An Investigation into the Mechanisms of Sludge Reduction Technologies

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

Master of Science
In
Environmental Engineering

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June 1, 2009
Blacksburg, VA

Keywords: sludge reduction technologies, Cannibal, thermal hydrolysis, shear, sonication, ozone, anaerobic digestion, biosolids

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Abstract

Anaerobic digestion has been the preferred method for reducing and stabilizing waste sludge from biological wastewater treatment for over a century; however, as sludge volumes and disposal costs increase, there has been a desire to develop various methods for reducing the volume of sludge to be treated, improving the performance of the digesters, and increasing the energy value of the sludge. To this end, there have been numerous pretreatment and side-stream systems studied and developed over the past several decades with the overall goal of reducing the volume of biosolids to be disposed of in landfills or by land application. These technologies can be broken into four large groups: mechanical, thermal, chemical and biological, although there is often overlap between groups.

This research approached the evaluations of these technologies through several methods in the hopes of developing effective tools for predicting the performance of each technology. Batch digestion studies mimicking several of these treatment methods and extensive analytical work on samples from full-scale installations were conducted to determine the effectiveness of each technology. From these studies a simple batch digestion methodology was developed to analyze the effectiveness of the Cannibal solids reduction process on wastewater streams that have never been exposed to it. Batch digestion of sludges pretreated with ozone, mechanical shear and sonication provided insight into the effectiveness of each technology. Extensive analytical work on samples collected from full-scale installations of thermal hydrolysis, mechanical shear and the

Cannibal process provided some insight into the workings of each process and potential leads as to how to further characterize and evaluate each process.

Acknowledgements: I would like to thank my advisor, Dr. John Novak, for his guidance throughout this research, the wealth of knowledge that he was able to provide and the freedom to conduct this research in a way that allowed me to develop further academically and professionally. I would also like to thank my committee members, Drs. Gregory Boardman and, especially, Charles Bott whose passion for the field of wastewater engineering was my original impetus to pursue this degree.

Funding for this research was primarily provided by the Water Environment Research Federation (WERF). Additional funding was provided by Malcolm Pirnie Inc. and Columbus, OH Water and Sewer Authority. Additional guidance, advice and information were provided by CH2MHill, Malcolm Pirnie, Inc., and Siemens Water and Wastewater Technologies. Also, the operators and managers at the Emporia, Christiansburg, Blacksburg and Pepper's Ferry, VA wastewater treatment plants willingly provided samples, data and operational advice.

The Novak research group provided invaluable help with sample collection, reactor monitoring and analysis, especially Jong Min Kim, Passkorn Khanthongthip and Charan Tej Tanneru. Special thanks to Chris Wilson for being an invaluable source of advice, an open ear when needed and a mutual source of sanity. Julie Pertruska and Jody Smiley deserve my special thanks for all the help, experience and knowledge they provided, not to mention their patience and willingness to provide advice.

Finally, I would like to thank my parents, family and friends for having the faith in me as I have pursued my degrees and for being a source of advice and grounding when needed.

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1 INTRODUCTION

Anaerobic digestion has been the preferred method for reducing and stabilizing waste sludge from biological wastewater treatment for over a century however, as sludge volumes and disposal costs increase, there has been a desire to develop various methods for reducing the volume of sludge to be treated, improving the performance of the digesters and increasing the energy value of the sludge. To this end there have been numerous pretreatment and side-stream systems developed and studied over the past several decades with the overall goal of reducing the volume of biosolids to be disposed of in landfills or by land application. These technologies can be separated into four large groups: mechanical, thermal, chemical and biological, although there is often overlap between groups. The primary goal of the pretreatment technologies is to disrupt sludge flocs and, to some degree, cause cell rupture or lysis. The reduction in mean particle size caused by these technologies short-circuits the rate-limiting hydrolysis step of anaerobic digestion which allows more rapid digestion, increased biogas production, lower volumes and a more stable product. Side-stream technologies incorporated into the activated sludge recycle stream are focused on reducing the overall plant yield and, in most cases, eliminating the need for anaerobic digestion because the sludge volumes for disposal are minimal.

This thesis investigates many of these technologies in the hopes of providing a thorough overview of the state of the knowledge and developing methods to evaluate the applicability of some of these processes to wastewater streams. The first section of this thesis is devoted to a literature review of each of the four categories discussed above.

Following the literature review, the thesis is broken into three chapters that provide the results of research conducted on several of these technologies. Chapter 2 considers the Cannibal solids reduction process and the development of a simple batch digestion method to evaluate the effectiveness of the Cannibal system on an activated sludge stream for conventional (non-Cannibal) activated sludge systems. Chapter 3 addresses the effect of ozone, mechanical shear and sonication on several different sludges through the use of batch digestion reactors. The Chapter 4 presents the results of analytical work that was conducted on samples collected from treatment plants that have full-scale installations which use several of these treatment technologies, including thermal hydrolysis, mechanical shear and the Cannibal system.

2 LITERATURE REVIEW

2.1 Wastewater Treatment: An Overview

Over the past two centuries wastewater treatment has developed from a non-existent field into a huge industry that has helped improve quality of life throughout the world. Wastewater treatment has developed from simple, small systems into huge treatment plants that receive millions of gallons of wastewater a day. The first systems were essentially septic tanks and lagoons, often utilizing anaerobic microorganisms to achieve treatment objectives (McCarty 2001), whereas the current systems utilize a variety of microorganisms to achieve stringent discharge limits. One factor that has remained constant since the beginning of wastewater treatment is the generation of sludge or biosolids. Within the traditional wastewater treatment plant (WWTP) there are two locations where sludge is generated: primary clarification and waste biomass from the activated sludge system/biological process. The sludge that is generated at these two locations is significantly different: those from the primary clarifier are typically readily degradable, whereas those from the biological process are more resistant to degradation. The treatment and disposal of these sludges is often a significant portion of WWTPs' expenses. Since the early twentieth century anaerobic digestion has been the preferred method for stabilizing the sludge generated during treatment of wastewater (McCarty 2001).

Anaerobic treatment initially required long residence times to achieve treatment objectives and, subsequently, huge tank volumes to attain those residence times, because of this need, anaerobic treatment was largely abandoned for secondary treatment of wastewater.

However, it was realized that anaerobic treatment of settled sludges had significant advantages and, with the installation of heating systems on the anaerobic digesters, significant reductions in residence times where achieved (McCarty 2001). There are two significant advantages of anaerobic digestion: the reduction of sludge total and volatile solids concentrations, which reduces the total volume to be disposed, and the generation of methane (CH_4) as an end product, which can be utilized as an energy source and often allows the digesters to be net energy generators.

Anaerobic digestion consists of three steps: hydrolysis, acidogenesis and methanogenesis. Each of these steps have been explained in detail in numerous texts (Grady et al. 1999, Tchobanoglous et al. 2003) and, other than hydrolysis, will not be covered by this manuscript. Hydrolysis is of concern because it is typically the rate-limiting step in the anaerobic digestion of sludges, especially of biological sludges. In hydrolysis the anaerobes break the sludge floc into smaller, more readily degraded particles. The floc is difficult to break apart because it contains biopolymers (proteins, polysaccharides, lipids) and fatty acids which act as a glue holding it together; these compounds are typically composed of long-chain structures which are difficult to break apart (Cui and Jahng 2006, Hogan et al. 2004). Once the flocs have been hydrolyzed to smaller particles the subsequent steps in the digestion process are free to be carried out by their respective anaerobes. Because of the long duration of the hydrolysis step there has been significant interest over the past several decades in developing methods to accelerate it from a process that requires days to complete to one that is achieved in hours or even minutes.

From the research that has been conducted on accelerating the hydrolysis step, four major categories of pretreatment technologies have been investigated, namely mechanical, thermal, chemical and biological. This manuscript will summarize each of these technologies and their respective applications to the treatment process. All of these technologies have one common goal that makes them appealing: the reduction of the final volume of sludge requiring disposal, and many have the additional benefit of increasing CH_4 production.

2.2 Mechanical Pretreatment

2.2.1 Introduction

Mechanical pretreatment can be divided into two categories, both of which have been investigated to an extent in this research. One category of mechanical shear typically utilizes violent shearing methods to try to achieve cell lysis and includes such devices as stirred-ball mills, high-pressure homogenizers, blenders and other devices that exert high stresses on the sludge. Sonication is the other category of mechanical shear and could be considered the more refined and less abusive method; in reality, it can cause much greater stress on the sludge through localized pressure and temperature extremes around the horn of the sonicator (Hogan et al. 2004, Tiehm et al. 2001). Both of these types of mechanical pretreatment technologies have their own advantages and disadvantages that will be discussed in the following paragraphs. A process flow diagram illustrating a typical plant design with the installation of a shear device for sludge pretreatment is shown in Figure 2.1.

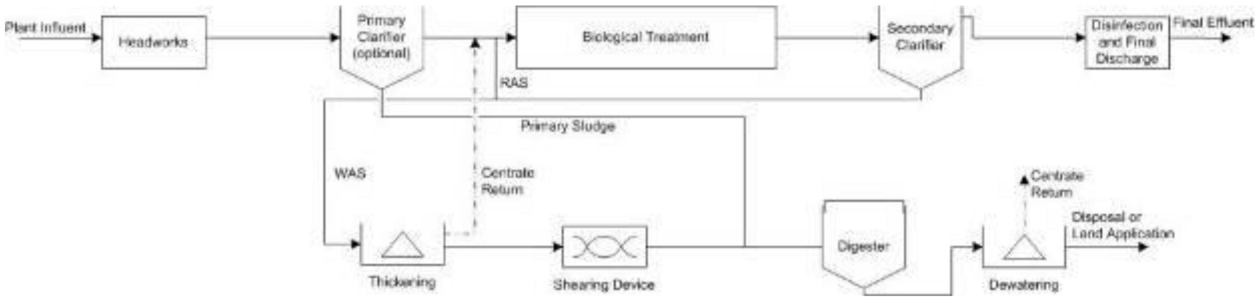

Figure 2.1- Shear Pretreatment Process Flow Diagram

2.2.2 Violent Shearing Devices

Studies have been conducted utilizing several types of violent mechanical shearing devices including stirred-ball mills and high-pressure homogenizers to determine their feasibility for sludge pretreatment or for modifying the return activated sludge (RAS) line to reduce the sludge yield in the activated sludge system (Camacho et al. 2002, Kopp et al. 1997, Lehne et al. 2000, Novak et al. 2007b, Strunkmann et al. 2006). Of important note is that mechanical shear devices are best applied only to secondary (biological) sludge because its degradability is significantly less than primary sludge, which gains little benefits from mechanical treatment (Lehne et al. 2000). It was found that mechanical shear causes floc disruption and hydrolysis over a short exposure time (Kopp et al. 1997).

One of the most important considerations with mechanical shearing is the energy imparted to the sludge because of a direct correlation between the energy imparted and the amount of cell disruption (Kopp et al. 1997, Liu et al. 2005). Low energy input will cause floc disruption, which allows the microorganisms within the flocs to access additional organic matter, and reduction in mean particle size, which can result in increased volatile solids reduction (VSR) in digesters when used as a pretreatment or a reduction in overall yield in the activated sludge process when used to treat RAS (Camacho et al. 2002, Kopp et al.

1997, Lehne et al. 2000). The one disadvantage to a low energy input is a deterioration in the settling characteristics of the sludge due to the floc dispersion and lighter particles (Seka and Verstraete 2003). To achieve cell lysis, higher energy must be imparted to the sludge which also implies a greater operational cost. However, the degradability is improved when the cells are lysed (Camacho et al. 2002, Liu et al. 2005).

An example of a propriety shear device is the Microsludge™ system which combines caustic addition with high-pressure homogenization by passing the sludge through a small orifice and impacting it on a plate (Novak et al. 2007b). It was found that WAS treated with this system had an approximately eight percent increase in VS reduction and elimination of foaming issues in bench scale reactors (Novak et al. 2007b).

One constant factor that several researchers found was when the total solids (TS) of the sludge were increased there was a decrease in required energy input (Kopp et al. 1997, Lehne et al. 2000). It was also found that with improved digestion and dewatering resulting from the mechanical shearing there was an increased concentration of nitrogen species being returned to the activated sludge system including poorly degradable organic nitrogen (Kopp et al. 1997, Strunkmann et al. 2006).

In summary, the digestion improving pathway followed by mechanical shear devices and many of the other pretreatment devices is cell and floc disruption which increases digestion rate resulting in reduced volatile solids (VS), increased sludge density and improved dewaterability (Kopp et al. 1997).

2.2.3 Sonication Pretreatment

Sonication, or ultrasound, is the use of sound energy between the frequencies of 20 kHz and 10 MHz which is typically caused by the rapid vibration of an object often referred to as a horn or transducer (Cao et al. 2006, Hogan et al. 2004). This rapid vibration causes alternating compression and rarefaction, that is, areas of high and low pressure, respectively, which result in excessive localized temperature and pressure (>5000°K and several hundred atmospheres) (Show et al. 2007, Tiehm et al. 2001). These extreme conditions are caused by the formation of cavitation bubbles that rapidly form and burst. Cavitation bubbles are classified as stable, where the bubble does not expand to its collapse radius due to the sound pressure during the rarefaction cycle being insufficient, or transient cavitation, where the pressure is sufficient enough to cause collapse within a few acoustic cycles (Show et al. 2007). The collapse or resonant radius is the point where the cavitation bubble ruptures and causes the localized extremes; it is directly proportional to the frequency of the sound waves (Tiehm et al. 2001).

The extreme conditions caused by sonication result in floc dispersion and subsequent reduction of mean particle size often through pyrolysis of volatile compounds (Braguglia et al. 2008, Hogan et al. 2004, Show et al. 2007, Tiehm et al. 2001). Hydroxyl radicals can also form during sonication and will react with non-volatile compounds in the bulk liquid (Tiehm et al. 2001, Zhang et al. 2007).

Researchers have found that the solids concentration of sludge affects the efficiency of sonication and, as with many of the other pretreatment technologies, a more concentrated sludge produces better results than a thinner sludge (Mao and Show 2006, Show et al. 2007, Zhang et al. 2008). Another parameter that affects the performance of sonication on sludge is the frequency that the device is operated at with lower frequencies causing more disruption due largely to the higher hydro-mechanical shearing effects (Tiehm et al. 2001).

When discussing sonication there are several terms which need to be defined and are listed below in Table 2.1.

Table 2.1- Common Sonication Terminology

Terminology	Definition	Units	Source
Ultrasonic Intensity	Power supplied per horn or transducer area	W/cm^2	Tiehm et al.2001
Ultrasonic Density	Power supplied per sample volume	W/mL	Tiehm et al.2001
Ultrasonic Dose	Energy supplied per sample volume	W-s/mL	Tiehm et al.2001
Specific Ultrasonic Dose (SUD)	Power supplied for an exposure time per unit volume and mass of sample	W-s/kg-solids	Muller 2006

In the literature, there has been no uniform method of reporting the energy imparted to the sample. Table 2.2 presents literature reported values and where possible provides them in terms of specific ultrasonic dose to promote uniformity and ease of comparison.

Table 2.2- Literature Reported Sonication Values

Source	Intensity (W/cm2)	Density (W/mL)	Dose (W-s/mL)	SUD (W-s/kg-solids)	Location
Show et al. 2007	0-92	0-0.52	ND	ND	Pretreatment
Cao et al. 2006	ND	0.25-0.50	ND	ND	Recycle
Zhang et al. 2008	125	0.80	1440	9.3×10^7	Pretreatment
Xie et al. 2007	13.70	ND	ND	ND	Pretreatment
Muller 2006	15.03	0.59-0.94	107-170	ND	Pretreatment and Recycle
Riedel 2009	15.03	0.3	90	$1.4\text{-}1.5 \times 10^6$	Pretreatment to batch digester

As can be seen in Table 2.2, there is a significant range of reported values which makes it difficult to decide on an optimal dose. However, of all the available units to report sonication values in, the SUD allows reproducibility because it accounts for the solids concentration of the sludge so it can be readily adapted to different sludges.

There are several common equations that are utilized when discussing sonication, the first of which is specific energy (Espec):

$$E_{spec} = \frac{Pt}{VTS} \quad (1)$$

Where P is power imparted, t is time of treatment, V is volume of sludge treated and TS is the total solids concentration of the sludge (Braguglia et al. 2008).

Another useful equation is the degree of disintegration equation which has can be expressed in two ways:

$$DD = \frac{(SCOD_{treated} - SCOD_{untreated})}{COD_{max}} \times 100\% \quad (2)$$

Where $SCOD_{treated}$ and $SCOD_{untreated}$ are the soluble COD of the treated and untreated sludge, CODmax is the maximum COD after complete chemical mineralization when the sludge is treated with H_2SO_4 or NaOH (Braguglia et al. 2008, Tiehm et al. 2001).

The other form of the degree of disintegration equation is as follows:

$$DD = \frac{SCOD_i - SCOD_f}{TCOD_i - SCOD_i} \times 100\% \quad (3)$$

Where $SCOD_i$ and $SCOD_f$ are the soluble COD before and after treatment and $TCOD_i$ is the total COD before treatment (Cui and Jahng 2006). This equation removes the variability of chemical mineralization, which is due to the use of different chemicals to achieve complete mineralization.

In summary for sonication treatment of sludge, its primary method for floc and cell disruption is the formation of cavitation bubbles that implode and cause localized extreme conditions. There is also some effect from the formation of hydroxyl radicals because they are strong oxidizing agents that could lyse cells or directly degrade organic matter. The most import parameters to consider when utilizing sonication is optimizing the solids concentration and the frequency of the device, typically higher for the former and lower for the latter provide the best results.

2.2.4 Disadvantages of Mechanical Pretreatment

There are four major disadvantages to mechanical shearing devices. One is the high energy input required to operate these devices, which is an issue with many of the pretreatment technologies; however, much of this energy can be recouped with the improved digestion of the sludge and the increased biogas production that can be utilized for power generation. The second disadvantage is maintenance required for many of these devices, especially the violent ones, due to the high stresses that are exerted on the mechanical parts during operation. The third disadvantage is with scaling these devices up to full-sized applications because many of them have only been utilized in lab-scale applications and may not be feasible for use in larger applications. The final disadvantage is that sludge settling and dewatering properties often deteriorate.

2.3 Thermal Pretreatment

2.3.1 Introduction

Thermal pretreatment or the thermal hydrolysis process (THP) is a technology that has been utilized since the early twentieth century in some form or another (Camacho et al. 2008). THP was first marketed under the names of Zimpro™ and Porteus™ as a method for reducing digester volumes and residence time by utilizing temperatures in excess of 200°C, however, they were plagued with several problems including fouling of heat exchangers, odors and refractory compounds in the dewatering centrate that caused issues throughout the WWTPs where they had been installed (Camacho et al. 2008). Because of these issues, most installations of these processes were abandoned, but the appeal of THP remained. Throughout the 1970s and 1980s numerous studies were conducted to determine the effects of thermal treatment on sludges and in the mid-1990s a new THP process entered the market under the name of Cambi™. This technology addressed some of the issues of the previous THP systems by operating at lower temperatures (160-180°C) and by utilizing steam instead of heat exchangers for primary heating of the sludge. Since then, there have been in excess of a dozen installations of the Cambi system along with the development of at least one other propriety process (Veolia's Biothelys™ system) that operates in a similar fashion. A simplified process flow diagram is illustrated in Figure 2.2.

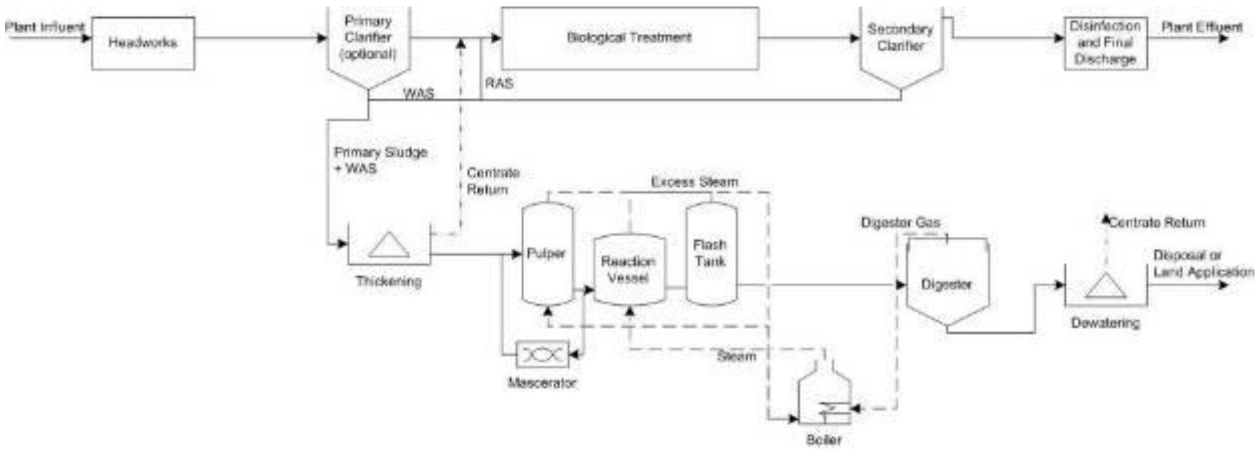

Figure 2.2- Cambi Process Flow Diagram

In its current installations the THP process consists of four primary steps that are outlined below:

1. Thickening- WAS and primary sludge is thickened to 15-20% using centrifuges, belt filter presses or other dewatering devices.
2. Pulping- The thickened sludge is pre-heated to 80-100°C using recycled steam from the main reactor and is homogenized using a recycle loop and macerator.
3. Reactor- The homogenized sludge is fed from the pulper in batch operation and is brought to 160-180°C and several bars pressure using steam. The reactor is maintained at these conditions for approximately 30 minutes and produces a product that meets Class A biosolids standards and causes no filamentous bulking problems in the digester.

4. Flash Tank- Treated sludge is transferred to this tank by the opening of a valve which causes a rapid drop in pressure drawing the sludge from one tank to the other and causing some degree of cell lysing. The sludge is cooled to the digester temperature in this tank.

2.3.2 Studies of THP

As was mentioned previously, there has been interest in thermal hydrolysis for several decades, so there are numerous studies that have been conducted to determine optimal conditions. One of the significant studies was conducted by Stuckey and McCarty in 1984 with the objective of determining the optimal temperature for thermal hydrolysis of sludge. They conducted batch studies with sludge that was thermally pretreated at temperatures ranging from 150-275°C then subsequently digested for 34 and 81 days. From this study they found that a temperature of 175°C is optimal because it balances the hydrolysis of recalcitrant compounds to soluble ones and soluble organic compounds to insoluble compounds (Stuckey and McCarty 1984). This statement was also supported by research conducted by Fdz-Polanco and colleagues who found that the biodegradability of pretreated sludge decreased after a certain temperature was achieved because of the increase of these recalcitrant compounds (Fdz-Polanco et al. 2008). Another study found that temperature is the most important parameter for thermal pretreatment and that treatment time has little effect (Carrere et al. 2007). Stuckey and McCarty also found that digestion after pretreatment at mesophilic temperatures (30-40°C) resulted in greater bioconvertibility at all pretreatment temperatures than digestion at thermophilic temperatures (>50°C) (Stuckey and McCarty 1984).

In their most recent article, Bougrier and colleagues presented a concise summary of most of the studies that have been undertaken on thermal hydrolysis and the conditions investigated which is reproduced below in Table 2.3.

Table 2.3- Literature review on impacts of thermal treatments on waste activated sludge mesophilic anaerobic digestion (Bougrier et al. 2008)

Reference	Thermal Treatment	Anaerobic Digestion	Results
Haug et al. 1978	175°C, 30 min	CSTR, HRT= 15 d	Increase of CH_4 production from 115-186 ml/g COD_{in} (+62%)
Stuckey and McCarty 1978	175°C, 60 min	Batch, 25 d	Increase of convertibility of COD to CH_4 from 48 to 68% (+42%)
Li and Noike 1992	175°C, 60 min	CSTR, HRT= 5 d	Increase of gas production from 108 to 216 ml/g COD_{in} (+100%)
Tanaka et al. 1997	180°C, 60 min	Batch, 8 d	Increase of methane production (+90%)
Fjordside 2001	160°C	CSTR, 15 d	Increase of biogas production (+60%)
Gavala et al. 2003	70 °C, 7 d	Batch	Increase of CH_4 production from 8.30 to 10.45 mmol/g VS_{in} (+26%)
Barjenbruch and Kopplow 2003	121 °C, 60 min	CSTR, 20 d	Increase of biogas production from 350 to 420 ml/g VSS_{in} (+20%)
Kim et al. 2003	121 °C, 30 min	Batch, 7 d	Increase of biogas production from 3657 to 4843 l/m^3 WAS_{in} (+32%)
(Dobhanyos et al. 2004	170 °C, 60 s	Batch, 20 d Thermophilic	Increase of biogas production (+49%)
Valo et al. 2004	170 °C, 60 min	Batch, 24 d	Increase of biogas production (+45%)
Valo et al. 2004	170 °C, 60 min	CSTR, 20 d	Increase of CH_4 production from 88 to 142 ml/g COD_{in} (+61%)
Graja et al. 2005	175 °C, 40 min	Fixed film Reactor, HRT= 2.9 d	65% reduction of TSS
Bougrier et al. 2006a	170 °C, 30 min	Batch, 24 d	Increase of CH_4 production from 221 to 333 ml/g COD_{in}

			(+76%)
Bourgrier et al. 2006b	170 °C, 30 min	CSTR, 20 d	Increase of CH_4 production from 145 to 256 ml/g VS_{in} (+51%)

Recently, Bougrier and colleagues have conducted several studies on thermal hydrolysis that are especially concerned with the effects on the proteins, lipids and carbohydrates contained within the floc and cells (Bougrier et al. 2006b, Bougrier et al. 2007b, Bougrier et al. 2008). In one of these studies they found that the exocellular carbohydrates that are contained in the exocellular polymeric substances (EPS) are hydrolyzed at lower temperatures, whereas proteins, which are typically intracellular, require a higher temperature to be released by cell lysis. At these higher temperatures the solubilized carbohydrates react with themselves and the soluble proteins that have been released from the cells to form organic compounds like melanoidins or Amadori compounds which contribute to the brown color of the supernatant of thermally treated sludges (Bougrier et al. 2008).

