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The Effect of Thermochemical Pretreatment on The Dewaterability and Biodegradability of Waste activated sludge

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# THE EFFECT OF THERMOCHEMICAL PRETREATMENT ON THE DEWATERABILITY AND BIODEGRADABILITY OF WASTE ACTIVATED SLUDGE

by

Nishant Rao

# A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

# **MASTER OF SCIENCE**

Department of Chemical Engineering

## ABSTRACT

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# THE EFFECT OF THERMOCHEMICAL PRETREATMENT ON THE DEWATERABILITY AND BIODEGRADABILITY OF WASTE ACTIVATED SLUDGE

By

# Nishant Rao

Waste activated sludge was pretreated at short reaction times - on the order of 10 seconds to 150 seconds and at temperatures ranging from 140°C to 310°C. Two types of hydrolyses were carried out. One was at neutral pH (autohydrolysis) and the other at pHs of 10.5 and 11.5 (alkaline hydrolysis). The sludges pretreated at neutral pH showed good dewaterability with 26% solids being obtained in the filter cake. Solubilisation of the sludges increased with increasing pretreatment temperatures with a solubilisation of 75.8% being achieved with autohydrolysis at 290°C. With alkaline hydrolysis, a solubilisation of 48.8% was achieved at 240°C at a pH of 10.5. Pretreatment increased the biodegradability of the sludges significantly. An increase in methane generation of 96.3% over the control was seen for the alkaline hydrolysis of pH 10.5 at 240°C. A cost analysis showed that the pretreatment scheme was commercially viable.

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## **CHAPTER I : INTRODUCTION**

Wastewater handling and treatment has advanced considerably from the time when wastewater plants used to just effect solids removal from the waste streams and discharge the clarified liquid stream into freshwater, regardless of the characteristics of the discharge stream. For quite some time now, due to growing environmental concerns, stricter controls have been enforced on the quality of the discharge streams from wastewater treatment plants. This has forced the addition of secondary treatment facilities, such as activated sludge treatment, to waste water treatment plants.

Activated sludge treatment involves the removal of soluble and insoluble organics from a wastewater stream by a flocculant microbial suspension<sup>1</sup> composed mostly of bacteria, protozoa, and fungi. This microbial biomass is allowed to come into contact with the waste stream in an aeration basin for about six to eight hours where the microbes are responsible for assimilating most of the organic matter. The removal of organics and the formation of flocs is due to the tendency of the microorganisms to secrete a polysaccharide gel. The substrate is trapped in the gel and metabolised to carbon dioxide and water. A sizeable fraction is converted to cellular mass. The biomass is then separated from the liquid stream in a sedimentation tank. That part of the biomass which results from synthesis during substrate utilisation is wasted and the rest is recycled to the aeration basin, providing a continuous source of biomass. A diagram of a typical

activated sludge treatment plant is shown in Figure 1.1.

The separated biomass is commonly referred to as waste activated sludge (WAS) and consists largely of bacterial cells. Waste activated sludge represents approximately two-thirds of the volume of sludge from a typical wastewater plant having a secondary treatment facility<sup>3</sup>, the other part being made up by primary sludge.

Though activated sludge treatment is efficient in the removal of organics from the waste stream (85-95% biological oxygen demand (BOD) removals are achieved<sup>2</sup>), it introduces some additional problems. One is that the organics have not been disposed of but only converted to another form that still requires disposal. The various disposal techniques available for sludge include land filling, ocean disposal, composting, incineration and digestion. Another problem is that WAS is generally known to be only about 30-50% biodegradable by anaerobic treatment<sup>4</sup>. This means poor utilisation of a potential energy source and also means that the effluent from the anaerobic digesters is not completely inert. A third problem is that of poor dewaterability of WAS due to the amount of bound water associated with the flocs and that in the cells. The various sludge disposal techniques all need the sludge to be dewatered and in some cases well digested for low disposal costs. This is because a major portion of the cost of disposal is taken up by transportation costs to the disposal site<sup>5</sup>. A poorly dewaterable sludge will mean increased cost of transportation per unit weight of dry sludge or , in the case of incineration, more fuel costs due to high water evaporation load.



Figure 1.1: Flow diagram of a typical Activated Sludge Treatment Plant [2]

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To overcome these and other sludge related problems such as odor and pathogenic activity, researchers have suggested and studied heat treatment of the sludge as an answer. Various types of pretreatment have been tried, most involving the cooking of the sludge for periods from half an hour to several hours at various pH values. Even though they have been shown to overcome the above mentioned problems, these pretreatments have been of limited commercial success.

This work described in this thesis investigated the effect of thermochemical pretreatment on waste activated sludge at very short residence times - on the order of ten seconds to a few minutes. The pretreatment was carried out in two regimes. One was at neutral pH (autohydrolysis) and the other was at high pH (alkaline hydrolysis).

Various tests including filtration, total and volatile solids, total and soluble chemical oxygen demand (COD) and anaerobic digestion were carried out on the pretreated sludge to determine the effect of the pretreatment. A conceptual process design and cost analysis were made to evaluate the commercial impact of the thermal pretreatment.

## **CHAPTER II : LITERATURE REVIEW**

## 2.1 Introduction

Waste activated sludge from biological treatment of municipal wastewater is composed mostly of biological cells<sup>4</sup>. A typical composition of bacteria ( on a dry weight basis ) is lipids, 10-15%; protein, 50%; carbohydrates, 10-30%; RNA, 10%; DNA, 3-4%<sup>6</sup>. In addition the bacterial cell wall accounts for 20-30% of the dry weight of the cell. The cell wall is a structural framework consisting of parallel polysaccharide chains covalently cross-linked by peptide chains<sup>7</sup>.

In a study conducted on pure compounds such as amino acids, DNA, RNA, collagen, albumin, ribose, deoxyribose and glucose (the building blocks of the cell), most of them were found to be easily biodegradable<sup>4</sup>. On the other hand untreated WAS was only partially biodegradable. It was concluded that structure and organisation were important in controlling biodegradability (and also dewaterability) which appeared to be related to the accessibility of degradative sites to enzymes.

To date, much research has been conducted on various pretreatment schemes aimed at improving substrate availability in the anaerobic digestion of WAS and at physical modification of WAS to improve dewaterability. Various other strategies(which do not involve pretreatment) have also been tried to improve sludge characteristics<sup>9,10</sup>. These rely mostly on existing equipment to increase their efficiency or on process modifications.

#### 2.2 Solubilisation

## 2.2.1 Undigested sludges

Yang et al.<sup>1,1</sup> in their study on pure cellulose reported a solubilisation of about 85% after cooking the cellulose with a 6% sodium hydroxide liquor for one hour at 250°C. They found that the alkali cooked liquor had a substantial inhibitory effect on methane generation in serum bottles though digestion in an anaerobic filter gave a much better gas production - 68% that of a pure glucose feed.

Ray et al.<sup>12</sup> reported a 44% solubilisation of chemical oxygen demand (COD) after 12 hours for a 1% solids feed concentration with an inexpensive pretreatment scheme. The process involved the addition of low levels (5 to 60 meq/L) of sodium hydroxide followed by mixing for several hours at either ambient or digester temperature. They found gas production and COD removal to increase by about 30% upon anaerobic digestion of the treated sludge (NaOH - 30 meq/L) when compared with the control.

Haug et al.<sup>13</sup> observed that thermal treatment of WAS at about 175°C for 30 minutes led to more than 60% solubilisation of the suspended solids. The COD reduction of the liquor in anaerobic filters was as high as 75%, much higher than that of the untreated control. They also found that while there was no significant improvement in the digestibility of raw primary sludge, pretreatment of WAS at 100°C improved the gas production by 14% and by 70% at 175°C. Pretreatment at temperatures higher than 200°C was found to lead to the formation of inhibitory substances. Another aspect of the

pretreatment was found to be improved dewatering with formation of cakes of 30 to 40% solids without any chemical addition.

It was also found that solubilisation alone could not account for the increase in COD reduction<sup>14</sup>. Haug attributed this to a 50-80% increase in biodegradability taking place during the heat treatment.

McCarty *et al.*<sup>15</sup> studied the effect of heat treatment, for a period of one hour, on municipal refuse and found the greatest solubilisation at high pH with about 85% solubilisation of COD at pH 13 and a reaction temperature of 200°C. They ran a continuous digester, 50% of whose effluent was recycled back to the digester's influent, after being treated for a period of one hour at pH 13 and 200°C. They found that methane production per unit volatile solids was 49% higher than that for the digester without recycle.

A major limitation was found to be inhibition of methane production in digesters, noticeable whenever the concentration of heat treated lignin products exceeded 1 g/L<sup>15,16</sup>.

