VOLATILE FATTY ACID PRODUCTION DURING THERMOPHILIC AEROBIC DIGESTION PRE-TREATMENT

BY

KAREN BONNIE M^{c}INTOSH

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Civil Engineering
University of Manitoba
Winnipeg, Manitoba

THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

*****

COPYRIGHT PERMISSION PAGE

VOLATILE FATTY ACID PRODUCTION DURING THERMOPHILIC AEROBIC DIGESTION PRE-TREATMENT

BY

KAREN BONNIE McINTOSH

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

ABSTRACT

This study was initiated to demonstrate the application of thermophilic aerobic digestion pre-treatment as a method of producing volatile fatty acids (VFA) for potential use as a denitrification carbon source. In order to achieve this goal, volatile fatty acid production and nitrogen release were examined under two oxygenation states with detention times ranging from 6 to 24 hours at 55°C. The semi-continuous laboratory scale reactors, with 3 L operating volumes, were fed primary solids obtained from the City of Winnipeg's North End Water Pollution Control Centre.

VFAs accumulated under all oxygen-deprived conditions (O_2 flow rate: 0.025 $m^3/m^3 \cdot h$; ORP: -330 mV to -390 mV) and the production rate increased with increasing retention time from 0.029 mg HAc/mg VS·d at 6 hours to 0.057 mg HAc/mg VS·d at 24 hours. VFAs were consumed under the oxygen-satisfied condition (O_2 flow rate: 0.14 $m^3/m^3 \cdot h$; ORP: -10 mV to -225 mV). The VFA specific production rate did not appear to vary with the influent solids concentration.

Acetic acid constituted the largest fraction of VFAs in both the oxygen-satisfied and oxygen-deprived experiments and ranged from 59.6% to 64.3%. The oxygen-satisfied condition exhibited much higher propionic acid concentrations (average of 30.3%) than did the oxygen-deprived conditions (average of 17.2%).

Ammonia nitrogen accumulated under all conditions studied, but more so with a decreasing oxygen supply and increasing retention time. Under the oxygen-deprived condition, the 6 hour SRT/HRT exhibited the lowest ammonia nitrogen increase of 41.6% while the 24

hour SRT/HRT exhibited the highest at 142.8%. The soluble organic carbon to ammonia ratio increased with a decreasing oxygen supply and detention time. Returning the VFA-rich supernatant to the plant influent would increase the overall chemical oxygen demand to ammonia ratio and aid in the denitrification process.

This thesis is dedicated to my father

who encouraged me to do my graduate studies

but never got the chance to see me finish.

ACKNOWLEDGEMENTS

I would like to thank my family for their support and encouragement and Dr. Oleszkiewicz for his patience and insights. In addition, I wish to express my sincere gratitude to the City of Winnipeg's Water and Waste Department for providing financial and technical support and the primary sludge used in this study.

CONTENTS

		Page
ABSTRACT		iii
ACKNOWLEDGEMENTS		vi
LIST OF ILLUSTRATIONS		xi
LIST OF TABLES		xiii
CHAPTER 1 - INTRODUCTION		1
CHAPTER 2 - LITERATURE REVIEW		3
2.1	**BIOLOGICAL NITROGEN REMOVAL PROCESS**	3
	2.1.1 Forms of Nitrogen	3
	2.1.2 Theory of Nitrogen Removal	3
	2.1.3 Summary	7
2.2	**DUAL DIGESTION PROCESS**	7
	2.2.1 Technology Development	7
	2.2.2 Treatment Configuration	8
	2.2.3 Summary	9
2.3	**THERMOPHILIC AEROBIC DIGESTION ENVIRONMENTAL AND OPERATIONAL PROCESS CONTROL PARAMETERS**	9
	2.3.1 Temperature	10
	2.3.2 Influent Solids	12
	2.3.2.1 Solids Retention Time	12
	2.3.2.2 Solids Concentrations	13
	2.3.2.3 Solids Loadings	13
	2.3.3 Oxygen Requirements	13
	2.3.4 Oxidation Reduction Potential	14
	2.3.5 pH and Alkalinity	17
	2.3.6 Summary	18
2.4	**THERMOPHILIC AEROBIC DIGESTION PERFORMANCE**	19
	2.4.1 Organic Carbon Transformation	19
	2.4.1.1 Volatile Solids Reduction	19
	2.4.1.2 Chemical Oxygen Demand Solubilization	21

2.4.2 Volatile Fatty Acids 22
2.4.3 Ammonia Nitrogen 24
2.4.4 Settleability/Dewaterability 25
2.4.5 Microbial Metabolism in TAD Reactor 27
2.4.6 Summary 31

CHAPTER 3 - RESEARCH OBJECTIVES 33

CHAPTER 4 - EXPERIMENTAL DESIGN: METHODS AND ANALYTICAL PROCEDURES 34

4.1 EXPERIMENTAL SET-UP AND OPERATION 34
4.1.1 Sludge Source 34
4.1.2 System Configuration 34
4.1.3 Operation 37

4.2 EXPERIMENTAL SAMPLING 39
4.2.1 Sludge Sampling 39
4.2.2 Discharge Gas Sampling 39

4.3 LABORATORY ANALYSIS AND DISCUSSION OF METHOD ERROR 40
4.3.1 Solids 40
4.3.1.1 Analysis Method 40
4.3.1.2 Method Error 40
4.3.2 Dissolved oxygen 42
4.3.2.1 Analysis Method 42
4.3.2.2 Method Error 42
4.3.3 Discharge Gas - Methane, Carbon Dioxide and Air 42
4.3.3.1 Analysis Method 42
4.3.3.2 Method Error 42
4.3.4 pH and Alkalinity 44
4.3.4.1 Analysis Method 44
4.3.4.2 Method Error 44
4.3.5 Soluble Chemical Oxygen Demand 44
4.3.5.1 Analysis Method 44
4.3.5.2 Method Error 45
4.3.6 Volatile Fatty Acids 46
4.3.6.1 Analysis Method 46
4.3.6.2 Method Error 46
4.3.7 Ammonia Nitrogen 46
4.3.7.1 Analysis Method 46
4.3.7.2 Method Error 47

*4.3.8 **Sludge Dewaterability*** 47
4.3.8.1 Analysis Method 47
4.3.8.2 Method Error 47

CHAPTER 5 - RESULTS AND DISCUSSION 48

5.1 ACCLIMATION 48

5.2 ENVIRONMENTAL AND OPERATIONAL PROCESS CONTROL PARAMETERS 49
5.2.1 Influent Solids 49
5.2.1.1 Influent Solids Concentrations 49
5.2.1.2 Solids Loading 53
5.2.2 Oxygen Supply 53
5.2.3 Dissolved Oxygen 55
5.2.4 TAD Discharge Gas 55
5.2.5 Oxidation Reduction Potential 56
5.2.6 Alkalinity 59
5.2.7 pH 63
5.2.8 Summary 64

5.3 THERMOPHILIC AEROBIC DIGESTION PERFORMANCE 65
5.3.1 Particulate Organic Carbon Transformation 65
5.3.1.1 Volatile Solids Reduction 65
5.3.1.2 Chemical Oxygen Demand Solubilization 70
5.3.2 Volatile Fatty Acids 75
5.3.2.1 Volatile Fatty Acid Production 75
5.3.2.2 Volatile Fatty Acid Composition 78
5.3.2.3 Volatile Fatty Acid Contribution to Chemical Oxygen Demand 83
5.3.3 Ammonia Nitrogen 84
5.3.3.1 Ammonia Nitrogen Production 84
5.3.3.2 Soluble Organic Carbon to Ammonia Ratio 87
5.3.4 Settleability/Dewaterability 88
5.3.5 Summary 89

CHAPTER 6 - ENGINEERING SIGNIFICANCE 92

6.1 FULL SCALE IMPLICATIONS OF EXPERIMENTAL RESULTS 92
6.1.1 Comparison of TAD Results with Conventional Fermentation Processes 92

6.1.2 Impact of Supernatant Recycle to Treatment Plant 94
6.1.3 Applicability of Lab Scale Results to Full Scale Results 96
6.1.4 Summary 96

6.2 BENEFITS OF DUAL DIGESTION PROCESS 96
6.2.1 Particulate Organic Carbon Transformation 96
6.2.2 Pathogen Reduction 98
6.2.3 Digester Foaming Control 100
6.2.4 Digester Gas Yield 100
6.2.5 Dewaterability 102
6.2.6 Summary 102

CHAPTER 7 - CONCLUSIONS AND RECOMMENDATIONS 104

7.1 CONCLUSIONS 104

7.2 RECOMMENDATIONS 107

BIBLIOGRAPHY 109

APPENDIX A - METABOLIC PATHWAYS 117

APPENDIX B - DATA 121

APPENDIX C - BALANCE CALCULATIONS AND BALANCE ERRORS 145

APPENDIX D - RECYCLE CALCULATIONS 149

LIST OF ILLUSTRATIONS

	Page
Figure 1. Nitrogen cycle in biological nitrogen removal.	4
Figure 2. Growth reaction rate constant as a function of temperature.	11
Figure 3. Measured ORP values relative to various sludge digestion regimes.	16
Figure 4. Biochemical model of acetate production in TAD under (a) microaerobic and (b) anaerobic conditions.	29
Figure 5. Thermophilic aerobic digester schematic.	35
Figure 6. Thermophilic aerobic digester set-up.	36
Figure 7. Average error of primary solids measurements.	41
Figure 8. Average error of TAD solids measurements.	41
Figure 9. Average error of discharge gas measurements.	43
Figure 10. Average error for SCOD measurements	45
Figure 11. Influent primary solids concentrations during OS24.	50
Figure 12. Influent primary solids concentrations during OD24.	51
Figure 13. Influent primary solids concentrations during OD18.	51
Figure 14. Influent primary solids concentrations during OD12.	52
Figure 15. Influent primary solids concentrations during OD6.	52
Figure 16. Variation of ORP with oxygenation state.	57
Figure 17. ORP trace patterns for OS24 and OD24.	58
Figure 18. Comparison of percent volatile solids measured in TAD influent and TAD effluent during OS24, OD24, OD18, OD12, and OD6.	66
Figure 19. Comparison of grams of total VS measured during OS24, OD24, OD18, OD12, and OD6.	68

Figure 20. Aerobic digester percent VS reduction design curve. 69

Figure 21. Primary and TAD Sludge soluble chemical oxygen demand concentrations during OS24 experiment. 73

Figure 22. Primary and TAD Sludge soluble chemical oxygen demand concentrations during OD24 experiment. 73

Figure 23. Primary and TAD Sludge soluble chemical oxygen demand concentrations during OD18 experiment. 74

Figure 24. Primary and TAD Sludge soluble chemical oxygen demand concentrations during OD12 experiment. 74

Figure 25. Primary and TAD Sludge soluble chemical oxygen demand concentrations during OD6 experiment. 75

Figure 26. Variation of specific VFA production rate with feed VS concentration during OD24. 78

Figure 27. Percent VFA distribution during OS24. 81

Figure 28. Percent VFA distribution during OD24. 81

Figure 29. Percent VFA distribution in OD18. 82

Figure 30. Percent VFA distribution in OD12. 82

Figure 31. Percent VFA distribution in OD6. 83

Figure 32. Increase in ammonia nitrogen in thermophilic aerobic reactors. 85

Figure 33. Comparison of soluble organic carbon to ammonia nitrogen ratios. 87

Figure 34. Percent solids capture in centrifuge. 89

Figure A1. Glycolysis. 118

Figure A2. The Entner-Doudoroff Pathway. 119

Figure A3. The Pentose Phosphate Pathway. 120

LIST OF TABLES

	Page
Table 1. Average Influent Primary Sludge Solids Concentrations with Standard Deviations	50
Table 2. Solids Loading to Thermophilic Aerobic Digesters	53
Table 3. Maximum Oxygen Requirement Based on Volatile Solids Oxidised	54
Table 4. TAD Discharge Gas Constituents	56
Table 5. Comparison of Measured to Expected Total Alkalinity	59
Table 6. Quantity of Bicarbonate Alkalinity Available to Neutralise Additional VFA	62
Table 7. Comparison of pH Variations in the TADs	64
Table 8. Calculated TAD Temperature ··Detention Time Products for OS24, OD24, OD18, OD12 and OD6	69
Table 9. Chemical Oxygen Demand Solubilization Efficiency	71
Table 10. COD Specific Solubilization Rate as a Function of Oxygenation State and Retention Time.	72
Table 11. VFA Specific Production Rate as a Function of Oxygenation State and Retention Time	76
Table 12. Average Percent Volatile Fatty Acids Constituents	79
Table 13. Average Soluble Chemical Oxygen Demand Attributed to the Presence of Volatile Fatty Acids	84
Table 14. Un-ionized Ammonia Percentage versus Temperature and pH	86
Table 15. Comparison of SCVFA Production in TAD with other Conventional Fermentation Processes at Ambient Temperatures	93
Table 16. Comparison of Volatile Fatty Acids Composition Produced in Various Full Scale and Pilot Projects	93
Table 17. Average Composition of NEWPCC Wastewater	94

Table 18. Estimated Effects of TAD Supernatant Recycle on Influent Flow Concentrations 95

Table 19. Volatile Solids Degradation in Dual Digestion Process 97

Table D1. Supernatant Recycle Volumes 151

Table D2. Estimated Effect of TAD Supernatant Recycle on Influent Flow Concentrations 151

CHAPTER 1

INTRODUCTION

The province of Manitoba has surface water quality objectives which define minimum levels of protection for different uses. These uses include domestic consumption, industrial use, agricultural use, recreation and maintenance of aquatic species, wildlife, and waterfowl (Williamson, 1988a). To protect both aquatic and wildlife, objectives are included for numerous parameters including un-ionized ammonia (NH_3), dissolved oxygen, toxic metals and pesticides. The maximum acceptable NH_3 concentration is defined by the ambient pH and temperature and ranges from 0.0184 to 0.05 mg/L in water with a temperatures of 0 to 30°C and a pH of 6.5 to 9.0. Currently these limits are often being exceeded in the Red and Assiniboine Rivers due to large quantities of ammonia being released from the City of Winnipeg's wastewater treatment facilities in combination with the pH, temperature and low flow.

In order to actualise the provincial regulations for un-ionized ammonia, the City of Winnipeg executed a study into the possibility of modifying their existing wastewater treatment plants to achieve nitrogen removal. A full scale study on nitrification was undertaken at the North End Wastewater Pollution Control Centre (NEWPCC). In spite of the fact that a high degree of nitrification was achieved, the long term sustainability of the process was found to be arduous. Consequently, the city approached the Environmental Engineering Department at the University of Manitoba to investigate various possibilities of ammonia removal in pure oxygen

reactors. Bench scale reactors were subsequently set-up and operated to study both nitrification using a closed single stage activated sludge pure oxygen reactor, and nitrification-denitrification using a pre-denitrifying closed activated sludge pure oxygen reactor. Results from the nitrification-denitrification experiments indicated that a carbon deficit hindered pre-denitrification (Oleszkiewicz *et al.*, 1995).

According to literature, numerous carbon sources have been used for denitrification at other locations such as, brewery wastes, methanol and volatile fatty acids (VFA) produced through fermentation processes. Methanol is used in many locations as a readily assimilable carbon, however, it has the drawback of continuous price increases.

During many thermophilic aerobic digestion (TAD) studies reports of VFA increases have been made. For example, Baier and Zwiefelhofer (1991) reported VFA increases of 146% from 2470 mg/L to 6081 mg/L after aerobic thermophilic pre-treatment at the Thun Treatment Plant and Kelly (1990) working with an autothermal thermophilic aerobic digester (ATAD) at Salmon Arm, BC, found VFA concentrations of up to 10,000 mg/L were reached in the first stage digester. Since this method of VFA production has not been fully investigated, this study was initiated using primary sludge obtained from the NEWPCC. Although not examined in this study, the VFAs produced would potentially be used as a carbon source for denitrification. In order to achieve this goal, the effects of retention time, oxygen delivery and influent characteristics on the conversion of volatile solids to short chain volatile fatty acids and nitrogen release are examined.

CHAPTER 2

LITERATURE REVIEW

2.1 BIOLOGICAL NITROGEN REMOVAL PROCESS

2.1.1 Forms of Nitrogen

Nitrogen occurs in water and wastewater in four forms: organic nitrogen, ammonia nitrogen (NH_4^+-N), nitrite (NO_2^-), and nitrate (NO_3^-). The harmful effects of ammonia nitrogen and nitrate nitrogen on the receiving body of water are well documented by many researchers. The negative effects include: deoxygenation due to nitrification of ammonia, toxicity by un-ionized ammonia, and an increase in algae blooms causing water quality deterioration. Significant concentrations of nitrates in drinking water also cause a condition known as methamoglobinaemia in infants (Metcalf and Eddy, 1991)

2.1.2 Theory of Nitrogen Removal

Nitrogen removal during wastewater treatment is generally accomplished by one of three methods: assimilation, denitrification, and volatilization (as ammonia gas with pH increase) (Oleszkiewicz, 1995-a). The steps involved in biological nitrogen removal are illustrated in Figure 1.

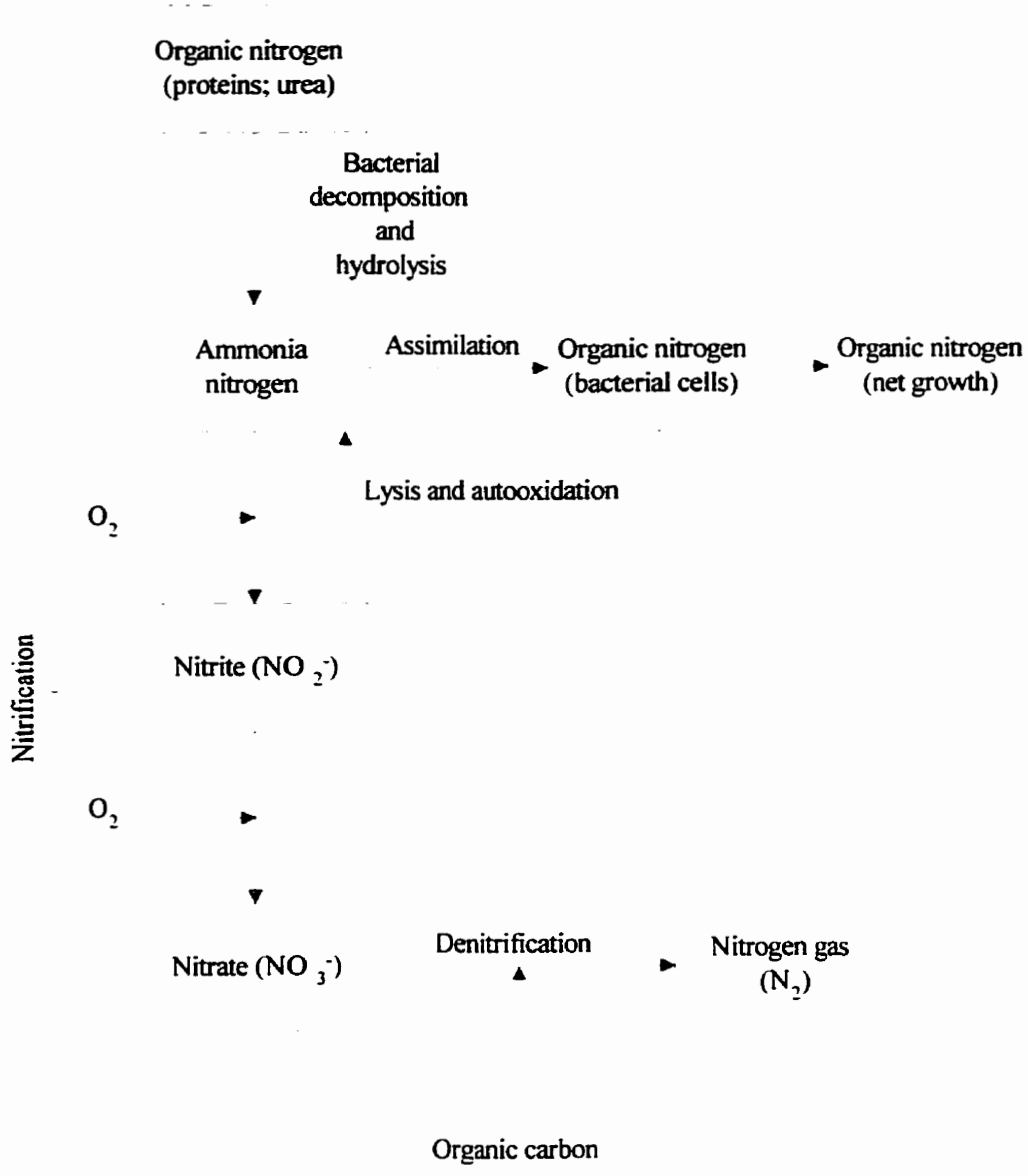


Figure 1. Nitrogen cycle in biological nitrogen removal. Process involves four biochemical steps: hydrolysis & deamination, assimilation, nitrification, and denitrification (Metcalf and Eddy, 1991).

Nitrification is carried out by autotrophic micro-organisms which use inorganic carbon

as the carbon source. The reaction is in two steps as follows (Metcalf and Eddy, 1991):

1) Oxidation of ammonium to nitrite by the members of the genera *Nitrosomonas* and *Nitrosococcus*

$$55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_5H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3 \qquad (1)$$

2) Oxidation of nitrite to nitrate by the members of the genera *Nitrobacter* and *Nitrosocystis*

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7O_2N + 3H_2O + 400NO_3^- \qquad (2)$$

Denitrification is accomplished by facultative heterotrophs (e.g. *Pseudomonas*) which use organic carbon as a source of energy and carbon and NO_3^- as the final electron acceptor. The following is a typical stoichiometric equation for denitrification (EPA, 1993):

$$NO_3^- + 5/6CH_3OH + 1/6H_2CO_3 \rightarrow 1/2N_2 + 4/3H_2O + HCO_3^- \qquad (3)$$

Assuming that anoxic conditions are maintained, the denitrification rate is solely limited by the amount and nature of the carbon source. The slowest denitrification rates correspond to endogenous carbon (carbon derived for cell lysis) and the highest are reported for methanol (Oleszkiewicz, 1995-b). Henze *et al.* (1994) indicated that the denitrification rates for directly

metabolisable COD (e.g. acetic acid) are 10-20 mg N/g VSS·h, easily degradable (e.g. lower amino acids) are 2 - 4 mg N/g VSS·h and the slower degradable components of the wastewater (e.g. complex carbohydrates, proteins) are 0.2 - 0.5 mg N/g VSS·h. Oleszkiewicz (1995-b), proposes that a typical specific rate is 10 mg NO_3^--N/g VSS·h.

Fass *et al.* (1994) evaluated the possibility of wastewater denitrification using VFAs as the sole carbon and electron source in an activated sludge culture continuously fed with a mixture of acetate, propionate, butyrate and valerate. They concluded that, acetate, propionate, butyrate and valerate can all act as carbon sources in denitrification. The five predominant strains in the denitrifying bacterial biomass were *Ochrobactrum anthropi*, *Moraxella lacunata*, *Pseudomonas testosteroni*, *Paracoccus denitrificans* and *Pasteurella gr. EF4*. Acetate, butyrate and valerate and the mixture of the 4 gave identical denitrification rates (20 mg NO_3^--N/g SS·h) and identical carbon consumption rates (60 mg C /g SS·h). Whereas propionate was almost not metabolised (3 mg NO_3^--N /g SS·h and 8 mg C /g SS·h).