There has also been research into the effect of chemical pretreatment before thermal pretreatment, typically utilizing bases such as NaOH and KOH (Bougrier et al. 2006b, Stuckey and McCarty 1984). Both studies found that alkaline addition had little effect on biodegradability of sludges treated in the optimal temperature range of 160-180 °C, however, Bougrier et al. found improvements at a temperature of 130 °C.

2.3.3 Additional Advantages of THP

Additional benefits that have been found for thermal pretreatment include:

- The improvement of filterability and disintegration of the sludge and the improvement of digestibility and dewaterability (Barr et al. 2008, Bougrier et al. 2007b, Carrere et al. 2007, Fdz-Polanco et al. 2008);
- A final product that meets Class A standards for land application (Camacho et al. 2008);
- The high temperatures ensure the destruction of foam causing organisms that can cause issues in digesters (Barr et al. 2008);
- Digester size can be significantly reduced because of the reduced residence time that is achieved by the acceleration of the hydrolysis phase and the ability to feed a sludge with a higher TS concentration (Barr et al. 2008);
- The system is typically a net energy producer because of the increased biogas quantity and quality that can be used to heat the boilers and generate power that exceeds the requirements of the THP system (Barr et al. 2008).

As with most of the other pretreatment technologies, higher solids concentrations result in better performance (Fdz-Polanco et al. 2008).

2.3.4 Disadvantages of THP

There are several disadvantages to THP systems that need to be considered:

- As was mentioned previously, there are higher concentrations of recalcitrant compounds that are difficult to remove and are recycled to the main biological process in the dewatering supernatant;
- The supernatant also contains high concentrations of nutrients that will affect the operation of the activated sludge system especially in plants where nutrient removal is a high priority;

- Due to the reduced particle size there have been issues with dewatering, especially using centrifuges, so Cambi typically utilizes belt filter presses for final dewatering (Barr et al. 2008);
- Depending on the influent wastewater stream, there can be issues with the heat exchangers clogging as happened at the installation in Dublin, Ireland because it was receiving wastewater with high fiber content from a pulp mill but the issue was solved by recycling digested sludge to the heat exchangers which raised the pH (Pickworth et al. 2006).

2.4 Ozone Pretreatment

2.4.1 Introduction

Ozone is a treatment technology that is receiving increased attention in both the water and wastewater industries primarily as a disinfectant alternative to chlorine species (Tchobanoglous et al. 2003). The chemical characteristics of ozone are listed in Table 2.4.

Table 2.4- Ozone Properties (Material Safety Data Sheet 2000)

Characteristic	Value
Chemical Formula	O_3
Molecular Weight	48 g/mole
Specific Gravity	2.144 g/L
Vapor Density	1.7
Solubility in Water	0.49 % by wt.

Ozone is a highly reactive, strong oxidant which has the potential to cause explosions when in contact with many organic compounds and can also create intermediaries that are as dangerous (Material Safety Data Sheet 2000). It is generated from air or pure oxygen using a high voltage electrical discharge called corona discharge and due to its short life span it is produced on site (Panda and Mathews 2008).

2.4.2 Ozone Usages in Wastewater Treatment

As was mentioned previously, ozone is receiving attention in wastewater treatment as a disinfectant before final discharge because of its ability to kill or inactivate bacteria and protozoa, including ones that are resistant to chlorine, and the lack of disinfection byproducts formed by it (Panda and Mathews 2008). There are other applications for ozone that are being investigated for use at wastewater treatment plants including usage as a pretreatment before digestion and as a side-stream reactor on the recycle loop to reduce the overall plant yield. Below are process flow diagrams illustrating ozone used as a pretreatment technology (Figure 2.3) and side-stream recycle (Figure 2.4).

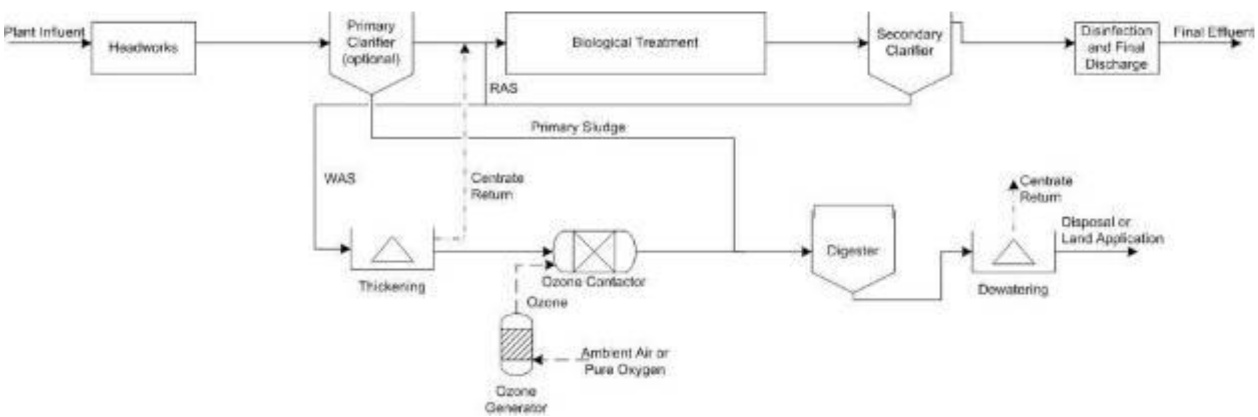

Figure 2.3- Sludge Pretreatment with Ozone Process Flow Diagram

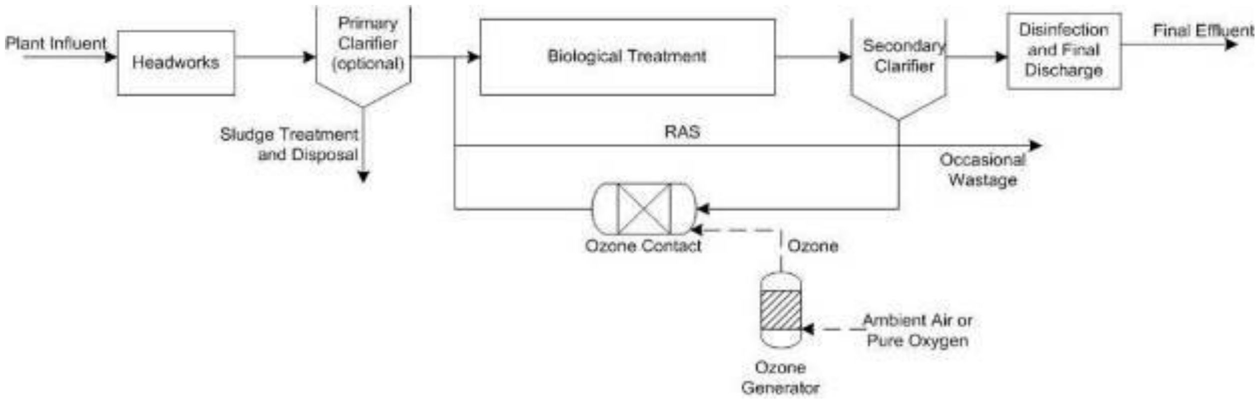

Figure 2.4- Side-Stream Ozone Treatment Process Flow Diagram

As a pretreatment for digestion of sludge, ozone serves to cause floc and cell disruption allowing better, more-rapid digestion (Ahn et al. 2002, Bernal-Martinez et al. 2007, Bougrier et al. 2006a, Bougrier et al. 2007a, Carballa et al. 2007, Chu et al. 2008, Manterola et al. 2008, Mines et al. 2008, Yeom et al. 2002, Zhao et al. 2007). There have also been studies investigating the usage of ozone pretreated sludge and dewatering centrate as a carbon source for nitrification (Ahn et al. 2002, Lee et al. 2005, Sakai et al. 1997, Yeom et al. 2002, Zhao et al. 2007). It has been investigated as a side-stream process attached to the return activated sludge line to treat a percentage of the RAS with the intention of minimizing sludge yield in the activated sludge process (Ahn et al. 2002, Boehler and Siegrist 2006, Kamiya and Hirotsuji 1998, Lee et al. 2005, Yeom et al. 2002).

Of important consideration for ozone treatment are the effects of temperature, dissolved oxygen and total solids upon the mass transfer coefficient (Manterola et al. 2008, Panda and Mathews 2008). The dose also affects the results of treatment of wastewater with ozone with literature reported values ranging from 0.05 to 0.50 g O_3/g TS (Bougrier et al. 2006a, Chu et al. 2008, Dogruel et al. 2007, Manterola et al. 2008, Mines et al. 2008, Sakai et al. 1997, Zhao et al. 2007). Typically, with higher ozone doses there is a greater solubilization of organic matter (Ahn et al. 2002, Manterola et al. 2008). When using ozone as a yield reduction technology on the return line in activated sludge processes there is a minimum dose required to achieve yield reduction (Kamiya and Hirotsuji 1998).

Ozone has direct and indirect treatment pathways which include the direct oxidation of organic material to carbon dioxide and the formation of hydroxyl radicals which react indirectly with compounds and organic material (Carballa et al. 2007, Chu et al. 2008).

2.4.3 Advantages of Ozone Treatment of Wastewater

Ozone treatment of wastewater has several advantages that make it an appealing technology, especially with increasingly stringent regulations. As a strong oxidant, ozone can break down or increase the bioavailability of many polycyclic aromatic hydrocarbons (PAHs), pharmaceutical and personal care products (PPCPs), dyes and other industrial byproducts that are becoming more prevalent in wastewaters and typically are not removed by conventional biological treatment (Bernal-Martinez et al. 2007, Carballa et al. 2007, Chu et al. 2008). It can help control the growth of bulking organisms in both the activated sludge process and digesters (Ahn et al. 2002). When used as a pretreatment technology prior to anaerobic digestion, it can potentially increase the production of methane (Bougrier et al. 2007a, Carballa et al. 2007). It also causes floc disruption and cell hydrolysis which releases soluble proteins and carbohydrates to the bulk liquid and improves degradability (Ahn et al. 2002, Zhao et al. 2007). Other advantages include:

- Decreased viscosity, improved settleablity and reduced odors (Bougrier et al. 2007a);
- Yield reduction in activated sludge systems (Kamiya and Hirotsuji 1998, Lee et al. 2005, Sakai et al. 1997);

- Potential carbon source for denitrification with equivalent energy to glucose (Ahn et al. 2002, Lee et al. 2005, Sakai et al. 1997, Yeom et al. 2002, Zhao et al. 2007);
- Increased mineralization of organic material (Bougrier et al. 2007a).

2.4.4 Disadvantages of Ozone Treatment of Wastewater

As with the other pretreatment technologies there are disadvantages to the use of ozone in wastewater treatment, which are listed below:

- Increased inert and colloidal COD due to the disintegration of sludge flocs and cells which often increases the non-biodegradable COD in the plant effluent due to recycling of dewatering centrate to the biological process or the use of ozone treatment on the RAS line (Boehler and Siegrist 2006);
- Decreased dewaterability, increased sludge volume index (SVI) and capillary suction time (CST) of digested sludge because of smaller particles (Ahn et al. 2002, Bougrier et al. 2006a, Bougrier et al. 2007a, Carballa et al. 2007);
- Decreased pH due to formation of carboxylic acid from organic material and consumption of alkalinity by the oxidation or organic material (Bougrier et al. 2007a);
- When used to minimize yield, phosphorus removal is reduced because one of the primary removal mechanisms is sludge wasting (Sakai et al. 1997);
- Ozone generation is an energy intensive process and requires significant capital investment in machinery (Panda and Mathews 2008);
- Mass transfer kinetics need to be optimized to the sludge characteristics (Lee et al. 2005, Panda and Mathews 2008).

2.5 Cannibal™ Yield Reduction Technology

2.5.1 Introduction to the Cannibal Process

The Cannibal solids reduction process is a proprietary technology that utilizes an anaerobic side-stream reactor to treat part of the RAS flow with the intention of reducing the overall plant yield. It has been installed in some form or another at more than twenty plants throughout the United States. An illustration of how the system is typically set up is presented in Figure 2.5.

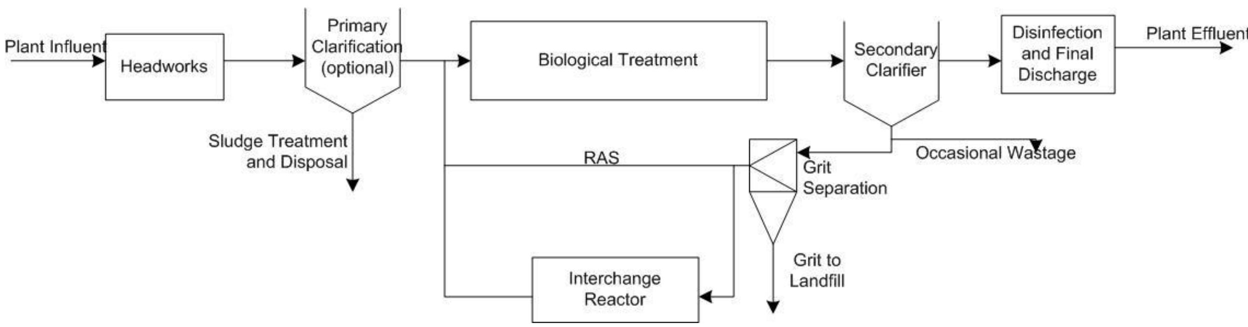

Figure 2.5- Cannibal Process Flow Diagram

2.5.2 Design Considerations for the Cannibal Process

The concept behind this system is that the anaerobic reactor, referred to as the interchange reactor, will select for different organisms than the activated sludge system. These organisms break down the aerobic sludge flocs releasing floc-bound EPS that is subsequently utilized as organic material for them to grow. The excess microorganisms from the interchange reactor are then recycled to the activated sludge system where they are degraded by the aerobes which regenerate the EPS and other organic material (Easwaran 2006, Novak et al. 2007a). The net result is a system that maintains a relatively constant substrate concentration through the release and uptake of different organic material depending on the zone, in essence cannibalizing itself.

The key component to maintaining a steady suspended solids concentration throughout the system is the optimization of the interchange rate through the interchange reactor. Through several studies conducted by Novak the optimal interchange rate has been determined to be around ten percent of the return sludge flow (Chon 2005, Easwaran 2006, Novak et al. 2007a).

Despite the installation of the Cannibal system at numerous plants it is not fully understood, but there are several characteristics that seem to affect the operational performance:

- The configuration of the activated sludge system has a significant effect on system efficiency with plug flow systems performing better than complete mix systems;
- There is no specific “Cannibal” microorganism, rather a unique microbial community develops that includes slower growing microorganisms that are typically washed out in conventional activated sludge systems; these microbes could include fermenters, iron reducers, polyphosphate accumulating organisms (PAOs) and Anamox organisms (Chon 2005, Goel and Noguera 2006, Novak et al. 2007a);
- The operation of the solids separating unit, which includes fine screens and cyclone grit removal, is essential in preventing the accumulation of inorganic material in the system, especially when there is no primary clarification, however this solids removal is a small portion of the overall plant yield;
- Endogenous decay contributes to the overall yield reduction (Goel and Noguera 2006).

Additional design considerations for the Cannibal process include:

- The applicability of the system to particular wastewater streams and treatment setups, e.g. industrial wastewaters and advanced treatment systems like membranes;
- The nutrient removal capabilities, especially phosphorus, since there is little wasting that allows for the removal of excess PAOs and the possible formation of inorganic phosphorus compounds due to higher cation concentrations both resulting in the build up of phosphorus in the system and increased levels in the plant effluent (Goel and Noguera 2006);
- The applicability of the system to larger treatment plants.

2.6 Summary of Sludge Pretreatment and Reduction Technologies

Each of the systems investigated in this literature review have their respective advantages and disadvantages that have been covered in depth previously, however several of the key ones will be summarized here:

- Advantages:
    - Improvement of sludge digestibility and dewaterability (pretreatment) or yield reduction (side-stream treatment)
    - Decreased digester and solids handling footprint
    - Reduction of odors
    - Production of stable product that meets many regulations for land application and is appealing for that use
    - Energy self-sustaining and often provider with proper utilization of increased biogas production
    - Potential carbon source for nutrient removal

- Disadvantages:
    - Production of recalcitrant byproducts that are difficult to remove
    - Increased nutrient recycle to activated sludge process
    - Energy intensive, especially if not properly recouped through co-generation
    - Scale-up issues, both from lab to full-scale and small to large scale
    - Additional odors during pretreatment requiring advanced treatment
    - Minimal number of full-scale installations for comparison

Cost-benefit analyses of these technologies are essential to determining the applicability of each to specific treatment plants; however, as treatment costs and volumes continue to rise while available area decreases, these technologies will become more appealing.

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3 MANUSCRIPT I: "SHORT-TERM ANAEROBIC BATCH STUDIES AS AN INDICATOR OF THE APPLICABILITY OF THE CANNIBAL™ PROCESS TO A RETURN ACTIVATED SLUDGE STREAM"

3.1 Abstract

The Cannibal™ solids reduction process is a proprietary technology that utilizes an anaerobic side-stream reactor to treat part of the return activated sludge (RAS) flow with the intention of reducing the overall sludge yield. It has been installed in some form or another at more than twenty plants throughout the United States.

The objective of this study was to develop a method for easily evaluating the applicability of the Cannibal system to a wastewater stream that has never used a Cannibal system. To achieve this goal, small, short-term batch digestion studies were conducted and were analyzed daily for SCOD. It was thought that a greater release of soluble COD might indicate that the system was more susceptible to solids reduction using the Cannibal process. Sludges from operating Cannibal plants, lab Cannibal systems and non-Cannibal plants were assessed. From these data clear correlations could be observed with better operating Cannibal systems typically having a greater SCOD release. Several conventional treatment plants were used to test this model and similar release patterns were observed for these plants, which were interpreted to indicate the relative applicability of the Cannibal system.

3.2 Introduction

The Cannibal™ solids reduction process is a proprietary technology that utilizes an anaerobic side-stream reactor to treat part of the return activated sludge (RAS) flow with the intention of reducing the overall sludge yield. It has been installed in some form or another at more than twenty plants throughout the United States. An illustration of how the system is typically set up is presented in Figure 3.1.

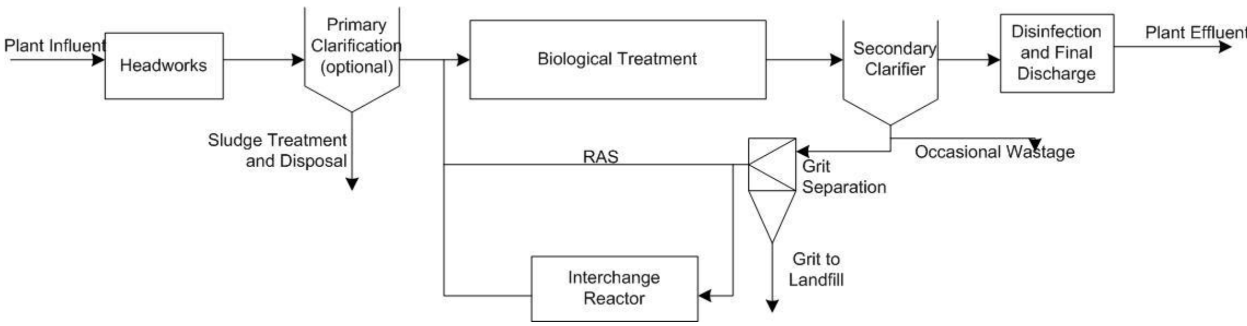


Figure 3.1- Cannibal Process Flow Diagram

The concept behind this system is that the anaerobic reactor, referred to as the interchange reactor, will select for different organisms than the activated sludge system. These organisms break down the aerobic sludge flocs releasing floc-bound EPS that is subsequently utilized as organic material for them to grow. The excess microorganisms from the interchange reactor are then recycled to the activated sludge system where they are degraded by the aerobes which regenerate the EPS and other organic material (Easwaran 2006, Novak et al. 2007a). The net result is a system that maintains a relatively constant substrate concentration through the release and uptake of different organic material depending on the zone, in essence cannibalizing itself.

The key component to maintaining a steady suspended solids concentration throughout the system is the optimization of the interchange rate through the interchange reactor.

Through several studies conducted by Novak the optimal interchange rate has been determined to be around ten percent of the return sludge flow (Chon 2005, Easwaran 2006, Novak et al. 2007a).

Despite the installation of the Cannibal system at numerous plants it is not fully understood, but there are several characteristics that seem to affect the operational performance:

- The configuration of the activated sludge system has a significant effect on system efficiency with plug flow systems performing better than complete mix systems;
- There is no specific "Cannibal" microorganism, rather a unique microbial community develops that includes slower growing microorganisms that are typically washed out in conventional activated sludge systems; these microbes could include fermenters, iron reducers, polyphosphate accumulating organisms (PAOs) and Anamox organisms (Chon 2005, Goel and Noguera 2006, Novak et al. 2007a);
- The operation of the solids separating unit, which includes fine screens and cyclone grit removal, is essential in preventing the accumulation of inorganic material in the system, especially when there is no primary clarification, however this solids removal is a small portion of the overall plant yield;
- Endogenous decay contributes to the overall yield reduction (Goel and Noguera 2006).

The objective of this study was to develop a simple method for quickly evaluating the efficacy of installing a Cannibal interchange reactor on the RAS stream of a treatment plant to reduce the overall plant yield. To achieve this goal short-term anaerobic batch studies were conducted on several sludges provided from full-scale installations of the

Cannibal system, lab scale versions of the Cannibal system and on several treatment plants that had never been exposed to Cannibal conditions.

3.3 Materials and Methods

3.3.1 Sludge Samples

Samples of sludge were provided by several plants that have been operating the Cannibal system. These samples were collected from the feed to the interchange reactor and were transported to the lab under conditions that maintained 4°C to minimize biological activity. For the non-Cannibal plants, the samples were collected from the RAS line. Details of the plants are included in Table 3.1.

Table 3.1- Treatment Plants Investigated

Plant Name and Location	Treatment System	Treated Flow (MGD)	Pre-Cannibal Yield (lb TSS/lb BOD)	Post-Cannibal Yield (lb TSS/lb BOD)
Peru, Indiana	Anoxic Selctor + 3 Siemens VLRs in series (upgrade w/ Cannibal)	4.0	0.8	0.1
Emporia, Virginia	Oxidation ditches in series with 2 Cannibal reactors	0.9	0.60	0.35
Big Bear, California	No data on plant configuration.	2.0	1.0	0.8
Morongo, California	SBR (only operated for short period before Cannibal came on line)	0.2	Unknown	0.1-0.2
Pepper's Ferry, Radford, Virginia	Approaching plug flow	3.0	1.21	N/A
Christiansburg, Virginia	Approaching plug flow	2.0	0.61	N/A
Blacksburg, Virginia	Complete mix	5.4	1.89	N/A

3.3.2 Batch Reactor Setup

The setup for the batch studies utilized 500 mL bottles that were filled with approximately 450 mL of sludge. The bottles were sealed with rubber stoppers and gas was vented through water traps.

Each reactor was sampled at least once daily and, during the initial several days after startup, twice daily. Samples were centrifuged and the centrate was filtered through 0.45 μm nitrocellulose filters for soluble COD analysis.

COD analysis was conducted photometrically using Hach High Range COD tubes (Hach Company, Loveland, CO) which had a range of 20-1500 mg/L COD and are USEPA approved.

Initial and final total and volatile solids were measured according to Standard Methods (A.P.H.A. et al. 1995).

3.4 Results and Discussion

Data from the lab reactors compared to yield data from the full-scale processes provided insight into the effectiveness of the Cannibal system and led to the development of a method for determining how a plant will respond to the installation of the Cannibal process. Raw data is provided in Appendix A. Results for the SCOD release are presented in Figure 3.2a and b.