Hiraoka *et al.*<sup>17</sup> studied the effect of thermal pretreatment of WAS at low temperatures (60-100°C) for 30-60 minutes. They found a significant increase in volatile acids concentration with thermal pretreatment at 60°C, a 130% increase over the untreated WAS. Gas production by anaerobic digestion from the pretreated WAS was 40-50% higher than that of the control.

Stuckey and McCarty<sup>1</sup> studied the effect of thermal pretreatment on the biodegradability and toxicity of WAS. They found that WAS bioconvertibility increased with increasing temperature up to

a maximum of 175°C (one hour reaction time), and this resulted in an increase in methane production of 27% over the control. Above 175°C a sharp decrease in bioconvertibility was noted. This was attributed to the formation of toxic compounds.

Stuckey and McCarty<sup>4</sup> also found a COD solubilisation between 45-55% at neutral pH. Their studies also indicated that 85% of the organics after thermal pretreatment (with addition of 300 meq/L of NaOH) were biodegradable compared with about 53% for the untreated control.

Teletzke<sup>17</sup> pretreated sewage sludge between temperatures of 65°C and 150°C for times ranging from 30 seconds to 60 minutes and reported a 26% increase in methane generation for a 60 minute cooking time at 120°C.

Everett<sup>19</sup> carried out a heat treatment of sewage sludges at 180°C for 30 minutes over a pH range of 2-12. He found solubilisation to increase with increasing temperature and amount of acid (hydrochloric acid) or alkali (sodium hydroxide) added, with a minimum solubilisation at around neutral pH. Alkali treatment was seen to give slightly lesser solubilisation than acid treatment. Everett<sup>20</sup> also found that greater solubilisation was achieved at longer reaction times.

Bachmann *et al.*<sup>21,22</sup> treated agricultural residues between temperatures of 175°C and 225°C for periods up to two hours and found that autohydrolysis of the above materials gave rise to intermediates that were highly bioconvertible to methane. They also observed that three stage autohydrolysis gave better results than

either single or two stage autohydrolysis. Each stage involved separating the solids from the effluent of the previous stage and redissolving them in deionised water to make up the effluent of that stage. With three stage treatment 43% of the initial COD was found to be solubilised.

# 2.2.1.1 Summary

The various pretreatment methodologies used by the researchers has been summarised in Table 2.1. The most noticeable feature is the fact that nearly all of them used very long reaction This gave rise to toxic conditions when temperatures above times. 175°C were used. This posed a barrier to the fact that increased biodegradability could be achieved with increased reaction temperature. One reason for the toxicity could be that, with increased temperature, biodegradable compounds were being converted into toxic ones. This reasoning is supported by the fact that Bachmann et  $al.^{21,22}$ did not report any toxicity even though they used temperatures higher than 175°C. This is because they separated the soluble and insoluble fractions after every stage, thus ensuring that no soluble compound would be toxified.

# 2.2.2 Digested sludges

Pretreatment of digested sludges has been studied by researchers to see whether increased biodegradability can be achieved by treating digester effluent.

Substrate	Catalyst	Temperature	Time	Reference
WAS	None Ca(OH) <sub>2</sub> NaOH HCl	1 <b>50-250°C</b>	1.0 hr	4,42
PS WAS Mixed	None HCl NaOH	100-225°C	0.5 hr	13
WAS	None NaOH	1 <b>50-275°C</b>	1.0 hr	8
WAS PS/WAS	None	171-218°C	1.0 hr	31
WAS	None	60-100°C 60°C`	1.0 hr 2.0 hr	17

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 Table 2.1 : Summary of pretreatments by other researchers [5]

PS - Primary Sludge

Effluents from digesters receiving WAS were treated at 175°C for one hour by McCarty *et al.*<sup>23</sup>. The data obtained indicated an overall improvement of 21% in biodegradability.

Anaerobically digested wheat straw was treated for an hour for temperatures between 100°C and 200°C<sup>21</sup>. The pretreatment carried out at 200°C showed a 47.1% biodegradability of the soluble fraction, nearly four times that of the control. This was accompanied by a 40% COD solubilisation.

The effect of parameters such as pH, temperature and retention time on the thermal pretreatment of digested sludge was studied<sup>6</sup>. pH was varied between 2 and 12, temperature between 140°C and 260°C and retention times between 1 and 30 seconds. Solubilisation was found to be the highest with alkaline hydrolysis, approaching 58%, while acid hydrolysis gave values of around 34%. Increasing temperature and retention time were also seen to increase the degree of solubilisation, with values of 71% being attained (0.25% NaOH, 230°C, 10 sec. retention time).

# 2.3 Dewaterability

In an article enumerating the various techniques for dewatering wastewater sludges, Vesilind *et al.*<sup>24</sup>, noted that WAS had poor dewatering characteristics because of it is associated with a lot of bound water (density generally less than 1.08). They found that WAS had a tendency not to get picked up by the filter cloth in standard vacuum filters and that it plugged the pores of the filter cloth rapidly

(called blinding). They found that WAS could be thickened to up to 6% solids by flotation and only up to 10% solids using solid bowl centrifuges.

Christensen and Dick<sup>25</sup> found the specific resistance of a flocculant slurry to be a very strong function of suspended solids concentration at low concentrations and relatively independent of suspended solids concentrations at higher concentrations. They also noted that due to differing conditions in various labs, specific resistance measurements were not as accurate and comparable as they should be. In this they disagreed with Kavanagh<sup>26</sup> who had earlier stated that specific resistance was independent of solids concentration.

In a related study Christensen and Dick<sup>40</sup> also found that measurement of specific resistance using a pressurised filtration cell and a computerised data acquisition system had several advantages over the traditional Buchner funnel filtration apparatus.

Mean cell residence time in the activated sludge aeration basin was found to be significant in the dewatering characteristics of activated sludge samples<sup>23</sup>. Optimum dewatering rates were obtained for residence times greater than seven days. It was also found that increase in particle size in a sludge matrix might be expected to improve dewatering characteristics.

Everett<sup>19</sup> investigated the effect of pH on the heat treatment of sludges with respect to specific resistance of the cake. He found the initial pH to have a great effect on the final specific resistance of the cake, with high pH giving rise to a high specific resistance and vice

versa. The difference in specific resistance between a pH of 2 and a pH of 12 was on the order of  $10^4$  m/kg.

Everett<sup>20</sup> also studied the effect of reaction time on the specific resistance of the sludge at various temperatures. He found that treating WAS at a temperature of  $210^{\circ}$ C for 30 minutes lowered the specific resistance to a value of  $1 \times 10^{11}$  m/kg from a value of  $2.05 \times 10^{15}$  m/kg for the untreated sample.

Lawler *et al.*<sup>29</sup> studied the effect of anaerobic digestion on particle size and dewaterability of municipal sludges. They found digestion to improve dewaterability by preferential destruction of particles of small size.

In a patented scheme, Brown *et al.*<sup>30</sup> found that dewatering time of anaerobic digested sludge was reduced substantially by subjecting the sludge to aeration for about 4 hours and then allowing it to settle for no more than two days.

Haug *et al.*<sup>31</sup> investigated the effects of thermal pretreatment in field scale projects with temperatures ranging from 171°C to 218°C for 30 minutes. They found dewaterability to increase with thermal pretreatment to the extent that a cake of about 45% solids could be formed using a plate and frame press, with the addition of small amounts (0-2 g/kg) of polymer.

Teletzke<sup>32</sup> studied the effect of briefly heating sewage sludge at temperatures between 190°C and 230°C for a period of time up to 240 seconds which was inversely proportional to the temperature selected. He observed that this improved the dewatering characteristics of the insoluble solids while producing less color and BOD in the supernatant liquid. He also found that a heating temperature of 200-225°C between 180 seconds and 5 seconds gave optimum results.

Ishida et al.<sup>33,34</sup> have reported a scheme wherein sludge is first adjusted to a pH below 3.5 and then treated at temperatures between 60 and 200°C for times between one and ten minutes. Upon treating a sludge, of 5% solids adjusted to a pH of 2.0, at 100°C for 5 minutes they observed a decrease in sludge viscosity from 5600 cp to 620 cp. This gave a higher digestion rate and led to lower stirring power and costs.

Dewatering of packing house wastes was improved<sup>35</sup> by heating them for 5 minutes at 180°F (82°C) after first fermenting them for 24 hours at 78°F (25°C). A four fold increase in cake solids concentration was seen for the treated sludge over the control.

The Zimpro process, which involves wet air oxidation of the sludge, is a pretreatment scheme that is prevalent commercially. The drawback of this process is in the very large amounts of soluble COD produced in the outlet stream which creates an excessive load on the waste water plant. In contrast, very good cake solids are obtained.

#### 2.4 Summary

The work of most of the the previous researchers involved very long pretreatment times. This needed a lot of energy to maintain the sludge at reaction temperature. The researchers also reported an

inhibition to methane formation from the sludges pretreated at temperatures above 170°C. This work investigated the effect of short reaction times on the dewaterability and toxicity of sludges. The economic feasibility of such a pretreatment scheme was also investigated.

