 2

Introduction

High-rate digester has a continuous mixing system which provides better contact between the seeded and fresh sludge thereby increasing the effective volume of the reactor. Mixing is a very important operation in HR reactor, reducing thermal stratification, dispersing the substrate for better contact with the active biomass and reducing scum buildup (Vesilind et al.). Beyond that, for this specific research, since the digestion is conducted under medium salinity conditions, mixing also helps to dilute the inhibitory substances or adverse pH and temperature feed characteristics. On the other hand, opposite views was also reported by some researchers that mixing could destroy organism or obligate interspecies associations and thus decrease the digestion performance (David, et. Al). However, the effect of mixing depends on many factors, such as digester size, configuration, organic loading and method of mixing. Three different mixing methods were used in this study and they were (1) Mixing with pumping only (2) two-hour gas recirculation (3) four-hour gas recirculation. The performances of these mixing methods were evaluated in the following section by testing the TSS and VSS content from different sample points.

Material and Methods

(1) Mixing with pumping only

Pump recycle was conducted from June 23, 2008 to September 8, 2008, 6 mixing hours per day, and two peristaltic pumps were used as recycle-driven device with the flow rate of 2L/min and 300 ml/min per minute. Two flow routes were applied in this type of recycle, as shown in figure 1. In route 1 (blue line), sludge was pumped from port 1 to port 4 and was pumped from port 2 to port 3 in route 2 (orange line). For most of the duration recycle route 1 was applied and
route 2 was only used occasionally. Sludge was sampled each day from port 4 and TSS and VSS was analyzed.

![Diagram of the mixing system](image)

**Figure B-1: Pump recycles only for mixing HR reactor**

(2) Two-hour gas recirculation

On September 18, 2008, the reactor was mixed with the biogas from top port from 11:30 p.m. to 1:30 p.m. Sludge was sampled from port 1, 2, 3, and 4 and the TSS, VSS, and COD was measured. The configuration of the mixing system was showed in Figure 4-2.

(3) Four-hour gas recirculation

On September 26, 2008, the reactor was mixed with the biogas from top port from 1:00 p.m. to 5:00 p.m. Sludge was sampled from port 1, 2, 3, and 4 and TSS and VSS were measured as an indicator of well mixing.

**Results and Discussion**

The TSS and VSS of different mixing method were measured for different sample ports and the average value and statistical analysis results were summarized in table 1. The standard
deviation indicated the spread of values in the solid sample. The COV presented the precision of the solid sample analysis.

Table B-1: Statistical analysis of different mixing methods

<table>
<thead>
<tr>
<th></th>
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<th>Two-hour gas recirculation</th>
<th>Four-hour gas recirculation</th>
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<tr>
<td></td>
<td>TSS (g/L)</td>
<td>VSS (g/L)</td>
<td>TSS (g/L)</td>
</tr>
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<td>-</td>
<td>-</td>
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<td>8.648</td>
</tr>
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<td>COV</td>
<td>-</td>
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<td>57.9%</td>
</tr>
</tbody>
</table>

For the mixing by pump, sludge was only sampled from port 4 and no sample from other ports. Therefore the statistic analysis of pump recycle in table 1 was blank. Even though, we can still conclude that the pump might not provide good mixing effect with the following observation. The original TSS content for HR reactor is around 10.25 g/L, however, TSS dramatically decreases to an approximate value of 3.5 g/L a few days later. Even if some of the solid was digested, most of the solid settled to the bottom, resulting in a fast solid content decrease. Therefore the pump did not provide a good mixing. Compared with two-hour gas recirculation, four-hours recirculation provides a smaller standard deviation and a smaller COV value even from 4 total different sampling ports, predicting that the HR reactor was well mixed by four-hour gas recirculation. From September 26, 2009 forward, four-hour gas recirculation is applied as a good mixing method.
APPENDIX C: THE SOLIDS CALCULATION IN PERIOD 2

- **LR VSS Destruction:**

Initial VSS values at the start of Period 2

\[
\text{Initial VSS} = 9.7 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 23.5\text{gal} = 862.88g
\]

The total VSS taken out

\[
VSS_{\text{out}} = 57.43g
\]

The total VSS fed in

\[
VSS_{\text{in}} = 3058g
\]

The final VSS measured after mixing sludge

\[
VSS_{\text{final}} = 17.1 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 30\text{gal} = 1941.9g
\]

The mass balance for the LR VSS destroyed

\[
\text{VSS reduced} = VSS_{\text{initial}} + VSS_{\text{in}} - VSS_{\text{out}} - VSS_{\text{final}} = 1921.1g
\]

% Removal

\[
\text{LR VSS removal(\%)} = \frac{\text{VSS reduced}}{VSS_{\text{initial}} + VSS_{\text{in}}} \times 100 = 49
\]

- **Estimation of the VSS destruction of LR based on biogas back-calculation method:**

Min. VS reduction = \[
\frac{1412 \text{ L gas}}{1.12 \text{ g VS destroyed}} = 1260.4 \text{g VS destroyed}
\]