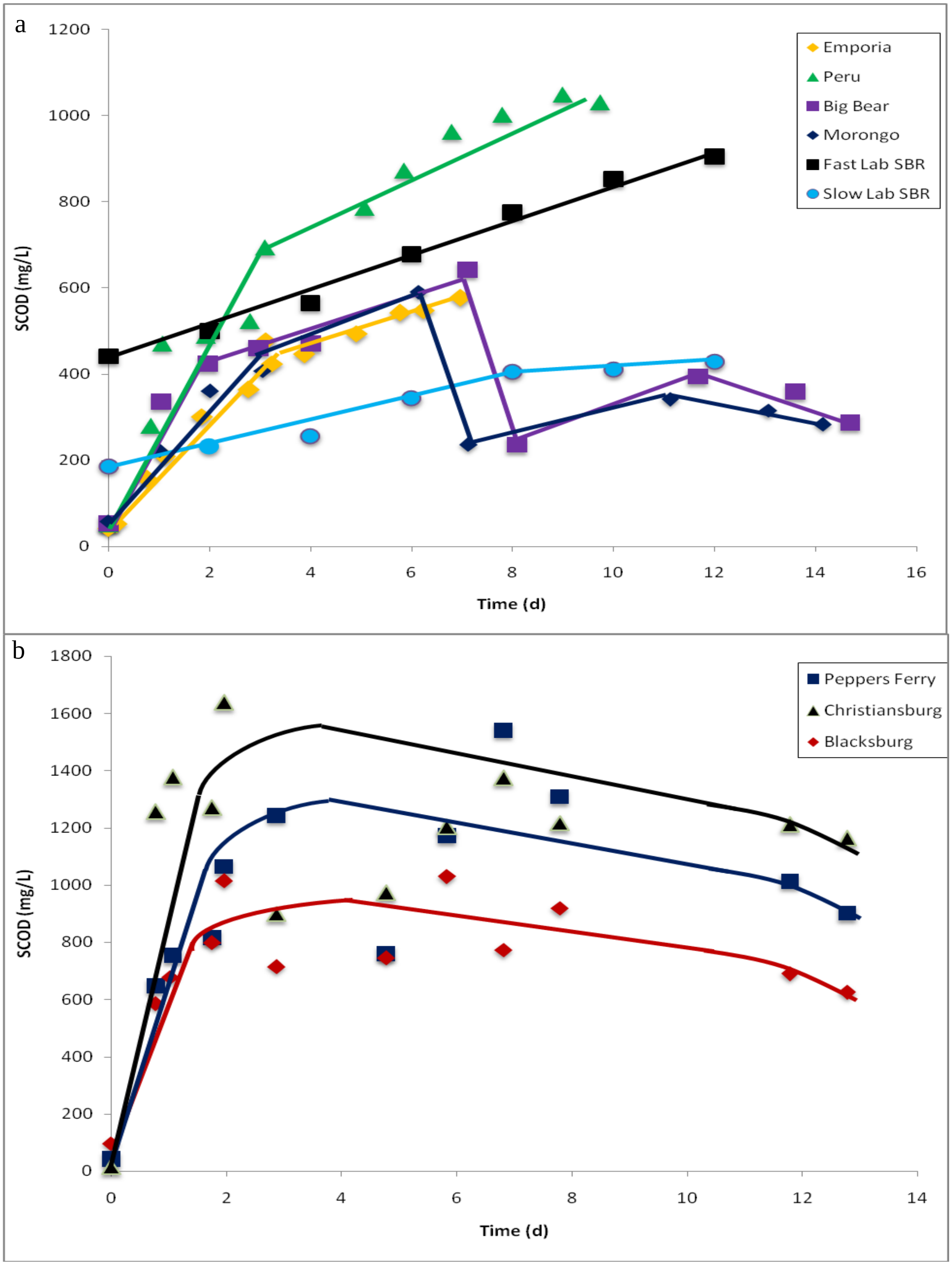


Figure 3.2(a) Cannibal and (b) Conventional SCOD Release in Batch Reactors

Before discussing Figure 3.2 a and b in detail, it is important to clarify the differences between the plants. Some details of each plant's configuration were provided in the materials and methods section; however, in this section additional information about plant performance is provided. The plants at Peru, Indiana and Morongo, California are two of the best operating Cannibal installations in the United States and Big Bear, California and Emporia, Virginia are two of the worst performing. The Peru plant operates with an anoxic selector system followed by a Siemens VLR system which is essentially an oxidation ditch on its side. Emporia is a high sludge age system (SRT> 35 days) with two oxidation ditches in series. Morongo, California is a sequencing batch reactor (SBR) system. No additional information was provided for Big Bear, although the change in yield is primarily assumed to be due to the additional screenings and grit separation for the Cannibal system. The Fast and Slow Lab SBRs are two side-by-side sequencing batch reactors that are being operated by one of the author's colleagues in the lab. The Fast SBR mimics a well operating Cannibal system with a high substrate pressure that is achieved by a short feeding time period. The Slow SBR mimics a poorly operating system with a low substrate pressure which is achieved by feeding the same overall concentration as the Fast SBR but over a longer time period. Blacksburg, Christiansburg and Pepper's Ferry are three plants that have never been exposed to the Cannibal process.

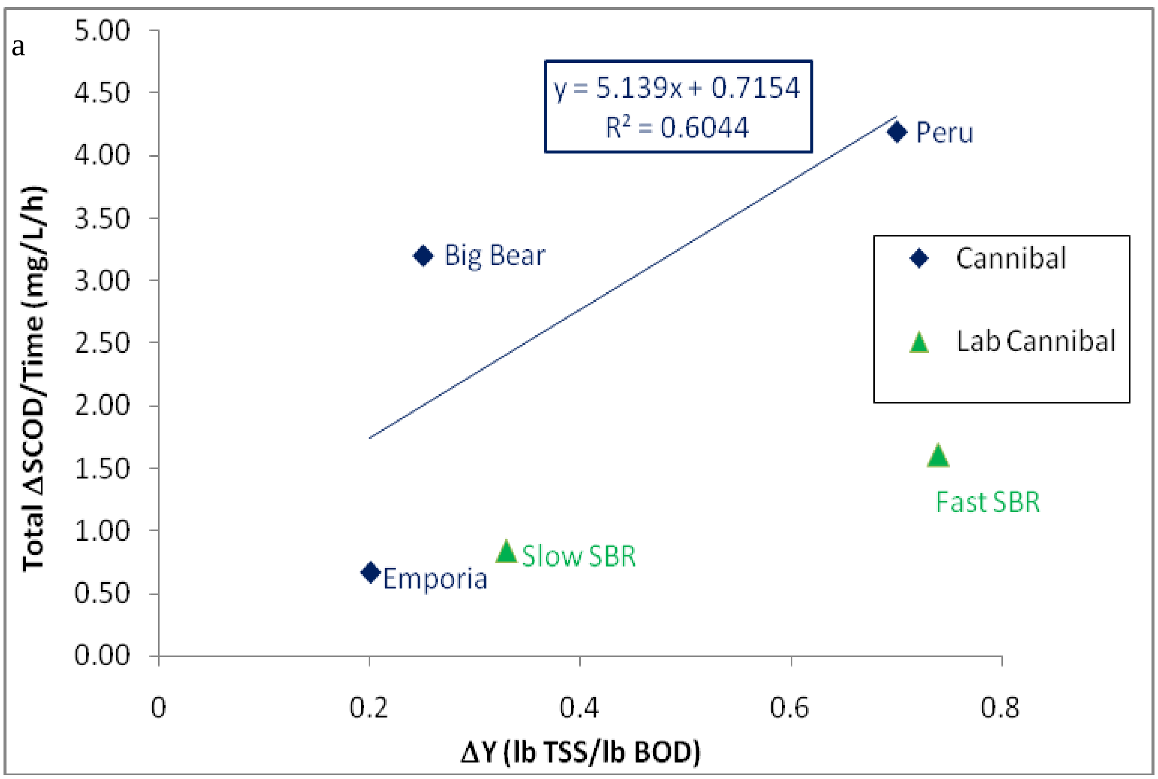
Data in Figure 3.2a show the results of SCOD release over time for the Cannibal plants and the distinction between the well and poorly operating plants is readily apparent. The data points for the lab SBRs were collected by the researcher operating those reactors, who conducted similar batch experiments, although SCOD was not directly measured. To estimate the COD release, the protein, polysaccharide and total VFAs on an oxygen demand basis were summed together and multiplied by a conversion factor of 2 to produce an accurate surrogate for SCOD. The conversion factor was based on an estimated average COD for the organics tested. In Figure 3.2b the results of the batch studies conducted on the conventional treatment plants are presented. All data series have trend lines drawn in to provide an approximate average.

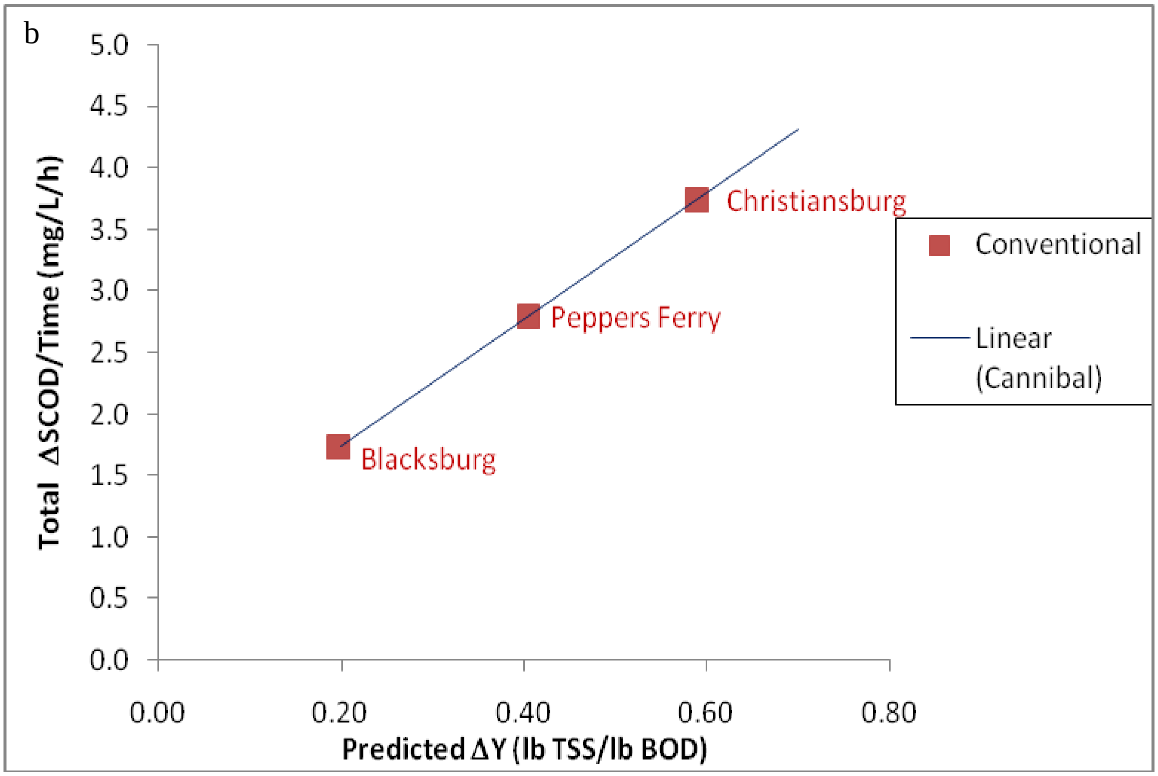
With the full-scale Cannibal sludges the release rate is fairly similar until almost three days into the operation, at which point the Peru sludge showed a significant increase in the SCOD concentration which, at the end of the test period, resulted in a final concentration of close to 800 mg/L higher than the poorly functioning plants. After about 5 days of operation, Big Bear underwent a dramatic decrease in SCOD release. This was assumed to be due to biodegradation. Although the Emporia tests were concluded much earlier than the other reactors, it may have followed a similar pattern to Big Bear if it had been allowed to continue operating. The two lab reactors followed smoother and more regular trends over their operation, although they started at higher concentrations than any of the full-scale samples. Both lab reactors mimic their respective performance category with regards to general concentration range, i.e. the slow feed SBR remained in the 200-300 mg/L range while the fast feed SBR released up to 800 mg/L. Despite being one of the best operating Cannibal plants, Morongo tended to follow the trends of the poorer operating plants. There are two possible explanations for this occurrence:

1. Because it is operating so well, most of the organic material has already been degraded in the activated sludge process.

2. The yield without a Cannibal system could have been low. This plant was designed and operated as a Cannibal system so there were no data for "conventional" operation for comparison. For this reason, it was not included in the assessment.

When looking at the release over time of SCOD in the non-Cannibal sludges in Figure 3.2b, all three plants have more irregular release patterns, but three distinct trends can be observed. Blacksburg and Pepper's Ferry appear to follow a similar pattern with a lower release rate than Christiansburg and a more significant tailing off near the end of operation; Christiansburg has a much greater release and does not tail off as significantly as the other two plants. From this assessment of these three plants it is possible to hypothesize that Blacksburg and Pepper's Ferry would not function as well as Christiansburg if Cannibal systems were installed at each plant.





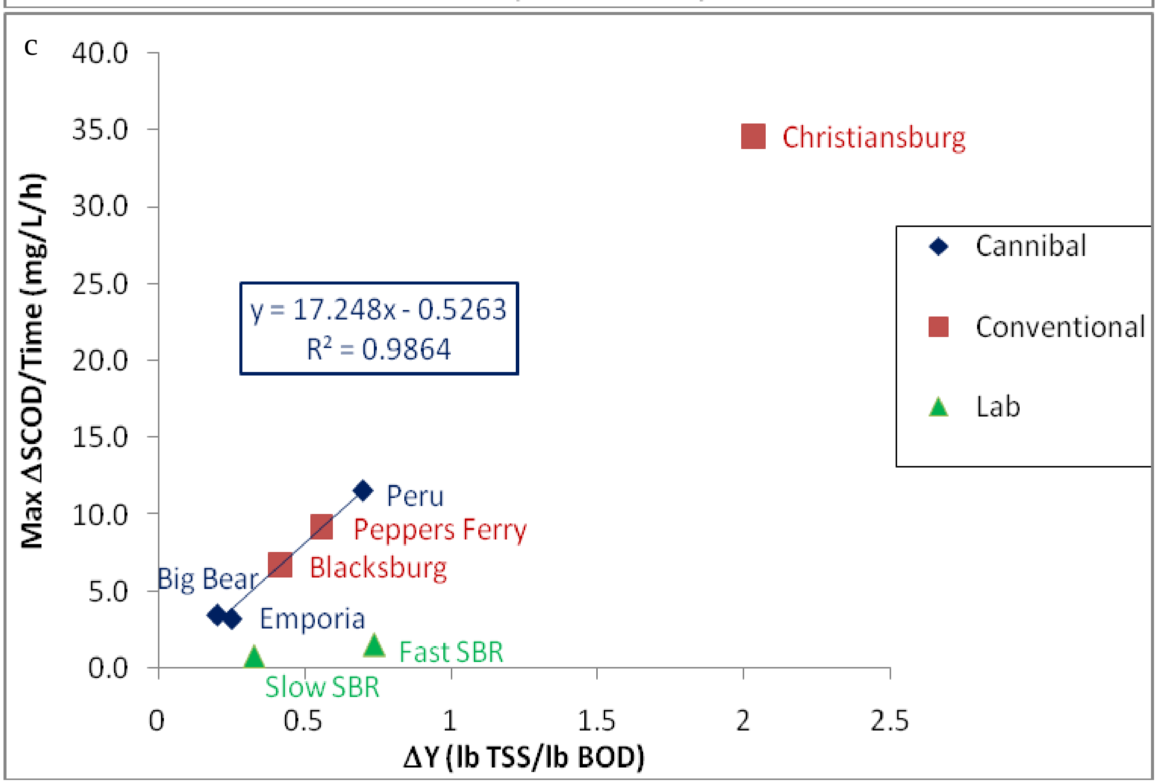


Figure 3.3 (a) Total ΔSCOD Release Normalized to Time vs. ΔY, (b) Expected ΔY for Conventional Plants and (c) Max ΔSCOD Release Normalized to Time vs. ΔY

Figure 3.3a presents the total change in SCOD over the experiment time for each Cannibal plant and the lab SBRs plotted against the change in yield that each plant has observed since the installation of the Cannibal system. A liner regression was run on the full-scale Cannibal plants and the derived equation was used to predict the changes in yield for the three conventional plants studied as illustrated in Figure 3.3b. These expected yields are also provided in Table 3.2. Figure 3.3c presents the data for the maximum SCOD change normalized to the time required to achieve that value. This provided a better R^2 value for the liner regression on the Cannibal plants. The change in yields calculated for the conventional plants based on this regression were slightly higher for Blacksburg and Pepper's Ferry, but unrealistically high for Christiansburg (i.e. ΔY= 2.04 lb TSS/lb BOD). The change in yield values for the conventional plants calculated by the liner regression in Figure 3.3a reinforce the conclusion that of the three conventional plants tested, Christiansburg would likely experience the greatest benefit from an upgrade to a Cannibal system.

Table 3.2- Expected ΔY for the Conventional Treatment Plants Based on Regressions from Figure 3.3a

Conventional Treatment Plant	Expected ΔY from Figure 3.3a (lb TSS/lb BOD)
Blacksburg	0.20
Pepper's Ferry	0.41
Christiansburg	0.59

There are several other analyses that could provide valuable insight into the operation of Cannibal systems, but, unfortunately, these could not be pursued in this study. The first of these analyses is a purely observational investigation and consists of determining when a sludge turns black in these batch digesters because when that occurs it has been found to indicate that the microorganisms have become acclimated to the anaerobic environment and the Cannibal “phenomenon” has begun (Chon 2005). This blackening of the sludge could also be correlated to oxidation reduction potential values and would likely be at a highly negative or reduced value when this occurred. This environment would result in the reduction of iron and sulfate which explains the blackening of the reactors. Although the blackening characteristic was not rigorously observed during these studies, it was noted for several of the reactors and it was found that the sludges that had been previously exposed to the Cannibal environment turned black more rapidly than those from conventional systems (e.g. Morongo was black within 3 days, while the conventional reactors required 1-2 weeks). Within the conventional systems, there was a difference in blackening times, with Pepper’s Ferry being the first to change and Christiansburg being the last, which, if this is an indication of applicability of Cannibal to a system, contradicts the hypothesis presented based on SCOD release. However, several of the lab studies conducted on Cannibal systems have found that there is an approximately 30 day acclimatization period for wastewater that has never being exposed to Cannibal conditions (Chon 2005, Easwaran 2006, Goel and Noguera 2006, Novak et al. 2007a), which helps to explain the longer time frame for the sludges in these batch reactors to turn black. This is an aspect of the Cannibal system that should be investigated further and has potential to be a good indicator for Cannibal applicability to a treatment plant.

Two, the reason the fast feed system works better than the slow feed system is thought to be due to the presence of a high substrate concentration during the feeding period. High substrate concentrations would also occur for a plug flow system at the head of the reactor where the feed entered. Therefore, one possible indicator of the potential for Cannibal to be successful is the flow pattern in the activated sludge system. It was observed that the Blacksburg plant is a complete mix plant while Christiansburg is more plug flow. Pepper's Ferry appears to be somewhat in between. This observed flow pattern is consistent with the soluble COD release amount shown in Figure 3.2b. Proof of this would require that the flow configuration be determined more precisely from dye studies and that a Cannibal system be implemented at each of these plants.

This is also consistent with the Peru, IN plant where a selector was used. In the selector, a higher substrate concentration is maintained and this likely influenced the characteristics of the sludge, making it more amenable to solids destruction by the Cannibal process.

3.5 Conclusions

From this study several conclusions can be derived:

- Successfully operating Cannibal plants tend to have a greater SCOD release from the feed to the interchange reactor than poorer performing plants as measured in small batch reactors. These SCOD releases over time can be compared to SCOD releases that occur in similar batch reactors using conventional activated sludge and it is possible that a preliminary assessment of the effectiveness of Cannibal based on soluble COD release can be made.
- Further studies are needed to determine the overall success of this approach.
- Along with the SCOD release, there are several other characteristics including reactor blacking, SVI and plant effluent quality that could potentially be used to judge a Cannibal plant's effectiveness and that could be utilized to create a more

comprehensive model for evaluating the applicability of the Cannibal system to a conventional treatment plant including release of iron or measurement of biologically reducible iron.

3.6 References

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Goel, R. K., and Noguera, D. R. (2006). "Evaluation of sludge yield and phosphorus removal in a Cannibal solids reduction process." *Journal of Environmental Engineering*, 132(10), 1331-1337.

Easwaran, S. P. (2006). "Developing a mechanistic understanding and optimization of the Cannibal^{TM} process phase II," Virginia Polytechnic Institute and State University, Blacksburg.

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4 MANUSCRIPT II: "BATCH STUDIES ON DIFFERENT SLUDGES TO DETERMINE THE APPLICABILITY OF SHEAR, SONICATION AND OZONE AS PRETREATMENT PROCESSES"

4.1 Abstract

This study was undertaken to determine the digestibility of several different sludges that had been pretreated with shear, sonication or ozone. The study was conducted by exposing each sludge to the different pretreatment methods then digesting them for extended time periods in batch digesters.

Several conclusions were derived from these experiments and included a more rapid increase of SCOD in digesters that are fed with pretreated WAS. The most significant changes in concentrations (TS, VS, and COD) tended to occur during the first week of batch digestion. There appeared to be a degree of floc disruption and EPS disintegration caused by pretreating the WAS with the different technologies, with the greatest effect from shearing and ozone. None of the pretreatment methods resulted in an increase in overall digestion but they tended to increase the rate of digestion early in the digestion process.

4.2 Background

This study was undertaken to determine the effect of several pretreatment technologies on the digestibility of several different sludges that had been pretreated with shear, sonication or ozone. The first set of tests was conducted using two activated sludges from local WWTPs that were exposed to two different shear durations or a dose of ozone. The second set of tests was conducted on sludge from one of the WWTPs in Columbus, OH, which was primarily interested in the applicability of shear and sonication to their sludge; however ozone was added to the experiment to provide additional data.

Below is a review of the available literature on the three pretreatment technologies followed by the results and conclusions found in this study.

4.3 Mechanical Pretreatment

Mechanical pretreatment can be divided into two categories: “violent” or “refined”. Violent pretreatment refers to those methods that utilize mechanical devices that smash, accelerate, or shear sludge and include stirred-ball mills, high-pressure homogenizers, blenders and other devices that exert high stresses on the sludge. Sonication is the other category of mechanical shear and could be considered the more refined and less abusive method; in reality it can cause much greater stresses on the sludge through localized pressure and temperature extremes around the horn of the sonicator (Hogan et al. 2004, Tiehm et al. 2001). Both of these types of mechanical pretreatment technologies have their own advantages and disadvantages and these will be discussed in the following paragraphs. A process flow diagram illustrating a typical plant design with the installation of a shear device for sludge pretreatment is shown in Figure 4.1.

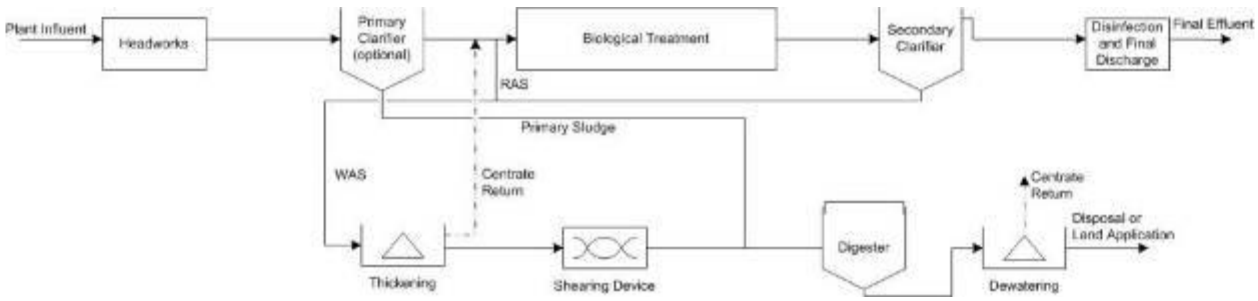


Figure 4.1- Shear Pretreatment Process Flow Diagram

4.3.1 Violent Shearing Devices

Studies have been conducted utilizing several types of violent mechanical shearing devices including stirred-ball mills and high-pressure homogenizers to determine their feasibility for sludge pretreatment or for modifying the return activated sludge (RAS) line to reduce the sludge yield in the activated sludge system (Camacho et al. 2002, Kopp et al. 1997, Lehne et al. 2000, Novak et al. 2007b, Strunkmann et al. 2006). Of important note is that mechanical shear devices are best applied only to secondary (biological) sludge because its degradability is significantly less than primary sludge, which gains little benefits from mechanical treatment (Lehne et al. 2000). It was found that mechanical shear causes floc disruption and hydrolysis over a short exposure time (Kopp et al. 1997).

One of the most important considerations with mechanical shearing is the energy imparted to the sludge because of a direct correlation between the energy imparted and the amount of cell disruption (Kopp et al. 1997, Liu et al. 2005). Low energy input will cause floc disruption, which allows the microorganisms within the flocs to access additional organic matter, and reduction in mean particle size, which can result in increased volatile solids reduction (VSR) in digesters when used as a pretreatment or a reduction in overall yield in the activated sludge process when used to treat RAS (Camacho et al. 2002, Kopp et al. 1997, Lehne et al. 2000). The one disadvantage to a low energy input is a deterioration in the settling characteristics of the sludge due to the floc dispersion and lighter particles (Seka and Verstraete 2003). To achieve cell lysis, higher energy must be imparted to the sludge which also implies a greater operational cost. However, the degradability is improved when the cells are lysed (Camacho et al. 2002, Liu et al. 2005).

One constant factor that several researchers found was when the total solids (TS) of the sludge were increased there was a decrease in required energy input (Kopp et al. 1997, Lehne et al. 2000). It was also found that with improved digestion and dewatering resulting from the mechanical shearing there was an increased concentration of nitrogen species being returned to the activated sludge system including poorly degradable organic nitrogen (Kopp et al. 1997, Strunkmann et al. 2006).

In summary, the digestion improving pathway followed by mechanical shear devices and many of the other pretreatment devices is cell and floc disruption which increases digestion rate resulting in reduced volatile solids (VS), increased sludge density and improved dewaterability (Kopp et al. 1997).

4.3.2 Sonication Pretreatment

Sonication, or ultrasound, is the use of sound energy between the frequencies of 20 kHz and 10 MHz which is typically caused by the rapid vibration of an object often referred to as a horn or transducer (Cao et al. 2006, Hogan et al. 2004). This rapid vibration causes alternating compression and rarefaction, that is, areas of high and low pressure, respectively, which result in excessive localized temperature and pressure (>5000°K and several hundred atmospheres) (Show et al. 2007, Tiehm et al. 2001). These extreme conditions are caused by the formation of cavitation bubbles that rapidly form and burst. Cavitation bubbles are classified as stable, where the bubble does not expand to its collapse radius due to the sound pressure during the rarefaction cycle being insufficient, or transient cavitation, where the pressure is sufficient enough to cause collapse within a few acoustic cycles (Show et al. 2007). The collapse or resonant radius is the point where the cavitation bubble ruptures and causes the localized extremes; it is directly proportional to the frequency of the sound waves (Tiehm et al. 2001).