# **CHAPTER III : MATERIALS AND METHODS**

## 3.1 Pretreatment Substrate

Most of the pretreatment runs in this study were carried out using WAS obtained from the Lansing Wastewater Treatment Plant. One pretreatment run, however, was made with WAS and sludge from the dissolved air flotation unit of the Battle Creek Wastewater Treatment Plant.

### 3.2 Pretreatment Methodology

Each batch of substrate WAS from the wastewater treatment plants was pretreated in a high temperature plug flow reactor system<sup>36</sup> as described by Allen *et al.*<sup>37</sup>. Pretreatments were carried out at several temperatures ranging from 100°C to 290°C. The nominal residence time in the flow reactor was 7 to 150 seconds, based on the slurry feed, although actual residence times were slightly lower because the flow rates of steam was added to the slurry to attain the high temperatures.

For the alkaline hydrolysis runs, the WAS in the feed tank was adjusted to the desired pH by the addition of sodium hydroxide.

# 3.3 Flow Reactor Configuration

A schematic diagram of the reactor system used (MBI High Temperature Flow Reactor, Michigan Biotechnology Institute, Lansing, Michigan) is shown in Figure 3.1. The reactor is fed from a 20 liter

HIGH TEMPERATURE FLOW REACTOR



Figure 3.1: Schematic diagram of the MBI High Temperature Flow Reactor.

feed tank by a Moyno pump (moving cavity positive displacement pump, Robbins-Meyer, Springfield, Ohio) with 18 stages, which was designed to handle slurries at up to 1650 psig and flow rates from 1 to 8 L/min. The reactor is constructed of 0.5 inch o.d. Carpenter-20 stainless steel tubing with a 0.048 inch wall thickness. The reactor volume was initially 190 ml but later was increased to 2154 ml by means of additional tubing. High temperatures were attained by the injection of steam from a boiler through a series of drill holes in the tube wall near the inlet of the reactor. A 1 mm orifice is located at the exit of the reactor at which the reaction mixture is flashed adiabatically from reactor pressure and temperature to atmospheric pressure and about The flash steam is then condensed as the slurry passes 100°C. through the heat exchanger and the pretreated sludge is then cooled to room temperature and collected at the heat exchanger outlet. Temperature is controlled by steam addition and residence time is controlled by the mass flow rate of the sludge plus condensed steam addition. Operating pressure is typically about 50 psig above the • steam saturation pressure at the desired reactor temperature to ensure complete condensation of the steam in the reactor.

The samples of the pretreated sludges were taken after allowing the reactor to come to equilibrium at the desired temperature. The samples were then stored at 4°C until further tests were conducted on it.

#### 3.4 Dewaterability Studies

The apparatus for measuring sludge dewaterability and cake



Figure 3.2 : Schematic diagram of filtration apparatus

•

solids consisted of a 11 cm Buchner funnel connected to a 500 ml measuring cylinder as shown in Figure 3.2. A Whatman No. 1 filter paper, which was tared for initial weight, was used in the funnel. The process consisted of adding a 250 ml sample of the sludge to the funnel, applying a vacuum of 26 inches of mercury, and recording the volume of filtrate produced as a function of time. The solids content of the cake formed was calculated by weighing a wet sample of cake, drying it at 105°C, and weighing the dry sample. Correction for the tare weight was made.

The effect of polymer addition on dewaterability of the pretreated sludges was studied by mixing the polymer (Optimer cationic flocculant #7139, Nalco Chemical Company, Naperville, Illinois) with the sludge before adding the sample to the Buchner funnel. The polymer, which was obtained in a concentrated form, was first prepared for use with the sludge using the directions given by Nalco representatives. This involved the transfer of 2 ml of the concentrate into 198 ml of water in a 600 ml beaker and the subsequent mixing of the same for 30 seconds using a Braun high shear mixer. Measured quantities of the prepared polymer (up to a level of 40 ppm of polymer) were then added to the sludge with constant mixing until a change in the physical appearance of the sludge was seen. This mixture was then transferred to the funnel.

## **3.5** Digestion Studies

The biodegradability and digestibility of the pretreated



Figure 3.3 : Schematic diagram of a serum bottle with stopper and crimp

sludges were determined by a batch digestion procedure using serum bottles which was a modification of the serum bottle technique for cultivation of anaerobes as described by Miller *et al.*<sup>38</sup>.

A schematic of the serum bottles used is shown in Figure 3.3. The serum bottles were of either 50 ml or 100 ml capacity, capped with a butyl rubber stopper and crimped with an aluminum seal to ensure anaerobic conditions. These were incubated in a room maintained at 37°C. A 10% inoculum was used for all the digestion studies. To maintain a constant supply of inoculum, untreated and pretreated sludge from initial pretreatment runs were mixed. Fifty ml each of this mix were stored in 100 ml serum bottles and refrigerated. An initial seed culture was obtained from the Jackson Wastewater Treatment Plant and was used as the inoculum for the mixed sludge. This inoculated sludge was incubated for 10 days. Five ml of this was transferred to the next serum bottle at the end of the 10 days and thus a continuous supply of inoculum was obtained.

This method had two advantages, one being that a stable seed culture was maintained, thus enabling comparisons between different pretreatment runs. The second was that since the inoculum grew on mixed untreated and pretreated sludge, acclimatisation to the pretreated sludge was achieved.

#### **3.6 Analytical Methods**

#### 3.6.1 Solids

Total solids and volatile solids concentrations were

determined gravimetrically, for the sludge samples using the procedure suggested in Standard Methods<sup>39</sup>. Total solids were given by the residue upon evaporation at 105°C. Volatile solids were defined to be the loss on ignition at 575°C, with the residue being inorganic ash. Total and volatile suspended solids were estimated in the same way after filtering the sample through a Whatman No.1 filter paper.

# 3.6.2 Chemical Oxygen Demand

Chemical oxygen demand (COD) of the various samples was determined by the colorimetric method using standard range reagents in twist cap vials (OI Corporation). Soluble COD was determined on total samples after centrifuging the samples for ten minutes at 14,000 rpm. Potassium hydrogen phthalate, whose theoretical COD value is known (1.176 mg  $O_2/mg$ ), was used as a standard.

The principle behind the COD test is the fact that most compounds are oxidised by a boiling mixture of chromic and sulfuric acids. Potassium dichromate reacts with oxidisable compounds in the sample, catalysed by sulfuric acid and mercuric sulfate. The change in color due to the reduction of the dichromate acts as an indicator of the amount of COD present in the sample and is read at 640 nm in a spectrophotometer.

# 3.6.3 Gas Composition

Gases were analysed on a Gow-Mac Gas Chromatograph with a Porapak Q column using a thermal conductivity detector. Helium

at a flow rate of approximately 25 ml/min was used as the carrier gas. Gas sampling was done with A-2 Pressure Lok syringes (Dynatech, Precision Sampling Corp., Baton Rouge, LA) using 0.5 ml of sample from the head space of the serum bottles. The build-up of pressure in the constant volume head space of the serum bottles was translated into the number of moles of gases produced. The equation used for this is shown in Equation 3.1 and its derivation is shown in Appendix A.

$$n_i = \alpha V_g \times 3.934 \times 10^{-4} \text{ mmoles}$$
 ... (3.1)

where,

n<sub>i</sub> - number of moles of component i in head space

 $\alpha$  - area of component i of the gas mixture from

the GC reported as a percentage of the total area

 $V_g$  -volume of the head space

This method of gas sampling was used over the usual one of measuring the volume of gas produced because of its simplicity and precision.

## **3.6.4** Volatile Fatty Acids

Volatile fatty acids were detected from a 2  $\mu$ l sample on a Varian Gas Chromatograph using a column with Chromosorb WAW as the support and GP-10% SP-1200/1% H<sub>3</sub>PO<sub>4</sub> as the phase with helium as the carrier gas. The column was connected to a hydrogen flame ionisation detector and was run isothermally at 120°C. The injection port and detector were maintained at 150°C and 180°C respectively.
3.6.5 pH

The pH of the samples was measured electrometrically using a Corning pH meter with a glass electrode and a silver chloride reference cell.

## **CHAPTER IV : RESULTS AND DISCUSSION**

## 4.1 Introduction

The results of five of the pretreatment regimes are presented in this section. Henceforth each pretreatment will be designated a series and individual levels that comprise a series will be referred to as runs. Thus, if on a certain day the sludge was pretreated at temperatures from 140°C to 220°C with increments of 20°C, each would be termed a run. All the runs, collectively, for that day would comprise one series.

A synopsis of the various conditions in each series is tabulated in Table 4.1.