Similarly, Æsøy. A and H. Ødegaard, (1994) investigated how efficiently biologically hydrolysed sludge is utilised as a carbon source. Their results showed that only the volatile fatty acids in the hydrolysed sludge were utilised as a carbon source. Their maximum denitrification rate was 23.6 mg NO_3^--N /g VSS·h.

The required carbon to nitrogen ratio is reported to range depending on the design and type of treatment process. The optimal C/N ratio is generally agreed to be 0.94 to 1.05, when methanol is used as the carbon source (Narkis *et al.*, 1979, Smith *et al.*, 1972 and Timmermans and Van Haute, 1983). EPA (1993) report values for methanol utilisation from 2.5 to 3.0 g methanol per gram of nitrate nitrogen reduced. Caponetto and Oleszkiewicz (1993) found that

the ratio of carbon utilised to be approximately 1 g SOC/g NO_3^--N.

The stoichiometric consumption ratio between soluble COD and nitrate was found to be 4.5 ± 0.6 mg COD_s/mg NO_3^--N by Æsøy. A and H. Ødegaard, (1994). Abufayed and Schroeder (1986) recommend a COD/N ratio of greater than 7 for an efficient denitrification process. A C/N ratio of 4-6 g BOD_5/g total N was suggested by Rusten and Eliassen (1993).

2.1.3 Summary

Nitrogen has many harmful effects on the receiving body of water, including the toxicity of ammonia, eutrophication, and deoxygenation. In the nitrification-denitrification process, denitrification is solely limited by the nature and amount of carbon assuming that anoxic conditions are maintained. Acetate, propionate, butyrate and valerate can all be used as a carbon source in denitrification. Acetate, butyrate and valerate however, have higher denitrification rates (20 mg NO_3^--N /g SS·h) and carbon consumption rates (60 mg C /g SS·h) over propionate (3 mg NO_3^--N /g SS·h and 8 mg C /g SS·h). The amount of carbon required to nitrogen varies depending on the design and treatment process. In general a COD/N ratio of greater than 7 is required for efficient denitrification.

2.2 DUAL DIGESTION PROCESS

2.2.1 Technology Development

Anaerobic mesophilic digestion of primary and secondary sludges from wastewater treatment has been a common practice in Europe for more than 35 years. However, rising

demands in sludge quality for agricultural land application left the sludge produced unable to meet the sludge standards. Dual digestion, which is also known as aerobic thermophilic pre-treatment (ATP) was consequently developed by the Union Carbide Corporation in 1975 (Messenger *et al.*, 1989) to meet this rising demand and is now widely used in Europe as a means of effective pasteurisation of sludge (Baier *et al.*, 1991).

2.2.2 Treatment Configuration

The dual digestion process consists of a thermophilic aerobic digestion (TAD) reactor upstream of the conventional mesophilic anaerobic digester. The TAD reactor operates at elevated temperatures, which means faster rates of biological reactions, faster sludge stabilisation, shorter retention times, smaller tanks, lower capital costs, and a pasteurised product. TAD reactors operate at short retention times of normally 1 day or less (EPA, 1990). The operation cycle is discontinuous; several times per day the aeration and mixing are stopped and stabilised sludge is discharged from the reactor to the sludge/sludge heat exchanger thus lowering the level in the reactor (EPA, 1990). Gravity thickened cold raw sludge is then fed to the second chamber of the exchanger. TAD sludge is thickened prior to digestion to minimise the required tank size and to limit the energy requirements for mixing and heating (EPA 1990).

In the exchanger raw sludge is preheated while the TAD reactor effluent cools down to mesophilic temperatures (40°C). The preheated raw sludge is then transferred to the TAD reactor where aeration and mixing start again. No additional raw sludge is fed for a period of time to maintain the undisturbed detention required for disinfection. The period of undisturbed detention time depends on the temperature and is controlled by the time-temperature

requirements for disinfection. This type of feeding avoids short circuiting and contamination of the pasteurised sludge. Depending on the operating conditions, TAD reactors may be either autothermal (ATAD) or an external source of heat may be required.

The cooled TAD effluent is then fed to the mesophilic anaerobic digester which operates with a 8 to 10 day retention period. Shorter retention periods can be achieved as compared to the conventional mesophilic digester since the feed is partially treated and "conditioned".

2.2.3 Summary

The dual digestion or aerobic thermophilic pre-treatment process consist of an thermophilic aerobic digestion reactor with a ± 1day retention period upstream of a 8 to 10 day mesophilic digester. Shorter periods in the mesophilic digester are achievable as compared to the conventional mesophilic digester since the sludge has been pre-treated in the TAD reactor.

2.3 THERMOPHILIC AEROBIC DIGESTION ENVIRONMENTAL AND OPERATIONAL PROCESS CONTROL PARAMETERS

Thermophilic aerobic digestion products are markedly affected by the characteristics of the wastewater and environmental and operational parameters. Environmental and operational parameters include dissolved oxygen (DO), pH, temperature, oxidation-reduction potential (ORP), solids retention time (SRT), hydraulic retention time (HRT), and solids loadings.

2.3.1 Temperature

Although both chemical and biochemical reactions are likely occurring in TAD reactors, biochemical reactions are assumed the predominant chemistry. Since bacterial growth and sequential sludge degradation rates respond to temperature, Hamer and Bryers (1985) proposed the division of five regimes of growth as follows:

1)	Psychrophilic	10°C
2)	Mesophilic	15-35°C
3)	Thermotolerent strains	40-50°C
4)	Thermophilic	50-70°C
5)	Caldoactive	75°C

In aerobic processes, for temperatures up to 40°C, the reaction rate behaviour of a biological process is usually expressed in the following form:

$$K_T = K_{Tref}\,\Theta^{(T-Tref)} \qquad (4)$$

where,

K_T = reaction rate constant at temperature, T

K_{Tref} = reaction rate constant at reference temperature

Θ = temperature activity coefficient,

T = temperature, °C

Tref = reference temperature, °C

Typical reported values of Θ range from 1.00 to 1.08. This relationship results roughly in a doubling of the reaction rate of a biological process with an increase of 10°C in temperature (Metcalf and Eddy, 1991). Kambhu and Andrew (1969) report that at temperatures beyond 45°C the reaction rate does not follow the Arrhenius relationship but is expressed as a series of connected straight line segments with a maximum occurring at 55°C and decreasing to zero at a temperature of 75°C as shown in Figure 2.

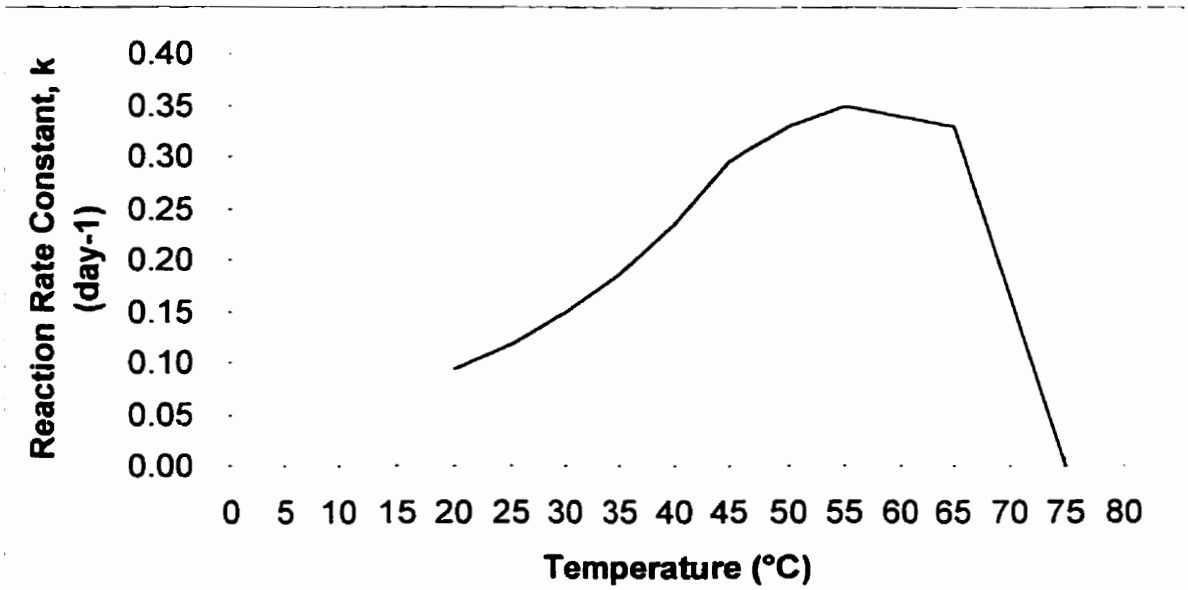


Figure 2. Growth reaction rate constant as a function of temperature. Reaction rate constant is assumed to be 0.094 day^{-1} at 20°C with a temperature coefficient of 1.047 (Kambhu and Andrew, 1969).

In aerobic processes, optimal temperatures exist but because of the large number of bacterial strains, no clear optimums are apparent (Grueninger, 1984). As with aerobic processes, the activity in obligate anaerobic processes increases, but to a lesser extent. It is generally accepted that two optimum activities are observed at 35°C and at 53°C.

Sonnleitner and Feichter (1983a) found that as the temperature increases in the thermophilic range, the number of competing strains decreases. For example, 100 to 1000 times fewer organisms could grow at 70°C than at 50-55°C. In addition, at these higher temperatures (70°C) the maintenance energy needs are relatively high for repair and replacement of cellular structures destroyed in the high temperature environment. For this reason, Loll (1984) suggests that an aerobic thermophilic degradation system should not be operated above 65°C (decay rate increases as the temperature increases above 65°C).

2.3.2 Influent Solids

2.3.2.1 Solids Retention Times

The solids retention time (SRT) is the average time allowed for a micro-organism to remain in the reactor. The SRT is an operational parameter which can be used as a selective factor by imposing a stress on bacterial communities (Elefsiniotis, 1993). TAD reactors operate at short retention times of normally 18 to 24 hours (Baier and Zwiefelhofer, 1991). However, longer detention times have been used. For example, Messenger (1989) at Milnerton utilised a first stage thermophilic reactor with a 1.25 day retention period. Similarly, the pre-treatment reactor at Thun operated with a 1.57 day residence time and at the same time experienced VFA increases of 146% from 2470 to 6081 mg/L.

2.3.2.2 Solids Concentrations

The EPA ATAD Design Manual recommends that sludge is thickened to 4-6% TSS (of which at least 2.5% is mostly biodegradable volatile solids) (EPA, 1990). However, this guideline is based on heat production rather than VFA production. This concentration can usually be accomplished by gravity thickening. In previous dual digestion studies, average total solids (TS) concentrations ranged from 3.0% (Pagilla *et al.*, 1996) to 3.8% and volatile solids (VS) concentrations were approximately 3.0% (Messenger *et al.* 1989).

2.3.2.3 Solids Loadings

Solids loadings for thermophilic reactors have been reported to vary. Loading rates of 12-15 kg TS/m^3·d are considered intermediate (Jewel *et al.*, 1982). However, loadings as high as 30 kg TS/m^3·d in pre-treatment facilities have been reported (Kelly, 1990; Messenger, 1989).

2.3.3 Oxygen Requirements

The amount of oxygen consumed to volatile solids oxidised is dependent on the composition of the volatile solids. Theoretical oxygen requirements are about 2.9 kg O_2/kg of fats (palmiepic acid), 1.65 kg O_2/kg of protein ($C_4H_{6.1}O_{1.2}N$), 1.6 kg O_2/kg of carbohydrate (glucose) and 1.4 kg O_2/kg of biomass (Elefsiniotis, 1993). For the typical ratio of fats, proteins, and carbohydrates in municipal sludge the design oxygen requirement is concluded to be about 2 kg O_2/kg VS destroyed (Kelly, 1990). For comparison sake, Morgan *et al.* (1984) reports values from 2.03 to 2.60 kg O_2/kg VS destroyed, Jewell (1978, 1979) reports values

from 1.57 to 4.59 kg O_2/kg VS destroyed, and Loll (1984) and Wolf (1982) suggests valves of 0.7 to 1.0 kg O_2/kg VS destroyed.

It is well known that higher temperatures increase the vapour pressure, diffusivity and ionization of many compounds, and decrease viscosity and gas solubility (Zeikus 1979). Hamer and Bryer (1985) however, showed on the basis of work by Scheibel (1954), that the oxygen diffusion coefficient in water increases markedly with increasing temperature and the increase largely compensates for the reduction in oxygen solubility with increasing temperatures.

Oxygen transfer efficiency (OTE) in ATADs has often proven to be higher than that measured with the standard ASCE aeration tests. Jewell and Kabrick (1980) found the oxygen transfer efficiency was only 2-3% when measured at 60°C in water using the DeLaval aerator. However, during operation at design temperatures with sludge, OTE always exceeded 12% and was sometimes as high as 23%. Jewell and Kabrick concluded that the ASCE standard tests do not necessarily reflect OTE in ATAD systems. Boulanger (1995) reports OTE of 31% under anoxic conditions and 67% under aerated anaerobic conditions. Due to the difficulty in measuring OTE, design is usually based upon empirical values such as air flows with a given type of aeration system (Boulanger, 1995).

2.3.4 Oxidation Reduction Potential

Oxidation reduction potential (ORP) is a measurement of the activity of oxidation-reduction reactions in an aqueous environment. ORP in a sewage sludge solution is affected by many parameters, including pH , DO, NOx and PO_4 concentrations (Peddie *et al.*, 1988).

The ORP can also indicate the aerobic state of a solution as reported by Boulanger

(1995) and Koch *et al.* (1988). Koch *et al.* (1988) showed that for a Bio-P pilot plant. 50 to 100 mV could be interpreted as aerobic respiration or oxygen reduction, -75 to -225 mV interpreted as anaerobic respiration (anoxic) or nitrate reduction, and -300 to -450 mV interpreted as anaerobic fermentation or organic reduction. Boulanger (1995) set target ORP values as follows: oxygen-deprived: ORP $\leq$ -200 mV; oxygen-satisfied: -200 $\leq$ ORP $\leq$ 100; oxygen-excess: ORP $\geq$ 100. Figure 3 illustrates measured values of ORP relative to various sludge digestion regimes.

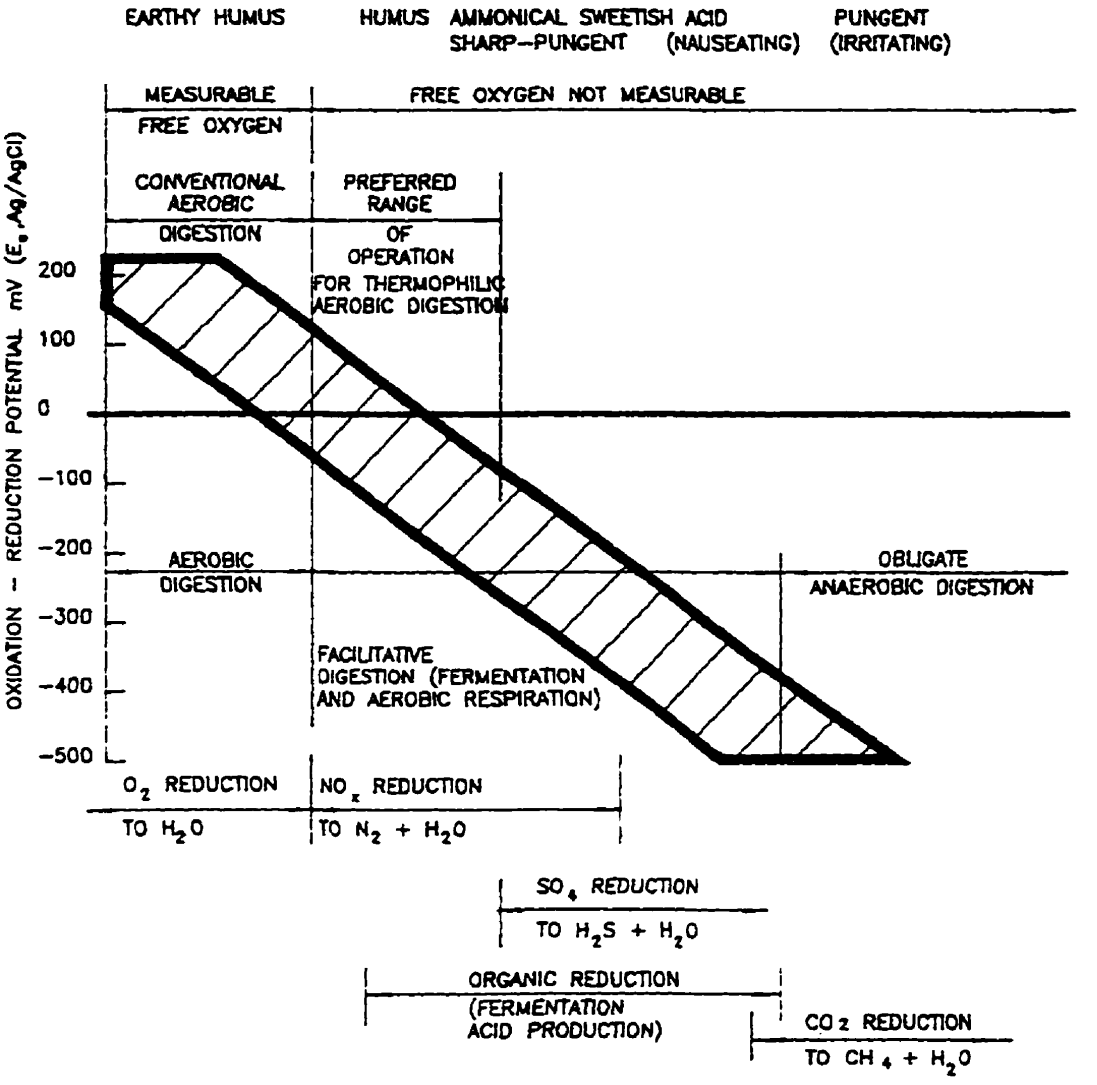


Figure 3. Measured ORP values relative to various sludge digestion regimes. The operating conditions described by ORP are represented by the cross hatched diagonal. From left to right in descending values of ORP, biological activity changes from aerobic respiration to anaerobic respiration and fermentation processes. In TAD reactors, oxidised salts such as nitrates are either unavailable or limited and anaerobic respiration would not be a dominant reaction as shown (Kelly, 1990).

2.3.5 pH and Alkalinity

pH is defined as the negative log of the activity of the hydrogen ion in solution. The concentration range suitable for the existence of most biological life is quite narrow and critical. In wastewater the optimum pH is neutral and should be controlled over a range of about 6 to 9 (Sawyer and McCarty, 1967). Low pH inhibits bacterial activity and most bacteria cannot live below pH 4.

Alkalinity is defined as the ability of a wastewater to resist changes in pH caused by the addition of acids. Alkalinity results from the presence of hydroxides, carbonates, bicarbonates, borates, silicates, phosphates and other bases (Metcalf and Eddy, 1991).

In the British Columbia studies, the alkalinity was always found to be high and increased to over 2,000 mg/L $CaCO_3$ (Kelly, 1990). The alkalinity increase is believed to be largely in response to ammonia formation. Ammonia, when released into the bulk liquid, creates alkalinity by forming a weak base (the weak base buffers acids in a pH range of about 8 to 10). Sears (1995) reports that the conversion of non-ammonia TKN to ammonia adds 3.59 mg of alkalinity per mg of ammonia formed.

pH depressions that could occur in a nitrifying environment are not typically experienced since nitrification is suppressed at thermophilic operating temperatures and since the TAD process is immediately self-buffering through ammonia alkalinity. With a feed sludge pH of 6.5, pH values in the TAD reactor are typically near 7.2 (Deeny, 1991). Matsch and Drnevich (1977) found that at thermophilic temperatures, the pH of the digested sludge increased with detention time. This increase in pH is thought to be from ammonia buffering. Other buffering compounds likely present are weak acids such as phosphoric acid (pH range 6

to 7), carbonic acid (pH range 6 to 8) and acetic acid (pH range 4 to 6) (Kelly, 1990).

Kelly (1990) indicates that when poor aeration is used, alkalinity may be needed at start-up as was the case at Salmon Arm where lime was required at start-up in the first generation ATAD digester. Therefore, it appears that the addition of alkalinity is not necessary nor does the process become acidic if not maintained in balance as long as there is proper aeration.

In contrast to thermophilic aerobic digesters, acidic conditions are observed in mesophilic aerobic digesters due to the nitrification of the ammonia. Alkalinity requirements are 7.1 mg of ($CaCO_3$) alkalinity per milligram of NH_4^+-N oxidised (Oleszkiewicz, 1995-b). Consequently, the H^+ ions created during nitrification may result in pH depressions as low as 3.5. In anaerobic digesters, the production of methane and carbon dioxide (bicarbonates) provides the required alkalinity. This occurs once the digestion process is in balance.

2.3.6 Summary

Thermophilic aerobic digestion products are influenced by the wastewater characteristics, the environmental parameters and the operational parameters. Thermophilic temperatures range from 50-70°C while mesophilic temperatures range from 15-35°C. Beyond 45°C the reaction rate does not follow the Arrhenius relationship but is expressed as a series of straight lines with a maximum occurring at 55°C and decreasing to zero at 75°C.

The solids retention time may be used as a selective factor by imposing stress on a bacterial community. In TAD reactors the retention time is normally 18 to 24 hours, although, retention periods as high as 1.57 days have been reported. The feed solids concentration is

normally quite high and ranges from 3% - 6% TS of which at least 2.5% is biodegradable VS. Solids loadings to pre-treatment reactors are also high and are in the 30 kg TS/m^3·d range.

The amount of oxygen consumed to VS oxidised is dependent on the composition of volatile solids. For an average municipal sludge the design oxygen requirement is about 2 kg O_2/kg VS destroyed. At the higher temperatures, oxygen is less soluble in water despite the increased oxygen diffusion coefficient. Standard ASCE aeration tests have proven to be unreliable in TAD systems and consequently the design is usually based upon values such as air flows with a given type of aeration system. Reported oxygen transfer efficiencies have ranged from 12% to as high as 67% at thermophilic temperatures.

The ORP is frequently used to indicate the aerobic state of a TAD solution. As the ORP decreases from 100 mV to below -300 mV, the aerobic state changes from aerobic respiration to anaerobic respiration and fermentation processes.

In TAD reactors the alkalinity increases due to ammonia formation. pH depressions are not experienced due to the ammonia self-buffering and since nitrification is suppressed at thermophilic temperatures. Consequently, pH values in a TAD reactor are typically around 7.2.

2.4 THERMOPHILIC AEROBIC DIGESTION PERFORMANCE

2.4.1 Organic Carbon Transformation

2.4.1.1 Volatile Solids Reduction

Organic material in either soluble or solid form is degraded by microbial activity during thermophilic pre-treatment. In a completely mixed reactor it is generally believed that

the degradation rate is controlled by the availability of oxygen, temperature, and by the residence time. This rate can be adjusted accordingly by the mixing characteristics, the presence of inhibitors and sludge nature (Ponti *et al.*, 1995).

If aerobic sludge conditioning is a result of oxidation reactions, it follows that the extent of conditioning might be controlled by the rate of oxygen consumption or, equivalently, by the rate of biological heat generation, and that these rates should be maximised for optimum conditioning. In keeping with this idea, Hawash *et al.* (1994) report that volatile solids reduction rates increase with increasing air flow from 0.16 to 0.50 $m^3/m^3/min$.