The extreme conditions caused by sonication result in floc dispersion and subsequent reduction of mean particle size often through pyrolysis of volatile compounds (Braguglia et al. 2008, Hogan et al. 2004, Show et al. 2007, Tiehm et al. 2001). Hydroxyl radicals can also form during sonication and will react with non-volatile compounds in the bulk liquid (Tiehm et al. 2001, Zhang et al. 2007).

Researchers have found that the solids concentration of sludge affects the efficiency of sonication and, as with many of the other pretreatment technologies, a more concentrated sludge produces better results than a thinner sludge (Mao and Show 2006, Show et al. 2007, Zhang et al. 2008). Another parameter that affects the performance of sonication on sludge is the frequency that the device is operated at with lower frequencies causing more disruption due largely to the higher hydro-mechanical shearing effects (Tiehm et al. 2001).

When discussing sonication there are several terms which need to be defined and are listed below in Table 4.1.

Table 4.1- Common Sonication Terminology

Terminology	Definition	Units	Source
Ultrasonic Intensity	Power supplied per horn or transducer area	W/cm^2	Tiehm et al.2001
Ultrasonic Density	Power supplied per sample volume	W/mL	Tiehm et al.2001
Ultrasonic Dose	Energy supplied per sample volume	W-s/mL	Tiehm et al.2001
Specific Ultrasonic Dose (SUD)	Power supplied for an exposure time per unit volume and mass of sample	W-s/kg-solids	Muller 2006

In the literature, there has been no uniform method of reporting the energy imparted to the sample. Table 4.2 presents literature reported values and where possible provides them in terms of specific ultrasonic dose to promote uniformity and ease of comparison.

Table 4.2- Literature Reported Sonication Values

Source	Intensity (W/cm2)	Density (W/mL)	Dose (W-s/mL)	SUD (W-s/kg-solids)	Location
Show et al. 2007	0-92	0-0.52	ND	ND	Pretreatment
Cao et al. 2006	ND	0.25-0.50	ND	ND	Recycle
Zhang et al. 2008	125	0.80	1440	$9.3x10^7$	Pretreatment
Xie et al. 2007	13.70	ND	ND	ND	Pretreatment
Muller 2006	15.03	0.59-0.94	107-170	ND	Pretreatment and Recycle
Riedel 2009	15.03	0.3	90	$1.4\text{-}1.5x10^6$	Pretreatment to batch digestion

As can be seen in Table 4.2, there is a significant range of reported values which makes it difficult to decide on an optimal dose. However, of all the available units to report sonication values in, the SUD allows reproducibility because it accounts for the solids concentration of the sludge so it can be readily adapted to different sludges.

In summary, for sonication treatment of sludge, its primary method for floc and cell disruption is the formation of cavitation bubbles that implode and cause localized extreme conditions. There is also some effect from the formation of hydroxyl radicals. The most import parameters to consider when utilizing sonication is optimizing the solids concentration and the frequency of the device, typically higher for the former and lower for the latter provide the best results.

4.3.3 Disadvantages of Mechanical Shear Pretreatment

There are three major disadvantages to mechanical shearing devices. One is the high energy input required to operate these devices, which is an issue with many pretreatment technologies, however, much of this energy can be recouped with the improved digestion of the sludge and the increased biogas production that can be utilized for power generation. The second disadvantage is maintenance required for many of these devices, especially the violent ones, due to the high stresses that are exerted on the mechanical parts during operation. The final disadvantage is with scaling these devices up to full-sized applications because many of them have only been utilized in lab-scale applications and may not be feasible for use in larger applications.

4.4 Ozone Pretreatment

4.4.1 Introduction

Ozone is a treatment technology that is receiving increased attention in both the water and wastewater industries primarily as a disinfectant alternative to chlorine species (Tchobanoglous et al. 2003). The chemical characteristics of ozone are listed in Table 4.3.

Table 4.3- Ozone Properties (Material Safety Data Sheet 2000)

Characteristic	Value
Chemical Formula	O_3
Molecular Weight	48 g/mole
Specific Gravity	2.144 g/L
Vapor Density	1.7
Solubility in Water	0.49 % by wt.

Ozone is a highly reactive, strong oxidant which has the potential to cause explosions when in contact with many organic compounds and can also create intermediaries that are as dangerous (Material Safety Data Sheet 2000). It is generated from air or pure oxygen using a high voltage electrical discharge called corona discharge and due to its short life span it is typically produced on site (Panda and Mathews 2008).

4.4.2 Ozone Usages in Wastewater Treatment

As was mentioned previously, ozone is receiving attention in wastewater treatment as a disinfectant before final discharge because of its ability to kill or inactivate bacteria and protozoa, including ones that are resistant to chlorine, and the lack of disinfection byproducts formed by it (Panda and Mathews 2008). There are other applications for ozone that are being investigated for use at wastewater treatment plants including usage as a pretreatment before digestion and as a side-stream reactor on the recycle loop to reduce the overall plant yield. Below are process flow diagrams illustrating ozone used as a pretreatment technology (Figure 4.2) and side-stream recycle (Figure 4.3).

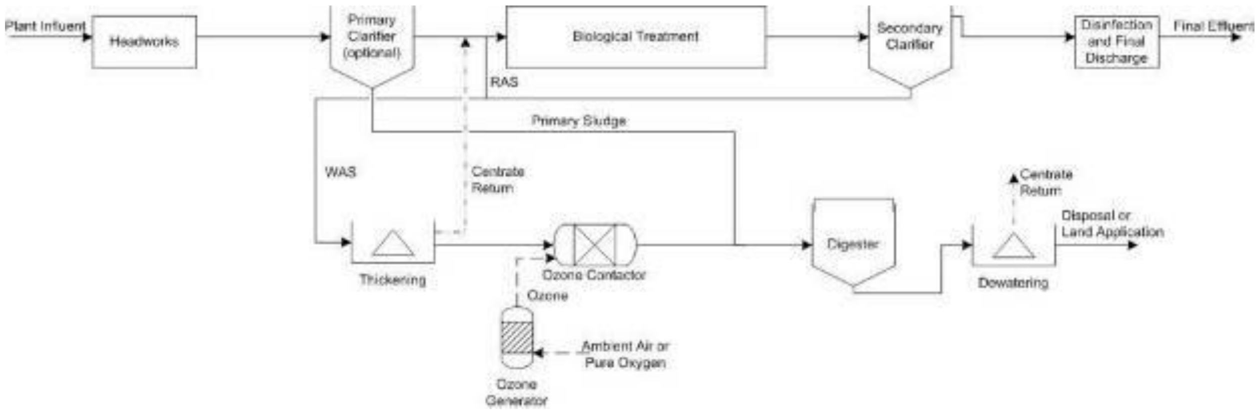


Figure 4.2- Sludge Pretreatment with Ozone Process Flow Diagram

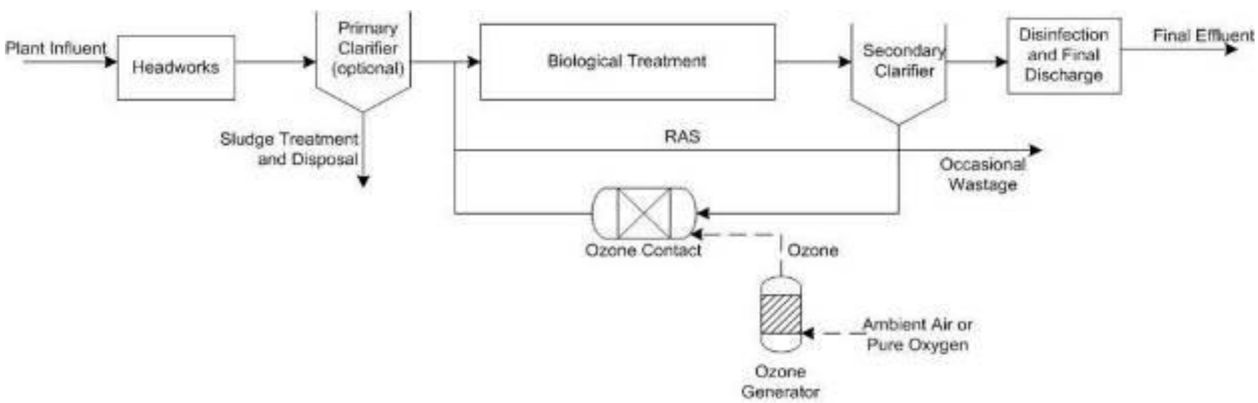


Figure 4.3- Side-Stream Ozone Treatment Process Flow Diagram

As a pretreatment for digestion of sludge, ozone serves to cause floc and cell disruption allowing better, more-rapid digestion (Ahn et al. 2002, Bernal-Martinez et al. 2007, Bougrier et al. 2006a, Bougrier et al. 2007a, Carballa et al. 2007, Chu et al. 2008, Manterola et al. 2008, Mines et al. 2008, Yeom et al. 2002, Zhao et al. 2007). There have also been studies investigating the usage of ozone pretreated sludge and dewatering centrate as a carbon source for nitrification (Ahn et al. 2002, Lee et al. 2005, Sakai et al. 1997, Yeom et al. 2002, Zhao et al. 2007). It has been investigated as a side-stream process attached to the return activated sludge line to treat a percentage of the RAS with the intention of minimizing sludge yield in the activated sludge process (Ahn et al. 2002, Boehler and Siegrist 2006, Kamiya and Hirotsuji 1998, Lee et al. 2005, Yeom et al. 2002).

Of important consideration for ozone treatment are the effects of temperature, dissolved oxygen and total solids upon the mass transfer coefficient (Manterola et al. 2008, Panda and Mathews 2008). The dose also affects the results of treatment of wastewater with ozone with literature reported values ranging from 0.05 to 0.50 g O_3/g TS (Bougrier et al. 2006a, Chu et al. 2008, Dogruel et al. 2007, Manterola et al. 2008, Mines et al. 2008, Sakai et al. 1997, Zhao et al. 2007). Typically, with higher ozone doses there is a greater solubilization of organic matter (Ahn et al. 2002, Manterola et al. 2008). When using ozone as a yield reduction technology on the return line in activated sludge processes there is a minimum dose required to achieve yield reduction (Kamiya and Hirotsuji 1998).

Ozone has direct and indirect treatment pathways which include the direct oxidation of organic material to carbon dioxide and the formation of hydroxyl radicals which react indirectly with compounds and organic material (Carballa et al. 2007, Chu et al. 2008).

4.4.3 Advantages of Ozone Treatment of Wastewater

Ozone treatment of wastewater has several advantages that make it an appealing technology, especially with increasingly stringent regulations. As a strong oxidant, ozone can break down many polycyclic aromatic hydrocarbons (PAHs), pharmaceutical and personal care products (PPCPs), dyes and other industrial byproducts that are becoming more prevalent in wastewaters and typically are not removed by conventional biological treatment (Bernal-Martinez et al. 2007, Carballa et al. 2007, Chu et al. 2008). It can help control the growth of bulking organisms in both the activated sludge process and digesters (Ahn et al. 2002). When used as a pretreatment technology prior to anaerobic digestion, it can potentially increase the production of methane (Bougrier et al. 2007a, Carballa et al. 2007). It also causes floc disruption and cell hydrolysis which releases soluble proteins and carbohydrates to the bulk liquid and improves degradability (Ahn et al. 2002, Zhao et al. 2007). Other advantages include:

- Decreased viscosity, improved settleablity and reduced odors (Bougrier et al. 2007a);
- Yield reduction in activated sludge systems (Kamiya and Hirotsuji 1998, Lee et al. 2005, Sakai et al. 1997);
- Potential carbon source for denitrification with equivalent energy to glucose (Ahn et al. 2002, Lee et al. 2005, Sakai et al. 1997, Yeom et al. 2002, Zhao et al. 2007);
- Increased mineralization of organic material (Bougrier et al. 2007a).

4.4.4 Disadvantages of Ozone Treatment of Wastewater

As with the other pretreatment technologies there are disadvantages to the use of ozone in wastewater treatment, which are listed below:

- Increased inert and colloidal COD due to the disintegration of sludge flocs and cells which often increases the non-biodegradable COD in the plant effluent due to recycling of dewatering centrate to the biological process or the use of ozone treatment on the RAS line (Boehler and Siegrist 2006);
- Decreased dewaterability, increased sludge volume index (SVI) and capillary suction time (CST) of digested sludge because of smaller particles (Ahn et al. 2002, Bougrier et al. 2006a, Bougrier et al. 2007a, Carballa et al. 2007);

- Decreased pH due to formation of carboxylic acid from organic material and consumption of alkalinity by the oxidation of organic material (Bougrier et al. 2007a);
- When used to minimize yield, phosphorus removal is reduced because one of the primary removal mechanisms is sludge wasting (Sakai et al. 1997);
- Ozone generation is an energy intensive process and requires significant capital investment in machinery (Panda and Mathews 2008);
- Mass transfer kinetics need to be optimized to the sludge characteristics (Lee et al. 2005, Panda and Mathews 2008).

4.5 Materials and Methods

4.5.1 Columbus Batch Digestion Studies

Thickened WAS, primary sludge and digested sludge were collected from the Columbus WWTP and shipped to Blacksburg. The WAS was treated in the following manners:

- 10 minute shearing with a Warring blender at 8-10,000 rpm, 10 minute cooling in water-jacketed beaker;
- 5 minute sonication at 20kHz, 166 W and sonication density of 0.33 W/mL using a Dukane DPC I 2120 generator and a Dukane 41C27 20kHz mounted probe with a tip diameter of 37.5 mm and no additional focusing horn, 5 minute cooling in water jacketed beaker;
- Ozone dose of approximately 0.13 mg O_3/mg TS using a Xetin Air Zone XT301 ozone generator with a generation rate of 300 mg O_3/h;
- Untreated control.

The initial reactors were 1 L Corning glass bottles with approximately 800 mL of sludge blended with a ratio of 1:1.5:1.5 digested:primary:WAS. Gas was collected in Tedlar bags and the volume was measured when the reactors were sampled. Reactors were maintained at 37 °C in a constant temperature room and mixed daily by hand agitation.

After approximately three and a half weeks of operation, the reactors were scaled up to 4000 mL of sludge in 10,000 mL Corning bottles. The initial reactors were sampled and the remaining 700 mL was used as seed for the new reactors. The difference was made up with 300 mL of digested sludge, 1500 mL of primary sludge and 1500 mL of treated WAS. These reactors were allowed to operate for approximately two weeks at which point 3000 mL was removed and replaced with 1500 mL of primary sludge and 1500 mL of treated WAS. Operation continued as before, except with weekly sampling for total and volatile solids, total and soluble COD, pH, ORP and gas volume measurement.

COD analysis was conducted photometrically using Hach High Range COD tubes (Hach Company, Loveland, CO) which had a range of 20-1500 mg/L COD and are USEPA approved. Soluble COD was measured on samples that were centrifuged long enough to have a supernatant that could be passed through a 0.45 μm nitrocellulose membrane filter.

Initial and final total and volatile solids, were measured according to Standard Methods (A.P.H.A. et al. 1995). Gas volume was measured by timed withdrawal from the Tedlar bags with a calibrated peristaltic pump. pH and ORP were analyzed using the appropriate probes from Accumet and Thermo Fisher. pH was adjusted as necessary with caustic or sodium bicarbonate addition.

Microscopy of treated and untreated WAS was conducted using a FEI Quanta 600 scanning electron microscope in low-vacuum mode. Samples were diluting 1:25 in distilled water and fixed on a 0.45 μm nitrocellulose membrane filter by vacuuming for 10 minutes. The filters with fixed samples were allowed to dry overnight in a desiccator.

4.5.2 Blacksburg Area WWTP Batch Digestion Studies

Thickened WAS was collected from two local WWTPs (Pepper's Ferry and Christiansburg) and transported to the lab. Both of these sludges were treated in the following manners:

- 1 minute shearing with a Warring blender at 8-10,000 rpm, no cooling;
- 10 minute shearing with a Warring blender at 8-10,000 rpm, 10 minute cooling in water-jacketed beaker;
- Ozone dose of approximately 0.13 mg O_3/mg TS using a Xetin Air Zone XT301 ozone generator with a generation rate of 300 mg O_3/h;
- Untreated control.

Reactors were approximately 500 mL in volume with 360 mL of sludge plus 90 mL of a seed sludge which was a 50:50 mix of primary and secondary sludge treated for 15 days at 37 °C and 2 days at 55 °C. All reactors were completely mixed and maintained at approximately 37 °C in an incubator. Gas was vented through water traps but not collected. Sampling occurred on days 0, 7, 14, 21, and 57.

COD analysis was conducted photometrically using Hach High Range COD tubes (Hach Company, Loveland, CO) which had a range of 20-1500 mg/L COD and are USEPA approved.

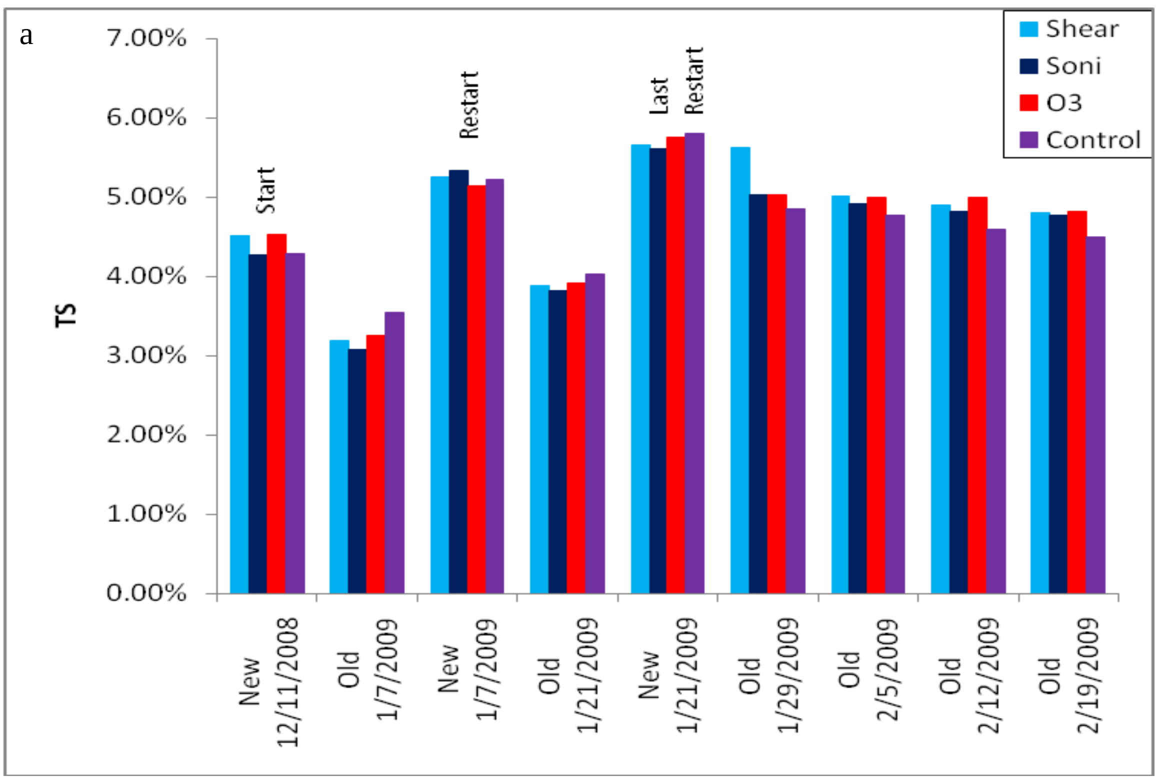
Initial and final total and volatile solids were measured according to Standard Methods (A.P.H.A. et al. 1995). pH was monitored with an Accumet pH probe and meter and adjusted if necessary using caustic or sodium bicarbonate addition.

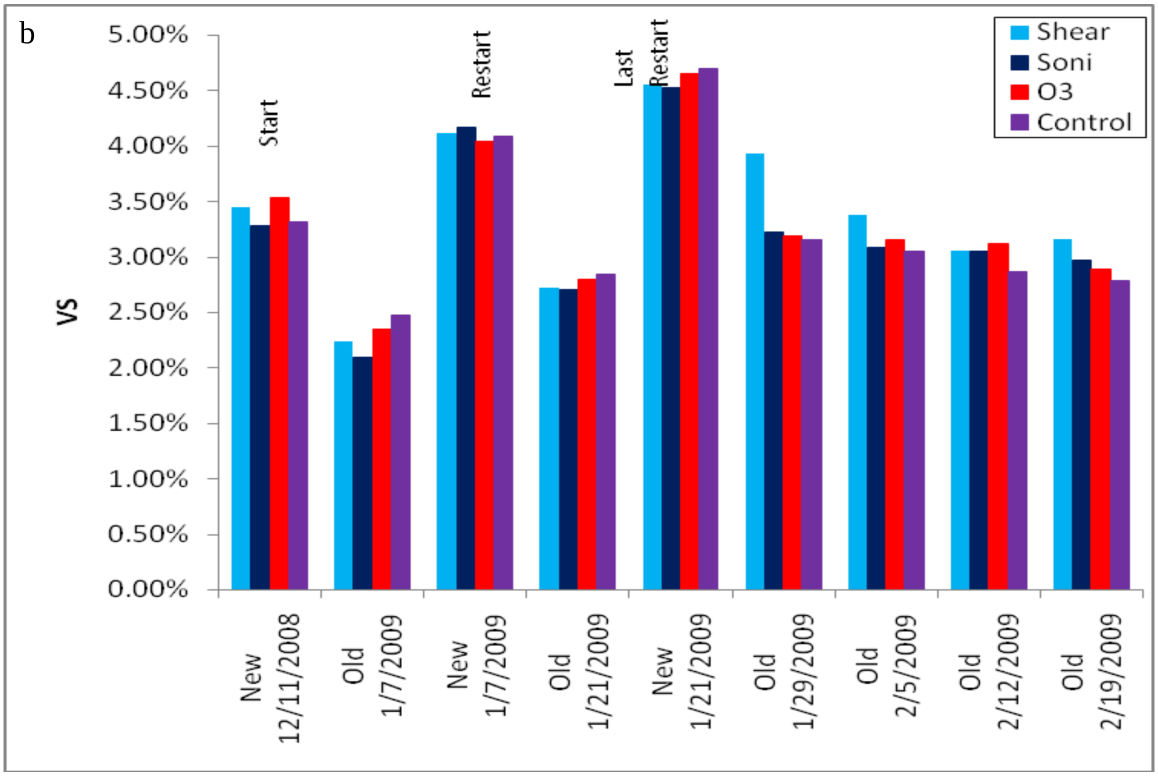
4.6 Results and Discussion

The raw data for these two studies are presented in Appendices B and C; however, several graphs will be utilized to illustrate the effects of the pretreatments on these samples.

4.6.1 Columbus Batch Digestion Studies

Figure 4.4 a, b and c illustrate the changes in TS and VS both over the entire study and after steady state conditions were achieved; i.e. after 21 January.





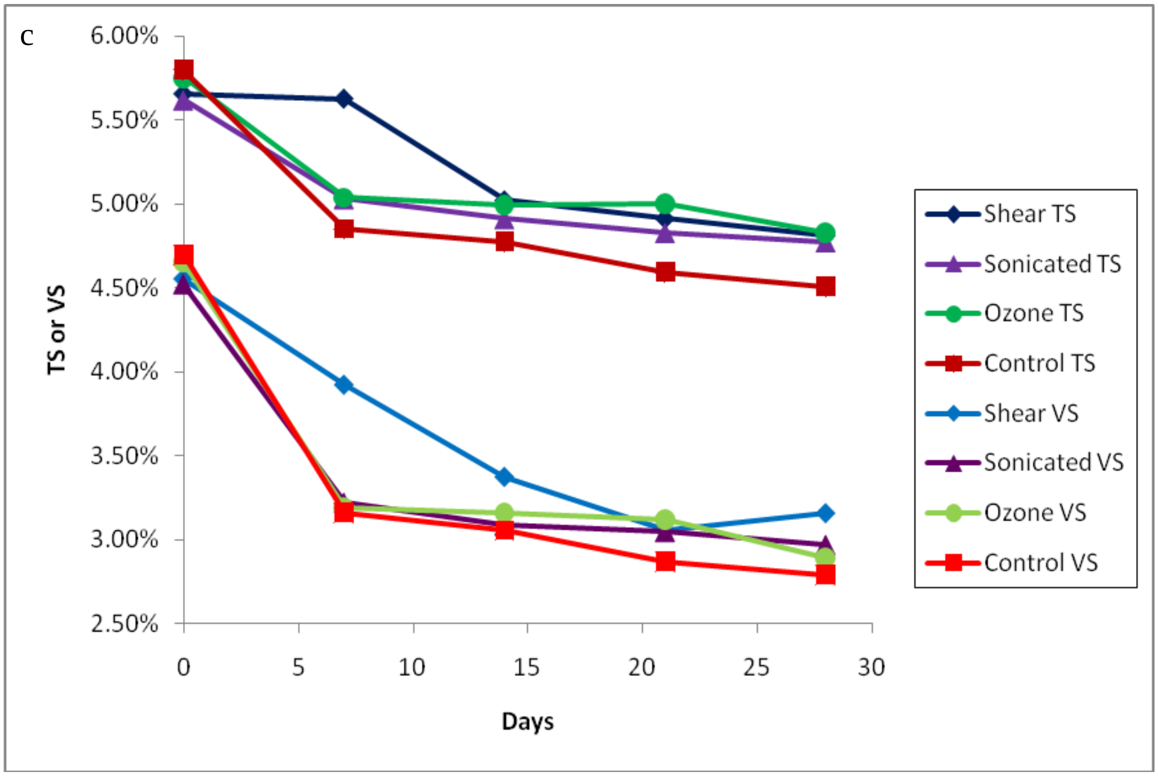


Figure 4.4- (a) %TS, (b) %VS and (c) 21 January to 19 February %TS and %VS Profiles for the Columbus Batch Reactors

From Figure 4.4a it can be observed that three of the reactors had a similar drop in TS within the first week, but the reactor with the mechanically sheared WAS lagged behind by about a week. Also, it can be seen that the control reactor started with a similar concentration as the ozonated reactor, but saw a more significant decrease in TS and was consistently lower in concentration than any of the other reactors.