#### 4.2 Physical Appearance

#### 4.2.1 Autohydrolysis runs

In the case of the autohydrolysis runs with the WAS, a general trend in the appearance of the pretreated sludge was observed. The sludge from the runs below a temperature of 180°C showed a granular gelatinous appearance with settling occurring very slowly. After settling, a whitish viscous layer was seen on top of the settled solids. These observations could be attributed to a partial breakdown of the cell wall and the slime layer coating the cells.

At around 200°C the pretreatment produced a sludge that did not show a granular nature like the preceding case but was homogeneous and viscous looking. This regime was also characterised

Series	Sludge	Type of	Temperature (°C)	
	origin	pretreatment	Range	Increment
• A	Lansing	Autohydrolysis	140-290	30
В	Lansing	Autohydrolysis	160-240	<b>30</b>
С	Lansing	Autohydrolysis	200-310	20
		Alkaline hydrolysis	180-240	20
D	Lansing	Alkaline hydrolysis	140-240	20
Ε	Battle Creek WAS	Autohydrolysis	140-220	20
	DAF	Autohydrolysis	160-200	20

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 Table 4.1 : Synopsis of conditions of pretreatment

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by poor settleability. This could be due to a more complete breakdown of the cell wall and with a complete breakdown of the slime layer of the cell.

Above a temperature of 220°C the sludge showed a fine grainy structure that settled out into a compact layer. A complete lysis of the cell wall and the slime layer could account for this behaviour.

The supernatants of the various runs showed an increase in color with increasing temperature.

## 4.2.2 Alkaline hydrolysis runs

The sludges from the alkaline hydrolysis runs on the other hand all tended to be very colloidal and were blackish in appearance. In all instances a small layer of black solids tended to settle out after about an hour, but the majority of the solids remained in suspension.

The supernatant of these runs tended to be very much darker in appearance when compared to those of the autohydrolysis runs. In addition they showed the same increase in color with temperature.

Figures 4.1 and 4.2 show the various trends described above.

# 4.3 Sludge Dewaterability

### 4.3.1 Autohydrolysis runs

The series A runs included runs at temperatures of 140, 170, 200, 230, 260 and 290°C. The pretreated sludges were filtered as described in the section on materials and methods. The results are shown in Figures 4.3 and 4.4. Figure 4.3 shows the filtration curves for the raw sludge (control) and the pretreated sludges of the 140°C



(a) From left to right : Raw sludge and sludges from the 140, 170, 200, 230, 260 and 290°C runs



(b) From left to right : Raw sludge and sludges from the 180, 200, 220, and 240°C runs

Figure 4.1 : Physical appearance of (a) Series A sludges and

(b) Series C sludges (alkaline hydrolysis)



(a) From left to right : Raw sludge and sludges from the 200, 220, and 240°C runs



(b) From left to right : Sludges from the 260, 280, 300 and 310°C runs

Figure 4.2 : Physical appearance of Series C sludges (autohydrolysis)



Figure 4.3 : Filtration curves for Series A sludges



Figure 4.4 : Filtration curves for Series A sludges

and 170°C runs, with and without the addition of the polymer. Figure 4.4 shows the curves for raw sludge and the 260°C and 290°C runs.

From Figure 4.3 it is evident that the sludges from the 140°C and 170°C runs have filtration rates about the same as the raw sludge. The raw sludge with polymer added, however, showed much better filtration rates. The addition of polymer to the 140°C and 170°C runs seemed to have a detrimental effect on the filtration rates. This could be because the addition of the polymer to the gelatinous sludge has a tendency to increase the gelatinous nature thus leading to slower filtration and faster clogging of the filter paper.

The sludge from the 200°C and 230°C runs showed very poor filtration rates, even with the addition of polymer. The sludge from the 260°C and 290°C runs, however, showed very good filtration rates as seen in Figure 4.4, comparable to that of the raw sludge with polymer addition. Addition of polymer to these sludges was found to have little effect on the filtration rates. Table 4.2 shows the solids content of the cakes that were formed. Note that 24 to 26% solids can be achieved by high temperature pretreatment.

Figures 4.5 and 4.6 show the filtration curves of some of the runs of series B. The other runs of that series showed poor filterability which agreed with the trend seen with the series A runs. Figures 4.5 and 4.6 show the filtration curves at two pump speeds of 39 and 79 rpm which had the effect of changing the retention time in the reactor from 10 seconds to 20 seconds respectively. Very similar results are seen

Run	% Solids in cake	
Raw w/p	9.5	
260°C	24.5	
260°C w/p	25.9	
290°C	26.4	
290°C w/p	<b>18.9</b>	

Table 4.2 : Solids content of cakes of series A

w/p - with polymer addition



Figure 4.5 : Filtration curves for Series B sludges(39 rpm pump speed)



Figure 4.6 : Filtration curves for Series B sludges(79 rpm pump speed)

in the two figures which shows that there is no appreciable difference in dewatering properties for the two retention times.

Series C was run after the reactor had an additional length of piping added to it which increased the residence time in the reactor from about 10 seconds to about 1.5 minutes. One more difference between this series and the previous ones was that series A and B were run at a constant pump speed while series C and those following it were run at a constant flow rate of sludge. Running at a constant pump speed did not provide a constant flow rate of sludge for all the runs in a series because the boiler pressure had to be increased to obtain higher temperatures in the reactor and this led to a higher back pressure on the pump driving the sludge. Thus as the temperature was increased, the flow rate of sludge decreased.

These differences seemed to shift the trend seen in series A and B to higher temperatures. Thus in Figures 4.7 and 4.8 sludges pretreated up to a temperature of 280°C showed filtration rates about the same as the raw sludge while the 300°C and the 310°C runs were slightly better than the raw sludge. Even though filtration rates of the pretreated sludges were about that of the raw sludge, the cake solids concentration of the pretreated sludges was much higher than that of the raw sludge. The solids content of the cakes obtained from the series C runs are reported in Table 4.3.

# 4.3.2 Alkaline hydrolysis runs

The alkaline hydrolyses of series C and D showed the same



Figure 4.7 : Filtration curves for Series C sludges



Figure 4.8 : Filtration curves for Series C sludges

	Run	% Solids in cake	
	Raw	13.0	
	Raw w/p	12.8	
	220°C	23.1	
	220°C w/p	26.6	
	240°C	22.5	
	240°C w/p	20.2	
	260°C	27.5	
	280°C	25.0	
	300°C	25.6	
•	300°C w/p	19.9	
	310°C	24.1	
	310°C w/p	18.8	

Table 4.3 : Solids content of cakes of series C

w/p - with polymer addition

trend among themselves as far as filtration was concerned. All the sludges that were treated in this manner did not filter at all and tended to clog the filter paper very quickly. This happened even when the pH of the pretreated sludges was adjusted to neutral before the filtration. Addition of different polymers did not seem to help either. Table 4.4 shows the pH of the pretreated sludges which was measured soon after the sludge was collected at the heat exchanger outlet. A decrease in pH is noticed with increasing temperature. This corresponds to the amount of alkali used up in the reaction.

## 4.4 Solubilisation

Solubilisation is one of the indices of biodegradability and digestibility of sludge, since increased solubilisation means an increased amount of sludge in a soluble form which is an easily digestible form of substrate. In this sense it is also an index of the effectiveness of pretreatment since the pretreatment aims at improving the biodegradability of the sludge.

In this study solubilisation was defined as the ratio of the soluble COD to total COD. Figures 4.9, 4.10 and 4.11 show the solubilisation data for series A, B, and C respectively. All the curves show an increasing solubilisation of the sludges with temperature. The effect of this increased solubilisation is clearly seen in the next section on biodegradability of sludges.

Figure 4.11 compares the solubilisation achieved in series C by autohydrolysis and alkaline hydrolysis. This figure shows that

Run	Series C	Series D	
Raw	10.5	11.50	
140°C		10.94	
160°C		10.65	
180°C	8.59	10.30	
200°C	8.15	9.91	
220°C	7.40	9.66	
240°C	7.05	9.27	

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Table 4.4 : pH of pretreated sludges of series C and D

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Figure 4.9 : Solubilisation curve for Series A sludges



Figure 4.10 : Solubilisation curves for Series B sludges



Figure 4.11 : Solubilisation curves for Series C sludges

alkaline hydrolysis allows us to achieve a much greater extent of solubilisation at lower temperatures than possible by autohydrolysis. Even allowing the raw sludge to sit overnight after adjusting its pH to 10.5 had the effect of increasing the amount solubilised from 1.8% to 24.8%.

# 4.5 Biodegradability and digestibility

Biodegradability like solubilisation is another index of the pretreatment on sludge since greater effectiveness is reflected in the increase in biodegradability exhibited by the sludges.

Figures 4.12 and 4.13 show the results of the batch biodegradability tests on the series A sludge samples. Two points of note about the results are highlighted here. One is the fact that all the pretreated sludges showed a greater gas production (per gram COD input) than the control. In general the amount of gas produced increased with increase in pretreatment temperature. This seems linked to the solubilisation data obtained, where the same trend was seen. Table 4.4 reports the ultimate gas production of the various runs.