Boulanger (1995), on the other hand, reports that total VS reduction is not affected by airflow rate. ATAD units operated in oxygen-deprived conditions did however possess higher concentrations of dissolved volatile solids in the supernatant than the ATAD units operated in oxygen-satisfied or oxygen-excess conditions. This suggests that the rate of oxidation of dissolved substrate under oxygen-deprived conditions are the same as under oxygen-excess conditions even though the solubilization rates are accelerated under the oxygen-deprived conditions (Boulanger, 1995).

Likewise, Mason (1987) demonstrated that oxygen limitation in an aerobic thermophilic reactor enhanced particulate solubilization and hence, conditioning. Mason obtained the highest suspended solids removal rates of approximately 18 and 11 g/L·d under the oxygen limited condition at residence times of 0.6 and 1.0 days respectively. Under oxygen excess conditions, very low total suspended solids removal rates were measured (approximately 0.25-6 g/L·d).

2.4.1.2 Chemical Oxygen Demand Solubilization

Chemical oxygen demand (COD) is defined as the oxygen equivalent of organic matter that can be oxidised by using potassium dichromate in an acidic medium using a silver sulphate catalyst at elevated temperatures (Metcalf and Eddy, 1991). During the determination of COD, organic matter is converted to carbon dioxide and water regardless of the biological assimilability of the substance. Consequently, the COD test is unable to differentiate between biologically oxidisable and biologically inert organic matter.

During the test amino nitrogen is converted to ammonia nitrogen. Eastman and Ferguson (1981) report that organic nitrogen accounts for 9.58 g COD/g organic N. The COD test is not affected by the ammonia concentration unless significant concentrations of free chloride ions are present (which is usually not the case with domestic sewage) (Boulanger, 1995; APHA *et al*, 1992). Nitrite however can produce 2.2 g COD/g nitrite. Volatile fatty acids contribute to the COD as follows (Eastman and Ferguson, 1981; cited in Boulanger, 1995):

Acetic acid	1.066 g COD/g acid
Propionic acid	1.512 g COD/g acid
Butyric acid	1.816 g COD/g acid
Valeric acid	2.037 g COD/g acid

Boulanger (1995), reports that total COD reduction is not affected by airflow rate. ATAD units operated in oxygen-deprived conditions produced higher concentrations of

dissolved COD in the supernatant than the ATAD units operated in oxygen-satisfied or oxygen-excess conditions. Similar to Boulanger's VS reduction results, this suggests that the rate of oxidation of dissolved substrate under oxygen-deprived conditions is the same as under oxygen-excess conditions even though the solubilization rates are accelerated under the oxygen-deprived conditions (Boulanger, 1995).

With their pilot scale ATAD system, Ponti *et al.* (1995a) noticed an increase in COD removal with a rise in the feed COD content. A strong reduction in degradation efficiency was experienced when sewage sludges with COD concentrations below 20 kg/m^3 were used and concentrations of up to 60 kg/m^3 COD were used without affecting the bacterial degradative efficiency.

2.4.2 Volatile Fatty Acids

In biochemical decomposition of organic matter a wide variety of saprophytic bacteria hydrolyse and convert the complex materials to low-molecular weight compounds. Among the low molecular-weight compounds formed are short chain fatty acids, such as acetic, propionic, butyric and to a lesser extent valeric and iso-valeric. These low molecular weight fatty acids are termed volatile acids because they can be distilled at atmospheric pressure.

Due to the limited oxygen supply, the concentration of soluble degradable organic compounds such as volatile acids is normally high in ATP reactors (EPA 1990, Baier 1989, Sixt 1987, Schaad 1988). For example, Baier and Zwiefelhofer (1991) reported VFA increases of 146% from 2470 mg/L to 6081 mg/L after aerobic thermophilic pre-treatment at the Thun treatment plant. About 54.5% of the total VFAs were comprised of acetic acid and

32.6% being propionic acid. Kelly (1990) working with an autothermal thermophilic aerobic digestion system at Salmon Arm, BC, found VFA concentrations of up to 10,000 mg/L in the first stage digester. Hamer showed an accumulation of up to 6000 mg/L acetate and 800 mg/L propionate in experiments involving biodegradation of yeast cells by thermophilic bacterial populations in a laboratory scale bioreactor (Hamer, 1987). Pagilla *et al.* (1996) discovered that the volatile fatty acid concentration in the TAD pre-treatment reactor increased to approximately three times the volatile acid concentration in the mixed sludge feed.

Chu *et al.* (1994) conducted a 2 stage pilot scale TAD process with a 6 day retention time, and air flow rates of 0.126 $m^3/m^3/h$ (anaerobic condition), 0.28 $m^3/m^3/h$ (microaerobic condition) and 0.6 $m^3/m^3/h$ (aerobic condition). The lowest aeration rate of 0.126 $m^3/m^3/h$ gave the highest acetate and total VFA concentration. When flow rates are increased, the net acetate concentrations fell rapidly. Likewise, Boulanger (1995) found in her experiments with 2 ATAD reactors in series with a 6 day HRT, that the concentration of acetic acid was greater in the oxygen-deprived experiment than with the higher airflow rates.

Mason *et al.* (1987) discovered that at thermophilic temperatures very little change in dissolved organic carbon (DOC) occurs under oxygen excess conditions but significant increases in DOC occurred at all residence times (0.6 - 5 days) when oxygen was limited. The largest DOC increase was with the 1 day residence time from approximately 900 to 4100 mg/l. No carboxylic acids were found under oxygen excess conditions. The amount of each acid produced varied with residence time, although clearly, acetate was produced in the highest concentration. Mason *et al.* (1987) observed acetate levels of approximately 2700 mg/L and total VFAs of approximately 3300 mg/L. The acetate concentrations were therefore 5 to 10

times the concentration of all other carboxylic acids in their TAD process.

Harrison and Pirt (1966) studied the influence of dissolved oxygen concentration on the metabolism and respiration of growing *Klebsiella aerogenes* NCTC 8017 using a continuous-flow culture technique under thermophilic temperatures. In the limited oxygen state (DO indistinguishable from zero & dissolved oxygen tensions below about 10 mm Hg), a decreasing oxygen supply resulted in increased production of fermentation products (butanediol, acetic acid, ethanol and lactate). Very large amounts of volatile acids (1280 mg carbon/L) were formed at pH 7.4 under oxygen limited conditions. Within the oxygen limited state, acetic acid accounted for the highest percentage of volatile acids, but with decreased oxygen supply, formic acid production increased until it accounted for about half as much glucose carbon as the acetic acid (i.e. the number of molecules of formic acid and acetic acid produced were equal).

2.4.3 Ammonia Nitrogen

Ammonia nitrogen exists in an aqueous solution as either ammonium ion or ammonia in accordance with the following equilibrium reaction:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \qquad (5)$$

The equilibrium is affected principally by temperature and pH. For example, Speece (1996) reports that at a pH of 7.0 the percentage of un-ionized ammonia is 0.6% at 25°C and 3.6% at 55°C. At a temperature of 55°C, the percentage of un-ionized ammonia is 1.2% and 27.4% for

pH values of 6.5 and 8.0 respectively.

Results from studying yeast cells by mixed thermophilic bacterial cultures indicate that at most residences times NH_4^+-N accumulated under all conditions, although at short residence times this was hardly detectable (Mason *et al.*, 1987). During studies conducted by Mason *et al.* (1987) ammonia concentrations of 500 to 1000 mg/L in the feed increased to twice this amount in the 1.5 to 3 day SRT digesters and three to four times this amount in the 5 day SRT digesters operating at 60°C, 65°C and 70°C. In Boulanger's ATAD pilot plant, the dissolved nitrogen increased with decreased airflow (Boulanger, 1995)

The presence of ammonia cannot be avoided during thermophilic aerobic degradation because ammonia is released by biological organisms during digestion. Ammonia is not subsequently nitrified because nitrification is suppressed at thermophilic temperature. Nitrates were not found present in any reports of operating digesters.

2.4.4 Settleability/Dewaterability

There have been a number of conflicting reports on the effect of high temperature digestion on dewaterability. Prakasam *et al.* (1990) measuring the capillary suction time (CST) at various polymer dosages found that mesophilic sludge required a lower polymer dosage than did the thermophilic sludge (10 vs. 22.5 kg/dry tonne) to achieve the minimum CST. Similarly, Jewell *et al.* (1978) in a single stage ATAD observed that the sludge dewaterability deteriorated significantly at all HRT's tested (3-8 days). With thickened primary and WAS, long periods of aeration were required in the ATAD system to achieve significantly increased dewaterability.

However, according to Baier and Zwiefelhofer (1991), dewaterability is improved with thermophilic treatment. They rationalise that the main hindrances to the water escape are non-uniform particle size distribution and non-optimal operation of sludge thickeners. A sludge with a high standard deviation of the gaussian particle size distribution curve will not release free water efficiently, because inter-particle volume is high and water release channels are clogged easily. Thermophilic treatment, by making particle size uniform, enhances free water release. Since the hydrolysis rate for aerobic thermophilic organisms is an order of magnitude higher than anaerobic mesophiles, cells exposed to high temperatures show a weakening of cell wall structure and an increase in membrane permeability. As a result, intracellular water is set free (Baier and Zwiefelhofer, 1991).

According to Deeny (1991), gravity thickening performance of hot ATAD effluent sludge is poor immediately after treatment because of thermal convection currents that occur in a thickening tank. If the sludge is allowed to cool, thickening performance is usually satisfactory. Values of 6% to 9% total solids by gravity thickening are typical for ATAD effluents and repeatedly, values up to 10% to 14% and even 18% have been reported (Deeny, 1991).

Kelly (1990) concludes that the ability to dewater sludge appears to be manifested in the sludge itself regardless of the digestion process. He came to this conclusion based on three British Columbia studies: Ladysmith showed improved dewaterability following digestion of primary sludge, Gibsons showed no change in dewaterability following digestion of mixed primary and biological waste sludge, and Salmon Arm showed a worsening in dewaterability following digestion of mixed primary sludge and biological waste sludge. The British Columbia

studies indicated that when sludges contain a high fraction of biological waste sludge, dewaterability worsened (Kelly, 1990).

Although there were conflicting reports on the ease of dewatering heat-treated sludge, all researchers who studied the characteristics of dewatered, heat-treated sludge agreed that heat-treated sludge exhibited a higher resistance to shear than did the dewatered mesophilically digested sludge (Woodley, 1961; Kelly, 1990, Prakasan *et al.*, 1990). For example, Woodley (1961) as reported in Kelly (1990) compared the dried solids characteristics of both mesophilic and thermophilic aerobically digested sludges. In these studies, which compared 15 to 35 day digestion periods, the 35°C mesophilic digested sludges, when allowed to dry, were granular and quite easy to break apart. The 52°C thermophilic sludges after drying were hand, fibrous, and difficult to pulverise. Likewise, the three TAD sludges from the British Columbia demonstration facilities, when dewatered on sand, left a felt-like odourless residue which was easy to lift as one single mat after only a few minutes of drying (Kelly, 1990).

2.4.5 Microbial Metabolism in TAD Reactor

A number of investigators have attempted to explain the different steps and pathways involved in VFA production in low oxygen-tension reactors. However, TAD is still considered a "blackbox" phenomenon. In low oxygen tension reactors, both oxidation and fermentation are occurring through the presence of facultative micro-organisms. The active thermophilic microflora in aerobic thermophilic sludges is very homogeneous and consists nearly exclusively of thermophilic *Bacilli*, of which more than 95% have been classified as type of *Bacillus stearothermophilus* (Sonnleitner and Fiechter, 1983b).

Fermentation is an energy yielding process in which organic molecules serve as both electron donors and acceptors. This is in contrast to *Respiration* which is an energy-yielding process in which an electron donor is oxidised using an inorganic electron acceptor. Fermentation accounts for much of the formation of organic acids, alcohols, aldehydes and ketones as by-products along with CO_2 and H_2O. In contrast, when no oxygen is present, carbon and sulphur compounds will be used as electron acceptors to produce methane or reduced sulphur biogas. This occurs in obligate anaerobic digestion reactors (Kelly, 1990).

Before metabolism can commence, the organic matter is hydrolysed by extracellular enzymes. The reaction rate is greatly affected by the pH and operating conditions. Complex carbohydrates such as cellulose and starch are hydrolysed to simple sugars, proteins to amino acids, and lipids to long-chain fatty acids.

Chu *et al.* (1996) developed a model to explain the fundamentals of substrate metabolism in TAD. To illustrate the model, an example *of E. coli* utilising glucose will be examined as shown in Figure 4.

Regardless of the presence or absence of oxygen, the first step in glucose metabolism is transport into the cell and subsequent catabolism into pyruvate (the breaking down of larger molecules into smaller ones with the release of energy). This may be accomplished in either the Embden-Meyerhof (glycolytic), the pentose phosphate or the Entner-Doudoroff pathways in which nicotinamide adenine dinucleotide (NADH) is generated (Appendix A). It is the further metabolism of pyruvate that differs between aerobic and anaerobic conditions.

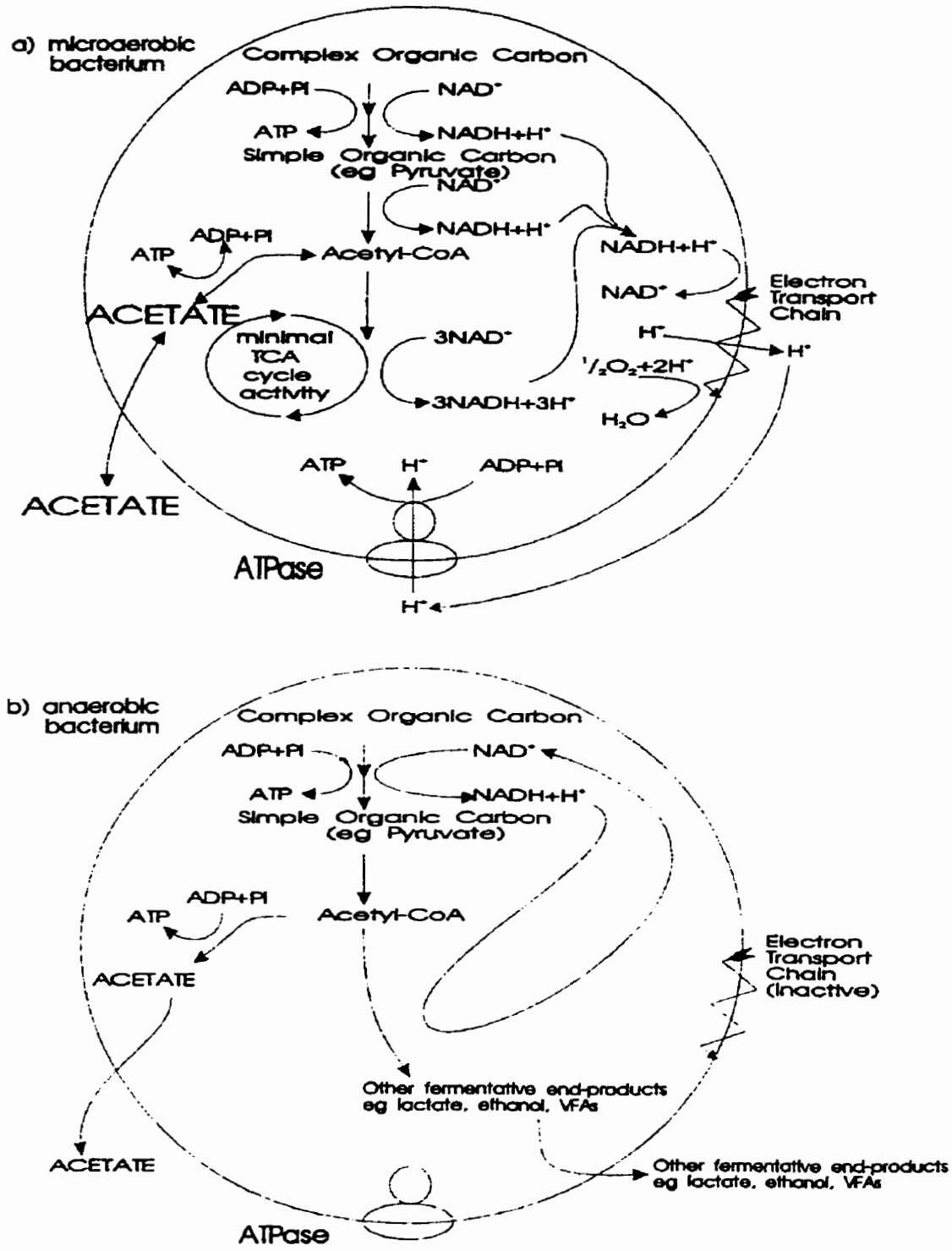


Figure 4. Biochemical model of acetate production in TAD under (a) microaerobic and (b) anaerobic conditions (Chu *et al.*, 1996).

In the microaerobic environment, NADH generated by both the glycolysis pathways and the tricarboxylic acid cycle (TCA) is reoxidised by the operation of the electron transport chain (Figure 4a). In the absence of O_2, NADH is not usually oxidised by the electron transport chain because no external electron acceptor is available (Figure 4b). The TCA cycle and pyruvate dehydrogenase reaction that generate large amounts of NADH are inoperative. Yet the NADH produced in the glycolytic pathway must still be oxidised back to NAD^+ or glycolysis will stop. Therefore, many micro-organisms to achieve a proper fermentation balance, slow or stop pyruvate dehydrogenase activity and use pyruvate or one of its derivatives as an electron and hydrogen acceptor in the reoxidation of NADH (Prescott *et al.*, 1993).

Under microaerobic conditions, the NADH produced during the oxidation of substrates can be reoxidized by operation of the electron transport chain. The flow of carbon is therefore uncoupled from the necessity to maintain redox balance via fermentation. Since the terminal electron acceptor, oxygen is limited in a microaerobic environment, the rate of transport of electrons down the respiratory chain is limited and in turn the rate of oxidation of NADH to NAD^+ is limited. In response to the limited capacity of the respiratory chain, the bacteria in a TAD process preferentially shuttle acetyl-CoA through an acetyl-phosphate intermediate to acetate, transferring the high energy phosphate bond to adenosine diphosphate (ADP), thus generating adenosine 5'-triphosphate (ATP). These reactions generate energy without the reduction of NAD+, as would be the situation if acetyl-CoA would have fed directly into the TCA cycle. Thus, by employing substrate level redox reactions and a limited flow of carbon through the TCA cycle, bacteria in a TAD process could limit the NADH

produced to meet the limited capacity of the respiratory chain to transport electrons; at the same time, they could maximise ATP production by channelling excess acetyl-CoA to acetate. If excess acetyl-CoA was not channelled to acetate, the limitations of the respiratory chain would result in the accumulation of NADH and limit the supply of NAD^+.

In a study by Varma *et al.* (1993) (cited in Chu *et al.*, 1996), under increasing O_2 limitation, 4 critical growth rates were revealed in which changes in by-product secretion patterns coincided with changes in metabolic pathway utilisations. The redox potential was identified as a likely trigger that led to shifts in metabolic rates.

Doelle *et al.* (1982) (cited in Chu *et al.*, 1996) suggested that the accumulation of NADH switches carbon flow towards acetic acid. Their results suggested that high glucose feed concentrations repress enzymes in the TCA cycle and electron transport chain. This condition results in high accumulated intracellular NADH concentrations, which ultimately switch the carbon flow in the direction of acetate production.

2.4.6 Summary

Organic material in either soluble or solid form is degraded due to microbial activity. There have been conflicting reports on whether total carbon solubilization is affected by airflow. TAD units operated under the oxygen-deprived conditions nevertheless possess higher concentrations of dissolved COD and VS in the supernatant, suggesting that solubilization and degradation rates are accelerated under the oxygen-deprived conditions. COD removal is reported to increase with increasing COD concentrations in the feed up to 60 kg/m^3 COD.

Short chain volatile fatty acids (e.g. acetic, propionic, butyric and valeric) are formed

during the biochemical decomposition of organic matter. Due to the limited oxygen supply, the concentration of VFAs is normally quite high in TAD reactors. Of the VFAs formed, acetate is always in the highest concentration followed by propionate. Total VFA and acetate concentrations are reported to decrease with increasing aeration rates.

The presence of ammonia nitrogen in TAD reactors cannot be avoided since ammonia is released by biological organisms as a result of digestion and is not subsequently nitrified. Ammonia nitrogen accumulations were found to increase with increasing retention time and decreasing airflow.

There have been conflicting reports on the dewaterability of thermophilic aerobic digested sludges as compared to mesophilic digested sludges. Some researchers have found that the dewaterability of TAD sludges deteriorates significantly while others have found that the dewaterability increases and attribute this increase to a more homogeneous particle size and a release of intracellular water. The intracellular water is said to be released due to the high temperature weakening of cell wall structure and increasing membrane permeability. Nevertheless, TAD sludge mats exhibit a higher resistance to shear.

TAD metabolism is still considered to be a "black box" technology, although, several researchers have suggested models. In TAD reactors both oxidation and fermentation are occurring by facultative micro-organisms under oxygen limited conditions.

CHAPTER 3

RESEARCH OBJECTIVES

As discussed in Chapter 1, volatile fatty acid generation has mostly been obtained by fermentation. Very few studies have examined volatile fatty acid production in thermophilic aerobic digesters. Due to the apparent need for an in-depth investigation of VFA production in thermophilic aerobic digestion of primary sludge, this study was initiated. Although not examined in this study, the VFAs produced would be used as a carbon source for a full-scale denitrifying wastewater treatment plant. To achieve this goal, the following objectives were set:

1) To determine the quantity and type of volatile fatty acids that could be produced in an aerobic thermophilic reactor operating at different oxygenation states and retention times.
2) To determine to what extent the nitrogen contained in the sludge would be released into solution in a TAD reactor operating a different oxygenation states and retention times.
3) To investigate the effect of influent characteristics on VFA production.
4) To estimate the full scale implications of experimental results.
5) To determine to what extent the TAD sludge is conditioned for further mesophilic digestion.

CHAPTER 4

EXPERIMENTAL DESIGN: METHODS AND ANALYTICAL PROCEDURES

4.1 EXPERIMENTAL SET-UP AND OPERATION

4.1.1 Sludge Source

Primary sludge was used in this study as a feed source and was obtained from the City of Winnipeg's North End Pollution Control Centre. The primary sludge, whose total solids content ranged from 2.9% to 8.1%, was collected three times per week (Monday, Wednesday, Friday) from the primary clarifier underflow lines. The sludge was then immediately shipped to the University of Manitoba's Environmental Engineering Laboratory. The sludge was subsequently passed through 0.5 cm screens and transferred to 20 L plastic containers for storage at 4°C. While at 4°C, this sludge was continuously mixed using a mechanical mixer located in a refrigerator.

4.1.2 System Configuration

Two laboratory-scale, semi-continuous reactors as depicted in the TAD schematic (Figure 5) and the reactor set-up photograph (Figure 6) were used in this research. Each completely sealed cylindrical plexiglas reactor had a total reactor volume of 6 L and an operating volume of 3 L. Each reactor was equipped with an on-line Canlab Baxter ORP probe inserted through the lid. The ORP probes were hooked up to a Fisher Scientific Accumet

Model 50 pH meter. Each reactor was also equipped with an effluent sludge overflow at the 3 L level. The effluent U-shaped Tygon tubing with a 1.6 cm inner diameter created an air block sealing the reactors. Effluent removal to waste buckets was by gravity.