Figure 4.4b illustrates the change in VS for every sampling event. It can be seen that there is a decrease in VS in the weeks after each reactor change-out which should occur when it is allowed to digest for several weeks. Figure 4.4c provides an illustration of the last four weeks of operation where the reactors were sampled. From this figure, it is quite clear that there is no significant improvement caused by any of the pretreatment technologies. In fact, shearing caused that reactor to lag behind the other three in VS reduction. This could be due to separation of some of the organisms, preventing efficient transfer of hydrogen from the hydrogen generators to the hydrogen utilizers (McCarty and Smith 1986). Although only the WAS was treated, it has been found that WAS contains a rich population of methanogenic archaea (Kim et al. 2004).

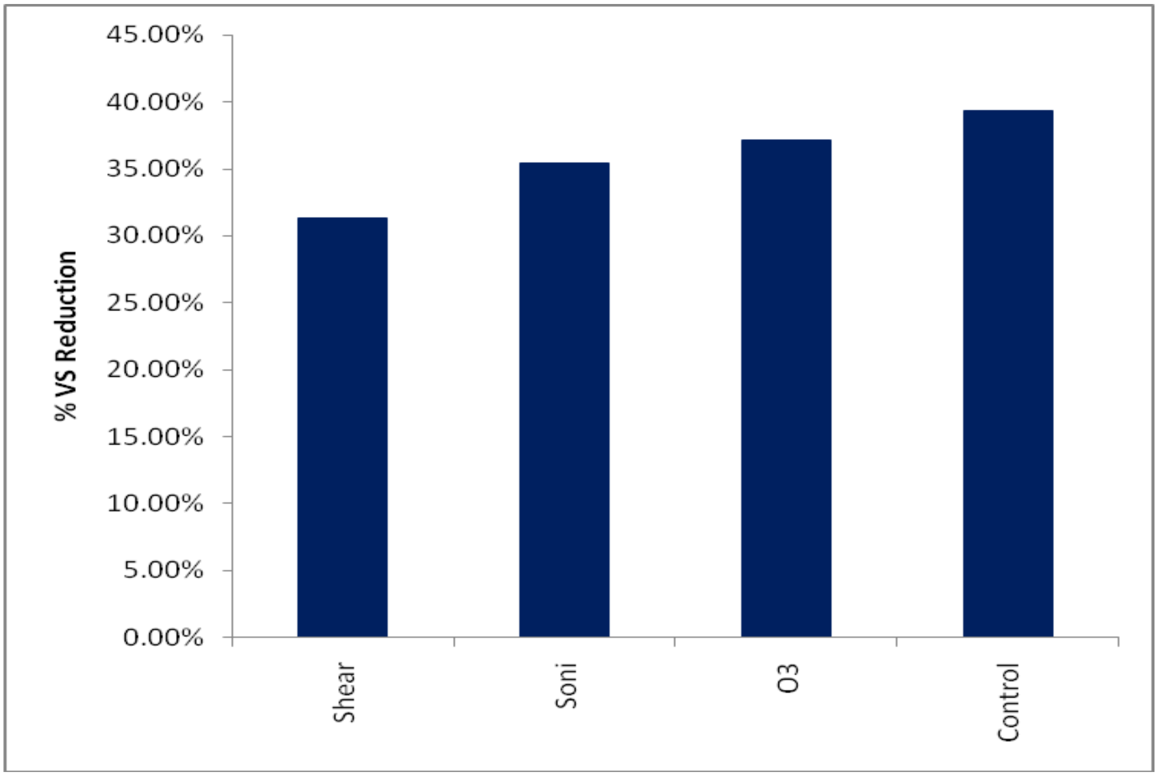
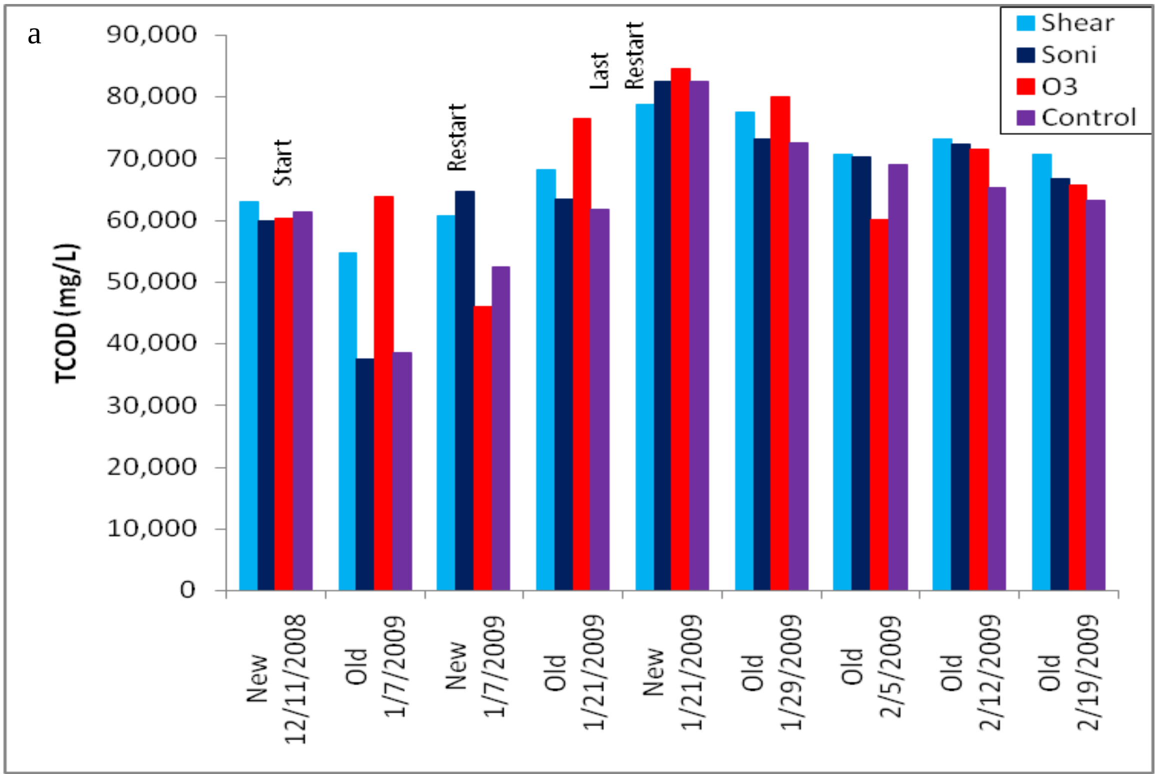
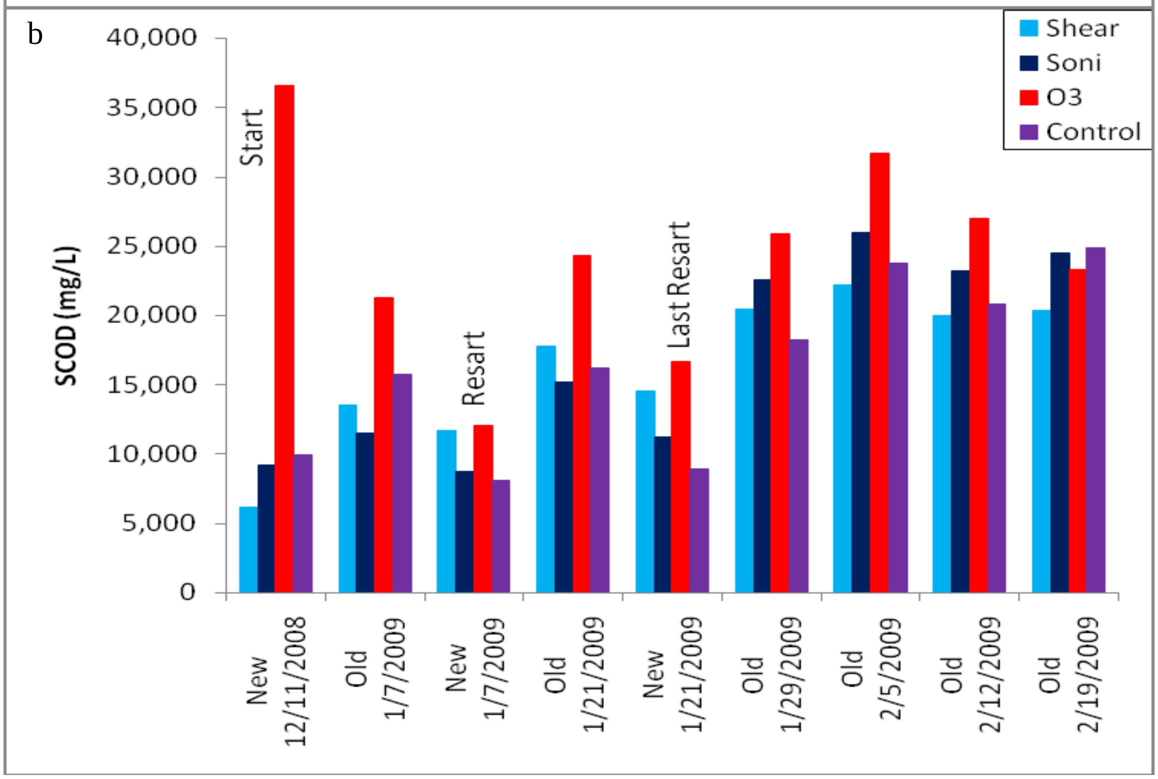


Figure 4.5- Columbus Batch Reactor Volatile Solids Reduction

Figure 4.5 illustrates the differences in VS reduction over the expiremental time period and it can be seen that the control reactor had the greatest reduction, which further reinforces the conclusion that these pretreatment technologies do little to improve the overall digestibility of the sludge at extended digestion times.


a
TCOD (mg/L)
90,000
80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
Start
Restart
Last Restart
Shear
Soni
O3
Control
New 12/11/2008
Old 1/7/2009
New 1/7/2009
Old 1/21/2009
New 1/21/2009
Old 1/29/2009
Old 2/5/2009
Old 2/12/2009
Old 2/19/2009


b
SCOD (mg/L)
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
Start
Resart
Last Resart
Shear
Soni
O3
Control
New 12/11/2008
Old 1/7/2009
New 1/7/2009
Old 1/21/2009
New 1/21/2009
Old 1/29/2009
Old 2/5/2009
Old 2/12/2009
Old 2/19/2009

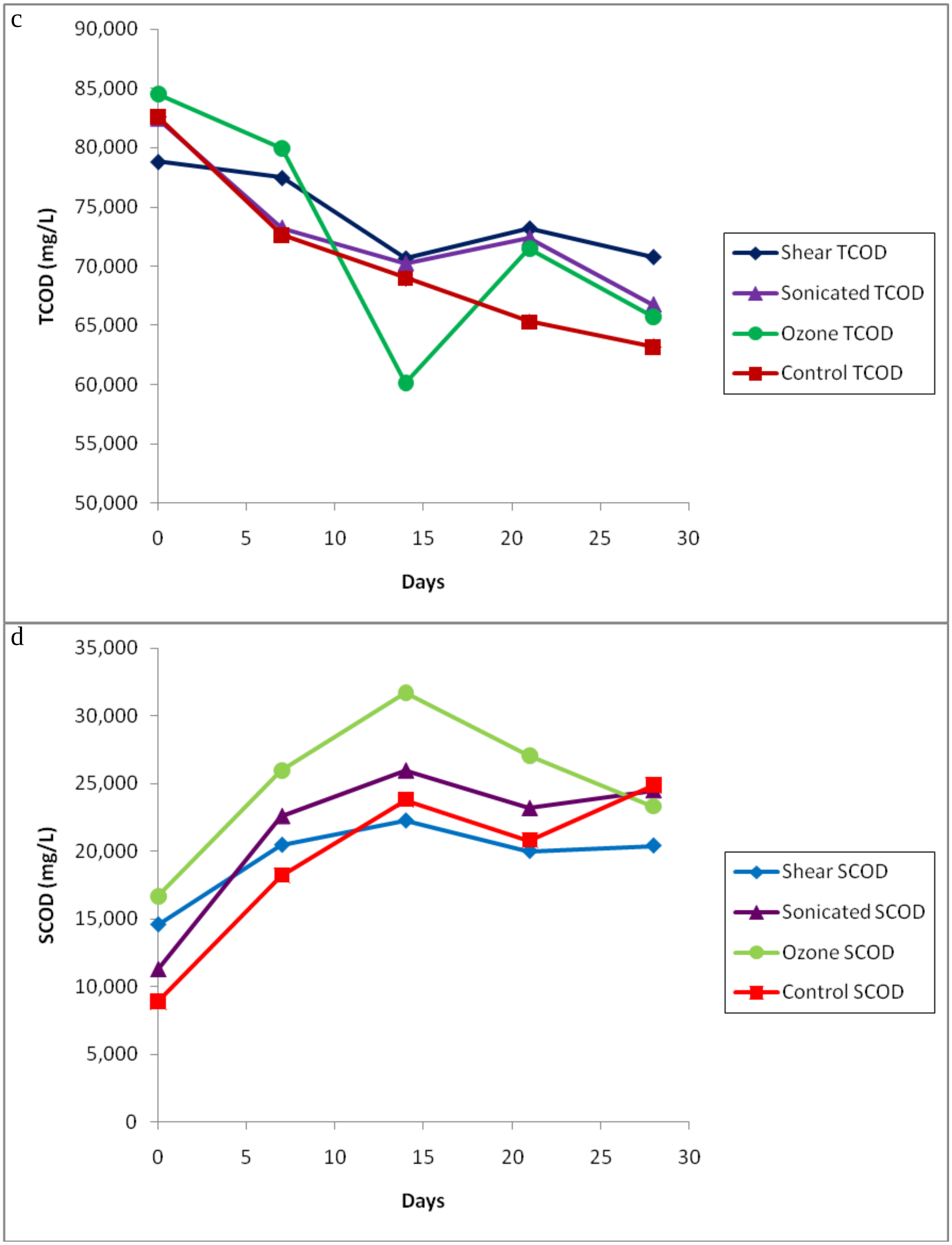


Figure 4.6 (a) TCOD, (b) SCOD and (c and d) 21 January to 19 February TCOD and SCOD Profiles for the Columbus Batch Reactors

The TCOD profile illustrated in Figure 4.6a presents a pattern that is consistent with the pattern shown by the TS profile. There is some reactor dependent variability from week to week. Figure 4.6b is of particular interest because most of these pretreatment technologies claim to solubilize flocs and cells which results in a greater concentration of SCOD in the bulk liquid. This unbound SCOD is thought to degrade more rapidly than with conventional digestion. This can be seen clearly when looking at the data from 21 January onward: all three reactors fed with the pretreated sludge have a significantly higher concentration of SCOD for the beginning which steadily increases until 5 February after which point the concentrations begin to decrease to a point were it remains fairly constant. The control reactor, on the other hand, starts from a much lower concentration and is never able to achieve the concentrations of SCOD that are achieved by the ozonated or sonicated reactors, although it does finally exceed the concentrations in the other reactors on 19 February. Figure 4.6c and d illustrate the TCOD and SCOD profiles for the last four weeks of operation. From these two figures it is again apparent that the pretreatment technologies have minimal improvement on the digestibility of the WAS, in fact the shear treatment seems to have a negative effect on SCOD after about 10 days of operation. The major effect of these pretreatment technologies is an initial increase in SCOD release which is readily apparent when the individual samples are compared as in Figure 4.7.

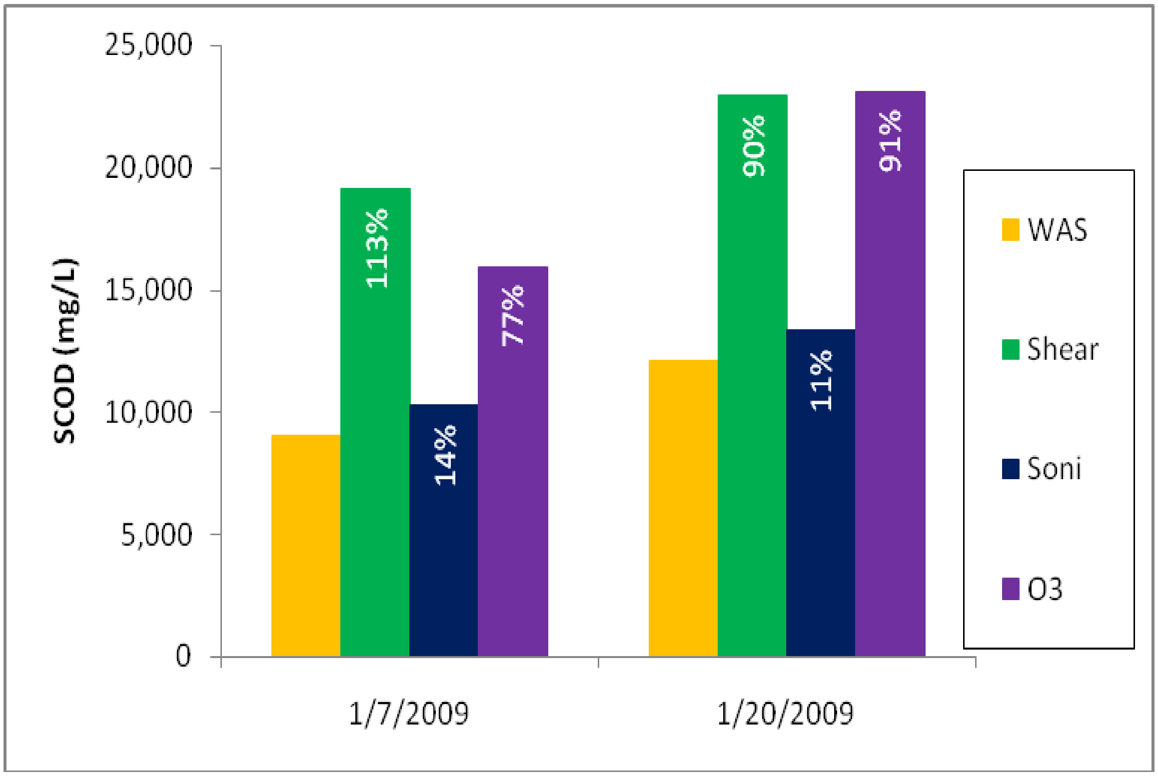


Figure 4.7- Initial Plant Samples SCOD

The percentages on each of the pretreated bars indicate the percent increase in SCOD when compared to the untreated WAS. From these numbers, it can readily be seen that sonication has little effect on the WAS, whereas the shear and ozone increased the initial soluble COD concentration.

Figure 4.8 presents images taken with a scanning electron microscope (SEM) in low vacuum mode of the treated and untreated WAS samples, all were diluted 1:25 and the magnification was approximately 2000-2500x. Figure 4.8a is an image of the untreated WAS in which the EPS is clearly present and in abundance. Figure 4.8b is an example of the sonicated WAS in which the floc structure and EPS is much more dispersed and in many sections not even present. Figure 4.8c is an image of WAS that had been sheared and which has the most dramatic lack of EPS of any of the images. Finally, Figure 4.8b is an example of the ozone treated WAS and in which there is also a distinct lack of EPS and floc material, but also some sort of multi-cellular organism that has been clearly damaged by the ozone treatment.

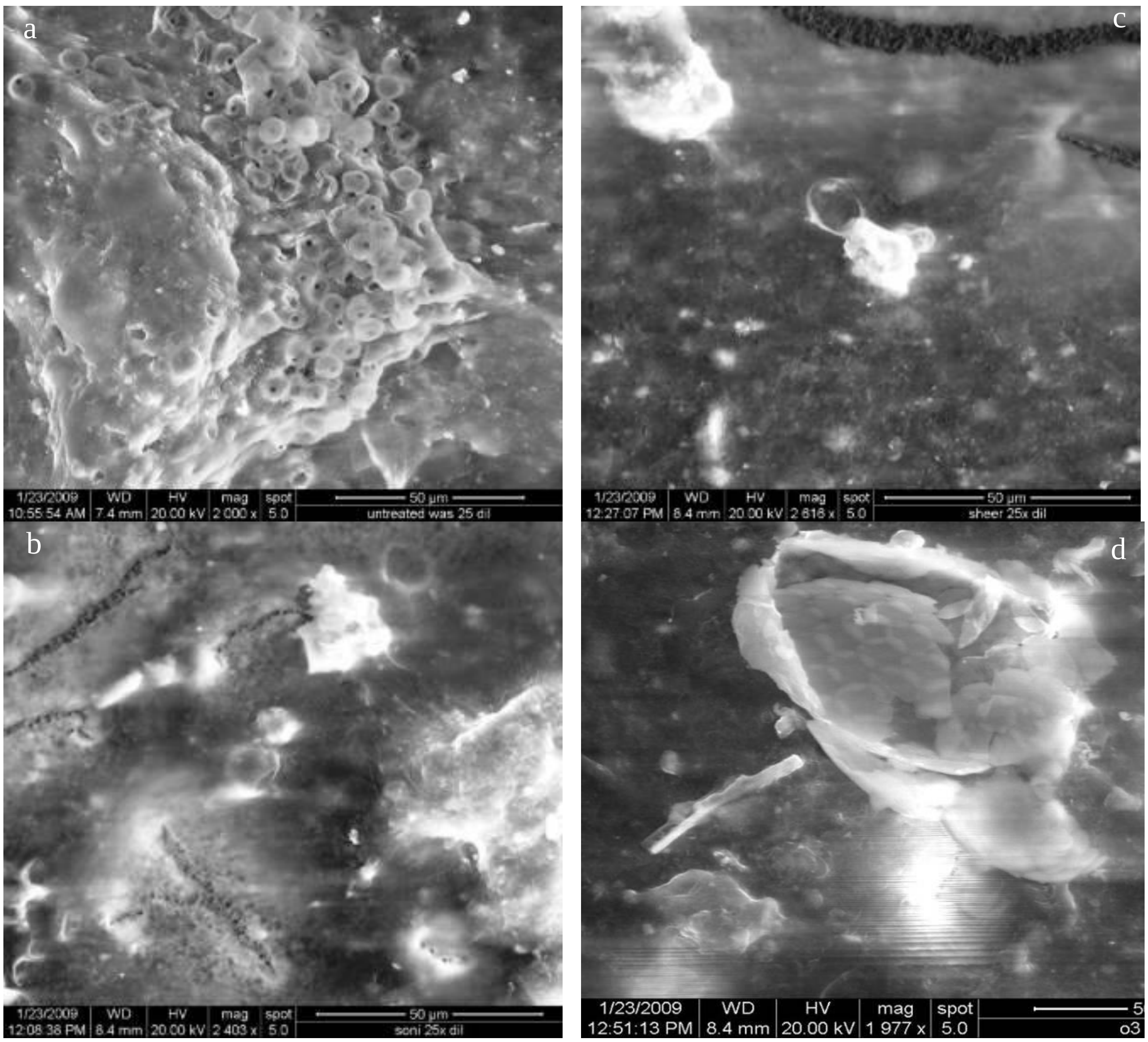


Figure 4.8 (a) Control, (b) Sonicated, (c) Mechanically Sheared and (d) Ozonated Scanning Electron Microscope Images of Samples Diluted 1:25 and Magnified Approximately 2000-2500X

There were some issues with the pH of the reactors dropping to 6.2 and below during the January draw-downs and refills; the ozone reactor dropped to 5.2-5.3 on two occasions. This was remedied initially by the addition of 1N NaOH to bring the pH up to near neutral levels but, when the pH continued to drop, $NaHCO_3$ as an approximately 1000 mg/L slurry as $CaCO_3$ was added to provide additional alkalinity. After that point, the pH remained above 7.

Gas collection was unsuccessful, with little volume accumulating in the Tedlar bags over the course of a week. This was more than likely due to poor sealing around the caps and on the vent lines to the bags. The volume of biogas produced can be estimated stoichiometrically based on the VSR and several chemical formulas for volatile solids, including $C_5H_7O_2N$, $C_{10}H_{19}O_3N$, $C_{16}H_{24}O_5N_4$, and CH_2O (Grady et al. 1999). Table 4.4 presents a range of theoretical biogas volumes for each reactor based on the VSR values compared to the measured values. As can be seen, the measured volumes were typically less than the theoretical volume, which reinforces the conclusion that the collection system was inadequate.

Table 4.4- Theoretical Biogas Volume Based on VSR and Measured Biogas Volume

Reactor	Theoretical Vol. Biogas Produced (L)	Measured Vol. Biogas Produced (L)
Control	43-80	48
Shear	33-62	27
Sonicated	37-69	15
Ozone	40-75	9

4.6.2 Blacksburg Area WWTP Batch Digestion Studies

As was mentioned in the materials and methods section, this study focused on comparing the effects of shear time and ozone dosing on two different sludges from local treatment plants. Both plants receive primarily municipal wastewater, although the Pepper's Ferry plant receives some additional industrial wastewater. Christiansburg is designed for a 4 MGD flow, but currently only treats 2 MGD; Pepper's Ferry treats 3 MGD.

Due to inadequate experimental planning, positive controls were not provided when the reactors were initially set up. To remedy this, an additional control was added and the 1 minute shear reactor can be considered to be a control because it was apparent that there was little difference in the sludge caused by the minute of shearing and the control which was set up later. Because of this the data from the control reactors is not presented and the original 1 minute shear reactors were treated as a control.