The other important point is in the shape of the curves for the various temperatures. It is seen that the curves for the 140, 170 and 200°C runs show no lag phase in the production of methane. On the other hand the higher temperature runs show a lag of about 3 to 5 days. This can be attributed to the formation of compounds in the higher temperature runs to which the inocula are not fully acclimated. These compounds do not seem toxic since, after the initial lag phase,



Figure 4.12 : Methane generation curves for Series A sludges



Figure 4.13 : Methane generation curves for Series A sludges

	Run	UMP	% above control	MMPR	
	Raw	5.925	_	0.642	
	140°C	6.683	12.8	0.738	
	170°C	6.168	4.1	0.624	
	200°C	8.052	35.9	1.081	
	230°C	7.623	28.7	1.210	
-	260°C	7.841	32.8	1.057	
	290°C	8.645	45.9	1.244	

Table 4.5 : Ultimate methane production of series A runs

UMP - Ultimate methane production at the end of 21 days (mmoles/g COD)

MMPR - Maximum methane production rate (mmoles/g COD/day)

the gas production resumes at a rate higher than of the control.

This same behaviour can be seen in the gas production data of the series C runs shown in Figure 4.14. As the pretreatment temperature increases, the lag in gas production seems to correspondingly increase. Again this seems to be due to the non acclimation of the inocula rather than to toxic inhibition for pretreatment temperatures below 300°C.

Figure 4.15 shows the results of digestion of the alkaline hydrolysis runs of series C. Comparing these curves with those of the autohydrolysis run of the same series (Figure 4.14) it can be seen that for the same temperature the alkaline hydrolysis gives a higher gas production.

Figure 4.16 presents the data of series D. In this case the sludge samples were inoculated after adjusting the pH of the sludges to neutral (pH 7) in order to avoid any shock to the inocula. The same trend as described for the series A runs are seen here; the increase in gas production with temperature of pretreatment and the increase in lag with temperature. In this series the 240°C run showed an increase of about 90% over the control. In contrast, Figure 4.17 presents the data obtained from the inoculation of the sludge samples without neutralisation. It can be seen that the lag in the production of methane decreases as the pH decreases to about neutral (refer Table 4.4).

The runs of series E were made with sludge from two sources. One was WAS of initial solids concentration of 5.69 g/l (0.569% solids). The other was DAF sludge 0f 56.1 g/l (5.61% solids)



Figure 4.14 : Methane generation curves for Series C sludges (Autohydrolysis runs)



Figure 4.15: Methane generation curves for Series C sludges (Alkaline hydrolysis runs)

- a Raw sludge w/o addition of catalyst (refer to Figure 4.14)
- b Raw sludge with addition of alkali



Figure 4.16 : Methane generation curves for Series D sludges (with pre-inoculation neutralisation)



Figure 4.17 : Methane generation curves for Series D sludges (without pre-inoculation neutralisation)



Figure 4.18 : Methane generation curves for Series E sludges (WAS)



Figure 4.19: Methane generation curves for Series E sludges (DAF)

Ru	n UMP	% above control	MMPR
Rav	v 3.655		0.464
200	°C 6.075	66.2	0.488
220	°C 5.833	59.7	0.538
240	°C 5.711	56.3	0.516
260	°C 4.551	24.5	0.424
280	°C 1.281	-65.0	· ·
300	°C 0.108	-97.0	

**Table 4.6 :** Ultimate methane production of series C autohydrolysis runs

UMP - Ultimate methane production at the end of 30 days (mmoles/g COD)

MMPR - Maximum methane production rate (mmoles/g COD/day)

Run	UMP	% above control	MMPR
Raw <sup>a</sup>	3.655	_	0.464
Raw <sup>b</sup>	4.535	24.1	0.500
180°C	5.936	62.4	0.656
200°C	5.760	57.6	0.715
220°C	7.173	96.3	0.727
240°C	6.974	90.8	0.657

 Table 4.7 : Ultimate methane production of series C alkaline hydrolysis

 runs

UMP - Ultimate methane production at the end of 28 days (mmoles/g COD)

- MMPR Maximum methane production rate (mmoles/g COD/day)
  - Raw<sup>a</sup> Raw sludge without alkali addition
  - Raw<sup>b</sup> Raw sludge with the addition of alkali

Run	UMP	% above control	MMPR
_			
Raw	3.457		0.360
140°C	5.006	44.8	0.443
160°C	5.482	58.6	0.561
180°C	5.483	58.6	0.515
200°C	5.565	61.0	0.477
220°C	6.023	74.2	0.490
240°C	6.555	89.6	0.408

Table 4.8 : Ultimate methane production of series D runs

UMP - Ultimate methane production at the end of 41 days (mmoles/g COD)

MMPR - Maximum methane production rate (mmoles/g COD/day)

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Run	UMP	% above control	MMPR	
Raw	4.615	_	0.665	
140°C	5.649	22.4	1.313	
160°C	6.369	38.0	1.216	
180°C	6.518	41.2	1.336	
200°C	6.669	44.5	1.094	
220°C	7.075	66.9	1.125	

Table 4.9 : Ultimate methane production of series E runs with WAS

UMP - Ultimate methane production at the end of 19 days (mmoles/g COD)

MMPR - Maximum methane production rate (mmoles/g COD/day)
 Run	UMP	% above control	MMPR	
Raw	5.290	_	0.667	
160°C	<b>6.99</b> 1	32.1	0.939	
180°C	7.183	35.8	0.913	
200°C	7.470	41.2	0.729	

Table 4.10 : Ultimate methane production of series E runs with DAF

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UMP - Ultimate methane production at the end of 19 days (mmoles/g COD)

MMPR - Maximum methane production rate (mmoles/g COD/day)

concentration. The DAF runs were diluted five times before seeding with inocula. These are shown in Figures 4.17 and 4.18. Tables 4.5 to 4.9 show the ultimate methane production of series C, D and E runs. From the data in these figures it is seen that the WAS sludges show a methane generation comparable to that seen in the earlier series. This indicates that the origin of the sludge does not make much of a difference if the source of the raw waste water is the same (waste water from municipal or industrial areas).

Another point that becomes evident on comparing Figures 4.17 and 4.18 is the fact that both the WAS and the DAF sludges generated approximately the same amount of methane. This indicates that the pretreatment has the same effect on the sludges, regardless of their solids concentration.

### 4.6 Discussion

#### 4.6.1 Sludge dewaterability

Though comparison between different series is difficult due to the varying compositions of the sludge obtained from the wastewater treatment plants, certain common trends across the series are evident.

For the autohydrolysis runs above a temperature of about 230°C, the sludge showed good filtration rates. Most of these sludges filtered within five minutes. Good filtration was also tied to good cake solids content as seen in Tables 4.1 and 4.2 where cake solids in the range of 25% were obtained. One other point is the fact that these

higher temperature runs did not show better filtration rates or cake solids with the addition of polymer. This represents a savings in polymer addition over the raw sludge.

With alkaline hydrolysis however, no filtration was possible with any of the runs. The colloidal nature of the sludges pretreated in this manner suggests that the fine particulates blind the filter paper, thus hindering the filtration process.

These trends in the dewaterability of the sludges can be related to their physical appearance which was discussed earlier. Sludges run at the lower temperatures appeared gelatinous and did not settle out well. These sludges showed poor dewatering characteristics and did not form good filter cakes. In contrast the sludges run at higher temperatures showed a fine grainy structure and settled out easily. These sludges filtered well and formed a good filter cake. The sludges of the alkaline hydrolyses were colloidal and correspondingly showed very poor filtration characteristics, which agreed with the findings of Everett<sup>19</sup>.

#### 4.6.2 Solubilisation and biodegradability

Kinetic evaluation of the overall process of anaerobic biodegradation of organic matter to methane has shown that solubilisation is usually the rate limiting step for the digestion of insoluble wastes. Thus, the greater solubilisation achieved due to the pretreatment leads to faster overall rates of digestion. It also leads to a greater conversion of substrate into methane as the gas production curves demonstrate.

Though most of the workers in this field have demonstrated the increase in biodegradability with pretreatment temperature, quite a few of them<sup>10,13</sup> have reported an optimum temperature of around 170°C to 200°C above which a decrease in biodegradability was seen. This was attributed to the formation of toxic compounds. One of the reasons for this decrease in biodegradability could be due to the fact that very long retention times, in the order of 30 minutes or longer, were used by nearly all the previous workers (see Table 2.1).

To find out whether this was the case, this study looked at reactor residence times on the order of 10 seconds to 2 minutes. From the graphs of gas produced over time, presented in the previous section, it is observed that even for temperatures up to 300°C no toxicity is seen, though there is a lag phase in the gas production at higher temperatures. Thus decreasing the time of pretreatment does seem to overcome the problem of toxicity.