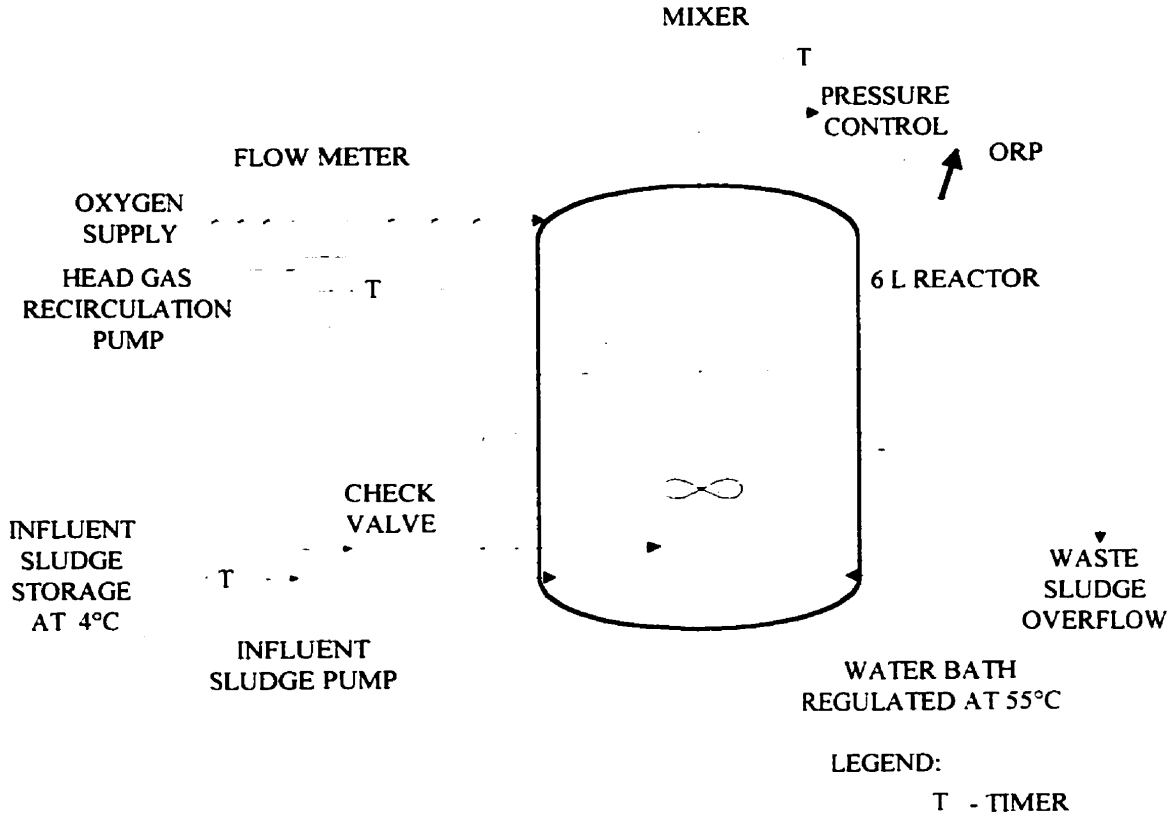


Figure 5. Thermophilic aerobic digester schematic.

Pure oxygen was fed into the headspace of the reactors while the pressure was

controlled to 5 cm of height through manometer gas vent systems. Oxygen flow was controlled by Cole Parmer 0-7 ml/min flowmeters.

The reactors were mixed by mechanical mixers and head gas recirculation. Each mixer consisted of a 6 to 600 rpm Cole Parmer pump (cat. number 7553-00) with an attached mixing rod. The rotation rate of the mixing rod was maintained at 400 rpm by a Cole Parmer Masterflex speed controller. The head gas was recirculated to the bottom of the reactors at two locations located 180° from each other. Head gas recirculation was done to improve the mixing, to increase the oxygen yield, and to minimise vent gas heat losses.

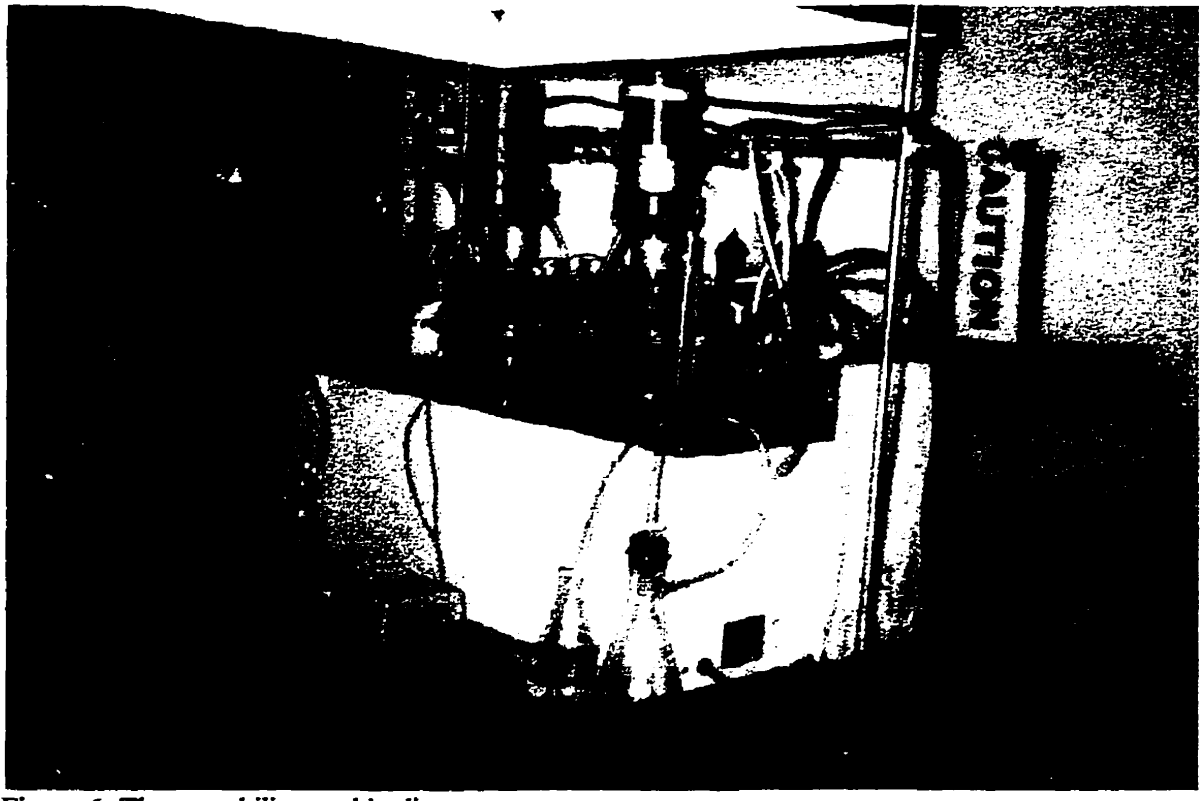


Figure 6. Thermophilic aerobic digester set-up.

Sludge was pumped from the refrigerator into the reactors by Robins and Meyers Moyno 500 progressive cavity pumps (model 20502). Two brass swing flap check valves were used in sequence in the feed line to each reactor to prevent the reactor contents from been siphoned out. The head space recirculation pumps, the mixing pumps and the Moyno pumps were all controlled by Paragon Electric Company Inc. single-channel electronic time controllers (model EC 4004/120).

Reactors were located in a water bath which acted as the primary heat source. Heat was also obtained from biological activity and mechanical mixing energies.

4.1.3 Operation

From June 1995 to September 1995 two 3 litre TAD reactors were operated in a semi-continuous mode at 55°C. A total of 5 runs were conducted to investigate the effects of selected operational and environmental parameters on the volatile fatty acid production during TAD utilising primary sludge. The research evolved into 2 stages, each exploring the influence of a particular parameter.

In Stage 1 the role of the oxygenation state was investigated while the solids/hydraulic retention time was maintained at 24 hours. Oxygenation states were defined by a combination of ORP patterns, oxygen input per volume of sludge per hour and DO trace patterns. Two oxygenation states were induced in the TADs as follows:

1) Oxygen-Satisfied (OS): microaerobic aerated / anoxic - O_2 flow rate: 0.14 $m^3/m^3 \cdot h$; ORP: between 0 to -225 mV; and DO greater than 0 mg/l.

2) Oxygen-Deprived (OD): anaerobic aerated condition - O_2 flow rate: 0.025 $m^3/m^3 \cdot h$; ORP: less than -300 mV; and DO equal to 0 mg/l.

Discharge gas was also sampled to confirm the difference in oxygenation states. Stage 1 reactors were seeded with mesophilically digested sludge obtained from the City of Winnipeg's North End Pollution Control Centre.

Stage 2 focused on the effects of solids/hydraulic retention time on VFA production. Retention times of 24, 18, 12 and 6 hours were studied under the oxygen-deprived condition (notated as OD24, OD18, OD12 and OD6 respectively). To achieve these nominal retention times, the digesters were fed every 3 hours a volume of 375, 500, 750 or 1500 ml for a 24 hour, 18 hour, 12 hour or 6 hour retention time respectively.

In both stages the reactors were fed every 3 hours to maintain the minimum 2 hr retention time required for disinfection at 55°C. Head gas recirculation pumps and mixing pumps were turned off 1 minute prior to feeding to allow for the rotational movement to dissipate. Primary sludge was then pumped from the refrigerator to the TAD reactors. Mixing and head gas recirculation resumed 10 minutes after feeding. This lag period allowed the excess sludge to overflow before the mixing started and minimized the contamination of the pasteurised sludge with the newly fed contaminated sludge. Actual solids retention times may be slightly larger than nominal hydraulic retention times due to slight settling which may occur during feeding.

4.2 EXPERIMENTAL SAMPLING

4.2.1 Sludge Sampling

Samples of TAD sludge were taken every day or every second day prior to feeding to avoid contamination. Samples were taken from the port located at the 2 L level. The sample port was first rinsed with a representative sample of the treated sludge before collecting the sample. Feed sludge samples were also taken at this time from the refrigerated 20 L containers. All sludge sample volumes were 200 mls. Sludge samples were then analysed for dissolved oxygen, pH, alkalinity, total solids and volatile solids.

Approximately 100 mls of the 200 ml sludge samples were then centrifuged for 15 minutes in a Damon/IEC Division IEC HN-S centrifuge. Next the supernatant was transferred to 1.5 ml test tubes and centrifuged for an additional 12 minutes in a Damon/IEC Centra-M centrifuge. The centrate was then collected and filtered through 0.45µm filters. Lastly, the filtrate was analysed for volatile fatty acids, chemical oxygen demand and ammonia nitrogen.

4.2.2 Discharge Gas Sampling

One millilitre discharge gas samples were collected 2 hours after feeding. Samples were collected with a syringe through a connector located in the gas recirculation line which was sealed with a rubber bung.

4.3 LABORATORY ANALYSIS AND DISCUSSION OF METHOD ERROR

4.3.1 Solids

4.3.1.1 Analysis Method

Total and volatile solids were measured, rather than the more usual suspended solids fractions because of the difficulty in filtering TAD samples. The total solids were found by measuring a known volume (5 ml) of sample into a ceramic crucible which had been previously fired and cooled in a desiccator for 1 hour and weighed. The samples were then dried for 4 hours in a Fisher Isotemp (Model 230F) oven at 104°C before being cooled in a desiccator for 1 hour and then reweighed. After weighting, volatile solids were determined by igniting the residue at 550°C for 1 hour in a Perfect Fire muffle furnace (model DTP-56 PN-E.FK). Samples were subsequently cooled and re-weighted. Solids analysis was performed as outlined in Standard Methods 2540B and 2540E (APHA *et al*, 1992).

4.3.1.2 Method Error

Method Error is a measure of the magnitude with which multiple analyses of a given sample disagree with each other (APHA, 1993). The method error was determined by first calculating the coefficient of variation for the two solids measurements taken per sample. Next the average coefficient of variation for each type of sludge was calculated and plotted (Figures 7 and 8). Primary sludge showed the highest variation between measurements with a volatile solids and non-volatile solids coefficient of variation of about 5% in the OD6 experiments. This high variation resulted because of the non-homogenous texture of primary sludge even after

blending. The primary sludge total solids error was usually less than 2%. The error of the TAD sludge TS and VS measurements were usually less than 3%.

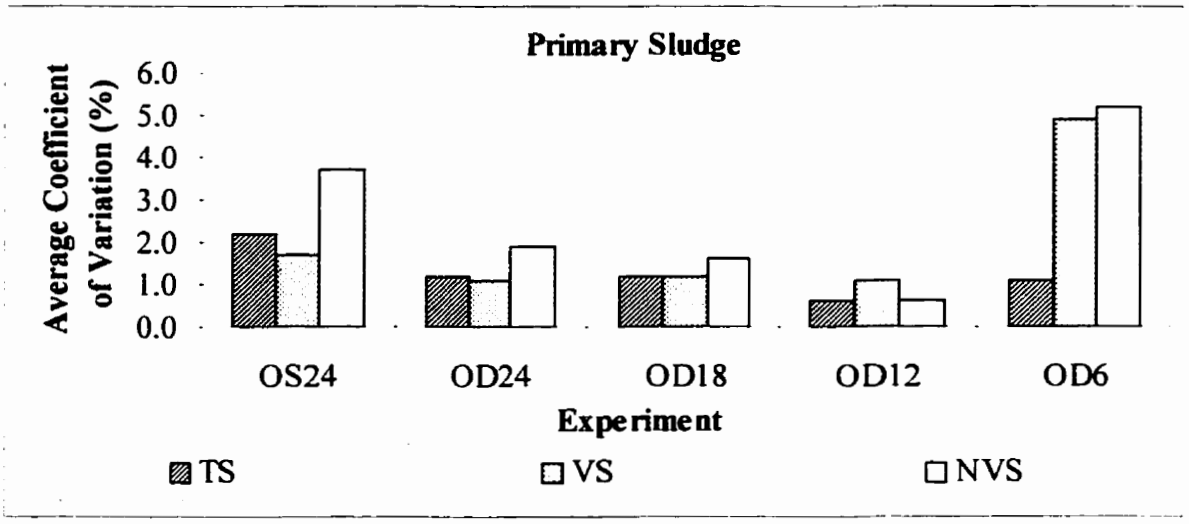


Figure 7. Average error of primary solids measurements.

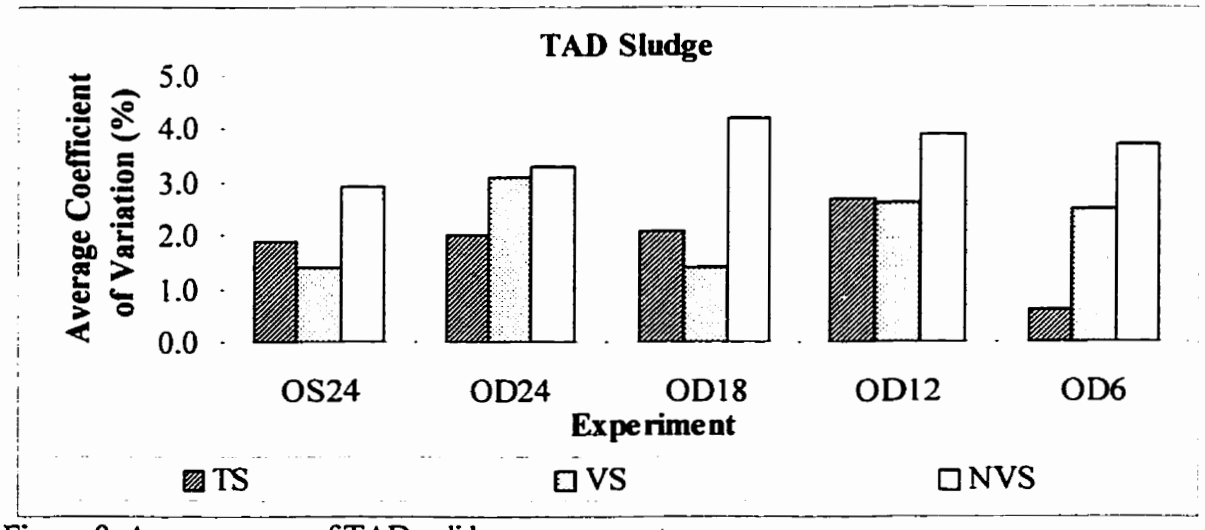


Figure 8. Average error of TAD solids measurements.

4.3.2 Dissolved oxygen

4.3.2.1 Analysis Method

Dissolved oxygen concentrations were measured using a YSI model 51B oxygen meter and YSI oxygen probe. The probe was calibrated each time samples were taken using the Winkler method.

4.3.2.2 Method Error

The YSI model 51B oxygen meter and YSI oxygen probe was deemed unsuitable for such an application. At such low dissolved oxygen levels (less than 0.5 mg/L) the meter and probe were not accurate and the readings fluctuated. Accuracy as stated by the manufacturer is ± 2 percent of the reading within 5 to 40°C.

4.3.3 Discharge Gas - Methane, Carbon Dioxide and Air

4.3.3.1 Analysis Method

Gas samples were injected in a Gow-Mac gas chromatograph which was standardised each day prior to use. The gas chromatograph used helium as the carrier gas. The gases were identified by comparing their retention times to standard gases. Concentrations were estimated by comparing the peak with known standards. Injections were done in duplicate. Method used was as outlined in Standard Methods 2720 C (APHA *et al.*, 1992).

4.3.3.2 Method Error

Figure 9 shows the average error obtained for discharge gas constituent

determinations. The error for gases which made up a large percentage of the total gas volume was very accurate at less than 3%. For gases which made up a small percentage of the total discharge gas, the error values were either zero or very high as was the case for the CO_2 component in OS24, and the CH_4 component in OD24 and OD18. The reason for this is that at low values, small discrepancies result in large coefficient of variation values. For example, if one measurement is 1 and the second is 2, the error is 47.1%; if one measurement is 90 and the other 91, the error is 0.8%; if both measurements taken are equal to 1, the error is 0%.

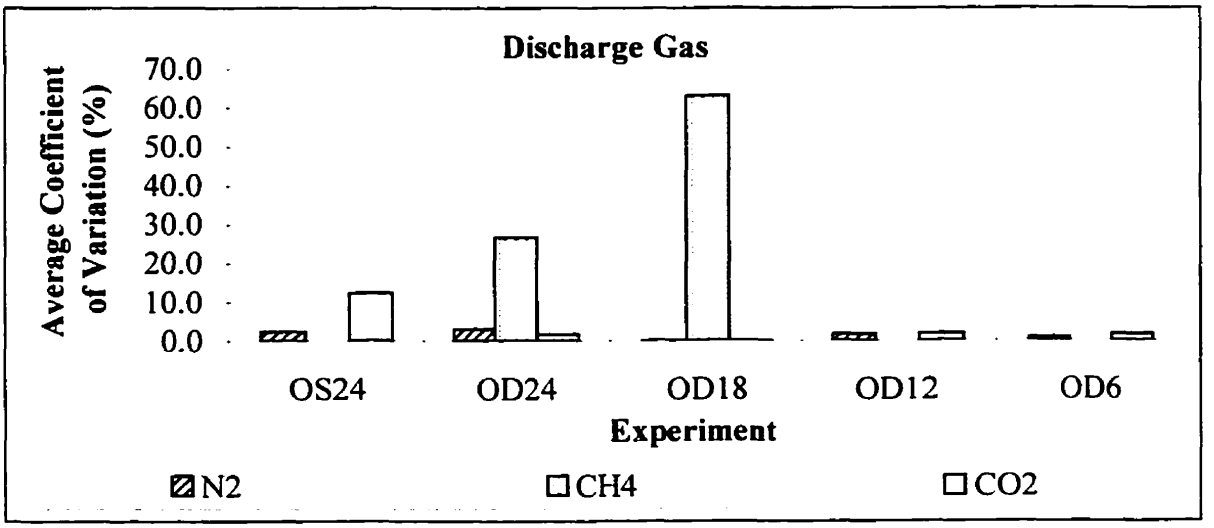


Figure 9. Average error of discharge gas measurements.

4.3.4 pH and Alkalinity

4.3.4.1 Analysis Method

Both pH and alkalinity were measured using a Fisher Accumet model 230 pH/ion meter. The meter was calibrated daily, prior to measurements, using two standard buffer solutions of pH 4.0 and 7.0. The probe was cleaned thoroughly with distilled water and dried after each sample. The reading was adjusted for 55°C.

Total alkalinity was measured by titrating the samples to an endpoint pH of 4.5 with 0.06 N sulphuric acid. Alkalinity was measured according to Standard Methods 2320 potentiometric titration method to preselected pH (A.P.H.A. *et al.*, 1992).

4.3.4.2 Method Error

pH probes were checked several times against other pH probes and meters in the laboratory and believed quite accurate.

4.3.5 Soluble Chemical Oxygen Demand

4.3.5.1 Analysis Method

Soluble chemical oxygen demand (SCOD) analysis was done in duplicate with dilutions of 1:10 and 1:20 according to Standard Methods Closed Reflux, Colorimetric Method (A.P.H.A. *et al.*, 1992). Primary sludge SCOD dilutions were always 1:10 because of its lower SCOD values while dilutions of both 1:10 and 1:20 were used for the TAD sludge. Samples intended for SCOD analysis were preserved by acidification with sulphuric acid and digestive acid to below pH 2. Once digested, the samples were allowed to sit for no more than 2 weeks

before colorimetric analysis was performed using a Bausch and Lomb Spectronic 21. The standards used were 0 mg/L, 10 mg/L, 20 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L, and 800 mg/L.

4.3.5.2 Method Error

Primary sludge SCOD measurements had an error of less than 4% as shown in Figure 10. The error of the TAD sludge was higher at 2.1% to 6.4%. The reason for the greater variability in TAD sludge SCOD measurements in OD18, OD12 and OD6 is unknown.

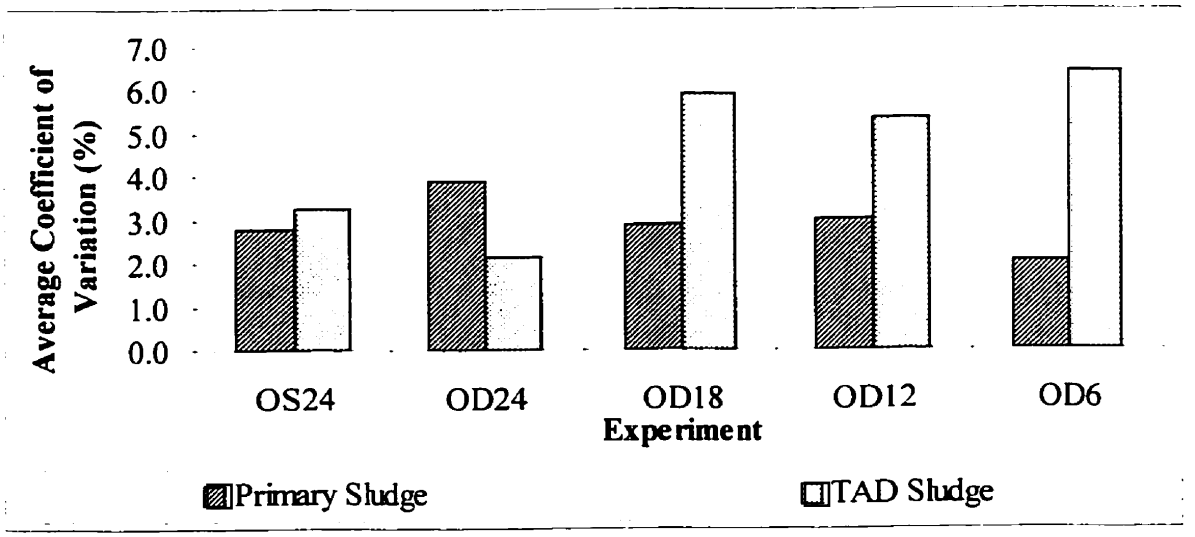


Figure 10. Average error for SCOD measurements.