Miax. VS reduction = \[
\frac{1412 \text{ L gas}}{0.75 \text{ g VS destroyed}} = 1882.2 \text{g VS destroyed}
\]
Typically, volatile solid (VS) includes volatile suspended solid and volatile dissolved solid. An assumption was made that the ratio of VSS to VS is 0.8 to calculate the equivalent of VSS destruction.

\[
\text{Min. VSS reduction} = 1260.4\text{gVS} \times 0.8 = 1008.32\text{g VSS}
\]

\[
\text{Max. VSS reduction} = 1882.2\text{gVS} \times 0.8 = 1505.76\text{g VSS}
\]

- **LR TSS Destruction:**

  Initial TSS values at the start of Period 2

  \[
  \text{Initial TSS} = 10.03\frac{g}{L} \times 3.7854\frac{L}{gal} \times 23.5\text{gal} = 892.24\text{g}
  \]

  The total TSS taken out

  \[
  TSS_{\text{out}} = 79.21\text{g}
  \]

  The total TSS fed in

  \[
  TSS_{\text{in}} = 3643.3\text{g}
  \]

  The final TSS after mixing

  \[
  TSS_{\text{final}} = 22.12\frac{g}{L} \times 3.7854\frac{L}{gal} \times 30\text{gal} = 2512\text{g}
  \]

  The mass balance for the HR VSS destroyed

  \[
  \text{TSS reduced} = TSS_{\text{initial}} + TSS_{\text{in}} - TSS_{\text{out}} - TSS_{\text{final}} = 1944.33\text{g}
  \]

  \%

  \[
  \text{LR TSS removal(%) = } \frac{\text{TSS reduced}}{TSS_{\text{initial}} + TSS_{\text{in}}} \times 100 = 42.87
  \]

- **HR VSS Destruction:**

  Initial VSS values at the start of Period 2
\[
\text{Initial VSS} = 9.75 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 23.5 \text{gal} = 867.33g
\]

The total VSS taken out

\[
\text{VSS}_{\text{out}} = 2149.91g
\]

The total VSS feed in

\[
\text{VSS}_{\text{in}} = 6130.5g
\]

The final VSS after mixing

\[
\text{VSS}_{\text{final}} = 16.79 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 30 \text{gal} = 1906.7g
\]

The mass balance for the HR VSS destroyed

\[
\text{VSS reduced} = \text{VSS}_{\text{initial}} + \text{VSS}_{\text{in}} - \text{VSS}_{\text{out}} - \text{VSS}_{\text{final}} = 2887.2g
\]

\[
\text{HR VSS removal(\%)} = \frac{\text{VSS reduced}}{\text{VSS}_{\text{initial}} + \text{VSS}_{\text{in}}} \times 100 = 41.26
\]

- **Estimation of the VSS destruction of HR based on biogas back-calculation method:**

  \[
  \text{Min. VS reduction} = \frac{2230 \text{ L gas}}{1.12 \text{ g VS destroyed}} = 1991 \text{ g VS destroyed}
  \]

  \[
  \text{Max. VS reduction} = \frac{2230 \text{ L gas}}{0.75 \text{ g VS destroyed}} = 2973 \text{ g VS destroyed}
  \]

Typically, volatile solid (VS) includes volatile suspended solid and volatile dissolved solid. An assumption was made that the ratio of VSS to VS is 0.8 to calculate the equivalent of VSS destruction.
Min. VSS reduction = 1991g VS × 0.8 = 1593g VSS

Max. VSS reduction = 2973g VS × 0.8 = 2379g VSS

- **HR TSS Destruction:**

  Initial TSS values at the start of Period 2

  \[
  \text{Initial TSS} = 10.25 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 23.5 \text{gal} = 1164g
  \]

  The total TSS taken out

  \[
  \text{TSS}_{\text{out}} = 2921g
  \]

  The total TSS feed in

  \[
  \text{TSS}_{\text{in}} = 7305.07g
  \]

  The final TSS after mixing

  \[
  \text{TSS}_{\text{final}} = 21.18 \frac{g}{L} \times 3.7854 \frac{L}{gal} \times 30 \text{gal} = 2405.2g
  \]

  The mass balance for the HR TSS destroyed

  \[
  \text{TSS reduced} = \text{TSS}_{\text{initial}} + \text{TSS}_{\text{in}} - \text{TSS}_{\text{out}} - \text{TSS}_{\text{final}} = 3142.87g
  \]

  % Removal

  \[
  \text{HR VSS removal(\%)} = \frac{\text{VSS reduced}}{\text{VSS}_{\text{initial}} + \text{VSS}_{\text{in}}} \times 100 = 37.11
  \]
APPENDIX D: THE COD MASS BALANCE CALCULATION IN PERIOD 2

- LR COD Mass Balance:

Calculation the COD removal of the LR reactor based on mass balance:

\[
COD_{in} = 5372.6g
\]

\[
COD_{out} = 441.2g
\]

\[
COD_{original} = 13.785 \frac{g}{L} \times 23.5\text{gal} \times 3.7854 \frac{L}{\text{gal}} = 1226.27g
\]

\[
COD_{residue} = 26.19 \frac{g}{L} \times 30\text{gal} \times 3.7854 \frac{L}{\text{gal}} = 2974.2g
\]

COD mass balance:

\[
COD_{removal}(\%) = \frac{COD_{original} + COD_{in} - COD_{out} - COD_{residue} \times 100}{COD_{total}}
\]

\[
= \frac{1226.27g + 5372.6g - 441.2g - 2974.2g \times 100}{1226.27g + 5372.6g} = 48.24
\]

- Percentage of LR methanized COD:

Produced methane: 905.16L at 23° C, 1Atm

\[
V = n \frac{RT}{p} = 1 \text{mol} \times \frac{0.08205 \frac{L \times Atm}{\text{mole} \times K}}{1 \text{Atm}} = 24.3L
\]

Mass of methane = 905.16L \times \frac{1 \text{mole}}{24.3 L} \times \frac{16g}{1 \text{mole}} = 596g

\[CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O\]

\[
\frac{COD}{CH_4} = \frac{2 \times 16 \frac{g}{\text{mole}} \times 2}{16 \frac{g}{\text{mole}}} = 4 \frac{g \text{ COD}}{\text{g CH}_4}
\]
Methanized COD = \(596 \text{g CH}_4 \times 4 \frac{\text{g COD}}{\text{g CH}_4} = 2384 \text{g CO}\)

\[
\text{Methanized COD} = \frac{\text{Methanized COD}}{\text{COD}_{\text{total}}} = \frac{2384 \text{g COD}}{6598.87 \text{g COD}} \times 100 = 36.13
\]

- **HR COD Mass Balance:**

Calculation the COD removal of the HR reactor based on mass balance:

\[
\text{COD}_{\text{in}} = 10561.9 \text{g}
\]

\[
\text{COD}_{\text{out}} = 4133.1 \text{g}
\]

\[
\text{COD}_{\text{original}} = 13.785 \text{g/L} \times 23.5 \text{gal} \times 3.7854 \frac{\text{gal}}{\text{L}} = 1226.27 \text{g}
\]

\[
\text{COD}_{\text{residue}} = 27.05 \frac{\text{g}}{\text{L}} \times 30 \text{gal} \times 3.7854 \frac{\text{gal}}{\text{L}} = 3071.85 \text{g}
\]

COD mass balance:

\[
\text{COD}_{\text{removal}}(\%) = \frac{\text{COD}_{\text{original}} + \text{COD}_{\text{in}} - \text{COD}_{\text{out}} - \text{COD}_{\text{residue}}}{\text{COD}_{\text{total}}} \times 100
\]

\[
= \frac{1226.27 \text{g} + 10561.9 \text{g} - 4133.1 \text{g} - 3071.85 \text{g}}{1226.27 \text{g} + 10561.9 \text{g}} \times 100 = 38.88
\]

- **Percentage of HR methanized COD:**

Produced methane: \(1440.31 \text{L at 23}^\circ \text{C, 1 Atom}\)

\[
V = n \frac{RT}{p} = 1 \text{mol} \times \frac{0.08205 \frac{\text{L \times Atom}}{\text{mole \times K}} \times 296.15 \text{K}}{1 \text{ Atom}} = 24.3 \text{L}
\]

Mass of methane = \(1440.31 \text{L} \times \frac{1 \text{mole}}{24.3 \text{ L}} \times \frac{16 \text{g}}{1 \text{mole}} = 948.35 \text{g}\)

\[
\text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]
\[
\frac{\text{COD}}{\text{CH}_4} = \frac{2 \times 16 \frac{\text{g}}{\text{mole}} \times 2}{16 \frac{\text{g}}{\text{mole}}} = 4 \frac{\text{g COD}}{\text{g CH}_4}
\]

Methanized COD = 948.35 g CH4 \times 4 \frac{\text{g COD}}{\text{g CH}_4} = 3793.4 g CO

\[
\text{Methanized COD(%)} = \frac{\text{Methanized COD}}{\text{COD}_{\text{total}}} = \frac{3793.4 g \text{ COD}}{11788.17 g \text{ COD}} \times 100 = 32.18
\]
VITA

Changjiang Shen was born in Anhui, China, in November, 1976. He earned the mechanical degree of Bachelor of Science from the Anhui Agricultural University in 1998, and then he worked as a mechanical designer in the Fuyang Tractor Factory for two years. He went to the Graduate School of Anhui Agricultural University majoring in mechanical engineering from 2000 to 2003. He received a Master of Engineering degree in mechanical engineering in 2003. From July, 2003, to May, 2006, he worked as an engine designer engineer at Anhui Jianghuai Automotive Co., Ltd, P.R. China. The author then joined the civil and environmental engineering program at Louisiana State University as a master student under the supervision of Dr. William M. Moe in January, 2007. The author’s study focused on the anaerobic digestion sludge applied to a saline industrial waste activated sludge.