Volatile fatty acid analyses were carried out on all the sludges being digested since a build up of fatty acids is an indication of an imbalance in the digestion process. Fatty acids at the end of the digestions were always found to be below levels which would indicate an incomplete digestion.

Another point that can be observed from the gas production curves is the fact that ultimate methane production tapers off between 7 to 9 mmoles per gram COD input. This is much lower than the theoretical value of 16.2 mmoles per gram COD (at 37°C). One reason for this could be that, because the COD test is a general one picking up oxidisable all compounds. it could have overestimated the biodegradable component of the sludge. Another explanation could be that the selection of mixed culture of organisms that arose due to the 10 day transfers of inocula was of such a nature that complete conversion to methane was not possible. This can be easily corrected by either changing the time between transfers or by introducing the necessary microorganisms into the system or by using a continuous system. When a COD balance was made on the digestion process it was found that the amount of gas produced per unit of COD destroyed was around the theoretical value of 16.2 mmoles/g COD. This confirms that the COD destroyed is converted to methane.

### CHAPTER V : PRELIMINARY PROCESS DESIGN AND COST ESTIMATION

### 5.1 Introduction

The objective of this study was to evaluate the feasibility of a pretreatment scheme that answered the problems of dewaterability and biodegradability posed by the WAS generated in secondary treatment facilities. From the discussion in the previous chapter it is evident that the pretreatment is effective in increasing the gas production from the sludge and also in increasing the dewaterability of the sludge. This chapter considers the implementation of the pretreatment scheme commercially as an addition to existing wastewater treatment plants. A preliminary process design for the pretreatment scheme has been developed and is presented in this chapter along with an estimate of the costs involved with this implementation.

To pretreat the sludges of the various series, they were all brought up to the desired reaction temperature from room temperature by the injection of steam. This method had two disadvantages. One was that a lot of energy in the form of steam had to be expended to bring the sludge up to reaction temperature. This could be very expensive if used commercially on a large scale. The other drawback was that the pretreated sludge was diluted due to the addition of the steam. Since one of the objectives was to produce a very compact sludge for disposal, the dilution would only lead to a higher filtration

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load.

An alternate scheme is to heat the incoming sludge by pretreated sludge from the reactor by means of a heat exchanger. This would lead to a large savings in the amount of heat to be supplied by the boiler. This would mean a substantial decrease in the operating costs of the boiler.

### 5.2 Proposed plant layout

For the purpose of the design and cost estimation a plant with existing thickening and filtration equipment was chosen as a basis for comparison. A conceptual layout of this plant is shown in Figure 5.1(a) (Scheme I). One proposed scheme is the addition of an anaerobic sludge blanket reactor to the basic plant which would serve two purposes. One would be to generate methane which could be put to a variety of uses. The other would be to bring about a reduction in solids due to the digestion. This would lead to a smaller quantity of solids to be disposed. These two advantages could be increased by incorporating the pretreatment methodology used in this study into the wastewater treatment plant (Scheme II). A schematic of such a proposed plant is shown in Figure 5.1(b). Two other options that were considered for their economic feasibility are shown in Figure 5.1(c) and 5.1(d). The case of using the pretreatment process without the addition of a digester is considered in Scheme III (Figure 5.1(c)). Since the raw WAS was observed to settle to about half its volume, the option of first allowing the WAS to settle before pretreating it, to reduce the



(a) Conceptual Plant ; basis of comparison



(b) Proposed Plant additions

Figure 5.1 Conceptual Plant Layouts



(c) Proposed Plant additions (Scheme III)



(d) Proposed Plant additions (Scheme IV)

Figure 5.1 (cont'd.).

equipment capacity, was considered. This is represented in Figure 5.1(d) (Scheme IV). The design and cost considerations for such additions to existing plants is considered in the following sections.

### 5.3 Process design

The design is based on a wastewater treatment plant of 20 mgd (75700 m<sup>3</sup>/day) capacity. This is the size of a wastewater treatment plant treating an average sized city. Generally about half a percent of the inflow is WAS though this may vary depending on the operational conditions in the plant. This WAS flow amounts to about 0.1 mgd (380 m<sup>3</sup>/day). Some of the assumptions made for the design included the following. The WAS was assumed to be at 20°C. This would be heated to 250°C by the reactor outlet stream which would be at 260°C, the reaction temperature. The outlet stream from the heat exchanger would be brought up to the reaction temperature by make up steam from the boiler. The reactor outlet stream, after being cooled in the heat exchanger, would be sent to the digester or to the thickener, as the case may be. A summary of the assumptions made for the design are presented in Table 5.1

The following three sections deal with equipment sizing for the first three schemes. For scheme IV sizing was done keeping in mind that only half the sludge volume would have to be treated.

### 5.3.1 Heat exchanger design

An enthalpy balance was used to calculate that the pretreated sludge would be cooled from 260°C to 36.7°C in heating the



### Table 5.1 : Design Assumptions

incoming WAS from 20°C to 250°C. Assuming an overall heat transfer coefficient of 225  $Btu/ft^2hr^{o}F$  (1098 kcal/m<sup>2</sup>hr<sup>o</sup>C) (from Perry's Chemical Engineers' Handbook<sup>41</sup>), the heat exchanger surface area was calculated to be 2733 ft<sup>2</sup> (254 m<sup>2</sup>)

#### 5.3.2 Boiler capacity

The amount of steam needed to raise the temperature of the sludge from 250°C to260°C was calculated to be 1037 lb/hr (471 kg/hr). This was assuming that the steam injected was at 260°C.

### 5.3.3 Pump capacity

For a flow rate of 380 m<sup>3</sup>/day and a pressure difference of 730 psi the pump power was calculated to be 40 hp (30 kW). The pressure difference was set 50 psi above the steam vapor pressure at the pretreatment temperature.

#### 5.4 Cost analysis

### 5.4.1 Capital costs

The cost analysis was made only on those pieces of equipment that were deemed to have a major impact on the pretreatment scheme. Various other aspects of setting up the new additions to the plant such as building materials, piping, reactor cost, instrumentation, electrical connections, installation and labor costs have been incorporated using a lang factor of 3.5 in this preliminary cost analysis.

Prices for the various equipment were obtained from sources such as Peters and Timmerhaus<sup>40</sup>, Perry<sup>41</sup> and Garzon-Lopez<sup>5</sup>. These

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were then scaled up to account for inflation using the Marshall and Swift index. The thickener and disposal costs were obtained from the EPA publication on sludge treatment costs. The capital and operating costs for the various schemes are reported in Tables 5.2 to 5.6.

#### **5.4.2** Operational costs

The main operating costs in the pretreatment process would be incurred by the pump and the boiler. Other equipment other than those of the pretreatment process that have been considered are the thickener and those for the disposal of the sludge. For scheme IV the cost of a settler was also included.

Based on the design considerations for the first three schemes, the pump power was calculated as 30 kW (15kW for scheme IV). Thus, assuming the cost of electricity to be 5 cents per kWhr, the pump operating costs would be \$36 per day.

Energy requirements for the boiler would be 29.9x10<sup>6</sup> Btu/day. This can be calculated knowing the enthalpy of steam at 260°C to be 1202 Btu/lb. This corresponds to a methane requirement, in the case of a methane fired boiler, of 846 m<sup>3</sup>/day (energy content of methane - 35336 Btu/m<sup>3</sup>). Part of this energy requirement can be made up by the methane generated in the digester. Assuming a WAS COD concentration of 10,000 mg/L and a methane generation of 7.871 mmoles/g COD (from the 260°C run of series A), a WAS flow rate of 380 m<sup>3</sup> gives a volumetric methane production of 761 m<sup>3</sup>/day. The deficit of 85 m<sup>3</sup>/day must be supplied externally and constitutes the operational cost of the boiler. This corresponds to \$13.6 per day (cost

	Capital cost (\$)	O & M costs (\$ / yr)	
Thickener	180,000	14,000	
Polymer	30,000	40,000	
Disposal	700,000	150,000	
Total annual cost	910,000	204,000	
Amortized cost <sup>a</sup>	148,100	204,000	

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### Table 5.2 : Scheme I equipment capital and O & M costs

a - Amortization over a period of 10 years with a 10% annual interest rate

	Capital cost (\$)	O & M costs (\$ / yr)
Thickener	180,000	14,000
Pump	75,600	13,140
Heat Exchanger	107,100	
Boiler	52,500	5,000
Digester	135,800	
Disposal	300,000	70,000
Total annual cost	851,000	102,140
Amortized cost <sup>a</sup>	138,500	102,140

### Table 5.3 : Scheme II equipment capital and O & M costs

a - Amortization over a period of 10 years with a 10% annual interest rate . •

Capital cost (\$)	O & M costs (\$ / yr)
180,000	14,000
75,600	13,140
107,100	
52,500	49,500
300,000	70,000
715,200	146,640
116,400	146.640
	Capital cost (\$) 180,000 75,600 107,100 52,500 300,000 715,200 116,400