4.3.6 Volatile Fatty Acids

4.3.6.1 Analysis Method

Centrifuged and filtered samples were diluted 1:10 with distilled water in duplicate. Volatile fatty acid determination was conducted using an Antek 3000 gas chromatograph equipped with a flame ionization detector (FID). Helium was used as the carrier gas. When samples could not be immediately analysed, they were preserved with one drop of phosphoric acid and then frozen in 1.5 ml test tubes. At the time of analysis, the samples were thawed at room temperature and mixed thoroughly. VFAs measured were acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acids.

4.3.6.2 Method Error

The calibration of the gas chromatograph was checked daily using standard solutions. Based on the standard solutions, the Antek 3000 G.C. appeared to be accurate within 5% in a range of 1 to 600. Due to the high concentration of VFAs being measured, problems were encountered with build-up on the column. To counteract this effect, distilled water was injected into the G.C. after every second or third sample to rinse the column.

4.3.7 Ammonia Nitrogen

4.3.7.1 Analysis Method

Ammonia samples were diluted 1:5 and preserved with sulphuric acid to a pH of less than 2. Samples were then stored at 4°C for no more than 7 days before analysis. Ammonia nitrogen was analysed using a Tecator Kjeltec Auto 1030 Analyser. Before analysis the pH was

adjusted by sodium hydroxide addition. Analyses were performed as outlined in Standards Methods Automated Phenate Method, Section 4500 (A.P.H.A. *et al.*, 1992).

4.3.7.2 Method Error

The Tecator Kjeltec Auto Analyser was standardised daily. Based upon technician experience with this analyser, the test is accurate to within ±2 percent.

4.3.8 Sludge Dewaterability

4.3.8.1 Analysis Method

A centrifuge was used to evaluate dewaterability on a few grab samples. To accomplish this, total solids tests were conducted on the non-centrifuged sludge. Next, 25 ml sludge samples were placed under 2550 g (4380 rpm) in a Damon/IEC Division IEC HN-S Centrifuge for periods of 1 to 14 minutes. The centrate volume was then recorded and the total solids of the centrate was measured using the procedure outlined in Section 4.3.1.1. From these measurements, the percent solids removal was calculated.

4.3.8.2 Method Error

Method error was not calculated for the dewaterability analysis since it is expected to be similar to that found in Section 4.3.1.2.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 ACCLIMATION

The original heterogeneous population in the bioreactor had to undergo acclimation to ensure successful and sustainable operation. Acclimation is a time-dependant process which can be influenced by the type of seed used, the characteristics of the feed, and the chosen operational and environmental conditions. Following the acclimation period, the microbial populations reach a steady state condition in which their abundance is in relative equilibrium with their environment.

In this study, acclimation of the mesophilically digested sludge obtained from the NEWPCC in the TAD reactors was accomplished within a period of 8 days (8 SRT/HRTs). The phenomenon was considered complete when the VFA production rate stabilized. The short acclimation period observed can be attributed to the combined action of a number of factors such as the high temperatures, suitability of the seed used, the digestibility of the primary sludge, favourable operating conditions and the small reactor volume. After achieving a steady-state condition, any further operational or environmental changes resulted in shorter acclimation periods of 4 days or less. Although the biomass was at a "steady-state" condition, fluctuations were still observed due to fluctuations in feed quality.

5.2 ENVIRONMENTAL AND OPERATIONAL PROCESS CONTROL PARAMETERS

5.2.1 Influent Solids

5.2.1.1 Influent Solids Concentrations

The average influent primary sludge solids concentrations are shown in Table 1 while Appendix B contains the experimental data. Average volatile solids ranged from 2.17% to 3.67% for the different experiments with an average of 2.88%. The average percent volatile solids is higher than the minimum value of 2.5% recommended by EPA for all experiments except for OD6. The volatile solids fraction varied from 53.23% to 72.41% with an average of 61.64%. The standard deviations are quite high because of the considerable differences in the quality of the sludge used.

Figures 11 to 15 illustrate that throughout the experimentation period there was a wide variation in the influent primary solids concentrations to the TAD reactors. One of the reasons for this variability is that the experiments were conducted during the summer months when the North End Pollution Control Centre experiences a great variability in influent flows and solids concentrations caused by wet-weather flow. Another reason is that the primary sludge was obtained from the primary hoppers in which the sludge blanket level varies. If the sludge blanket level is high, the solids at the bottom of the hoppers are more compact.

Table 1. Average Influent Primary Sludge Solids Concentrations with Standard Deviations

EXP.	PRIMARY SLUDGE		
	Total Solids (%)	Volatile Solids (%)	Volatile Solids Fraction (%)
OS24	3.84 ± 0.76	2.78 ± 0.48	72.41 ± 0.32
OD24	4.31 ± 0.84	2.82 ± 0.44	65.57 ± 0.50
OD18	5.14 ± 1.37	2.93 ± 0.53	57.04 ± 0.86
OD12	6.90 ± 0.68	3.67 ± 0.19	53.23 ± 0.52
OD6	3.62 ± 0.83	2.17 ± 0.54	59.96 ± 0.39
Mean	4.76	2.88	61.64
SD[a]	1.33	0.54	7.52

(a) Standard Deviation

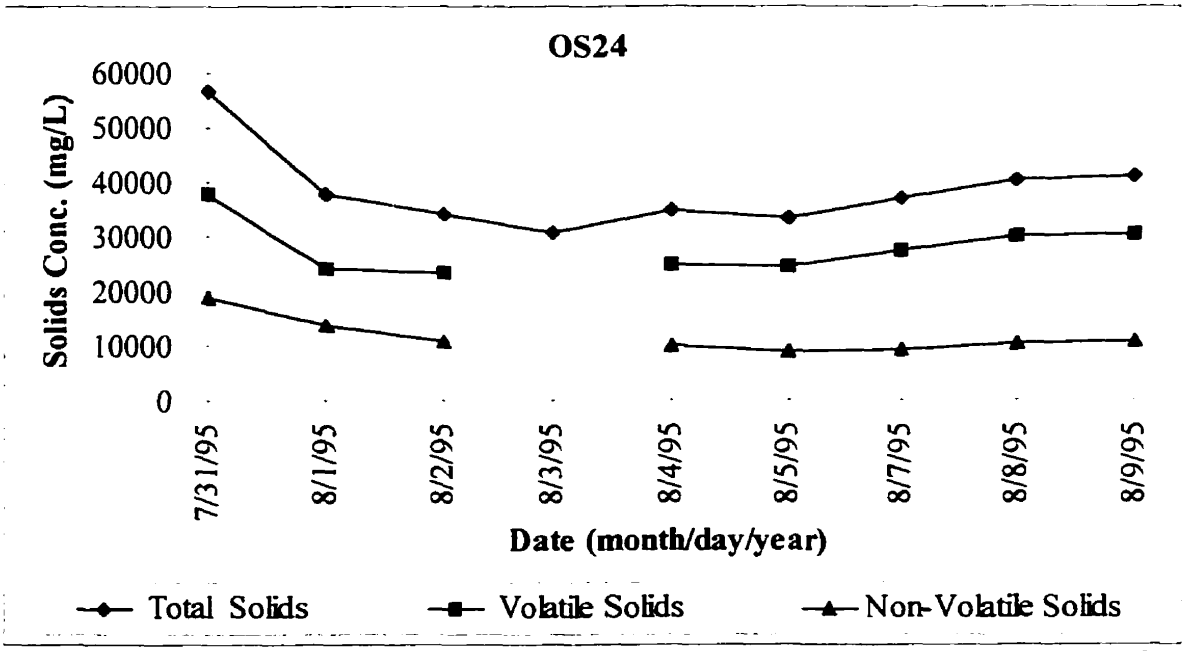


Figure 11. Influent primary solids concentrations during OS24. Volatile solids ranged from 25000 to 37740 mg/L with an average of 27837 mg/L throughout OS24.

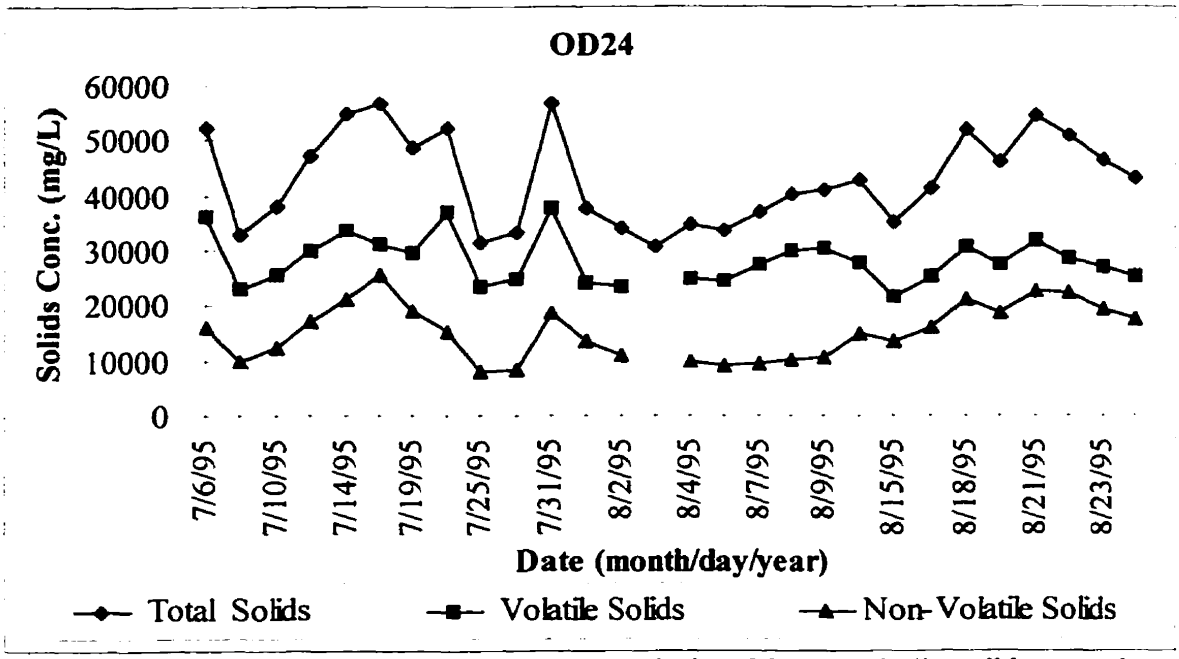


Figure 12. Influent primary solids concentrations during OD24. Volatile solids ranged from 22570 to 37740 mg/L with an average of 28234 mg/L throughout OD24.

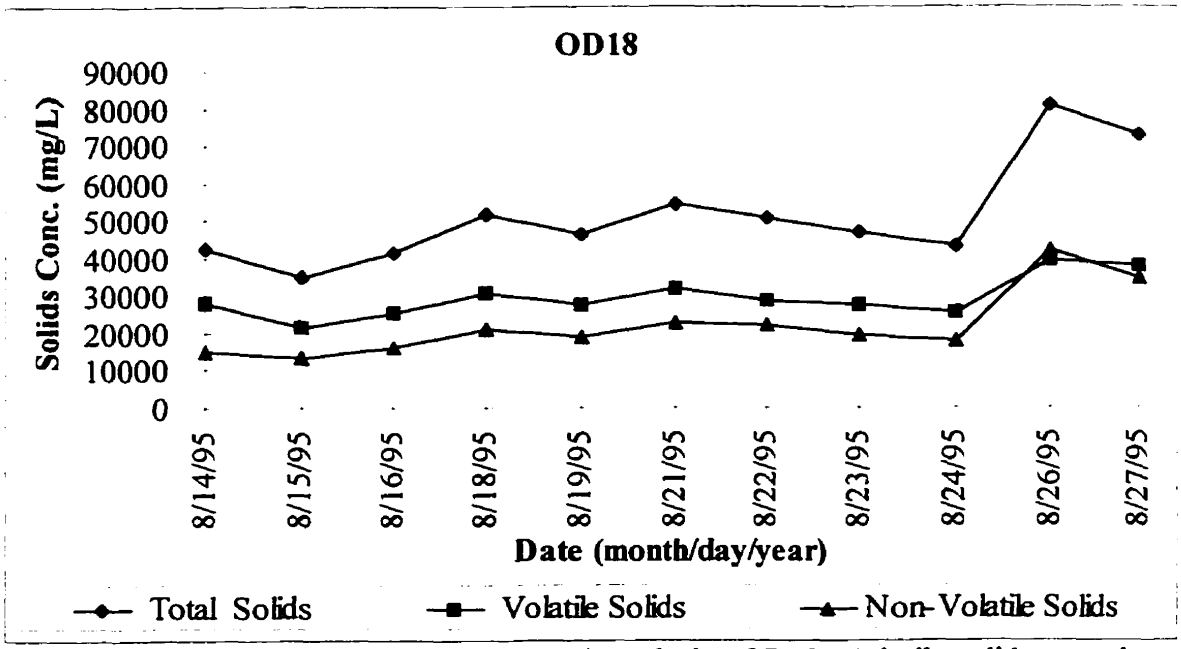


Figure 13. Influent primary solids concentrations during OD18. Volatile solids ranged from 21570 to 39230 mg/L with an average of 29342 mg/L throughout OD18.

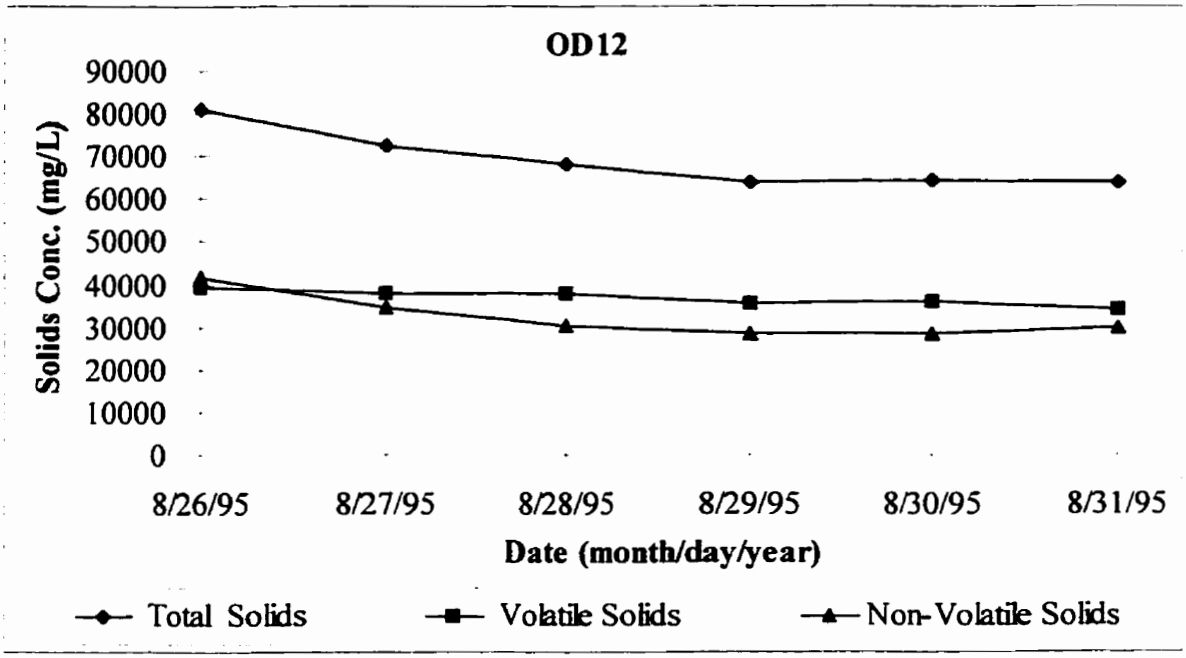


Figure 14. Influent primary solids concentrations during OD12. Volatile solids ranged from 34070 to 39230 mg/L with an average of 36727 mg/L throughout OD12.

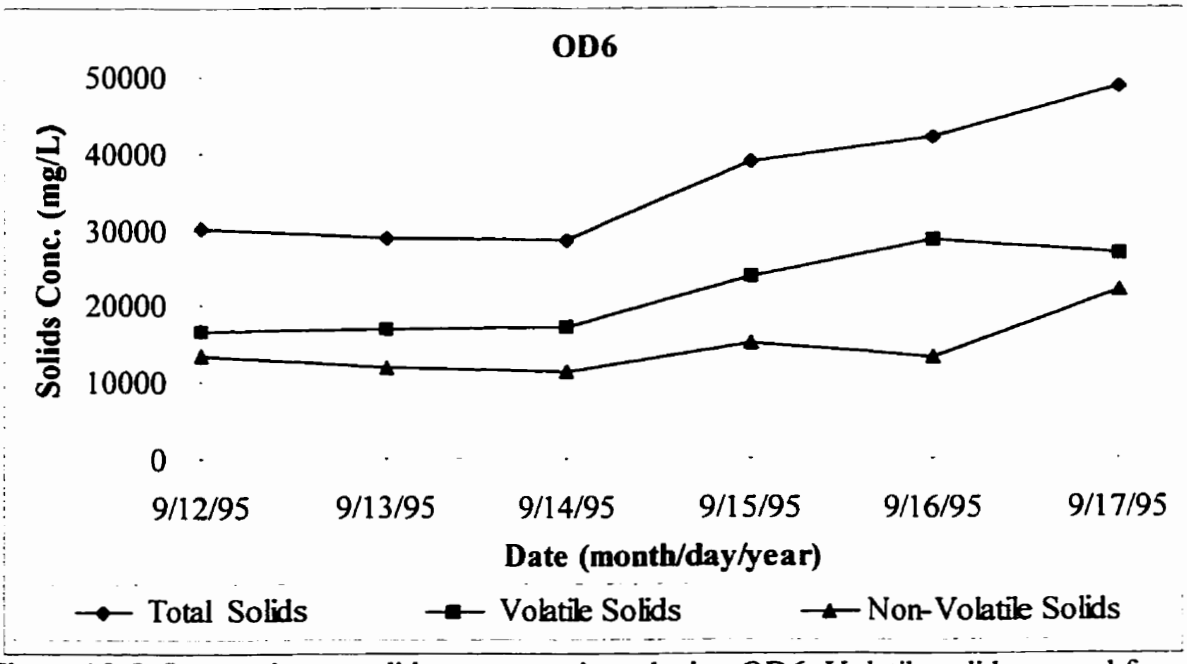


Figure 15. Influent primary solids concentrations during OD6. Volatile solids ranged from 16690 to 28650 mg/L with an average of 21690 mg/L throughout OD6.

5.2.1.2 Solids Loading

The average TS and VS loadings to OS24, OD24, OD18, OD12, and OD6 are shown in Table 2. The total solids loadings ranged from 38.44 to 144.69 kg TS/m^3·d. These loadings are higher than is typically experienced. For example, the highest reported value in literature is 30 kg TS/m^3·d (Kelly, 1990; Messenger, 1989). The high loadings encountered in this study are the result of short retention times and the high solids concentrations experienced in the TAD reactors.

Table 2. Solids Loading to Thermophilic Aerobic Digesters

Exp.	Total Solids (kg TS/m^3·d)	Volatile Solids (kg VS/m^3·d)
OS24	38.44	27.84
OD24	43.06	28.23
OD18	68.59	39.12
OD12	137.99	73.45
OD6	144.69	86.76

5.2.2 Oxygen Supply

The TAD reactors were aerated with 100% pure oxygen by volume. The oxygen flow rates during these experiments were 0.14 m^3/m^3·h for the OS experiment, and 0.025 m^3/m^3·h for the OD experiments. Based on the amount of volatile solids oxidised (Section 5.3.1.1) and

the amount of oxygen supplied, the maximum possible oxygen requirement (kg O_2/kg VS) was calculated (Table 3). The maximum oxygen requirement was 0.95 kg O_2/kg VS destroyed during the OS experiment and ranged from 0.18 to 0.55 kg O_2/kg VS destroyed during the OD experiments. The actual the oxygen requirement (amount of oxygen utilised) is much less since the oxygen transfer efficiency is not 100%. By comparison, the values reported in literature range from 0.7 to 4.59 kg O_2/kg VS with an average of about 2.0 kg O_2/kg VS.

Table 3. Maximum Oxygen Requirement Based on Volatile Solids Oxidised

Experiment	**Maximum Oxygen Requirement (kg O_2/kg VS)**
OS24	0.95
OD24	0.27
OD18	0.23
OD12	0.18
OD6	0.55

Since the theoretical oxygen requirements exceed the amount available in the OD experiments, both oxidation and fermentation must be occurring in the reactors through facultative micro-organisms. Even though one would expect to see some sort of trend under the OD conditions, this was not the case, most likely due to the heterogeneous nature of the primary sludge.

Even though the maximum oxygen requirement during the OS experiment was within the range reported, the actual oxygen requirement would be much less due to the oxygen transfer efficiency. Oxidation is most likely the primary metabolic process occurring in the OS reactor although fermentation may also be occurring on a lesser scale.

5.2.3 Dissolved Oxygen

Dissolved oxygen values were taken for the first 4 weeks of experimentation, and subsequently stopped due to the unreliable nature of the results been obtained. DO probes developed for use in biological systems do not have adequate temperature compensation above 45°C. In addition, it was observed that at low DO concentrations (less than 1 mg/L) the probes were inaccurate. Likewise, Boulanger (1995) found that the interference by carbon dioxide resulted in inaccurate DO levels below 1 mg/L.

5.2.4 TAD Discharge Gas

Discharge gases were measured as another means of defining the aerobic state. Microbial degradation of organic material in an anaerobic environment is linked with the production and release of biogas. Table 4 lists the average percent by volume of N_2, CO_2 and CH_4 measured in the TAD discharge gas grab samples throughout the experiments. In the oxygen-satisfied experiment no methane was present indicating that excess oxygen was been fed into the reactor (oxygen may have a 'toxic effect' on methanogens since they require an anaerobic environment). Since methane was found in all oxygen-deprived reactors, this illustrates that there was a difference in microbial populations present in the oxygen-deprived

and oxygen-satisfied reactors due to the oxygenation state.

The relatively low gas production obtained indicates that methanogenesis was successfully suppressed at the retention times studied. The results presented in Table 4 do not indicate any trend in constituent values with respect to the different oxygen retention times studied.

Table 4. TAD Discharge Gas Constituents

Experiment	N_2 (%)	CO_2(%)	CH_4(%)
OS24	84.4	15.6	0
OD24	51.1	46.7	2.2
OD18	64.8	34.3	0.9
OD12	53.2	45.3	1.5
OD6	67.9	31.1	1.0

5.2.5 Oxidation Reduction Potential

Figure 16 shows examples of daily ORP variations with oxygenation state. The oxygen flow rate of 0.14 $m^3/m^3 \cdot h$ produced ORP values which ranged between -225 mV and -10 mV. This range falls within the anoxic state and somewhere between the anoxic and aerobic states as described by Koch et al. (1988). Based on Boulanger's (1995) target trace ORP pattern, this state would be considered oxygen-satisfied. Immediately after feeding the ORP would decrease drastically and then slowly rise over the following 2½ hours. Under similar operating

conditions Chu *et al.* (1994) reported an ORP range of approximately -250 to 60 mV during their microaerobic aerated state.