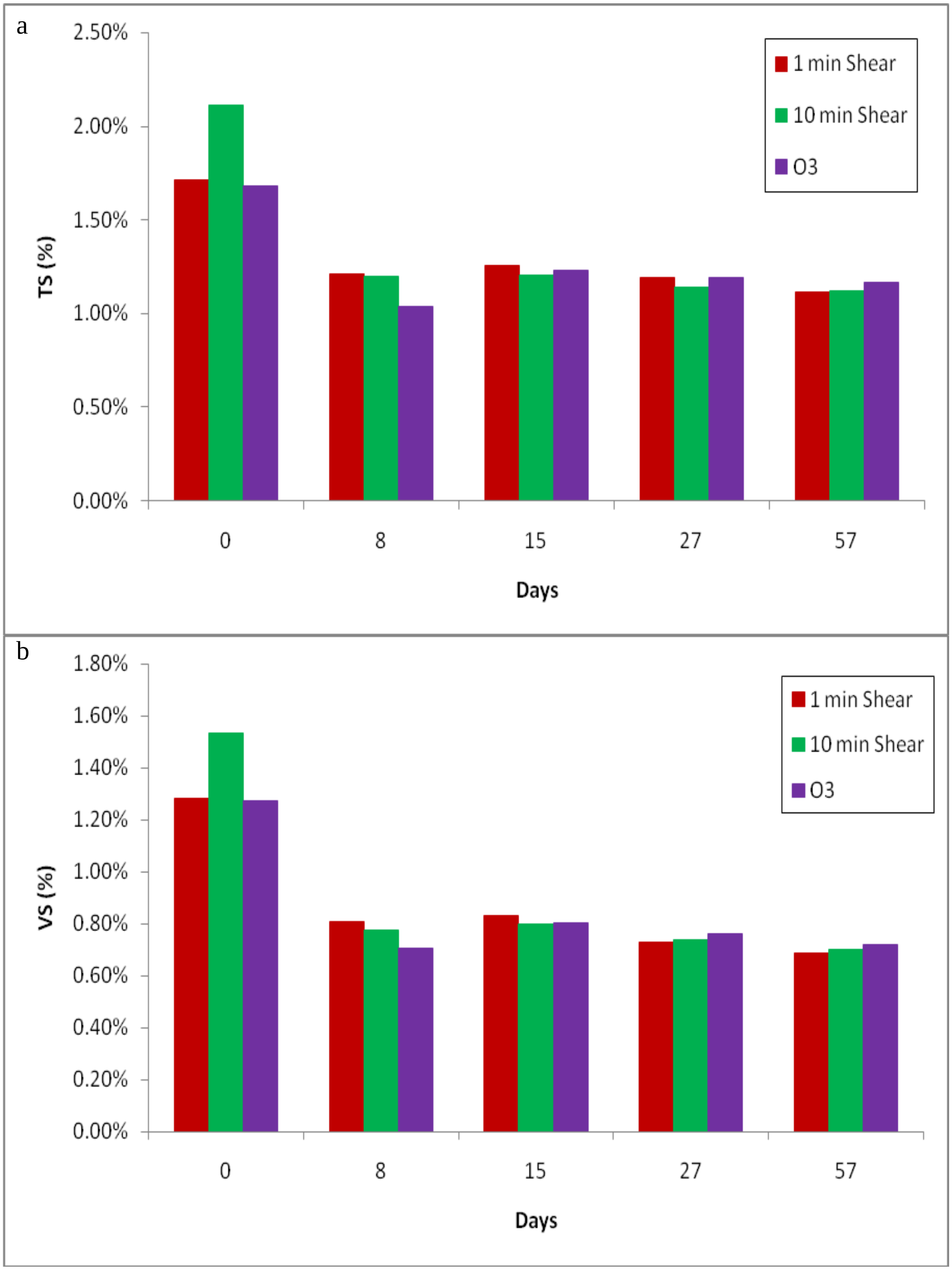


Figure 4.9 (a) TS and (b) VS Concentrations for Christiansburg Batch Reactors

As can be seen from Figure 4.9a, there is a decrease in TS during the initial week of operation, but after that point the TS remains fairly constant. There is also no significant difference between the treated and untreated reactors. In Figure 4.9b, the VS concentrations mirror the TS concentrations and what is significant is that there appears to be little overall decrease in VS over time after the initial week of digestion.

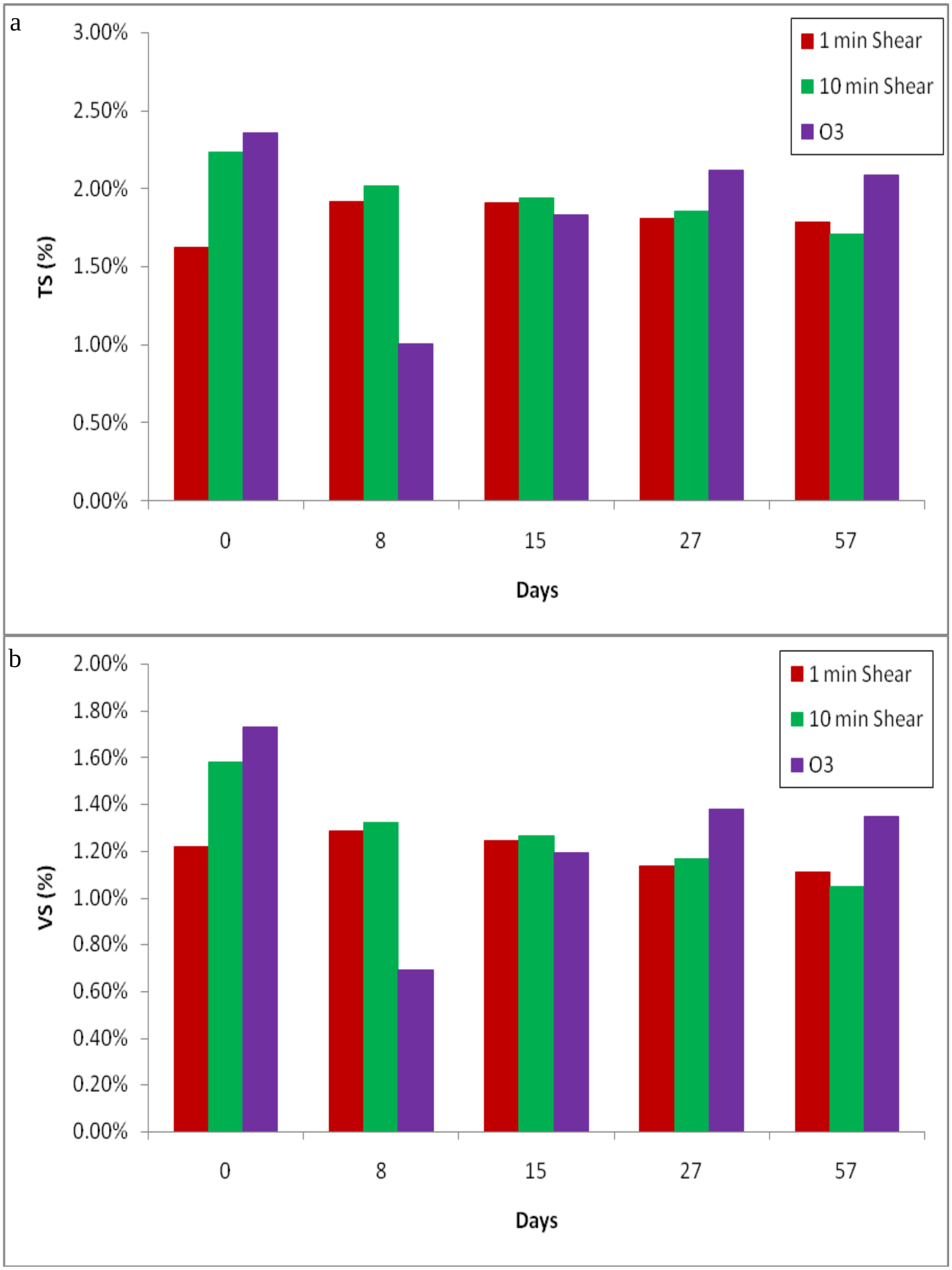


Figure 4.10 (a) TS and (b) VS Concentrations for Pepper's Ferry Batch Reactors

Figure 4.10 shows that there was little effect from any of the pretreatment technologies on the Pepper's Ferry sludge, although there was a slight decrease for the 10 minute shear and ozone reactors during the first week of operation. After that first week of operation, the TS and VS changed minimally. The initial significant drop in the ozone concentrations is likely due to inaccuracies in the measurement. It is not clear why the ozonation would influence the TS measurement while the other pretreatment techniques did not have this same effect.

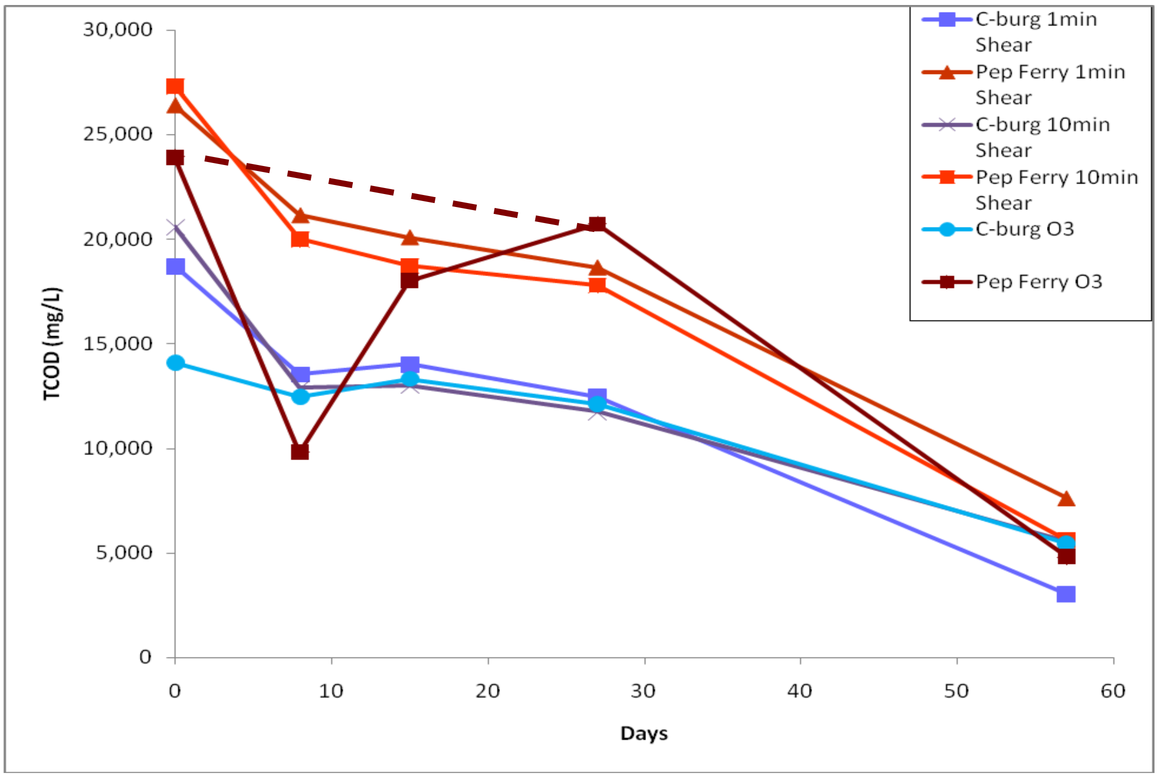


Figure 4.11- Christiansburg and Pepper's Ferry TCOD

Figure 4.11 illustrates a general decline in TCOD concentrations over the duration of the test. The most significant changes occurred during the first week of operation, which concurs with the TS and VS data presented above. It also shows that the 10 minute shear and ozone had little effect when compared with the 1 minute shear/control. The only unusual data series in this figure is the Pepper's Ferry ozone, which has an extreme initial decrease in concentration that is followed by and increase back to the range of the other Pepper's Ferry reactors. This could have caused by analytical error, so the dashed line was added as a hypothetical trend for that section of the data series. It is also important to note that the Pepper's Ferry reactors had a greater change in TCOD over the digestion period when compared to the Christiansburg reactors; this could be due to the higher initial TS concentrations in the Pepper's Ferry WAS.

4.7 Conclusions

Based on the data collected from these two studies there are several general conclusions that can be derived and are presented below:

- There is little difference in the overall improvement in digestibility of pretreated WAS compared to untreated WAS;
- The most significant changes in concentrations (TS, VS, and COD) tend to occur during the first week of batch digestion;
- Ozone had a greater initial impact on VS and SCOD than, shear which typically had a greater impact than sonication;
- Apparent floc disruption and EPS disintegration was observable when micrographs of the untreated and pretreated WAS were compared. Visually, it appeared that shear and ozone had greater effects on the floc structure than sonication did.

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5 MANUSCRIPT III: "WEF/WERF 05-CTS-3 EVALUATION OF PROCESSES TO REDUCE ACTIVATED SLUDGE SOLIDS GENERATION AND DISPOSAL"

5.1 Introduction

The generation of sludge has been a continual issue for every WWTP because of the increasing cost of handling and disposal (Tchobanoglous et al. 2003). Over the past several decades there have been numerous studies conducted to evaluate different methods for reducing the volume of sludge that has to be disposed. These studies have focused on two main pathways for reducing sludge volume: acceleration of the hydrolysis step of anaerobic digestion by thermally, mechanically or chemically short circuiting the process from a step that requires days to one that is completed in hours or even minutes; or reduction of yield from the activated sludge system by biological, mechanical or chemical treatment of a portion of the return sludge.

This study was undertaken with the objective of evaluating several of these pretreatment and side-stream technologies with the hope of developing a methodology for evaluating the feasibility of a particular treatment technology to a wastewater that has never been exposed to one of these technologies. It was hoped that this methodology would reduce the necessity of conducting costly and time-consuming pilot studies of these technologies by determining unique characteristics of sludges treated with these technologies.

A review of the available literature and the selection of the technologies to investigate was previously conducted, so this manuscript will focus on the results found from analytical work conducted on several sludges from different wastewater treatment plants that utilize the technologies (Sandino et al. 2008). The technologies selected for this work are as follows:

- Thermal hydrolysis, specifically Cambi™ THP;
- Mechanical shear, specifically Biogest AG Crown™ Press system;
- Biological side-stream yield reduction, specifically Cannibal™.

Difficulties arose in acquiring samples of these technologies because, of the three being investigated, only Cannibal has installations in the United States; the other two technologies, along with several others that were desired for investigation, have installations in other countries throughout the world. In addition to the full-scale applications of these technologies, the authors had access to data from a Cambi pilot study and lab-scale digestion study being conducted for District of Columbia Water and Sewer Authority (DCWASA).

5.2 Materials and Methodology

5.2.1 Sample Collection

Sample coolers, bottles and instructions were provided and shipped by CH2MHill's Corvallis, OR laboratories to the treatment plants that were utilizing one of the selected treatment processes. Most of these plants were located outside the United States; however there was one Cannibal™ plant within driving distance of Virginia Tech, which provided the opportunity to collect multiple samples and to witness how the process had been installed and the plant modified to optimize operation.

5.2.2 Sample Preservation

Depending on the analysis being performed on a sample, certain preservation procedures were implemented. All samples were shipped on ice to hinder additional biological activity. For iron and aluminum analysis a volume of sample was preserved using concentrated nitric acid. For COD analysis a volume of sample was preserved with concentrated sulfuric acid. Upon arrival, a volume of the non-acidified samples was centrifuged at approximately 17,700 x G on a Beckman-Coulter Avanti-JE high-speed, refrigerated centrifuge for 15 minutes; the centrate was filtered through a 0.45 μm nitrocellulose membrane filter and frozen until analysis for soluble COD, protein, polysaccharides, cations, anions and volatile fatty acids (VFAs). All other samples were stored in a 4 °C refrigerator until analysis. Analysis of samples was conducted within a week of arrival, with priority given to those procedures that required shorter hold times as specified by Standard Methods (A.P.H.A. et al. 1995).

5.2.3 Sample Analysis

Samples were collected from numerous locations throughout the plant and analyzed for pertinent characteristics as shown in Table 5.1.

Table 5.1- Sampling Locations and Analysis Performed

Sample Location	pH	TS/TSS VS/VSS	COD/ SCOD	Soluble Cations/ Anions	VFAs	Total Fe/Al	Protein Polysaccharides
Raw Influent	X	TSS/VSS	X	X		X	
Primary Sludge	X	TS/VS	X	X	X	X	X
Mixed Liquor	X	TSS/VSS	X	X	X	X	X
WAS/Process Feed	X	TS/VS	X	X	X	X	X
Post Process	X	TS/VS	X	X	X	X	X
Digested Sludge	X	TS/VS	X	X	X	X	X
Dewatering Centrate/Filtrate	X	TSS/VSS	X	X		X	
Final Effluent	X	TSS/VSS	X	X		X	

Analyses were conducted according to the methods described in Table 5.2. All samples for soluble fraction analyses (SCOD, cations, anions, proteins, polysaccharides and VFAs) were centrifuged and the centrate was filtered through 0.45 μm nitrocellulose membrane filters as previously described.

Table 5.2- Sample Analyses

Analysis	Method	Reference
pH	Accumet electrode with AgCl filling solution	N/A
Total and Volatile Solids Total and Volatile Suspended Solids (TS/VS and TSS/VSS)	Standard Methods 2450 A, B, D, E	(A.P.H.A. et al. 1995)
Total and Soluble Chemical Oxygen Demand (COD)	Hach High Range COD tubes (20-1500 mg/L COD)	(Hach Company, Loveland, CO)
Soluble Cations	Dionex DX-120 Ion Chromatograph with IonPac either CS16 5x250 mm or CS12 5x250 mm columns, CG16 5x50 mm guard column and either 25 mM methane sulfonic acid or 10 mN sulfuric acid as the eluents	N/A
Soluble Anions	Dionex DX-120 Ion Chromatagoraph with IonPac AS9-HC 4x250 mm column, AG9-HC 4x50 mm guard column and 9 mM sodium bicarbonate as the eluent	N/A
Volatile Fatty Acids (VFAs)	HP 5890 with flame ionization detector and Nukol Silca Capillary Column, 15 m x 0.53 mm x 0.5 mm film thickness; carrier gas pressurers: He= 17 mL/min N_2= 13 mL/min, Air= 450 mL.min, H_2= 45 mL/min; column pressure= 15 psi	N/A
Total Aluminum	Perkins-Elmer 5100 Flame Atomic Adsorption Spectrophotometer; gases= nitrous oxide, acetylene; wavelength= 309.3 nm, method detection limits= 5-100 mg/L	N/A
Total Iron	Perkins-Elmer 5100 Flame Atomic Adsorption Spectrophotometer; gases= air, acetylene; wavelength= 248.3nm, method detection limits= 0.3-10 mg/L	N/A
Protein	Frolund et al. modification of Lowry method, utilizing bovine serum albumin (BSA) and humic acid as standards; Bradford protein assay utilizing BSA as standard	(Bradford 1976, Frolund et al. 1995)
Polysaccharides	Colorimetric analysis using sulfuric acid and phenol with glucose as standard	(Dubois et al. 1956)

*N/A= not applicable

5.3 Results and Discussion

The results presented herein are divided into three sections based on the technology being investigated. Due to the nature of these results, the majority of them are presented as tables in Appendix D; however pertinent data points will be provided in these sections.

5.3.1 Thermal Hydrolysis Process (THP)

For the Cambi THP system there was only one full-scale installation available for this study, however, the authors also had access to data collected from the pilot and lab studies being conducted for DCWASA. The samples from the full-scale installation of Cambi were shipped from the treatment plant that serves Naestved, Denmark, which was one of the first installations of Cambi in the world. The DCWASA samples are from a small pilot study being conducted in two locations: the THP system is setup in Pennsylvania and the Cambi treated sludge is being digested in bench-scale mesophilic reactors at Virginia Tech. Table 5.3 contains the pertinent operating data for both applications.

Table 5.3- Cambi Plant Operating Characteristics

Characteristic	Naestved	DCWASA
Influent Plant Flow	5 MGD	~400 MGD
Flow to Cambi	ND	~1 gal/batch
Flow to Digesters	12,310 gpd	1 L/day
Dry Solids to Disposal	9,666 lb/day	~60 g/day**

*ND= no data available
**Lab digesters

In its current installations the THP process consists of four primary steps that are outlined below:

1. Thickening- WAS and primary sludge is thickened to 15-20% using centrifuges, belt filter presses or other dewatering devices.

2. Pulping- The thickened sludge is pre-heated to 80-100°C using recycled steam from the main reactor and is homogenized using a recycle loop and macerator.
3. Reactor- The homogenized sludge is fed from the pulper in batch operation and is brought to 160-180°C and several bars pressure using steam. The reactor is maintained at these conditions for approximately 30 minutes and produces a product that meets Class A biosolids standards and causes no filamentous bulking problems in the digester.
4. Flash Tank- Treated sludge is transferred to this tank by the opening of a valve which causes a rapid drop in pressure drawing the sludge from one tank to the other and causing some degree of cell lysing. The sludge is cooled to the digester temperature in this tank.

Due to the size of the DCWASA pilot study, these steps are most likely combined into one or two steps at the pilot plant and the digestion is separated by shipping time from the pilot plant to Virginia Tech.

Figure 5.1 presents several images of Cambi treated sludge.

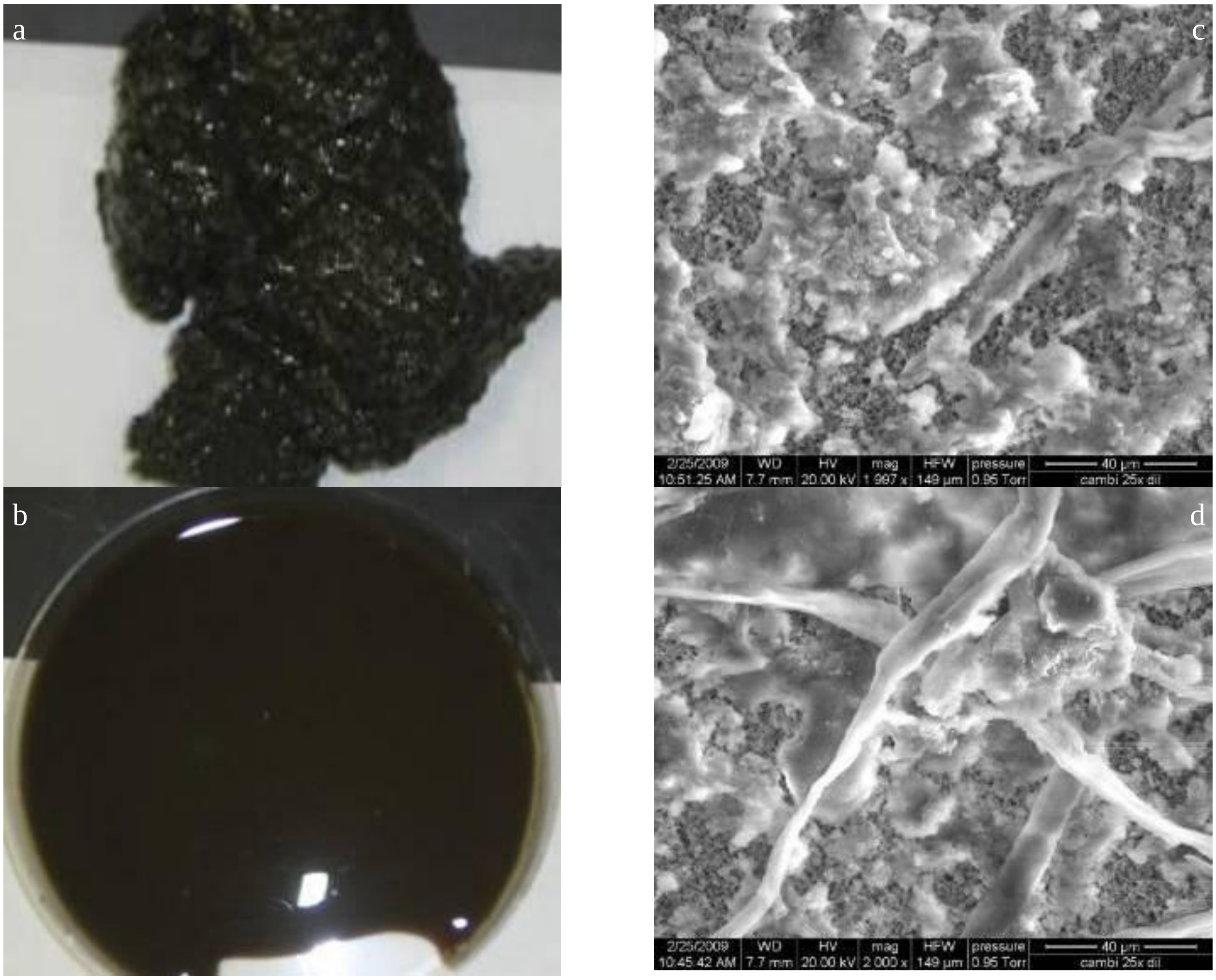
a
b
c
2/25/2009 WD HV mag HFW pressure 40 µm
10:51:25 AM 7.7 mm 20.00 kV 1 997 x 149 µm 0.95 Torr cambi 25x dil
d
2/25/2009 WD HV mag HFW pressure 40 µm
10:45:42 AM 7.7 mm 20.00 kV 2 000 x 149 µm 0.95 Torr cambi 25x dil

Figure 5.1 (a) Naestved Cambi Feed, (b) Naestved Cambi Effluent, (c) and (d) SEM Micrographs of DCWASA Cambi Effluent

Figure 5.1a and b are photographs of the influent and effluent of the Naestved Cambi process. As can be observed in Figure 5.1a, the influent has been thickened before being fed to the pulper, while the effluent shown in Figure 5.1b is much thinner due to the steam dilution, and more homogeneous in consistency due to the temperature and pressure increase. Figure 5.1c and d present low vacuum scanning electron microscope (SEM) images of a 1:25 dilution of the effluent from the DCWASA 150°C pilot unit at a 2000x magnification, which illustrates the dispersed nature and small size of the flocs. The long, string-like structures shown in Figure 5.1d could be some form of cellulose that was not degraded in the activated sludge and not destroyed by the heat and pressure. Although a picture of the discharge from the DCWASA pilot is not presented, it appeared to have a less homogeneous consistency when compared to the Naestved discharge.