## Table 5.4 : Scheme III equipment capital and O & M costs

a - Amortization over a period of 10 years with a 10% annual interest rate

	Capital cost (\$)	O & M costs (\$ / yr)	
Settler	100,000	12,500	
Pump	52,500		
Heat Exchanger	75,250		
Boiler	35,000		
Digester	91,000		
Thickener	120,000	10,000	
Disposal	300,000	70,000	
Total annual cost	773,750	92,500	
Amortized cost <sup>4</sup>	111,100	92,500	

## Table 5.5 : Scheme IV equipment capital and O & M costs

a - Amortization over a period of 10 years with a 10% annual interest rate

	Amortized Capital cost (\$)	O & M costs (\$ / yr)	Total annual cost
Scheme I	148,100	204,000	352,100
Scheme II	138,500	102,140	240,640
Scheme III	116,400	146,640	263,040
Scheme IV	111,100	92,500	203,600

# Table 5.6 : Comparison of costs of the various schemes

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of methane \$0.16/m<sup>3</sup>). Thus a total operating cost of \$49.6 will be incurred if the first three schemes are used. For scheme IV the boiler energy requirements would be 14.95 x10<sup>6</sup> Btu/day which corresponds to a methane requirement of 423 m<sup>3</sup>/day. Since the digester generates 761 m<sup>3</sup> of methane per day, there is a surplus of methane in the order of 338 m<sup>3</sup> per day. This makes up for the operating cost of the pump. These calculations have been summarised in Tables 5.2 to 5.5.

#### 5.4.3 Summary

Table 5.6 summarises the costs that are shown in Tables 5.2 to 5.5. From the table it is evident that scheme IV with initial settling of the WAS has the least costs associated with it. On the other hand, the process without pretreatment shows the highest costs, with a large share being due disposal costs of the sludge.

### **CHAPTER VI: CONCLUSIONS AND RECOMMENDATIONS**

### 5.1 Conclusions

Effect on dewaterability

Pretreatment of the sludge at high temperature had a positive effect both on the rate of filtration as well as on the solids content of the cake formed. Cake solids of about 25% were easily achieved with pretreatment. Polymer addition was found to have very little effect on the dewaterability of the sludges thus doing away with the necessity of polymer addition. This represented a savings in operating costs.

Effect on solubilisation

The pretreatment pH and temperature had a significant effect on the solubilisation of the sludges. Higher degrees of solubilisation were achieved at higher pretreatment temperatures. For the same temperature, alkaline hydrolysis resulted in higher solubilisation than that obtained by autohydrolysis. Values of around 35-45% were reached at the higher temperatures with a solubilisation of 75.8% being achieved at 290°C with autohydrolysis. Greater solubilisation was linked to higher biodegradability in the batch digestion tests.

Effect on digestibility

In general, an increase in pretreatment temperature brought about an increase in the digestibility of the sludges, as seen from the gas generation data. Pretreatment increased the rate of methane production as well as the total amount of methane produced from the sludge. An increase of 101% was seen in the rate of gas production for

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the series E run at 180°C The short retention times used have overcome the toxicity reported at higher temperatures by other researchers. Changing the residence time in the reactor from about 10 seconds to about 130 seconds did not seem to have much of an effect on the digestibility of the sludges.

### Commercial capability

From the section on process design and cost estimation, a preliminary evaluation showed that the proposed additions would be more cost effective than a process without pretreatment. The best option was the scheme with the settling of WAS so that a smaller amount of sludge would have to be treated.

### 5.2 Recommendations

One of the aspects that could be investigated is the fact that only about half the input COD is converted to methane. A better understanding of the reasons behind this could lead to methods by which a more complete conversion to methane is possible. This problem could be studied by also pretreating the digested sludge to see whether further digestibility is possible.

Another aspect that has to be studied is a continuously run pilot scale facility. One aim would be to compare the results of this process with those of the present study which made use of batch digestion assays. This study could be used to reach some optimum pretreatment conditions which could show an overall profit commercially. This study would also enable us to check the validity of the assumptions made in the design and cost estimation.

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### **APPENDICES**

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### Appendix A

### **Derivation of Equation 3.1**

The derivation of the equation used to calculate the amount of gas produced is outlined below.

For a mixture of gases, the mole fraction of a particular component of the gas is given by :

$$\mathbf{x}_i = \mathbf{n}_i / \mathbf{n}_t = \mathbf{P}_i / \mathbf{P}_t$$

where,

x<sub>i</sub> - mole fraction of component i

n<sub>i</sub> - number of moles of component i

n, - total number of moles in gas mixture

P<sub>i</sub> - partial pressure of component i

 $P_t$  - total gas pressure

From the ideal gas law,

 $n_t = P_t V_g / R T$ 

which gives,

 $n_i = P_i V_g / R T$ 

 $V_g$  - Volume of the head space in the serum bottle

Working in a closed system (serum bottle) and using pressure lok syringe,

 $P_i = \alpha / 100$  atmospheres

where  $\alpha$  is the area of component i of the gas mixture reported as a percentage of the total area from the GC.

This gives,

 $n_i = \alpha V_g / 100 R T$ 

Here,

T - 310 K

R - 0.082 cc atm / mmol K

Therefore,

 $n_i = \alpha V_g \times 3.934 \times 10^{-4}$  mmoles

This was the equation used to convert the percentage of component i obtained from the GC to mmoles of that component.

# Appendix B

### Tabulated data

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Volume of filtrate (ml)	Time for filtration (min:sec)						
	Raw	Raw w/p	140°C	140°C w/p	170°C	170°C w/p	
0	0:00	<b>0:00</b>	0:00	0:00	0:00	0:00	
25	0:14	0:06	0:10	0:08	0:07	0:16	
50	1:00	0:14	0:28	0:35	0:45	2:45	
75	2:30	0:25	1:10	2:00	3:00	11: <b>0</b> 0	
100	4:45	0:36	2:30	5:00	10:30		
125	8:00	0:52	5:00	12:00			
150	11:30	1:10	9:00				
175	16:00	1:34	16:00				
200	23:50	2:20					
225	4:30						

Table B.1 : Data for Figure 4.3

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Volume of filtrate (ml)	Time for filtration (min:sec)						
	Raw	Raw w/p	260°C	260°C w/p	290°C	290°C w/p	
0	0:00	0:00	0:00	0:00	0:00	0:00	
25	0:14	0:06	0:11	0:06	0:07	0:07	
50	1:00	0:14	0:22	0:16	0:18	0:18	
75	2:30	0:25	0:41	0:34	0:28	0:32	
100	4:45	0:36	1:00	0:55	0:40	0:45	
125	8:00	0:52	1:20	1:17		1:00	
150	11:30	1:10	1:38	1:38	1:00	1:12	
175	16:00	1:34	1:58	2:04	1:15 ·	1:23	
200	23:50	2:20	2:20	2:24	1:30	1:34	
225		4:30	2:40	2:50	2:00	1:44	
240		•	3:00				

Table B.2 : Data for Figure 4.4

Volume of filtrate (ml)	Time for filtration (min:sec)						
	Raw	Raw w/p	220°C	220°C w/p	240°C	240°C w/p	
0	0:00	0:00	0:00	0:00	0:00	0:00	
25	0:13	0:05	0:10	0:04	0:12	0:06	
50	0:45	0:08	0:34	0:13	0:26	0:13	
75	1:45	0:15	1:00	0:27	0:41	0:25	
100	3:20	0:22	1:30	0:44	1:01	0:40	
125	5:45	0:32	1:57	1:05	1:23	1:01	
150	9:30	0:45	2:25	1:30	1:44	1:23	
175	15:00	1:04	3:00	1:54	2:10	1:45	
200	22:00		3:35	2:28	2:38	2:10	
225		3:00	4:50	3:00	3:18	2:49	

Table B.3 : Data for Figure 4.5

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Volume of filtrate (ml)	Time for filtration (min:sec)						
	Raw	Raw w/p	220°C	220°C w/p	240°C	240°C w/p	
0	0:00	0:00	0:00	0:00	0:00	0:00	
25	0:13	0:05	0:12	0:06	0:13	0:05	
50	0:45	0:08	0:35	0:21	0:32	0:10	
75	1:45	0:15	1:07	0:57	0:53	0:17	
100	3:20	0:22	1:45	1:29	1:12	0:35	
125	5:45	0:32	2:21	2:00	1:29	0:53	
150	9:30	0:45	2:57	2:35	1:49	1:09	
175	1 <b>5:00</b>	1:04	3:36	3:11	2:11	1:25	
200	22:00		4:17	3:53	2:29	1:39	
225		3:00	5:20		3:15		