The oxygen flow rate of 0.025 $m^3/m^3 \cdot h$ consistently exhibited similar ORP trace patterns as those reported by Boulanger (1995) and Chu *et al.* (1994). ORP values remained relatively constant between -330 to -390 mV. This range falls within the anaerobic state defined by Koch *et al.* (1988) and the oxygen-deprived condition as defined by Boulanger (1995).

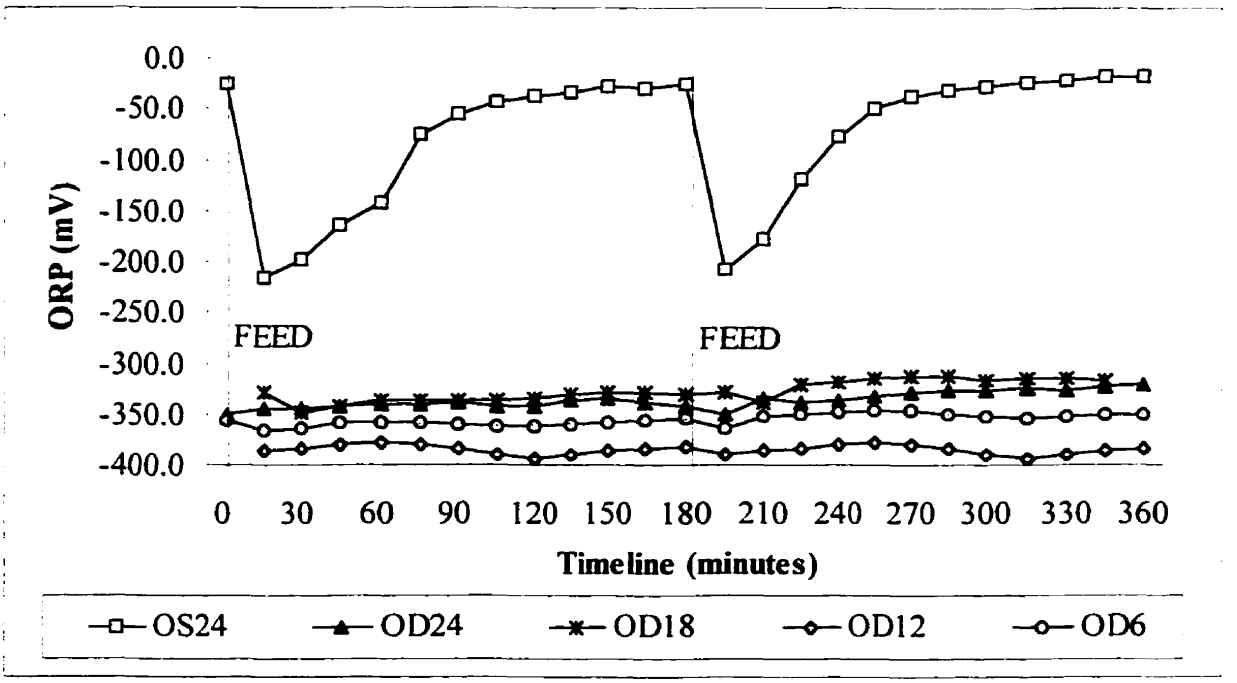


Figure 16. Variation of ORP with oxygenation state.

Oxygen transfer greatly increased as the rotational speed of the mixers increased for a

given oxygen flow. This is due to the smaller air bubbles which are formed as a result of the greater shearing of oxygen flows. This phenomenon occurred in the OS24 experiment. Initially the mixer rotational speeds were set at 200 rpm, however, the ORP values obtained from the OS24 reactor were considered too negative for the oxygen been supplied. At this time it was decided to increase the rotational speed to 400 rpm. With this mixer speed increase, the ORP values showed a dramatic increase as shown beyond 7/31/95 in Figure 17.

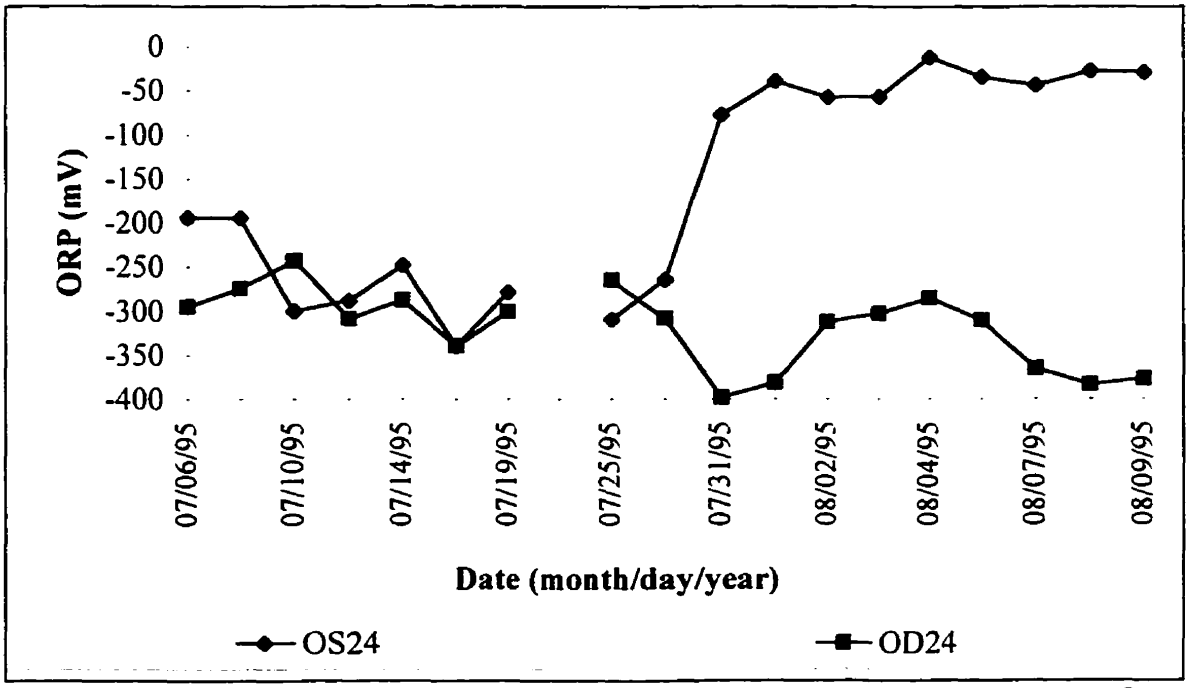


Figure 17. ORP trace patterns for OS24 and OD24. Initial mixer speed of 200 RPM and final mixer speed of 400 RPM.

5.2.6 Alkalinity

Table 5 summarises the total alkalinity concentrations recorded during the experiments. Also shown is the theoretical change in alkalinity expected from the increase in ammonia concentration (Section 5.3.3.1).

Table 5. Comparison of Measured to Expected Total Alkalinity

Exp.	Total Alkalinity			
	Primary Sludge	**TAD Sludge - Measured**	**Measured Increase**	**Theoretical Expected Increase**
	(mg/L as $CaCO_3$)	**(mg/L as $CaCO_3$)**	**(mg/L as $CaCO_3$)**	**(mg/L as $CaCO_3$)**
OS24	1257	2394	1137	70
OD24	1526	2501	975	1266
OD18	1909	2736	827	1075
OD12	2718	3276	558	1153
OD6	1556	1941	385	287

The alkalinity appears to increase with an increase in oxygenation. The amount of alkalinity produced in OS24 was far greater than what was expected from ammonification alone. Additional research is required to explain the differences between the theoretical expected increase and the measured alkalinity values presented in Table 5.

The alkalinity also increased in all OD experiments. This increase is most likely metabolism-generated, which is the increase in alkalinity in a wastewater resulting from the

metabolism of an organic compound with the release of a cation (Speece, 1996). Metabolism-generated alkalinity is determined by measuring the concentration of degradable cation-releasing organic components (such as proteins), the salts of organic acids or soaps, and sulphate/sulphite reduction. If no cation is released from the organic during biodegradation, no alkalinity will be generated as is the case with carbohydrates, sugars, organic acids, aldehydes, ketones and esters (Speece, 1996).

Total alkalinity increased during the OD experiments, as expected, since the biodegradation of nitrogenous organic compounds in an anaerobic or aerobic process result in an increase in alkalinity which is proportional to the quality of ammonium released. The alkalinity generated from protein or amino acids is as follows:

$$RCHNH_2COOH + H_2O \rightarrow RCOOH + NH_3 + CO_2 + 2H_2 \quad (6)$$

$$NH_3 + H_2O + CO_2 \rightarrow NH_4^+ + HCO_3^- \quad (7)$$

Ammonium bicarbonate is then generated, which in turn helps maintain a neutral pH in the system. The conversion of non-ammonia TKN to ammonia adds 3.5 mg of alkalinity per mg of ammonia formed.

The largest alkalinity increase due to ammonia occurred in the OD24 experiment and decreased as the retention time decreased. This is as expected since a longer digestion time results in greater hydrolyzation of organic nitrogen to ammonia.

Bicarbonate alkalinity (B Alk) is the total alkalinity minus the alkalinity of the salts of

VFA (due to neutralized VFA) with only the bicarbonate alkalinity available to neutralize additional VFA. Bicarbonate alkalinity is shown as follows, with the VFA expressed as acetic acid (Speece, 1996):

$$\text{B Alk} = \text{Total Alk} - (0.83)(0.85)(\text{VFA}) \quad (8)$$

where,

0.85 = 85% of VFA titrated at pH of 4.0.

0.83 = 50 E.W. $CaCO_3$/60 E.W. of HAc

E.W. = Equivalent Weight

VFA = 60 expressed as HAc

$HAc \rightarrow H^- + Ac^-$

Acetate Salt = Alkalinity

Any cation except H^- keeps Ac^- in the alkalinity form. A significant fraction of the bicarbonate alkalinity may be allocated to neutralize the CO_2/H_2CO_3 with only the excess available for neutralizing an increase in VFA. The concentration of bicarbonate alkalinity available to neutralize additional free VFA is know as the reserve bicarbonate alkalinity (Speece, 1996). The theoretical calculated bicarbonate concentrations are shown in Table 6.

The bicarbonate alkalinity concentrations increased under the higher oxygenation rate and decreased under the lower oxygenation rate due to the VFA concentrations (discussed in Section 5.3.2). Although the bicarbonate alkalinity concentration decreased under the OD

conditions, the concentrations are still high enough to buffer the system pH and have additional alkalinity available for the subsequent mesophilic anaerobic digestion step.

Table 6. Quantity of Bicarbonate Alkalinity Available to Neutralize Additional VFA

Exp.	Bicarbonate Alkalinity	
	Primary Sludge (mg/L as $CaCO_3$)	TAD Sludge (mg/L as $CaCO_3$)
OS24	162	2374
OD24	431	271
OD18	942	716
OD12	1295	841
OD6	890	839

Pfeffer (1981) discussed the effect of elevated temperature on the pH/alkalinity/gas composition. The temperature effect manifests itself in two ways: 1) by a change in the equilibrium constants for the bicarbonate system, and 2) by a change in the vapour pressure of water (cited in Speece, 1996). The lowered solubility of CO_2 in water results in only about half the concentration at 60°C as at 35°C. The reduced CO_2 solubility consequently reduces the alkalinity requirement at thermophilic temperatures. Pfeffer illustrated that a reactor operating at 40°C and producing a gas containing 40% CO_2 would require an alkalinity of about 2250 mg/L to maintain a pH of 7.0. The same reactor operating at 60°C would require only 1300 mg/L of alkalinity to maintain a pH of 7.0, due to the temperature dependent solubility of CO_2.

5.2.7 pH

The pH of a biological system dictates to some extent the possibility of survival and the reproduction rates of microbial species present. It is however, the micro-organisms themselves in many systems who dictate the pH. Table 7 shows the changes in pH between the TAD influent and effluent. In all experiments the pH remained neutral and did not require adjustment supporting the findings of Deeny *et al.*(1991). The pH increased during the oxygen satisfied experiment and either remained the same or slightly decreased during the oxygen deprived experiments. The "equilibrium" pH range attained is a function of the relative concentrations of proteins and amino acids utilised during the digestion process and the generation of VFAs. During the oxygen-satisfied experiment the low VFA concentrations combined with higher amination resulted in an increase in pH. Likewise, Elefsiniotis (1993) while studying acid phase digestion discovered that VFA concentrations below 400 mg/L resulted in an increase in pH, and no appreciable variation in pH (less than 0.3 units) occurred at concentrations ranging from 400 to 750 mg/L.

The lower pH values may be due to the build-up of volatile fatty acids. For example, acetic acid was present in the OD reactors in high concentrations (discussed in Section 5.3.2) and buffers in the 4 to 6 pH range. The pH depressions that could occur in a nitrifying environment were not experienced since the thermophilic operating temperatures in the reactors suppressed nitrification.

No correlation of pH to detention time was observed. This is in contrast to the results reported by Matsch and Drnevich (1977) who reported a pH increase with detention time.

Table 7. Comparison of pH Variations in the TADs

Exp.	Primary Sludge		TAD Sludge	
	Range	Average	Range	Average
OS24	5.70 - 6.15	5.93	6.80 - 7.40	7.06
OD24	5.70 - 6.50	6.14	5.90 - 6.40	6.15
OD18	6.00 - 6.5	6.26	5.75 - 6.15	5.98
OD12	6.00 - 6.30	6.13	5.85 - 6.10	5.93
OD6	5.90 - 6.95	6.32	5.90 - 6.20	6.02

5.2.8 Summary

The average total solids in the feed ranged from 3.62 to 6.9% while the average volatile solids ranged from 2.17 to 3.67% with an average of 2.88% throughout the different experiments. Due to the short retention times the solids loadings were much higher than those reported in literature for ATP systems.

The two different oxygenation states were primarily distinguished by the different ORP trace patterns and the oxygen supply to the reactors. DO measurements proved to be unreliable at 55°C and at low DO concentrations. The oxygen flow rate of 0.14 m^3/m^3-h resulted in an ORP range of between -225 mV and -10 mV which is defined by other researchers to be anoxic, microaerobic, or oxygen-satisfied. The oxygen flow rate of 0.025 m^3/m^3-h produced ORP values in the range of -330 to -390 mV which is defined as anaerobic or oxygen-deprived by other researchers. The discharge off gases verified the oxygenation state in each experiment mainly though the presence or absence of methane gas.

The alkalinity increased under all conditions studied and was found to increase with

increasing oxygen supply and retention time. The alkalinity increase during the OD experiment was most likely metabolism generated alkalinity from the nitrogenous organic compounds. The alkalinity increased with increasing retention time since the longer digestion time resulted in greater hydrolyzation of organic nitrogen to ammonia. Alkalinity was also formed from the salts of organic acids, however, this alkalinity is not available to neutralize additional VFA. The bicarbonate alkalinity concentration increased under the higher oxygenation rate due to the low VFA productions and decreased under the lower oxygenation rate due to the high concentration of VFAs produced. Although the bicarbonate alkalinity concentration decreased under the oxygen-deprived conditions, the concentration was still high enough to buffer the system pH in the neutral range and still have additional alkalinity available for a future mesophilic anaerobic digestion step. By operating at thermophilic temperatures the need for supplemental alkalinity is reduced. In all experiments this alkalinity increase is a strong incentive due to the relatively high costs of supplemental alkalinity.

5.3 THERMOPHILIC AEROBIC DIGESTION PERFORMANCE

5.3.1 Particulate Organic Carbon Transformation

5.3.1.1 Volatile Solids Reduction

For substrate degradation both hydrolysis and solubilization of the compounds must occur. The rate of hydrolysis generally depends upon the temperature, pH, nature of the biomass, particle size, type of substrate, and the remaining concentration of the biodegradable suspended matter (Eastman and Ferguson, 1981). Substrate solubilization can be estimated

from a number of non-specific parameters such as soluble COD, filtered TOC, TSS, and VSS.

Evidence that degradation took place is indicated by the decrease in particulate organic carbon as shown in Figures 18 and 19. The TAD reactors did very little as far as VS reductions. Figure 18 illustrates the reductions calculated by comparing the influent primary sludge and the digested sludge VS concentrations. The largest reduction of 15.3% was achieved in the anoxic reactor (OS24). The volatile solids reductions varied from 6.4 to 12.3 percent in the anaerobic aerated reactors (OD24, OD18, OD12, and OD6). It is evident that the retention time variation plays a minimal role in the degradation of particulate matter, at least in the range investigated.

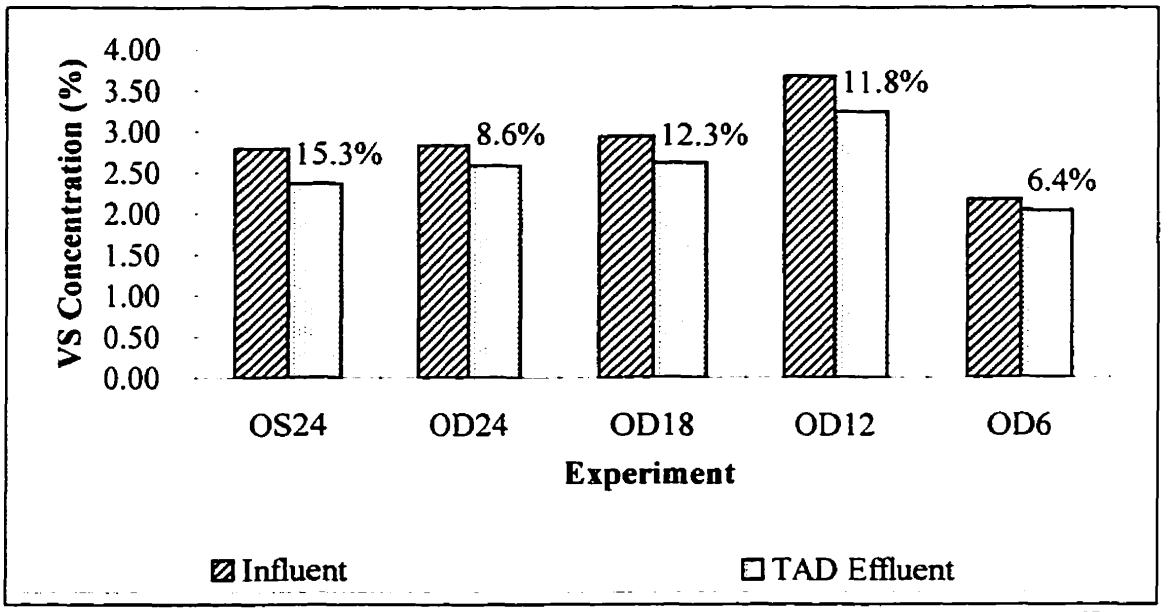


Figure 18. Comparison of percent volatile solids measured in TAD influent and TAD effluent during OS24, OD24, OD18, OD12, and OD6. Percent reductions are located above corresponding experiment.

Figure 19 also shows the volatile solids reductions calculated for the OS24, OD24, OD18, OD12, and OD6 experiments. In this case however, the calculations are based upon grams of total VS oxidised, rather than the difference in primary sludge and digested sludge VS concentrations to avoid errors from water evaporation. Detailed calculations are provided in Appendix C. The largest reduction of 17.0% was achieved in OS24. The volatile solids reductions varied from 6.7 to 12.4 percent in the OD reactors. The VS removal appears to increase with an increase in oxygen supply. This finding is similar to those results reported by Hawash *et al.* (1994).

Solids degradation increased with decreasing SRT/HRT until a maximum was reached at 12 hours. Based on this trend it appears as though solids degradation increases with an increasing solids loading. The 6 hour SRT/HRT exhibited the smallest VS reduction most likely indicating that at the shorter SRT/HRT the hydrolysis mechanisms or the production of extracellular metabolic intermediates limit the VS degradation rate (see Section 5.3.1.2).

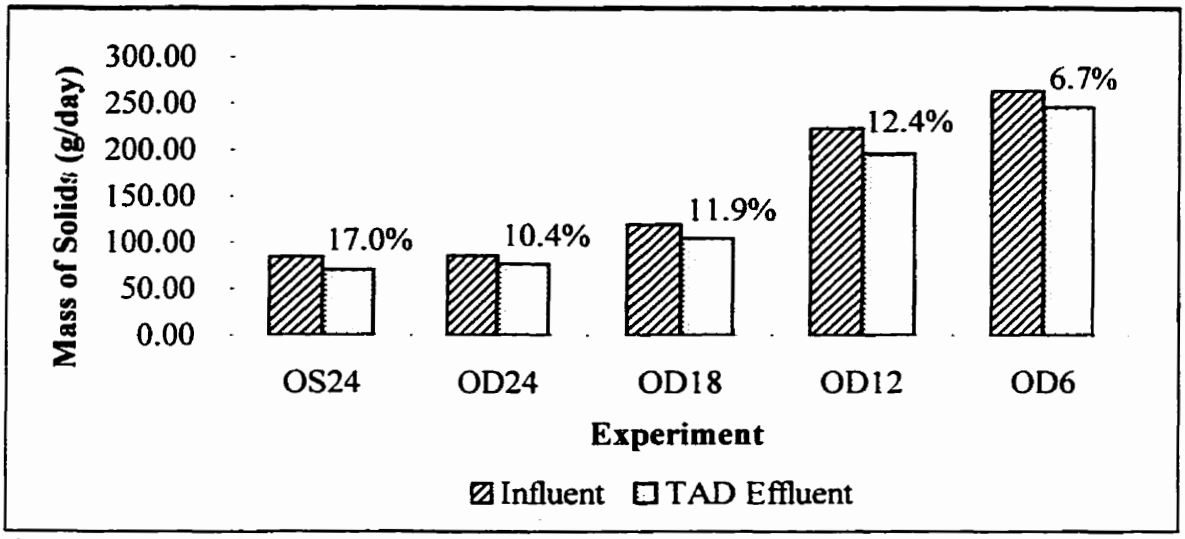


Figure 19. Comparison of grams of total VS measured during OS24, OD24, OD18, OD12, and OD6. Percent reductions are located above corresponding experiment.

To evaluate these results, temperature · detention time products were calculated (Table 8) and compared to the EPA design curve shown in Figure 20. The results of this study exceeded those values predicted by the EPA Design Curve in all instances. For example, for a system temperature · detention time product of about 55, the EPA Design Curve predicts a 9% VS reduction. The 55°C · day values obtained in this study are 17.0% and 10.4% during OS24 and OD24 respectively. Likewise, for a 13.8 temperature · detention time product in this study (OD6) a 6.7% VS reduction was observed while for the same temperature · detention time product, the EPA Design Curve predicts about only a 1% VS reduction. The relatively high percent VS reductions obtained indicate that the TAD process is very proficient with respect to solids removal.