Table 5.4- Concentration Changes Caused by Cambi THP and Digestion

Characteristic	Change Caused by Cambi (Naestved)	Change Caused by Digestion (Naestved)	Change Caused by Digestion (DCWASA)
TS	-40.9%	-42.6%	-40.3%
VS	-34.5%	-45.4%	-57.8%
TCOD	9.17%	-20.3%	-55.6%
SCOD	-39.8%	-74.2%	ND
Polysaccharides	101 %	-55.6%	ND
Lowery Protein	1227%	-78.1%	ND
Bradford Protein	68.7%	-42.5%	ND
Total VFAs (on HAc basis)	398%	-94.7%	-92.1%

*Negative (-) implies decrease
*ND= No Data Available

As can be seen in Table 5.4, the full-scale installation of the Cambi process and both the full-scale and lab-scale digesters cause a significant decrease in the TS and VS of the sludge. The decrease in TS and VS that occurred in the Cambi process is due to the direct injection of steam into the sludge in the reaction vessel which is the method utilized for increasing the temperature and pressure in the vessel. With the full-scale Cambi system, there is an increase in the total COD but a decrease in the soluble COD caused by the Cambi system. The decrease in SCOD does not seem to correlate with the dramatic increase in proteins and polysaccharides that are caused by the THP, nor does it correlate with the claims of cell hydrolysis and floc dispersion. The dramatic increase in proteins and polysaccharides does indicate a dispersion of flocs and rupturing of cells, so it is possible that the SCOD data could be inaccurate but, since there is no additional data with which to compare, it is impossible to make a conclusive statement about the change in SCOD caused by the THP process. The decrease of TCOD witnessed by both the full-scale and lab-scale digesters, along with the significant decrease in SCOD, proteins and polysaccharides, all indicate successful digestion of the Cambi treated sludge.

The changes in VFAs also correlate with what occurs in the Cambi process and with the digesters, i.e. the VFAs increase dramatically in the Cambi process due to the hydrolysis of a significant portion of the organic material in the feed sludge and are decreased by conversion to CH_4 and CO_2 in the digesters. The increase in VFAs caused by the THP correlates with the strong odors of the treated sludge which require appropriate capture and treatment of the headspace gases from the pressure vessel.

5.3.2 Mechanical Shear Process

Only one set of samples was acquired from a full-scale application of a mechanical shear process, in this case the Crown Press system, which is owned worldwide by Biogest AG and in the United States by Siemens. In this case the samples were shipped from the installation at the Rosedale WWTP which services North Shore City, located on New Zealand's northern island. Characteristics of the plant are included in Table 5.5.

Table 5.5- Rosedale WWTP Characteristics

Characteristic	Value
Flow Rate	14.1 MGD
Flow to Crown	26,417 gpd
Flow to Digesters	89,819 gpd
Dry Solids to Disposal	15,454 lb/d

The Crown system operates with several steps including thickening, homogenization and high pressure disintegration, which all occur before the sludge is digested. The objective of this treatment is to cause cell lysis, floc disruption and sludge homogenization. Based on a visual inspection of the samples received, it achieves the goal of homogenization with a sludge that is semi-gelatinous after treatment as shown in Figure 5.2.

Figure 5.2- Crown Press Effluent

A summary of the increase or decrease of several characteristics of the sludge that were caused by the Crown press and by digestion is shown in Table 5.6.

Table 5.6- Concentration Changes Caused by Crown Press and Digestion

Characteristic	Change Caused by Crown	Change Caused by Digestion
TS	2.24%	-39.6%
VS	3.05%	-38.5%
TCOD	16.3%	-29.1%
SCOD	46.2%	-61.5%
Polysaccharides	255%	-88.2%
Lowery Protein	711%	-77.8%
Bradford Protein	246%	-78.2%
Total VFAs (on HAc basis)	6.74%	-43.9%

*Negative (-) implies decrease

For all the above listed characteristics there was an increase caused by the Crown press which, in some cases, was dramatic. The three characteristics that can potentially provide the greatest insight into the efficacy of the Crown press are soluble COD, polysaccharides and proteins. Polysaccharides are often considered to be primarily bound in the sludge floc structure, while proteins are typically more prevalent within cells. Such dramatic increases in the concentrations of both of these compounds give creditability to claims of cell lysis and floc disruption and correlate to the increased SCOD concentrations. The increase in VFA concentration is typical for many of the pretreatment technologies and is attributable to the breaking up of cells and floc structure.

Within the digester all characteristics were significantly reduced with the least being TCOD. Without knowing how effective the digesters were before the installation of the Crown system it is impossible to comment on any improvement in digester performance, however the VS reduction is slightly lower than the generally held value of 50% for conventional digestion.

5.3.3 Biological Side-Stream Process

Of all the technologies investigated, the biological side-stream process, which has been realized commercially as the Cannibal System, provided the most samples and the best potential for developing a method for readily evaluating the system effectiveness and applicability to new or retrofitted treatment plants. The primary reason for this success was that Cannibal has been installed mainly in the United States and Virginia Tech has prior experience working with US Filter and Siemens on the Cannibal technology, which has allowed greater access to samples and treatment plants. The Cannibal system utilizes a side-stream anaerobic bioreactor on a part of the RAS stream to effect release of floc-bound polymeric substances which serve as a carbon source for the anaerobes and iron compounds. After several hours of residence time in this side-stream reactor, the treated RAS is returned to the activated sludge process where the anaerobes are degraded by the aerobes and the floc is regenerated utilizing the free iron compounds. The overall effect is a sort of endogenous decay with a reduction of plant yield of up to 50% or greater and a sludge age that is significantly higher than most conventional treatment systems.

As with the previous two technologies investigated, this section focuses on data collected from extensive analysis of field samples acquired from two treatment plants, one where Cannibal has been a success, the other where it has not achieved the desired yield reduction. The development of a simple and effective method for evaluating Cannibal's effectiveness is presented in another manuscript and includes an additional two Cannibal plants, two lab scale Cannibal systems and several conventional activated sludge plants. Characteristics of the Cannibal plants included in this manuscript are listed in Table 5.7.

Table 5.7- Cannibal Plant Characteristics

Characteristic	Peru, IN	Emporia, VA
Influent Flow	8.0 MGD	0.8 MGD
Plant Configuration	Anoxic + 3 Siemens VLRs in series	2 oxidation ditches in series,
Pre-Cannibal Yield	0.8	0.60
Post-Cannibal Yield	0.1	0.35

As was previously mentioned in Chapter 3, these two plants are near the extremes of the operating effectiveness of the Cannibal system, Peru being one of the best operating installations while Emporia is one of the worst operating. This statement is reinforced by the change in yield that was witnessed after Cannibal was installed at each plant: Peru achieved almost 90% yield reduction while Emporia had less then 50%. Previous research conducted at Virginia Tech, along with this study, has found that the Cannibal system apparently works better when installed at plants were the activated sludge process approaches plug flow and worse when installed on systems that are more complete mix. This evaluation is reinforced by the results found from running the short-term batch digestion studies that are discussed in the other manuscript in this thesis that focuses purely on the Cannibal system.

Presented in Table 5.8 are a selection of the results of the extensive analyses conducted on these two Cannibal plants and that provide a good indication of the operational effectiveness of these plants.

Table 5.8- Concentration Changes Caused by Two Cannibal Plants

Characteristic	Change Caused by Cannibal Bioreactor	
	Peru, IN	Emporia, VA
TS	51.0%	29.7%
VS	47.2%	31.4%
TCOD	-72.2%	4.8%
SCOD	-0.640%	61.4%
Polysaccharides	-22.6%	-27.0%
Lowery Protein	ND	123%
Bradford Protein	244%	1170%
Total VFAs (on HAc basis)	54.8%	39.3%

*Negative (-) implies decrease
*ND= No Data Available

Unfortunately, based on these numbers there appears to be no ready correlation as to what is occurring in the Cannibal reactor, however there are a few basic assessments that can be made based on the differences between the two plants. Of first note is the difference in the increases of TS and VS in the two plants, Peru's increase in both characteristics is significantly greater than the increase at Emporia. The TS concentration at Peru is approximately 42% greater than at Emporia in both the influent and effluent of the Cannibal bioreactor and the VS concentration is approximately 34% greater as well. This difference along with several of the other differences between the two plants and the apparently poor performance of the Emporia plant can be attributed to the excessively over-sized capacity of the activated sludge system which results in conditions approaching an extended aeration configuration where a significant portion of the organic material is already degraded before it enters the Cannibal bioreactor.

In regards to the other characteristics, Peru mimics what would occur in a conventional anaerobic digester where there is a decrease in TCOD, SCOD and floc bound polymeric substances, although based on the Bradford protein number there is a release of bound proteins which could indicate some cell degradation. On the other hand, Emporia witnesses almost a completely opposite effect on all characteristics especially SCOD. The Bradford protein concentration at Emporia increases almost five-fold compared to Peru, but when the actual concentrations are compared the effluent concentrations from both plants are similar (Emporia= 1.83 mg/L, Peru= 1.96 mg/L) and the influent concentration to Peru is about five times greater than to Emporia (Emporia= 0.144 mg/L, Peru= 0.540 mg/L). Both plants witnessed increases in the VFA concentrations, with Peru being greater by approximately 30%. This increase in VFAs can be attributed to the incomplete anaerobic digestion that occurs within the Cannibal bioreactor caused by the relatively short residence time which allows, at most, partial hydrolysis and acidogenesis. Other than the raw influent, both plants have low concentrations of VFAs throughout the plant and according to the operators at the Emporia plant almost no odor issues, which is an appealing characteristic.

5.4 Conclusions

Due to the lack of available samples with which to compare between each process, it is difficult to make many conclusive statements about each process; however, there are several statements that can be made to help direct future work.

For the Cambi system the conclusions from this study are as follows:

1. Based on visual and microscopic analysis of the Cambi treated sludge, the process does affect a degree of destruction of flocs and cells and produces a well homogenized digester feedstock. The increase in soluble proteins and

polysaccharides cause by the process does indicate a dispersion of flocs and cell lysis. Whether the degree of cell lysis is as extreme as marketed is hard to conclude from this research.

2. VS reduction over the Cambi process and the digesters correlates with many of the reports on full-scale Cambi applications. It also has the added benefit of the potential to decrease digester SRT, as illustrated by the DCWASA study where 15 days of digestion achieves as much or greater than typical 20+ day digestion.
3. Although not investigated in this research, the treatment of the dewatering centrate from the Cambi treated sludge poses issues due to its high concentrations of nitrogen species and recalcitrant compounds that are largely attributed to the brown color of the centrate.

For the Crown system the conclusion from this study are as follows:

1. The Crown process does achieve a degree of floc dispersion and cell destruction that improves the digestibility of the sludge; however, without a frame of reference, it is difficult to make any conclusions on how successful it has been. This is a technology that requires additional investigation, especially in regards to digester performance before and after the installation of the Crown system.

For the Cannibal system the conclusions from this study are as follows:

1. Of the three technologies investigated, Cannibal is the one that the authors have the greatest understanding of due to previous and concurrent work being conducted in the labs and a greater access to WWTPs that utilize this technology.

2. Based on a purely analytic investigation of the two plants, there is little to be stated conclusively about the Cannibal process; however, there is the distinct issue of the difference in operating performance. In reality, even though the Emporia plant is "not working well" it achieved an almost 50% decrease in plant yield because of the Cannibal system. In this respect, it is a successful installation of the Cannibal process although the performance needs to be improved to achieve the desired yield reduction. Therein lies the key to successful Cannibal operation, it does not require any special organisms to operate successfully once the system has acclimated; however, it seems to work better with particular activated sludge configurations (e.g. plug flow).
3. This research led to the development of a simple method for evaluating the effectiveness of the Cannibal system utilizing small batch reactors and comparing SCOD release over time. This method is discussed in detail in a preceding chapter in this thesis, although it requires additional refinement that could be achieved with a comprehensive comparison of all the treatment plants that are currently operating the Cannibal system.

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6 SUMMARY AND CONCLUSIONS

This research derived several conclusions that can be utilized to guide further research into the evaluation of sludge reduction technologies:

- The Cannibal biological side-stream yield reduction process can be evaluated by small, short-term batch reactors where the SCOD is analyzed daily. From these measurements a comparison can be developed that produces a trend based on how well the Cannibal system is performing. This trend is reflected by conventional treatment plants based on their operational configuration, so a correlation can be drawn between conventional plants that would perform well with an upgrade to the Cannibal system and those that would not. This comparison needs further development that can be realized by analyzing more Cannibal plants using the short-term batch methodology and analyzing for SCOD as well as monitoring the blackening of the reactors and the ORP. Additional clarity to this model can also be realized by investigating the effluent quality of the Cannibal treatment plants.
- In this study, ozone, shear and sonication had clear effects on the floc structure of sludge and potentially cause cell rupture or lysis. These processes should improve the digestibility of sludge, although, with the conditions utilized in this study, there was little difference between the pretreated and untreated WAS digestibility. It appeared that the greatest effect of these technologies on digestion occurred during the first week of operation.
- Thermal hydrolysis seems to have similar effects as ozone, shear and sonication on a microscopic level (i.e. floc dispersion). It results in significant release of bound

proteins and polysaccharides that are subsequently fed to the digester. Significant VSR (greater than 45-50%) is achieved during digestion, at a shorter SRT

Two additional considerations based on the initial project objectives are presented below.

- Extensive evaluation of a particular technology should be undertaken before installation because of the costs associated with each process and the issues that arise on a case by case level.
- A purely analytical approach to determining a characteristic or several characteristics that stand out for each pretreatment technology has potential to be a method for determining the applicability of a certain pretreatment technology to a sludge, however, due to the lack of sludges to compare, this was not realized in this study.

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Appendix A: Cannibal Batch Digestion Study Data

Table A1- Emporia SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	45	40	42.5	45	40	42.5	42.5
3:45:00	68	65	66.5	42	36	39	52.8
18:15:00	166	164	165	156	144	150	157.5
26:40:00	230	230	230	182	194	188	209.0
44:15:00	331	335	333	281	258	269.5	301.3
66:30:00	369	369	369	357	364	360.5	364.8
74:40:00	505	497	501	452	456	454	477.5
77:40:00	450	442	446	403	400	401.5	423.8
93:00:00	476	473	474.5	423	416	419.5	447.0
117:45:00	513	509	511	484	470	477	494.0
138:30:00	569	573	571	571	515	515	543.0
149:45:00	579	577	578	510	527	518.5	548.3

Table A2- Peru SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	49	54	51.5	49	54	51.5	51.5
20:00:00	394	402	398	156	170	163	280.5
25:30:00	384	420	402	538	541	539.5	470.8
46:25:00	698	679	688.5	299	280	289.5	489.0
67:10:00	750	742	746	290	312	301	523.5
74:25:00	990	969	979.5	409	410	409.5	694.5
91:55:00	1504	1484	1494	1208	1172	1190	1342.0
96:55:00	1550	1522	1536	1206	1246	1226	1381.0
115:25:00	1574	1548	1561	1238	1204	1221	1391.0
121:40:00	1078	1110	1094	440	516	478	786.0
140:25:00	1178	1204	1191	552	556	554	872.5
163:10:00	1288	1286	1287	632	644	638	962.5
187:10:00	1304	1316	1310	706	680	693	1001.5
215:45:00	1304	1319	1311.5	778	794	786	1048.8
233:30:00	1204	1212	1208	852	854	853	1030.5

Table A3- Big Bear SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	54	53	53.5	54	53	53.5	53.5
25:00:00	347	343	345	326	329	327.5	336.3
47:15:00	422	423	422.5	423	427	425	423.8
71:10:00	454	457	455.5	456	474	465	460.3
96:15:00	462	459	460.5	479	480	479.5	470.0
170:30:00	647	645	646	640	635	637.5	641.8
194:00:00	209	208	208.5	263	263	263	235.8
280:00:00	411	403	407	383	379	381	394.0
326:30:00	385	376	380.5	335	340	337.5	359.0
352:30:00	281	283	282	299	286	292.5	287.3

Table A4- Morongo SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	60	56	58	60	56	58	58.0
24:15:00	244	239	241.5	203	205	204	222.8
48:10:00	371	370	370.5	349	354	351.5	361.0
73:15:00	405	410	407.5	409	405	407	407.3
147:30:00	589	593	591	589	590	589.5	590.3
171:00:00	232	232	232	241	241	241	236.5
267:00:00	398	392	395	289	290	289.5	342.3
313:30:00	283	282	282.5	350	346	348	315.3
339:30:00	288	285	286.5	292	270	281	283.8

Table A5- Peppers Ferry SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	40	44	42	40	44	42	42.0
18:30:00	644	656	650	637	649	643	646.5
25:40:00	782	764	773	718	746	732	752.5
42:00:00	776	794	785	834	860	847	816.0
47:00:00	1114	1122	1118	1000	1018	1009	1063.5
68:45:00	1385	1445	1415	1050	1090	1070	1242.5
114:30:00	884	886	885	630	638	634	759.5
139:45:00	1466	1432	1449	892	894	893	1171.0
163:20:00	1664	1446	1555	1534	1516	1525	1540.0
186:45:00	1336	1314	1325	1286	1296	1291	1308.0
282:40:00	1368	1344	1356	670	668	669	1012.5
306:35:00	1004	1008	1006	782	808	795	900.5

Table A6- Christiansburg SCOD Release

	Reactor 1			Reactor 2			
Sample	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	17	12	14.5	17	12	14.5	14.5
18:30:00	1185	1208	1196.5	1298	1334	1316	1256.3
25:40:00	1338	1374	1356	1380	1416	1398	1377.0
42:00:00	1232	1262	1247	1282	1310	1296	1271.5
47:00:00	1614	1586	1600	1670	1688	1679	1639.5
68:45:00	1280	522	901	890	904	897	899.0
114:30:00	1144	1166	1155	784	802	793	974.0
139:45:00	1256	1238	1247	1166	1158	1162	1204.5
163:20:00	1398	1388	1393	1354	1360	1357	1375.0
186:45:00	1396	1420	1408	1028	1022	1025	1216.5
282:40:00	1260	1230	1245	1198	1164	1181	1213.0
306:35:00	1292	1318	1305	1024	1020	1022	1163.5

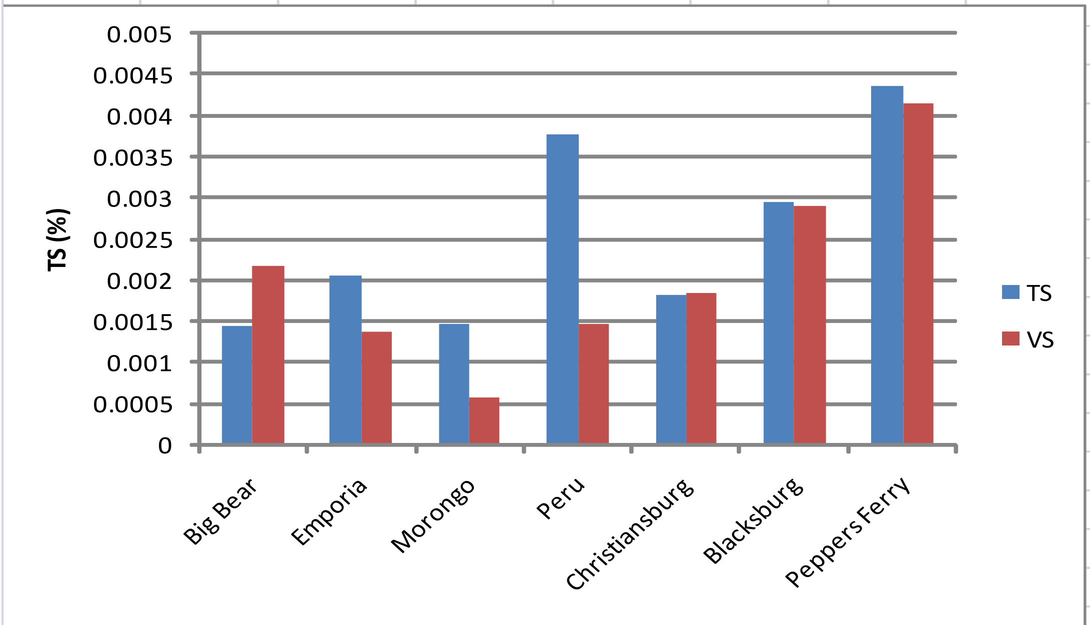
Table A7- Blacksburg SCOD Release

Sample	Reactor 1			Reactor 2			
	SCOD1	SCOD2	Avg	SCOD1	SCOD2	Avg	Avg SCOD
0:00:00	92	100	96	92	100	96	96.0
18:30:00	581	583	582	584	598	591	586.5
25:40:00	624	642	633	714	732	723	678.0
42:00:00	766	778	772	816	838	827	799.5
47:00:00	1010	1014	1012	1012	1028	1020	1016.0
68:45:00	846	836	841	594	588	591	716.0
114:30:00	686	692	689	814	794	804	746.5
139:45:00	1010	998	1004	1038	1078	1058	1031.0
163:20:00	798	784	791	708	806	757	774.0
186:45:00	1020	988	1004	836	836	836	920.0
282:40:00	682	704	693	692	688	690	691.5
306:35:00	722	714	718	504	566	535	626.5

Table A8- Change in TS and VS

Sample	ΔTS (mg/L)	ΔVS (mg/L)	ΔTS/Time (mg/L/h)	ΔVS/Time (mg/L/h)
Emporia 1	1,889	1,322	11.29	7.91
Emporia 2	2,211	1,433	13.22	8.57
Peru 1	3,856	1,356	16.51	5.81
Peru 2	5,611	2,544	24.03	10.90
Big Bear 1	1,378	2,078	3.91	5.89
Big Bear 2	1,611	722	4.57	2.05
Morongo 1	1,750	483	5.15	1.42
Morongo 2	2,011	883	5.92	2.60
Pep Frry 1	4,011	3,844	13.08	12.54
Pep Frry 2	4,700	4,389	15.33	14.32
Cburg 1	1,811	1,872	5.91	6.11
Cburg 2	1,678	1,711	5.47	5.58
Bburg 1	2,811	2,844	9.17	9.28
Bburg 2	2,978	2,822	9.71	9.21

Figure A1- Change in TS and VS



Appendix B: Columbus Batch Digestion Studies Data

Note: Red = CCOD data

Table B1- Shear Reactor Data

Date	Old/ New	TS (%)	VS (%)	TCOD (mg/L)	CCOD\ SCOD (mg/L)	SCOD/ TCOD	pH	ORP	Gas Vol (L)
12/11/2008	New	4.52%	3.44%	63,117	6,218	9.85%	6.48	ND	ND
1/7/2009	Old	3.20%	2.24%	54,685	13,590	24.85%	5.94	ND	7.75
1/7/2009	New	5.26%	4.11%	60,852	11,730	19.28%	6.12	ND	ND
1/21/2009	Old	3.89%	2.72%	68,145	17,770	26.08%	6.64	ND	12.46
1/21/2009	New	5.66%	4.56%	78,820	14,580	18.50%	6.04	ND	ND
1/29/2009	Old	5.63%	3.92%	77,468	20,450	26.40%	7.3	-269	9.14
2/5/2009	Old	5.02%	3.38%	70,691	22,240	31.46%	7.25	-249	3.45
2/12/2009	Old	4.91%	3.06%	73,220	20,000	27.31%	7.43	-261	6.2965
2/19/2009	Old	4.81%	3.16%	70,809	20,400	28.81%	7.69	-272	8.0955
2/26/2009	Old	4.86%	3.12%	ND	ND	ND	ND	ND	ND
3/5/2009	Old	5.23%	3.51%	ND	ND	ND	ND	ND	ND

Table B2- Sonication Reactor Data

Date	Old/ New	TS (%)	VS (%)	TCOD (mg/L)	CCOD\ SCOD (mg/L)	SCOD/ TCOD	pH	ORP	Gas Vol (L)
12/11/2008	New	4.28%	3.29%	59,891	9,178	15.32%	6.4	ND	ND
1/7/2009	Old	3.08%	2.10%	37,582	11,545	30.72%	6.98	ND	ND
1/7/2009	New	5.34%	4.18%	64,724	8,710	13.46%	6.26	ND	ND
1/20/2009	Old	3.82%	2.71%	63,358	15,240	24.05%	6.69	ND	9.97
1/20/2009	New	5.62%	4.52%	82,461	11,280	13.68%	5.96	ND	ND
1/29/2009	Old	5.03%	3.22%	73,236	22,610	30.87%	7.29	-278	10.19
2/5/2009	Old	4.91%	3.09%	70,234	25,980	36.99%	7.4	-300	1.27
2/12/2009	Old	4.83%	3.05%	72,391	23,200	32.05%	7.39	-246	2.40
2/19/2009	Old	4.77%	2.97%	66,759	24,520	36.73%	7.44	-239	0.599667
2/26/2009	Old	4.92%	2.98%	ND	ND	ND	ND	ND	ND
3/5/2009	Old	4.79%	2.95%	ND	ND	ND	ND	ND	ND