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Table B.4 : Data for Figure 4.6

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Volume of filtrate (ml)	Time for filtration (min:sec)						
	Raw	Raw w/p	220°C	220°C w/p	240°C	240°C w/p	
0	<b>0:00</b>	0:00	0:00	0:00	0:00	0:00	
25	0:07	0:03	0:06	0:02	0:07	0:04	
<b>5</b> 0	0:14	0:03	0:06	0:02	0:16	0:10	
75	0:22	0:10	0:38	0:15	0:35	0:19	
100	0:34	0:14	1:05	0:45	0:51	0:35	
1 <b>25</b>	0:47	0:19	1:35	1:15	1:07	0:49	
150	1:06	0:24	2:00		1:21	0:57	
175	1:30	0:29	2:26	2:00	1:39	1:04	
200	2:00	0:39	3:07	2:23	1:57	1:11	
225	3:30	1:00		2:52	2:15	1:47	

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Table B.5 : Data for Figure 4.7

Volume of filtrate (ml)		Time for filtration (min:sec)						
	Raw	Raw w/p	260°C	280°C	300°C	300°С w/р	310°C	310°C w/p
0	0:00	0:00	0:00	0:00	0:00	0:00	0:00	0:00
25	0:07	0:03	0:10	0:07	0:07	0:05	0:07	0:03
50	0:14	0:06	0:22	0:17	0:17	0:21	0:13	0:07
<b>75</b>	0:22	0:10	0:45	0:33	0:32	1:05	0:23	0:15
100	0:34	0:14	1:01	0:53	0:50	1:45	0:39	0:19
125	0:47	0:19	1:16	1:10	1:15	2:23	0:55	0:26
150	1:06	0:24	1:28	1:26	1:28	3:00	1:06	0:32
175	1:30	0:29	1:43	1:39	1:44	3:28	1:17	0:39
200	2:00	0:39	2:09	1:54			1:29	
225	3:30	1:00		2:19	2:13	4:17	2:04	0:57

# Table B.6 : Data for Figure 4.8

Temperature % Solubilisation Raw 5.94 140°C 12.45 170°C 14.73 200°C 21.46 230°C 32.05 260°C 37.10 290°C 75.81

Table B.7 : Data for Figure 4.9

Temperature	% Solubilisation		
	39 rpm	79 rpm	
Raw	9.27	9.27	
160°C	21.06	25.48	
180°C	31.78	27.41	
200°C	36.05	40.49	
220°C	42.41	40.61	
240°C	51.42	45.91	
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Table B.8 : Data for Figure 4.10

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Tempe	rature	% Solubilisation		
		Autohydrolysis	Alkaline hydrolysis	
Rav	×	1.78	24.82	
180°	C		39.68	
200%	C		47.92	
220%	C	29.44	48.80	
240%	C	34.69	45.96	
260%	C	41.17		
280%	C	45.57		
300%	С	50.00		
310°	C	50.09		

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Table B.9: Data for Figure 4.11

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	Raw	140°C	170°C	200°C
<u> </u>		<u></u>		•
0	0	0	0	0
1	0.225	0.189	0.202	0.218
3	0.993	0.969	0.885	0.868
4	1.716	1.619	1.621	1.467
5	2.169	2.309	2.241	2.403
6	2.711	2.993	2.846	3.574
7	3.509	3.923	-3.388	4.709
8	4.284	4.572	4.116	5.004
9	4.522	4.998		5.906
10 、	4.802	5.179	4.777	5.984
12	5.546	6.455	6.058	7.402
14	5.599	6.363	5.975	7.642
15	5.696			8.078
16	5.546	6.529	6.097	8.267
18	5.672	7.033	6.611	8.397
20	5.907	6.769	6.124	8.111
21	5.925	6.684	6.169	8.052

Table B.10 : Data for Figure 4.12

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	Raw	230°C	260°C	290°C
		0	0	0
0	0.005	U 0 1 1 2	U 0.050	U
1	0.225	0.115	0.050	0 414
3	0.993	0.403	0.211	0.414
4	1.715	0.926	0.405	0.462
5	2.169	1.850	0.663	0.312
6	2.711	3.347	1.498	0.629
7	3.509	3.644	2.753	1.317
8	4.284	4.373	3.613	2.876
9	4.522	5.145	4.068	3.806
10	4.802	5.518	4.975	4.363
12	5.546	6.188	6.323	5.806
14	5.599	6.735		7.860
15	5.696	7.419	7.089	8.344
16	5.546	7.685	7.333	8.398
18	5 762	7 624	7 871	8 645
20	5 907		1.011	0.072
20 21	5.707			

 Table B.11 : Data for Figure 4.13

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		s/g COD)	on ( mmole	ne producti	Metha		Day
300°C	280°C	260°C	240°C	220°C	200°C	Raw	
C	0	0	0	0	0	0	0
0.027	0.017	0.015	0	0.085	0.209	0.481	2
0.063	0.008	0.007	0.144	0.466	1.713	1.872	5
	0.008	0.022	2.209	2.618	3.629	2.592	9
0.061	0.008	0.206	3.184	3.740	4.467	2.806	12
0.018	0.008	1.478	4.101	4.101	5.077	2.976	15
	0.008	3.618	4.585	5.394	5.348	3.248	21
	0.008	4.191	5.646	5.676	5.779	3.557	25
0.108	1.281	4.551	5.711	5.833	6.075	3.655	30

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Table B.12 : Data for Figure 4.14

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Day	]	Methane produ	ction (mmoles,	/g COD)	
	Raw	180°C	200°C	220°C	240°C
0	0	0	0	0	(
3	0.341	0.516	0.415	0.618	0.352
6	1.842	2.537	1.952	2.492	1.949
9	3.154	4.452	4.098	4.674	3.919
15	4.157	5.213	5.054	5.944	4.894
19	4.420	5.718	5.498	6.676	6.901
24	4.544	5.926	5.555	6.803	6.916
28	4.535	5.936	5.760	7.173	6.974

Table B.13 : Data for Figure 4.15

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Day	<b></b>	Meth	ane produ	ction (mn	holes/g CO	D)	
	Raw	1 <b>40°C</b>	160°C	180°C	200°C	220°C	240°C
· 0	0	0	0	0	0	0	C
2	0.307	0.337	0.354	0.245	0.122	0.068	0.044
5	1.387	1.516	1.414	1.037	0.473	0.414	0.397
9	2.321	3.441	3.657	3.097	1.861	1.724	1.882
14	2.616	4.072	4.420	4.389	4.247	4.175	3.923
20	2.507	4.048	4.410	4.346	4.346	4.756	5.059
27	2.886	4.337	4.857	4.638	4.708	5.141	5.573
35	3.320	4.880	5.369	5.275	5.319	5.774	6.320
41	3.458	5.006	5.482	5.483	5.565	6.080	6.555

Table B.14 : Data for Figure 4.16

Day		Meth	ane produ	ction (mn	noles/g CO	D)	
•	Raw	140°C	160°C	180°C	200°C	220°C	240°C
0	0	0	0	0	0	- 0	0
2	0	0.008	0.025	0.003	0.007	0.087	0.057
7	0.002	0.006	0.003	0.003	0.057	0.120	<b>0</b> .1 <b>57</b>
10	0.012	0.023	0.084	0.155	0.257	0.467	0.706
13	0.009	0.051	0.144	0.354	0.831	1.408	1.828
17	0.033	0.108	0.404	1.398	2.557	2.982	3.216
22	0.042	0.168	1.433	2.648	3.108	3.494	3.817
28	0.102	0.200	2.247	2.967	3.473	3.607	4.127
43	0.216	0.354	3.727	.3.637	4.853	5.122	5.865
49	0.226	0.580	3.747	4.067	4.758	5.161	5.895

Table B.15 : Data for Figure 4.17

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Day		Methane	production (	mmoles/g CC	)D)	
<u></u>	Raw	140°C	160°C	180°C	200°C	220°C
0	0	0	0	0	0	0
2	0.691	1.101	0.995	1.112	1.042	0.850
4	2.020	3.728	3.426	3.784	3.230	2.513
6	2.866	4.575	5.193	5.492	<b>4.96</b> 1	4.762
9	3.461	4.982	5.732	6.019	5.993	6.194
12	4.262	5.767	6.606	6.930	6.836	7.183
19	4.615	5.649	6.369	6.578	6.669	7.075

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Table B.16 : Data for Figure 4.18

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Day	Meth	nane production	( mmoles/g C	0D)
<del></del>	Raw	160°C	180°C	200°C
)	0	0	0	0
	0.621	0.555	0.554	0.487
•	1.954	1.850	1.510	1.020
5	2.552	3.729	3.335	2.206
9	3.503	4.897	5.052	4.392
2	4.981	6.681	6.467	6.251
9	5.290	6.991	7.183	7.470

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Table B.17 : Data for Figure 4.19

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