Table 8. Calculated TAD Temperature · Detention Time Products for OS24, OD24, OD18, OD12 and OD6

Exp.	TAD Temperature · Detention Time Product (°C · days)
OS24	55.0
OD24	55.0
OD18	41.3
OD12	27.5
OD6	13.8

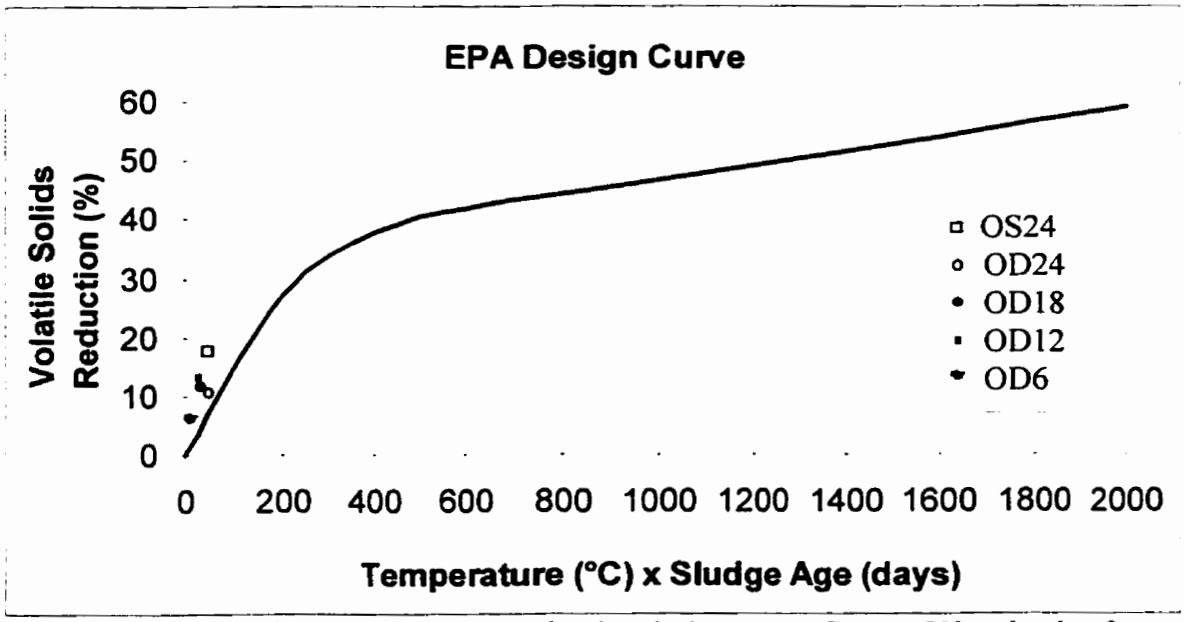


Figure 20. Aerobic digester percent VS reduction design curve. Greater VS reduction for every temperature · detention time product studied were achieved than those values predicted by the EPA Design Curve (EPA, 1990).

5.3.1.2 Chemical Oxygen Demand Solubilization

The extent of organic carbon transformation can be viewed from the perspective of soluble chemical oxygen demand (SCOD) creation. Table 9 shows how the percent SCOD increased under the OD conditions and decreased under the OS condition. The SCOD increase during the oxygen-deprived experiments is the result of substrate conversion from a particulate to a soluble state. The SCOD decrease under the oxygen-satisfied conditions is the result of slow solubilization of solid COD combined with VFA conversion to CO_2. Likewise, Boulanger (1995) found that the solubilization of solid COD occurred faster under oxygen-deprived conditions than under oxygen-excess conditions.

The SCOD percent increase during the anaerobic aerated (OD) experiments increased with increasing residence time from 65.9 % at a 6 hour residence time to 95.1% at a 24 hour residence time. The large increase in SCOD is attributed to the volatile fatty acids (Section 5.3.2). The results show that a 12 hour retention time provided adequate time for volatile solids conversion to soluble substrate by the biomass. Increasing the retention time beyond 12 hours did not improve the solubilization of organic particulates significantly. With a 6 hour SRT/HRT, the solubilization efficiency was much lower. It is most likely that with a 6 hour SRT/HRT, the micro-organisms are not remaining in the system long enough to reach their optimum soluble substrate production efficiency.

In comparison with results from mesophilic fermentation of primary sludge, Elefsiniotis (1993) found a sharp drop in the solubilization efficiency as the SRT reached 5 days and a plateau was achieved at longer SRTs of 10 and 15 days.

Table 9. Chemical Oxygen Demand Solubilization Efficiency

Exp.	Primary Sludge (mg/L)	TAD Sludge (mg/L)	Solubilization Efficiency* (%)
OS24	3695	1854	N/A**
OD24	3638	7097	95.1
OD18	3518	6861	95.0
OD12	4490	8683	93.4
OD6	2453	4070	65.9

* Solubilization Efficiency: net SCOD as percentage of feed SCOD
** Decrease in SCOD concentration

The SRT/HRT has a profound effect not only on the net SCOD concentration, but also on the specific solubilization rates of COD expressed as mg of net soluble COD per mg of VS per day as shown in Table 10. The specific solubilization rates were greatly influenced by the oxygenation state. During the OS experiment, the rate of oxidation of dissolved substrate was much higher than the solubilization rate resulting in what appears as a negative COD specific solubilization rate. During the OD experiments, the solubilization rates were much higher. Likewise, Boulanger (1995) also discovered that solubilization rates are accelerated under oxygen-deprived conditions.

The specific solubilization rate was also affected by the retention time since the solubilization rate increased with increasing retention time. The low rate at the 6 hour residence time may indicate that either the short residence time is imposing a stress on the metabolic activity or that the time available is too limited for substrate assimilation.

Table 10. COD Specific Solubilization Rate as a Function of Oxygenation State and Retention Time

Exp.	COD Rate (mg COD/mg VS·d)
OS24	N/A*
OD24	0.123
OD18	0.114
OD12	0.114
OD6	0.075

*Decrease in soluble COD concentration

Figures 21 to 25 illustrate the variations in influent and effluent SCOD throughout the different experiments. There was a great variability in the influent SCOD concentrations. This variability may be due to the varying hydraulic loads to the North End Sewage Treatment Plant throughout the summer months and the different retention times occurring in the hoppers where fermentation is occurring.

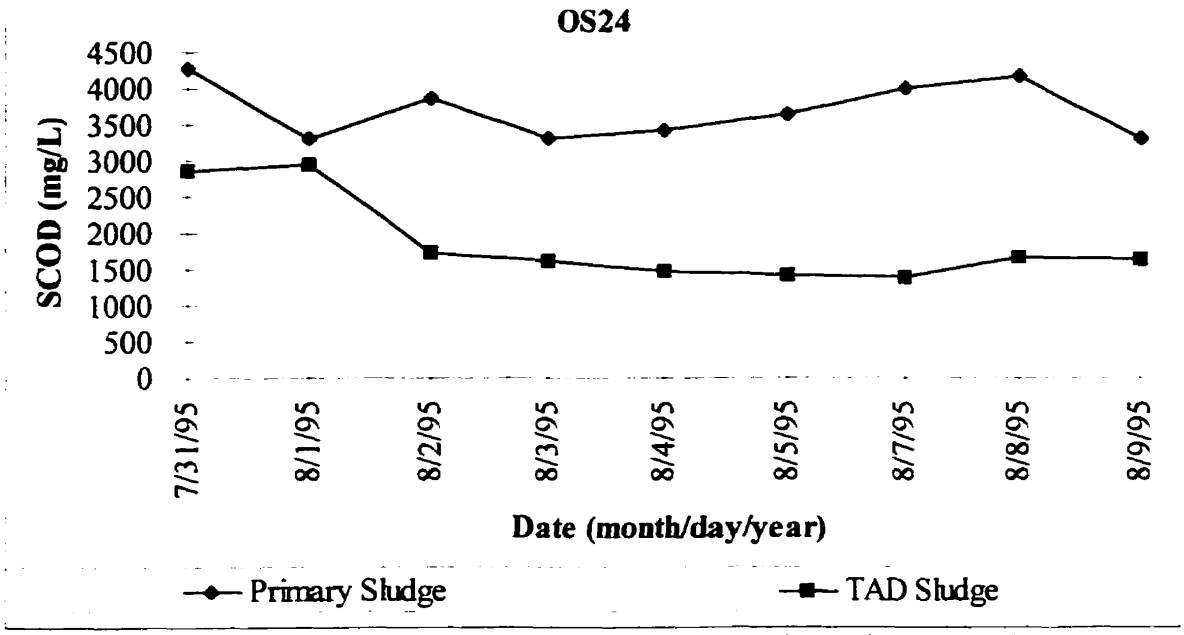


Figure 21. Primary and TAD sludge soluble chemical oxygen demand concentrations during OS24 experiment. SCOD concentrations decreased in TAD reaction.

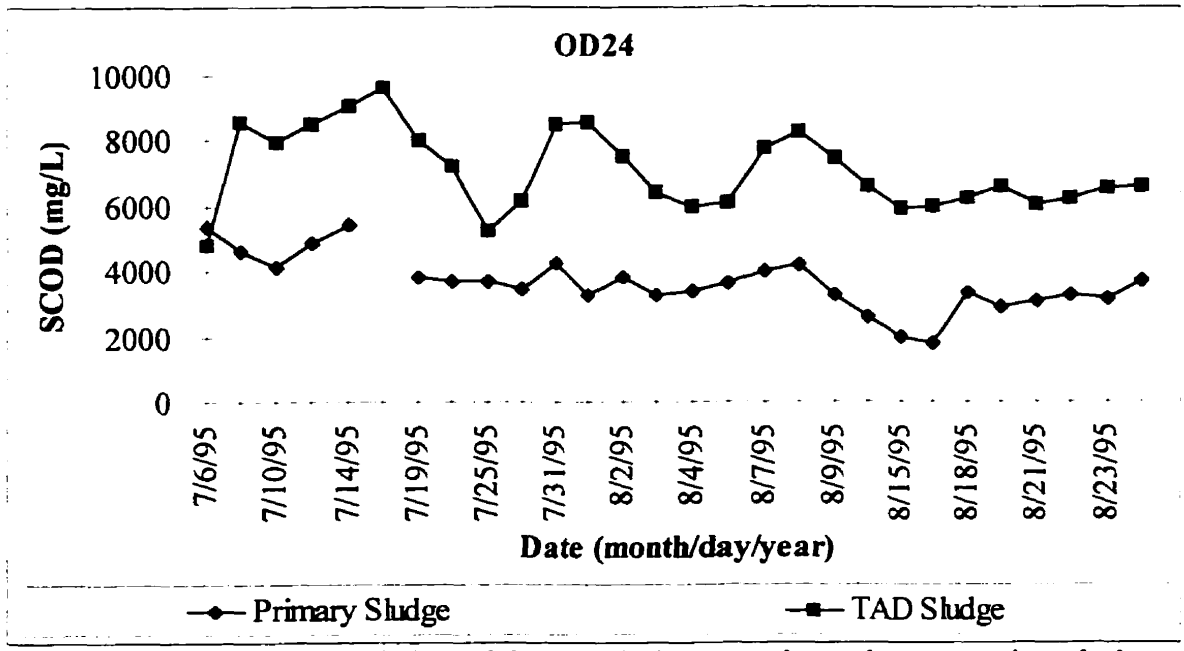


Figure 22. Primary and TAD sludge soluble chemical oxygen demand concentrations during OD24 experiment. SCOD concentration increased in TAD reaction.

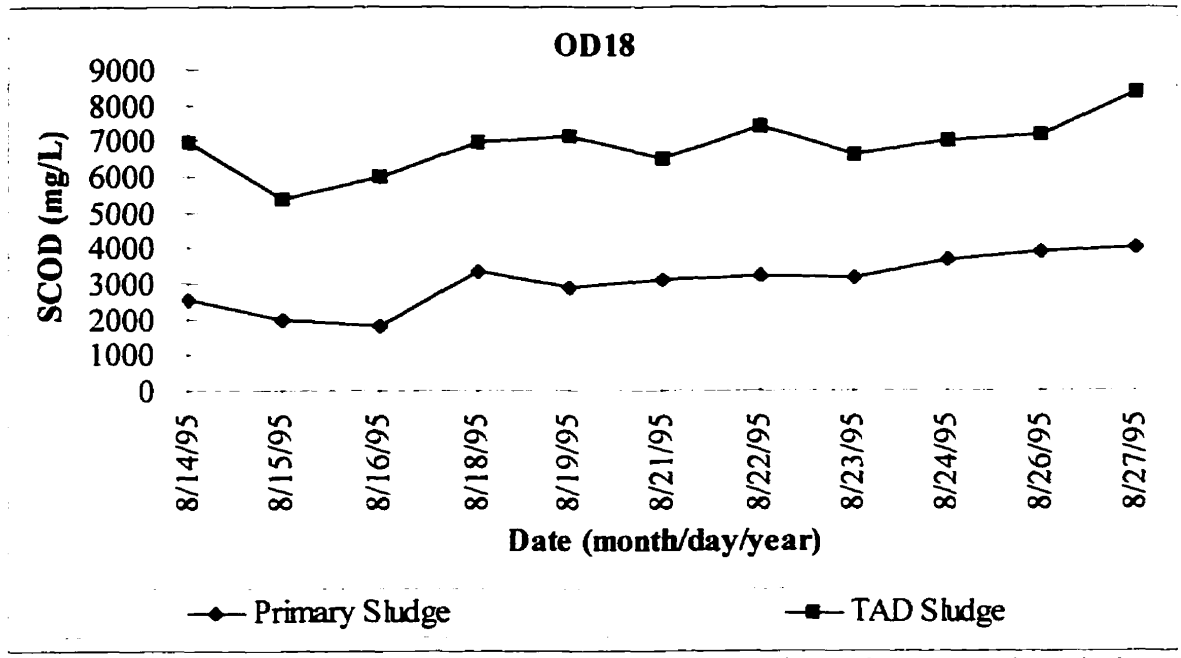


Figure 23. Primary and TAD sludge soluble chemical oxygen demand concentrations during OD18 experiment. SCOD concentration increased in TAD reaction.

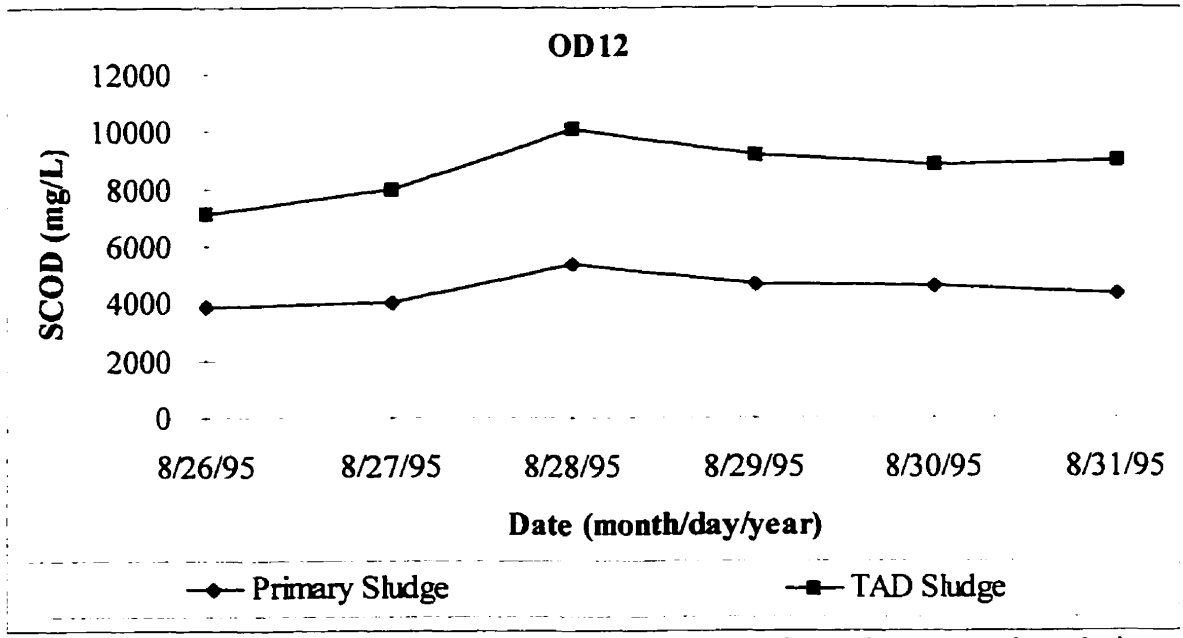


Figure 24. Primary and TAD sludge soluble chemical oxygen demand concentrations during OD12 experiment. SCOD concentration increased in TAD reaction.

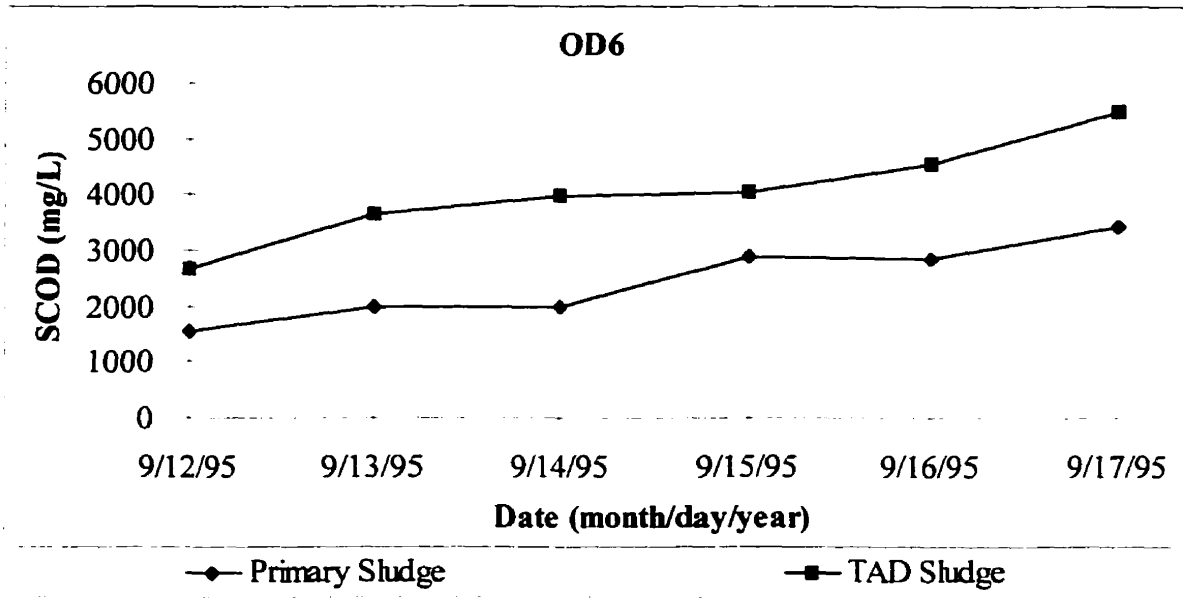


Figure 25. Primary and TAD sludge soluble chemical oxygen demand concentrations during OD6 experiment. SCOD concentration increased in TAD reaction.

During both the OD and OS experiments, the solubilization product concentrations in each reactor followed roughly the same trend associated with the strength of the primary sludge. No correlation was found between the COD removal and the concentration of COD in the feed as was reported by Ponti *et al.* (1995a).

5.3.2 Volatile Fatty Acids

5.3.2.1 Volatile Fatty Acid Production

Both the soluble organic compounds initially present in the sludge and the ones generated in the solubilization process are used by the acidogenic bacteria to produce a wide variety of compounds. The compounds produced are mainly in the form of short chain volatile

fatty acids (C_2-C_5).

All VFA samples were collected at the end of the feed cycle. At this time the ORP in the OS experiment was at its highest and the ORP in the OD experiments was still below -300 mV. High increases in VFA concentrations occurred in the OD experiments while VFAs were consumed during the OS experiment as shown in Table 11. Similar results have been found by numerous researchers (Chu *et al.*, 1994; Boulanger, 1995; and Mason *et al.*, 1987).

The change in VFA production in each experiment followed closely the same pattern observed during the solubilization process. The net VFA specific production rate (as acetic acid) expressed as mg VFA/mg VS·d, at steady-state operation is also presented in Table 11.

Table 11. VFA Specific Production Rate as a Function of Oxygenation State and Retention Time

Exp.	Primary Sludge		TAD Sludge		
	Total VFA (mg HAc/L)	**VFA/VS (mg HAc / mg VS)**	**Total VFA (mg HAc/L)**	**VFA/VS (mg HAc / mg VS)**	**Specific Production Rate (mg HAc / mg VS·d)**
OS24	1621	0.058	29	0.001	N/A*
OD24	1552	0.055	3172	0.112	0.057
OD18	1370	0.047	2949	0.101	0.054
OD12	2017	0.055	3567	0.097	0.042
OD6	943	0.043	1562	0.072	0.029

* Decrease in VFA concentration

With an average influent VFA concentration of 0.055 mg HAc/mg VS, the 24 hour oxygen-deprived condition resulted in the highest average specific production rate of 0.057 mg HAc/mg VS·d. The VFA production rate decreased under the OS24 condition due to the large VFA oxidation rate.

The specific production rate is also affected by the retention time. The VFA production increased with increasing retention time. As with COD solubilization, the maximum occurs in the 24 hour oxygen-deprived experiment. The low rate at the shorter retention times may indicate that the short SRT is imposing a strong stress on the metabolic activity of the acidogenic bacteria and/or that the available time is too limited for substrate assimilation. The reduction in specific production rate increase between the 24 hour and the 18 hour retention time may be due to the conversion of soluble VFAs to gaseous products or the conversion rate maybe reaching a plateau. The specific VFA production rates appear to be more dependent on the retention time than was COD solubilization. Perhaps the pathways utilised in VFA production from soluble products are more influenced than those utilised in hydrolysis.

The specific production rate did not appear to vary with the influent volatile solids concentration as shown in Figure 26.

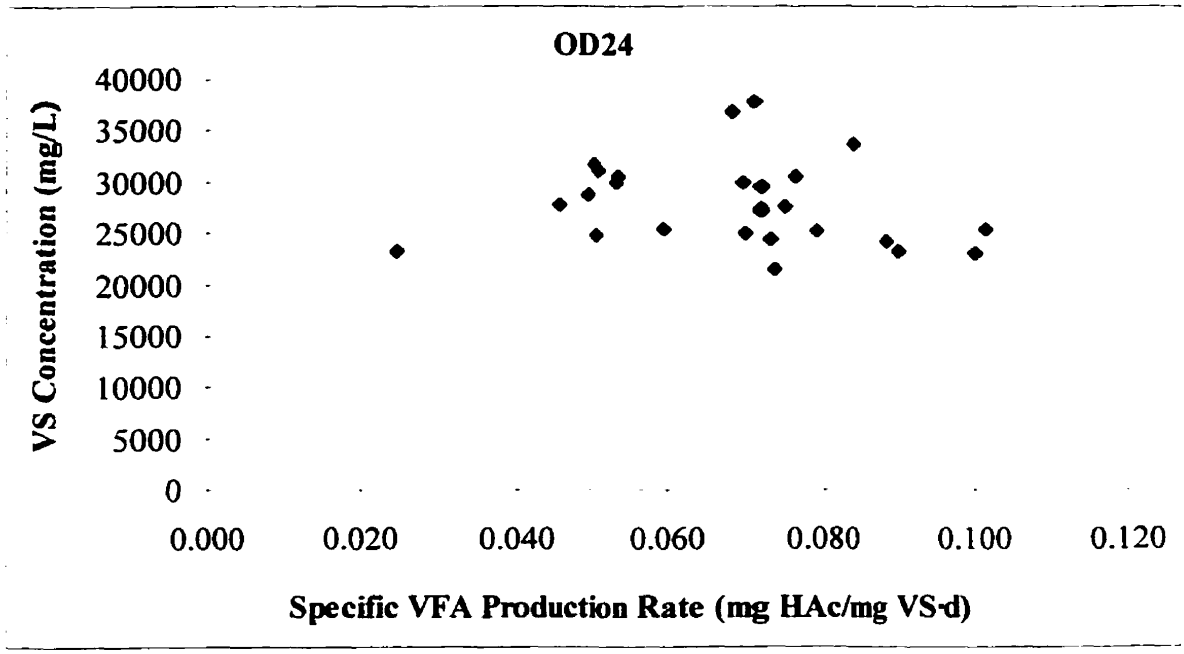


Figure 26. Variation of specific VFA production rate with feed VS concentration during OD24. No relationship appears to exist between the two parameters.