Table B3- Ozone Reactor Data

Date	Old/ New	TS (%)	VS (%)	TCOD (mg/L)	CCOD\ SCOD (mg/L)	SCOD/ TCOD	pH	ORP	Gas Vol (L)
12/11/2008	New	4.53%	3.53%	60,412	36,585	60.56%	ND	ND	ND
1/7/2009	Old	3.26%	2.35%	63,937	21,270	33.27%	5.3	ND	ND
1/7/2009	New	5.15%	4.05%	46,049	12,115	26.31%	5.92	ND	ND
1/22/2009	Old	3.92%	2.80%	76,554	24,300	31.74%	5.24	ND	6.30
1/22/2009	New	5.75%	4.65%	84,524	16,660	19.71%	5.44	ND	ND
1/29/2009	Old	5.04%	3.19%	79,946	25,930	32.43%	7.01	-267	2.79
2/5/2009	Old	5.00%	3.16%	60,152	31,690	52.68%	7.12	-277	1.95
2/12/2009	Old	5.00%	3.12%	71,490	27,040	37.82%	7.65	-270	2.40
2/19/2009	Old	4.83%	2.89%	65,752	23,300	35.44%	7.78	-283	1.98
2/26/2009	Old	5.03%	3.05%	ND	ND	ND	ND	ND	ND
3/5/2009	Old	5.28%	2.87%	ND	ND	ND	ND	ND	ND

Table B4- Control Reactor Data

Date	Old/ New	TS (%)	VS (%)	TCOD (mg/L)	CCOD\ SCOD (mg/L)	SCOD/ TCOD	pH	ORP	Gas Vol (L)
12/11/2008	New	4.28%	3.32%	61,404	9,965	16.23%	6.25	ND	ND
1/7/2009	Old	3.55%	2.47%	38,561	15,750	40.84%	6.34	ND	2.92
1/7/2009	New	5.23%	4.09%	52,426	8,120	15.49%	6.34	ND	ND
1/20/2009	Old	4.04%	2.85%	61,746	16,220	26.27%	6.98	ND	33.28
1/20/2009	New	5.80%	4.70%	82,593	8,900	10.78%	6.03	ND	ND
1/29/2009	Old	4.85%	3.16%	72,628	18,220	25.09%	7.23	-260	38.71
2/5/2009	Old	4.78%	3.06%	68,969	23,790	34.49%	7.53	-290	3.45
2/12/2009	Old	4.59%	2.87%	65,297	20,820	31.88%	7.36	-256	3.30
2/19/2009	Old	4.51%	2.79%	63,166	24,880	39.39%	7.35	-243	2.70
2/26/2009	Old	4.70%	2.88%	ND	ND	ND	ND	ND	ND
3/5/2009	Old	4.53%	2.82%	ND	ND	ND	ND	ND	ND

Table B5- Feed Sludge Data

Date	Old/ New	TS (%)	VS (%)	TCOD (mg/L)	CCOD\ SCOD (mg/L)	SCOD/ TCOD	pH
12/11/2008	Primary	4.79%	4.00%	64,801	5,105	7.88%	ND
1/7/2009	Primary	6.21%	5.22%	78,176	4,715	6.03%	5.29
1/20/2009	Primary	6.52%	5.57%	81,491	4,270	5.24%	5.13
12/11/2008	WAS	5.88%	4.34%	69,316	11,835	17.07%	ND
1/7/2009	WAS	6.15%	4.80%	80,373	9,025	11.23%	6.37
1/20/2009	WAS	5.94%	4.74%	91,856	12,100	13.17%	5.96
12/11/2008	Shear	5.71%	4.28%	77,844	16,140	20.73%	ND
1/7/2009	Shear	6.15%	4.73%	54,015	19,180	35.51%	ND
1/20/2009	Shear	5.74%	4.62%	80,099	22,970	28.68%	5.96
12/11/2008	Soni	5.70%	4.23%	72,712	24,660	33.91%	ND
1/7/2009	Soni	6.16%	4.72%	79,549	10,330	12.99%	6.15
1/20/2009	Soni	5.99%	4.82%	93,183	13,390	14.37%	6.03
12/11/2008	O3	5.76%	4.30%	72,269	20,325	28.12%	ND
1/7/2009	O3	6.14%	4.74%	85,156	15,980	18.77%	6.15
1/20/2009	O3	6.23%	4.98%	78,455	23,150	29.51%	5.73
12/11/2008	DS	2.64%	1.61%	18,742	2,255	12.03%	ND
1/7/2009	DS	3.36%	2.10%	30,436	1,040	3.42%	ND

Table B6- Cation Data (2/5/09)

Sample	Ca (mg/L)	Mg (mg/L)	K (mg/L)	NH4 (mg/L)	Na (mg/L)
Shear	313.2	336.8	534.8	1304.3	228.3
Soni	340.3	316.5	477.2	892.4	222.8
O3	354.3	330.3	509.0	1041.8	224.0
Control	357.6	320.1	480.1	859.0	224.6

Appendix C: Blacksburg Area Batch Digestion Studies Data

Note: *Red Italics* = SCOD data

Table C1- Seed Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
Day 0	3.53%	2.18%	22,707	*88*
Day 8	3.32%	2.05%	27,075	5,152
Day 15	3.07%	1.76%	29,700	4,815
Day 27	3.07%	1.83%	26,700	5,558
Day 57	3.24%	1.72%	19,550	3,600

Table C2- Christiansburg 1 min Shear Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	1.22%	1.04%	11,077	664
WAS 11/4	1.21%	1.09%	15,625	*151*
Day 0	1.71%	1.29%	18,718	2,637
Day 8-1	1.36%	0.92%	15,238	3,556
Day 8-2	1.07%	0.69%	11,850	2,994
Day 15-1	1.21%	0.81%	13,800	2,770
Day 15-2	1.30%	0.86%	14,225	2,238
Day 27-1	1.13%	0.68%	12,400	2,445
Day 27-2	1.25%	0.78%	12,525	2,030
Day 57-1	1.03%	0.63%	3,100	1,635
Day 57-2	1.20%	0.75%	2,900	1,945

Table C3- Peppers Ferry 1 min Shear Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	2.17%	1.62%	19,418	7,545
WAS 11/4	1.23%	1.06%	21,557	199
Day 0	1.62%	1.22%	26,390	1,185
Day 8-1	2.36%	1.55%	25,175	2,680
Day 8-2	1.48%	1.03%	17,088	2,854
Day 15-1	1.88%	1.22%	20,050	2,575
Day 15-2	1.95%	1.27%	20,100	2,800
Day 27-1	1.78%	1.11%	18,800	2,213
Day 27-2	1.83%	1.17%	18,475	2,623
Day 57-1	1.74%	1.08%	8,300	2,110
Day 57-2	1.83%	1.15%	6,900	2,910

Table C4- Christiansburg 10 min Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	1.22%	1.04%	11,077	664
WAS 11/4	1.97%	1.49%	15,850	*2,252*
Day 0	2.11%	1.53%	20,590	2,754
Day 8-1	1.48%	0.98%	15,138	2,824
Day 8-2	0.92%	0.57%	10,675	3,278
Day 15-1	1.20%	0.80%	12,550	2,070
Day 15-2	1.21%	0.80%	13,450	2,458
Day 27-1	1.13%	0.74%	11,625	1,973
Day 27-2	1.14%	0.74%	11,875	2,383
Day 57-1	1.14%	0.71%	6,350	1,210
Day 57-2	1.11%	0.69%	4,750	1,825

Table C5- Peppers Ferry 10 min Shear Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	2.17%	1.62%	19,418	7,545
WAS 11/4	1.95%	1.44%	23,582	2,215
Day 0	2.23%	1.58%	27,317	2,665
Day 8-1	1.90%	1.24%	17,913	3,276
Day 8-2	2.13%	1.41%	22,100	3,322
Day 15-1	1.88%	1.25%	17,900	2,885
Day 15-2	2.00%	1.28%	19,550	3,078
Day 27-1	1.84%	1.16%	17,725	2,435
Day 27-2	1.87%	1.18%	17,875	2,685
Day 57-1	1.86%	1.15%	6,500	2,735
Day 57-2	1.56%	0.94%	4,700	2,865

Table C6- Christiansburg Ozone Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	1.22%	1.04%	11,077	664
WAS 11/4	0.99%	0.83%	13,082	*410*
Day 0	1.68%	1.27%	14,100	1,661
Day 8-1	0.88%	0.60%	10,588	3,026
Day 8-2	1.19%	0.82%	14,338	2,704
Day 15-1	1.31%	0.86%	14,050	2,230
Day 15-2	1.15%	0.75%	12,600	1,858
Day 27-1	1.27%	0.82%	12,575	1,880
Day 27-2	1.11%	0.71%	11,650	1,553
Day 57-1	1.24%	0.78%	5,750	1,125
Day 57-2	1.09%	0.66%	5,150	900

Table C7- Peppers Ferry Ozone Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 11/3	2.17%	1.62%	19,418	7,545
WAS 11/4	2.05%	1.60%	17,457	*117*
Day 0	2.36%	1.73%	23,921	1,605
Day 7-1	0.96%	0.65%	10,288	1,284
Day 7-2	1.05%	0.73%	9,338	1,356
Day 14-1	2.04%	1.32%	20,175	1,690
Day 14-2	1.63%	1.07%	15,850	1,375
Day 26-1	2.06%	1.34%	19,050	1,463
Day 26-2	2.18%	1.42%	22,400	1,143
Day 57-1	2.01%	1.35%	5,550	700
Day 57-2	2.16%	1.35%	4,050	560

Table C8- Christiansburg Control Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 1/26	3.20%	2.85%	42,351	1,765
Day 0	2.62%	2.32%	26,533	1,995
Day 7-1	2.80%	2.39%	44,171	5,525
Day 7-2	2.37%	1.99%	41,622	6,243
Day 14-1	2.21%	1.50%	42,122	24,850
Day 14-2	2.90%	1.69%	37,851	23,350
Day 21-1	3.28%	1.74%	41,983	22,540
Day 21-2	2.81%	1.60%	38,468	20,180

Table C9- Peppers Ferry Control Reactor Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 1/26	2.96%	2.35%	27,020	105
Day 0	3.05%	2.35%	35,010	895
Day 7-1	2.72%	1.99%	41,283	5,573
Day 7-2	2.41%	1.77%	35,421	5,128
Day 14-1	2.33%	1.66%	31,390	7,225
Day 14-2	2.19%	1.56%	26,693	6,485
Day 21-1	2.27%	1.57%	29,129	4,980
Day 21-2	2.04%	1.40%	26,460	4,140

Table C10- Christiansburg 1 min Shear Reactor 2 Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 1/26	3.73%	3.42%	59,983	1,825
Day 0	2.70%	2.33%	34,863	2,520
Day 7	2.30%	1.98%	39,012	6,693
Day 14	2.94%	1.77%	38,280	18,690
Day 21	2.69%	1.52%	37,284	19,780

Table C11- Peppers Ferry 1 min Shear Reactor 2 Data

Sample	TS (%)	VS (%)	TCOD (mg/L)	CCOD (mg/L)
WAS 1/26	4.23%	3.39%	57,258	1,190
Day 0	3.49%	2.87%	41,328	1,495
Day 7	2.94%	2.13%	47,795	10,075
Day 14	2.89%	2.04%	43,944	13,050
Day 21	2.62%	1.79%	37,267	8,900

Appendix D: WEF/WERF Waste Activated Sludge Solids Reduction Process Study Data Summary

Abbreviations:

ND = No Data Available
BDL = Below Detection Limit
Polysacc = Polysaccharide
Lowery = Lowery Protein Assay
Bradford = Bradford Protein Assay

Table D1- Cannibal Data Summary

Tmt Plant- Date	Smpl Lctn	TSS\TS		VSS\VS		TCOD	SCOD	Polysac	Lowery	Bradford	Humic	Tot Fe	Tot Al	NH_4^+	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Acetic	Proprionic	Isobutyric	Butyric	Isovaleric	Valeric	Isocaproic	Hexanoic	Heptanoic	Total VFA
						Biopolymer								Soluble Cations					Soluble Anions					Volatile Fatty Acids									
		%	mg/L	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L as Hac
Empr- 6/17	Raw Inf	6.24%	357	4.15%	120	687	177	ND	ND	ND	ND	2.80	5.11	71.2	19.7	88.4	3.90	27.0	ND	ND	ND	ND	ND	52.3	3.88	0.715	0.445	0.836	0.202	BDL	0.122	BDL	56.3
Empr, VA- 8	Raw Inf	5.62%	357	4.49%	59.9	487	253	ND	ND	ND	ND	1.34	0.790	44.6	44.6	44.6	44.6	44.6	115.36	BDL	17.6	BDL	5.12	72.5	8.37	1.16	1.61	1.35	1.72	BDL	BDL	BDL	81.6
Peru, IN- 4/	Raw Inf	1.30%	45.3	0.17%	39.3	ND	ND	ND	ND	ND	ND	0.64	0.637	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peru, IN- 10	Raw Inf	2.27%	70.0	1.807%	14.3	199	95	ND	ND	ND	ND	ND	ND	10.7	8.53	146	34.2	60.9	346	BDL	BDL	78.7	BDL	5.63	0.829	0.468	0.699	0.333	0.636	0.388	1.27	4.41	10.2
Empr- 6/17	Mxd Lqr	2.12%	3,635	1.63%	795	3,900	21.5	0.264	9.04	ND	2.22	26.0	46.7	BDL	20.6	82.2	0.695	23.3	ND	ND	ND	ND	ND	2.89	0.069	0.056	0.102	BDL	BDL	BDL	BDL	BDL	3.03
Empr, VA- 8	Mxd Lqr	2.14%	4,140	1.498%	1,240	4,350	37	2.36	5.28	0.233	4.32	106	212	BDL	24.2	93.5	BDL	30.6	96.9	BDL	44.2	6.85	5.66	1.47	0.459	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.79
Peru, IN- 4/	Mxd Lqr	2.87%	5,003	0.62%	3,560	ND	ND	8.96	0.166	ND	2.93	153	85.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peru, IN- 10	Mxd Lqr	1.44%	14,156	0.752%	6,744	16,800	61.5	3.30	ND	0.263	ND	ND	ND	BDL	11.6	132	41.5	52.6	247	BDL	BDL	53.6	BDL	1.76	0.128	0.107	0.205	0.021	0.068	0.900	0.139	0.290	2.72
Empr- 6/17	Cann Inf	0.794%	7,756	0.600%	1,889	8,760	44.0	3.35	2.28	ND	1.29	33.5	101	BDL	20.8	81.0	1.47	24.6	---	---	---	---	---	3.02	0.051	0.062	BDL	BDL	BDL	BDL	BDL	BDL	3.10
Empr, VA- 8	Cann Inf	0.662%	5,989	0.446%	1,956	7,200	42	3.35	3.25	0.144	2.46	102	203	BDL	25.6	93.7	BDL	30.0	98.3	BDL	47.0	3.94	BDL	1.79	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.79
Peru, IN- 4/	Cann Inf	2.15%	20,943	1.06%	10,629	ND	ND	10.4	ND	ND	3.25	249	160	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peru, IN- 10	Cann Inf	2.26%	23,550	1.18%	11,267	25,167	78.5	3.30	ND	0.570	ND	ND	ND	34.4	43.5	144	50.7	31.7	263	BDL	BDL	BDL	11.6	1.45	0.087	0.171	0.235	0.112	0.019	0.619	0.156	0.097	2.24
Empr- 6/17	Cann Eff	0.848%	8,367	0.646%	1,989	9,724	60.0	0.835	6.56	ND	10.4	36.3	106	86.7	33.4	76.5	6.05	9.97	---	---	---	---	---	3.93	0.051	0.242	0.036	BDL	BDL	BDL	BDL	BDL	4.13
Empr, VA- 8	Cann Eff	1.04%	10,233	0.728%	3,067	7,000	78	4.06	5.76	1.83	11.2	47.3	113	41.5	51.9	85.9	12.5	17.4	90.4	BDL	15.6	BDL	41.0	2.67	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2.67
Peru, IN- 4/	Cann Eff	3.29%	32,010	1.63%	16,200	ND	ND	6.53	0.435	ND	5.15	228	173	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peru, IN- 10	Cann Eff	3.37%	33,456	1.67%	16,867	7,000	78.0	4.07	ND	1.96	ND	ND	ND	205.4	109	118	BDL	BDL	213	BDL	BDL	BDL	24.4	2.36	0.090	0.495	0.302	0.107	0.055	0.635	0.166	0.238	3.47
Empr- 6/17	Final Eff	0.176%	15.0	0.577%	ND	21.0	10.5	ND	ND	ND	ND	0.037	0.293	BDL	20.9	80.3	BDL	22.0	---	---	---	---	---	1.44	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.44
Empr, VA- 8	Final Eff	0.638%	4.92	0.529%	83.3%	32.5	30.5	ND	ND	ND	ND	ND	ND	BDL	26.7	92.9	BDL	28.9	100	BDL	47.7	9.75	BDL	0.123	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.12
Peru, IN- 4/	Final Eff	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.576	1.02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Peru, IN- 10	Final Eff	0.506%	6.13	0.463%	53.3%	63.0	62.0	ND	ND	ND	ND	ND	ND	BDL	10.7	135	32.7	61.9	268	BDL	0.68	83.5	BDL	2.35	0.352	BDL	0.378	0.171	0.207	0.691	0.237	0.354	3.63

Notes: The **red data points** indicate TSS/VSS

Table D2- Cambi Data Summary

Tmt Plant- Date	Smpl Lctn	TSS\TS		VSS\VS		CCOD TCOD\	SCOD	Polysac (Biopolymer)	Lowery (Biopolymer)	Bradford (Biopolymer)	Humic (Biopolymer)	Tot Fe	Tot Al	(total) NH_4^+ (Soluble Cations)	K^+ (Soluble Cations)	Na^+ (Soluble Cations)	Mg^{2+} (Soluble Cations)	Ca^{2+} (Soluble Cations)	Cl^- (Soluble Anions)	NO_2^- (Soluble Anions)	NO_3^- (Soluble Anions)	SO_4^{2-} (Soluble Anions)	PO_4^{3-} (Soluble Anions)	Acetic (Volatile Fatty Acids)	Proprionic (Volatile Fatty Acids)	Isobutyric (Volatile Fatty Acids)	Butyric (Volatile Fatty Acids)	Isovaleric (Volatile Fatty Acids)	Valeric (Volatile Fatty Acids)	Isocaproic (Volatile Fatty Acids)	Hexanoic (Volatile Fatty Acids)	Heptanoic (Volatile Fatty Acids)	Total VFA
		%	mg/L	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L as Hac
Nstvd- 5/1(	Raw Inf	**5.81%**	**229**	**3.73%**	**75.5**	ND	ND	ND	ND	ND	ND	1.49	3.85	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	Raw Inf	**5.65%**	**351**	**4.18%**	**92.0**	605	106	ND	ND	ND	ND	ND	ND	13.0	7.44	61.8	10.6	40.5	108	BDL	2.37	28.0	4.51	6.16	0.55	BDL	BDL	BDL	3.28	3.38	5.48	7.80	16.12
Nstvd- 5/1(	WAS	0.64%	6,219	0.40%	2,267	ND	ND	139	1,082	ND	411	382	449	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	WAS	0.49%	6,183	0.27%	2,700	**1,650**	382	232	ND	7.17	ND	ND	ND	9.31	35.2	147	39.0	98.4	255	BDL	28.0	101	49.2	16.6	2.19	BDL	BDL	BDL	0.943	1.67	2.29	3.37	22.1
Nstvd- 5/1(	THP Inf	13.4%	ND	8.63%	ND	ND	ND	210	178	ND	292	308	312	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	THP Inf	13.8%	ND	8.38%	ND	**28,900**	15,400	1,337	ND	201	ND	ND	ND	233	409	137	104	122	133	BDL	27.8	96.2	71.2	518	226	15.6	4.67	21.8	5.49	0.21	4.44	1.98	707
Nstvd- 200!	THP Inf	14.0%	ND	8.40%	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 5/1(	THP Eff	*2.92%*	*28,543*	*2.40%*	*5,105*	ND	ND	421	2,360	ND	1,629	246	292	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	THP Eff	*3.17%*	*ND*	*2.54%*	*ND*	**31,550**	9,270	184	ND	340	ND	ND	ND	667	415	123	136	123	167	BDL	28.0	107	353	2,308	654	327	482	303	91.9	45.0	21.2	79.1	3,519
Nstvd- 200!	THP Eff	8.10%	ND	4.86%	ND	972,025	27,375	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DCWASA	THP Eff	9.86%	ND	7.57%	ND	161,627	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2,278	593	329	52	95	BDL	31.5	BDL	BDL	2,985
Nstvd- 5/1(	Digested	4.28%	55,743	2.33%	19,048	ND	ND	269	517	ND	286	248	364	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	Digested	5.85%	ND	2.85%	ND	**6,000**	5,100	105	ND	195	ND	ND	ND	BDL	423	111	BDL	32.6	136	BDL	27.9	BDL	119	167	BDL	15.8	BDL	BDL	BDL	BDL	3.54	17.7	187
Nstvd- 200!	Digested	5.80%	ND	2.78%	ND	793,713	4,338	ND	ND	ND	ND	ND	ND	2.05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DCWASA	Digested	5.89%	ND	3.20%	ND	71,840	ND	ND	ND	ND	ND	ND	ND	**2,446**	ND	ND	ND	ND	82.1	BDL	BDL	1300	4.67	188	6.59	60.8	3.98	BDL	0.78	4.87	5.51	BDL	236
Nstvd- 5/1(	Centrate	**5.81%**	**535**	**2.80%**	**277**	ND	ND	37.4	63.2	ND	175	7.88	8.69	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	Centrate	**2.43%**	**321**	**1.33%**	**147**	3,300	1,926	ND	ND	ND	ND	ND	ND	1,101	251	136	BDL	35.0	200	BDL	28.1	124	103	53.4	3.91	8.02	0.24	0.54	0.44	2.15	1.50	8.68	67.3
Nstvd- 5/1(	Final Eff	**ND**	**ND**	**ND**	**ND**	ND	ND	ND	ND	ND	ND	35.2	412	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nstvd- 10/9	Final Eff	**1.05%**	**12.6**	**0.46%**	**7.30**	45.0	31.5	ND	ND	ND	ND	ND	ND	BDL	20.8	138	21.8	82.6	237	BDL	7.31	58.1	11.7	4.05	BDL	BDL	0.18	0.38	BDL	BDL	BDL	0.18	4.44

Notes: Nstvd- 2005 is average data for 2005 provided by the plant

The *blue TS and VS* data points for the Naestved THP effluent are values that do not correlate with the plant data or typical Cambi operation

The **red data points** indicate TSS/VSS, CCOD or total nitrogen

Table D3- Crown Data Summary

								Biopolymer						Soluble Cations					Soluble Anions					Volatile Fatty Acids									
Tmt Plant-Date	Smpl Lctn	TSS\TS		VSS\VS		TCOD	SCOD	Polysac	Lowery	Bradford	Humic	Tot Fe	Tot Al	NH_4^+	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Acetic	Proprionic	Isobutyric	Butyric	Isovaleric	Valeric	Isocaproic	Hexanoic	Heptanoic	Total VFA
		%	mg/L	%	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L as Hac
Rsdl- 5/9	Raw Inf	**5.78%**	**344**	**3.76%**	**101**	ND	ND	ND	ND	ND	ND	0.439	4.23	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Raw Inf	**4.23%**	**147**	**3.824%**	**22.5**	984	217	ND	ND	ND	ND	ND	ND	53.7	20.2	72.8	2.63	9.24	72.5	BDL	2.26	45.9	15.9	30.1	8.05	0.558	1.07	0.221	0.924	0.322	0.839	1.00	38.4
Rsdl- 5/9	Primary	4.62%	41,829	3.45%	10,552	ND	ND	7.49	ND	ND	29.0	49.3	51.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Primary	4.45%	ND	4.01%	ND	72,916	3,250	29.0	ND	9.17	ND	ND	ND	112	67.9	80.5	14.2	145	89.9	BDL	11.3	BDL	67.7	626	660	19.5	266	14.0	71.7	1.18	8.86	2.33	1,310
Rsdl- 5/9	Crown Inf	6.17%	48,933	4.37%	14,238	ND	ND	24.1	9.20	ND	6.53	41.6	40.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Crown Inf	5.43%	ND	4.39%	ND	61,408	3,660	72.0	ND	28.9	ND	ND	ND	198	177	64.5	11.5	3.08	80.4	BDL	BDL	125	154	765	329	95.2	136	131	17.3	52.6	2.97	1.16	1,238
Rsdl- 5/9	Crown Eff	6.38%	39,067	4.48%	11,638	ND	ND	191	74.6	ND	ND	37.9	38.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Crown Eff	5.48%	ND	4.555%	ND	71,439	5,350	151	ND	100	ND	ND	ND	295	259	94.4	27.5	6.27	88.5	BDL	11.2	46.4	209	775	388	98.8	137	171	17.4	58.9	0.634	13.8	1,321
Rsdl- 5/9	Digested	2.47%	19,295	1.527%	7,324	ND	ND	18.5	16.6	ND	31.0	36.1	55.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Digested	2.26%	22,022	1.605%	6,389	22,249	540	26.7	ND	38.0	ND	ND	ND	890	220	82.4	0.303	1.92	98.7	BDL	BDL	BDL	193	12.7	2.06	2.68	BDL	BDL	BDL	0.120	0.877	1.92	17.1
Rsdl- 5/9	Centrate	**3.43%**	**124**	**0.98%**	**88.7**	ND	ND	7.48	717	ND	ND	0.697	1.61	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Centrate	**0.908%**	**51.0**	**0.558%**	**22.7**	614	416	25.0	ND	17.7	ND	ND	ND	805	165	48.9	0.197	1.44	128	BDL	44.7	BDL	149	5.93	1.39	BDL	BDL	BDL	BDL	0.541	BDL	4.20	9.09
Rsdl- 5/9	Final Eff	**ND**	**ND**	**ND**	**ND**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Rsdl- 10/15	Final Eff	**0.741%**	**12.8**	**0.590%**	**2.83**	58.5	49.0	ND	ND	ND	ND	ND	ND	21.9	13.8	73.5	2.10	9.00	68.7	BDL	9.68	52.9	15.3	3.46	1.49	BDL	BDL	BDL	BDL	0.181	BDL	0.609	4.87

Notes: The **red data points** indicate TSS/VSS