5.3.2.2 Volatile Fatty Acid Composition

Identifying individual acids formed in the TAD reactors may furnish valuable information on both the suitability to act as a carbon source for denitrification and the metabolic pathways involved in the process. The VFAs identified include: acetic, propionic, butyric, iso-butyric, valeric, and iso-valeric.

Acetic acid is formed directly from the fermentation of carbohydrates and proteins, as well as the anaerobic oxidation of lipids via a number of metabolic pathways (Elefsiniotis, 1993). Propionic acid is formed primarily from carbohydrates, but it can also be produced in the digestion of proteins and lipids to a lesser extent. Butyric acid is mainly generated in the

digestion of proteins and lipids. Iso-butyric acid and the isomers of valeric acid are mostly associated with the fermentation of proteins (Elefsiniotis, 1993).

There are some notable differences in the composition of the VFAs produced between the two oxygenation states. The OS condition produced an average of 30.3% propionic acid whereas the OD conditions produced an average of 17.2%. This higher propionic acid concentration found in the OS experiment is balanced by a lower concentration of butyric and valeric acids as shown in Table 12. This is in contrast to Chu *et al.* (1997) who found that as aeration rates decrease, propionate accumulation increased. The percentage of acidic acid was the highest of all VFAs and comparable for both oxygenation states studied. Similar results have been found by other researchers who discovered that the amount of each acid produced varied with residence time, although, acetate was produced in the highest concentration (Chu *et al.*, 1994; Hamer, 1987; Mason *et al.*, 1987). This is expected due to the average organic composition of volatile solids in primary sludge reported in literature (carbohydrates - 38%; proteins - 27%, lipids - 27%; other - 8%) (Elefsiniotis, 1993).

Table 12. Average Percent Volatile Fatty Acids Constituents

Experiment	Acetate	Propionate	Iso-Butyrate	Butyrate	Iso-Valerate	Valerate
OS	61.1	30.3	2.3	2.3	2.0	2.0
OD24	61.5	18.5	3.5	8.1	6.0	2.4
OD18	64.3	15.9	3.5	7.8	5.7	2.8
OD12	59.6	17.8	3.0	11.8	5.3	2.5
OD6	63.8	16.5	3.6	9.7	4.9	1.5
Average (OD)	62.3	17.2	3.4	9.3	5.5	2.3

*All values expressed as acetic acid equivalence.

It is interesting to note that Kelly (1990) reports acetic acid values of 70% during his ATAD studies at Salmon Arm while the results from this study indicate that the percentage of acetate ranges from 59.6-64.3%. This difference may possibly be explained by the different sludges used or possibly by the difference in pH. At Salmon Arm, pH values of 6.8-8.61 were obtained while during this study pH values ranged from 5.75 to 6.4. According to Danesh (1997) the reduction of wastewater pH causes a drop in the percent acetic acid component and profusion of other acids such as butyric and valeric.

In the range studied the percent VFA distribution was not affected by retention time. The speculation can therefore be made that the majority of the acid-producing bacteria are equally influenced by retention time variations between 6 and 24 hours.

Figure 27 shows that under the OS condition there is a shift towards acetic and propionic acid. While Figures 28 to 31 illustrate that under the oxygen deprived conditions there is a shift towards acetic acid and the isomers of butyric and valeric acid. Although the percent VFA distributions are somewhat similar in the OS and OD experiments, it is important to remember that the VFA concentrations are much smaller in the OS experiment than in the OD experiments. During the OD experiments the shift towards the higher molecular weight acids can be primarily attributed to an increased protein fermentation rate due to the favourable environment as compared to the primary clarifier.

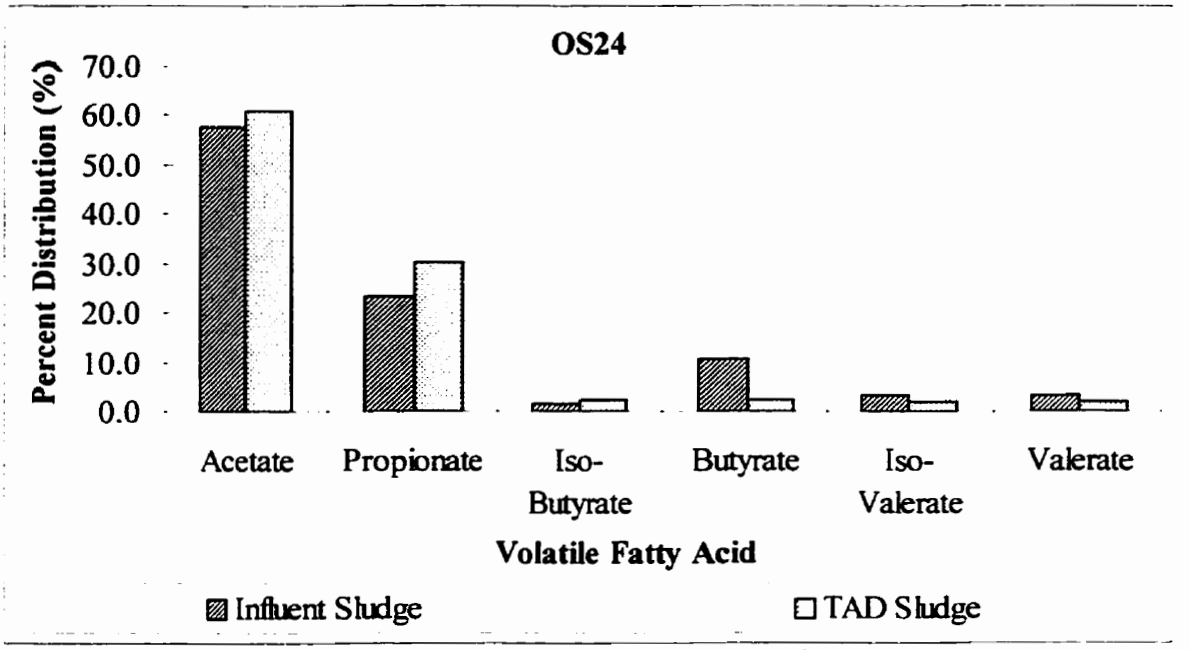


Figure 27. Percent VFA distribution during OS24. Percentage of acetate and propionate increased after thermophilic aerobic digestion.

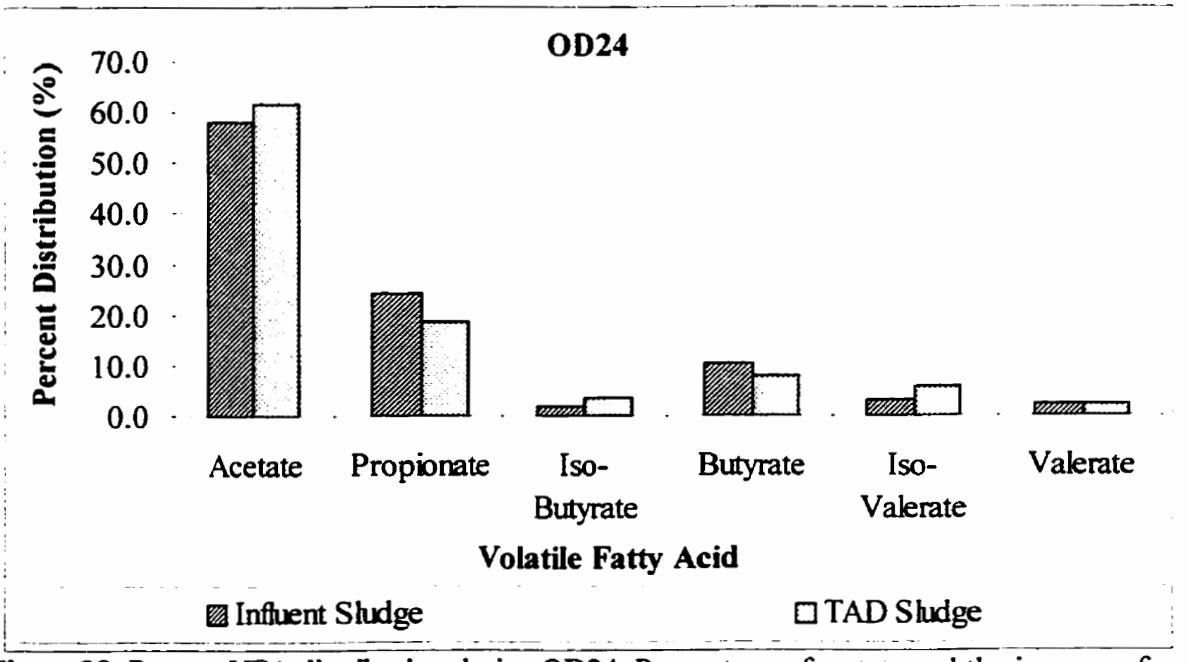


Figure 28. Percent VFA distribution during OD24. Percentage of acetate and the isomers of butyrate and valerate increased after thermophilic aerobic digestion.

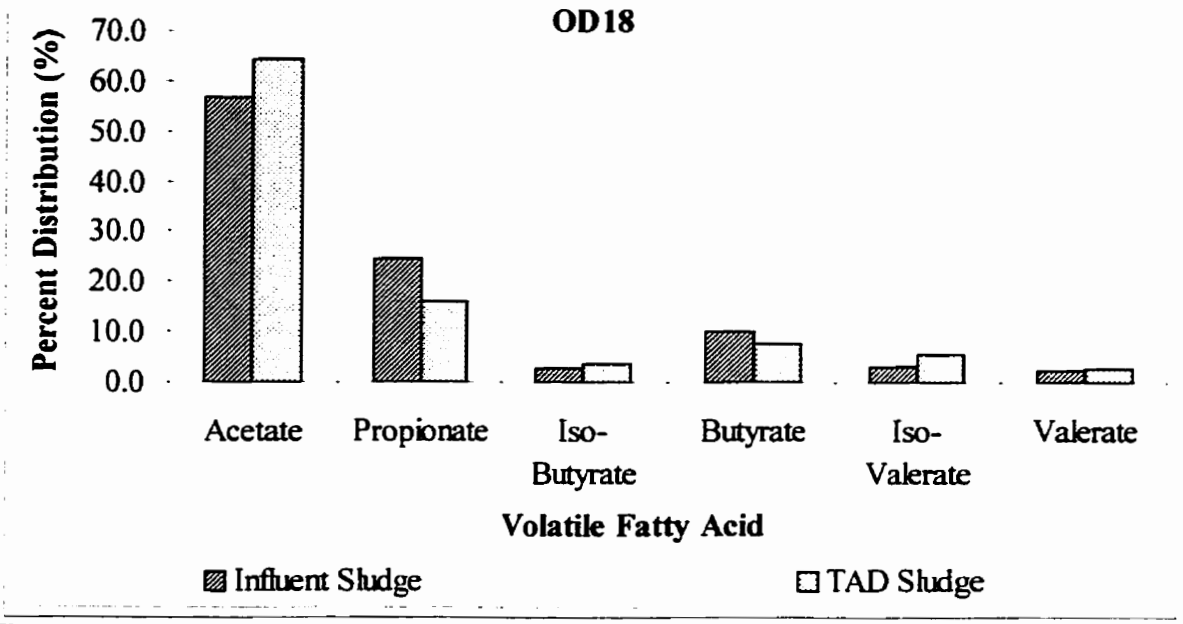


Figure 29. Percent VFA distribution in OD18. Percentage of acetate and the isomers of butyrate and valerate increased after thermophilic aerobic digestion.

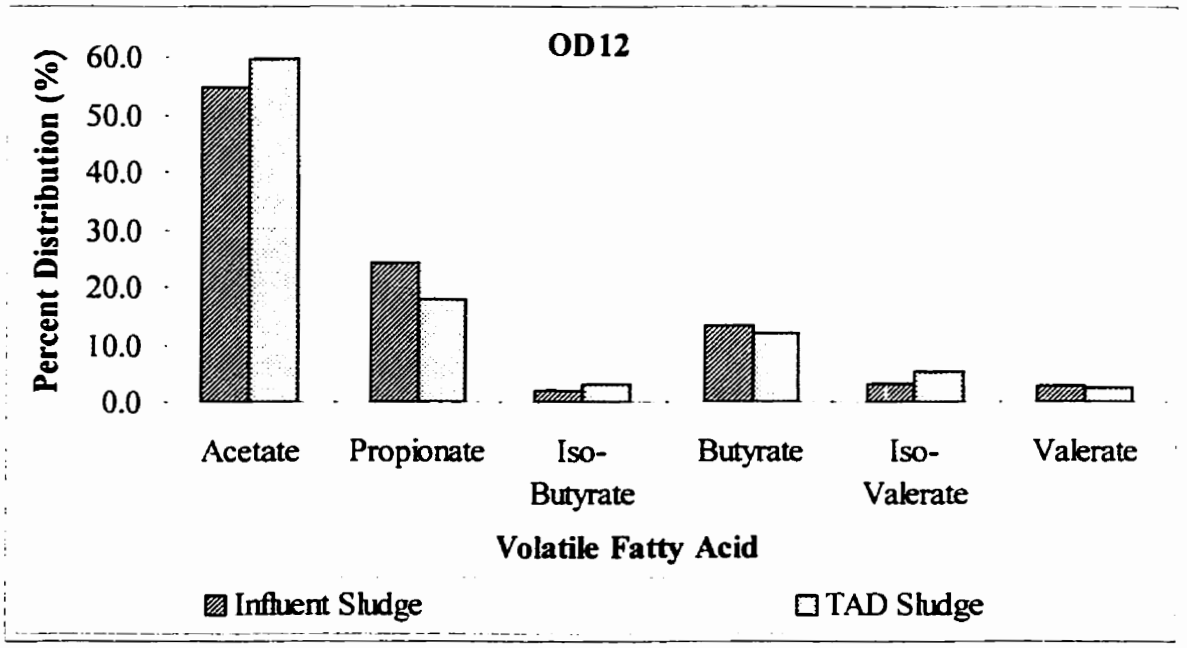


Figure 30. Percent VFA distribution in OD12. Percentage of acetate and the isomers of butyrate and valerate increased after thermophilic aerobic digestion.

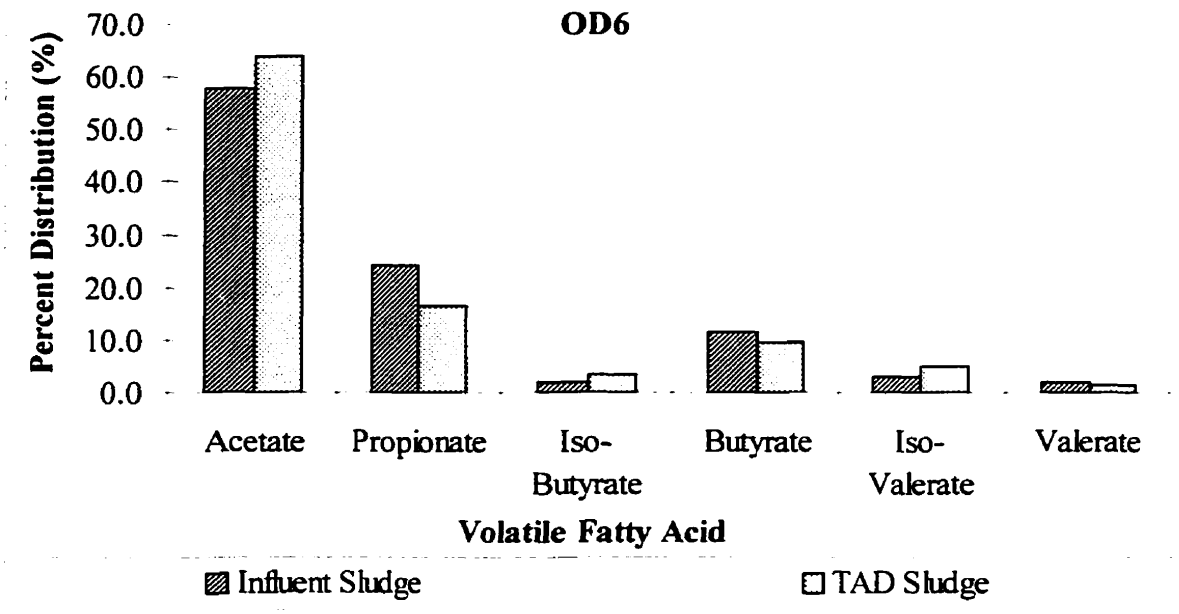


Figure 31. Percent VFA distribution in OD6. Percentage of acetate and the isomers of butyrate and valerate increased after thermophilic aerobic digestion.

5.3.2.3 Volatile Fatty Acid Contribution to Chemical Oxygen Demand

Using the conversion factors developed by Eastman and Ferguson (1981), the average amount of SCOD attributed to VFAs, was calculated as shown in Table 13. These results suggest that the SCOD content of the oxygen-deprived supernatant is easily biodegradable with SCOD percentage due to VFAs of over 60%. In comparison, VFAs accounted for only 2.4% of the SCOD content of the oxygen-satisfied supernatant. This suggests that the soluble COD content may not be easily biodegradable.

The percentage of SCOD due to VFAs increased with increasing residence time, however, beyond the 12 hr SRT/HRT the change was not substantial. This suggests that the rate of metabolism of soluble extracellular intermediate products to VFAs is independent of the

residence time above a certain minimum value and consequently, the conversion rate of soluble substrates to VFAs may have reached a plateau. The smaller percentage of volatile acid SCOD observed at the 6 hours SRT/HRT, indicates that the acid generation mechanisms are more affected by shorter SRT/HRT than are the hydrolysis mechanisms or the production of extracellular metabolic intermediates.

Table 13. Average Soluble Chemical Oxygen Demand Attributed to the Presence of Volatile Fatty Acids

Exp.	Average SCOD Concentration due to VFA (mg/L)		Average SCOD Concentration (mg/L)		% SCOD due to VFA	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
OS24	2615	44	3695	1854	70.8	2.4
OD24	2420	5061	3638	7097	66.5	71.3
OD18	2197	4678	3518	6861	62.5	68.2
OD12	3320	5847	4490	8683	73.9	67.3
OD6	1498	2443	2453	4070	61.1	60.0

5.3.3 Ammonia Nitrogen

5.3.3.1 Ammonia Nitrogen Production

The variation of influent ammonia nitrogen concentrations varied minimally from about 200 mg/L to 290 mg/L during the different experiments as shown in Figure 32. It was found that ammonia nitrogen accumulated under all conditions studied, however, more so with

decreasing oxygen supply and increasing retention time. For example, at a 24 hour residence time the percent ammonia nitrogen increase was 8.6% and 142.8% for the OS and the OD experiments respectively. During the OD experiments the ammonia nitrogen increase ranged from 41.6% during OD6 to 142.8% during OD24. Boulanger (1995) found that the same trend existed. Similar results were also found by Mason who observed that the ammonium ion (NH_4^+-N) accumulated under all conditions, although at short residence times this was hardly detectable.

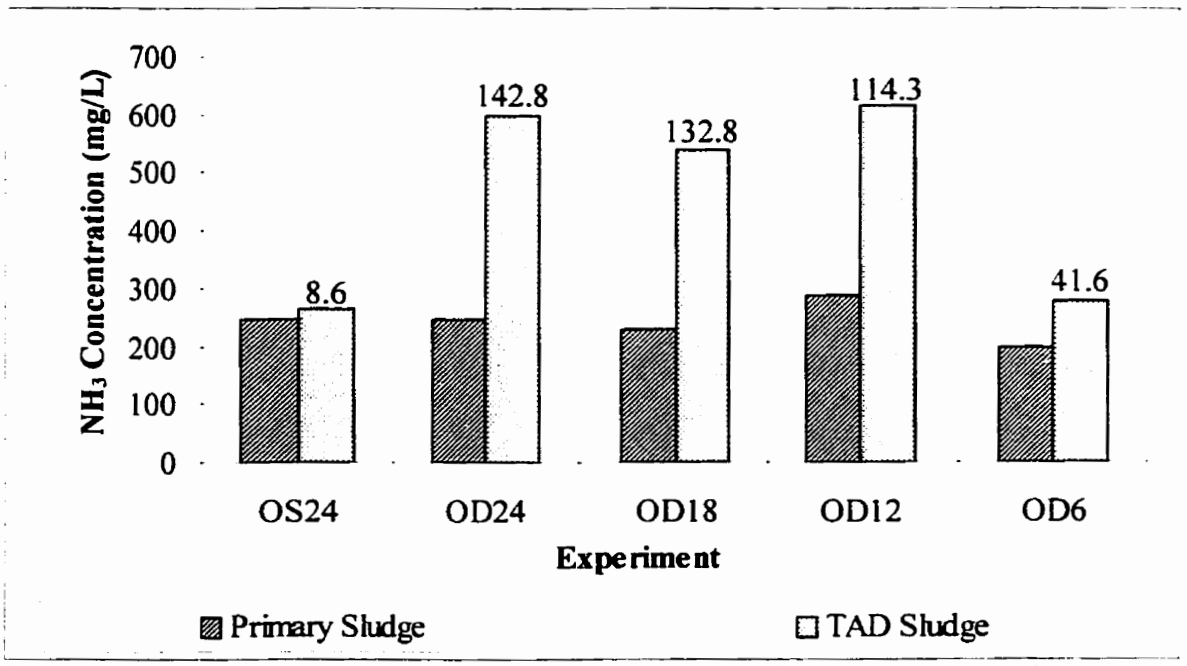


Figure 32. Increase of ammonia nitrogen in thermophilic aerobic reactors. Percent increase relationship to the influent concentration shown above respective experiment.

Ammonia nitrogen production is indicative of the deamination of the nitrogen containing fraction of the biomass and thus an increase in ammonia nitrogen content should reflect the extent of protein solubilization. This process probably occurs somewhat slower than the overall solubilization of the organic matter, hence the low level of accumulation of ammonia nitrogen at short residence times. The longer residence times resulted in consistently higher protein dissimilation. Some ammonia nitrogen was lost by stripping in the exhaust gases (strong ammonia odour was given off from manometer gas vent condenser water) and thus the measured concentrations can only be considered indicative of effective solubilization.

Ammonia ionization is controlled by pH and temperature (Table 14). With a pH of 7.06, the ammonia nitrogen concentration during OD24 was most likely comprised of about 4% un-ionized ammonia and 96% ionized ammonia. During the OD experiments the pH was lower and ranged from 5.93 to 6.15. Consequently, the equilibrium would have shifted even more towards the ammonium ion and the un-ionized ammonia concentration would have been less than 1%.

Table 14. Un-ionized Ammonia Percentage versus Temperature and pH

	Temperature (°C)		
pH	**25**	**35**	**55**
6.5	0.2	0.4	1.2
7.0	0.6	1.1	3.6
7.5	1.7	3.4	10.7
8.0	5.3	9.9	27.4

Source: Speece, 1996

5.3.3.2 Soluble Organic Carbon to Ammonia Ratio

The suitability of a wastewater for biological nutrient removal is usually determined by the COD/N ratio. In reality however, the micro-organisms involved in the denitrification process absorb only the available soluble fraction of the total COD. Therefore, total COD data may be misleading unless adequate time is provided in the treatment process for the solubilization of particulate organic matter. Consequently soluble organic carbon to ammonia nitrogen ratios (SOC: NH_3-N) have been presented here (Figure 33).

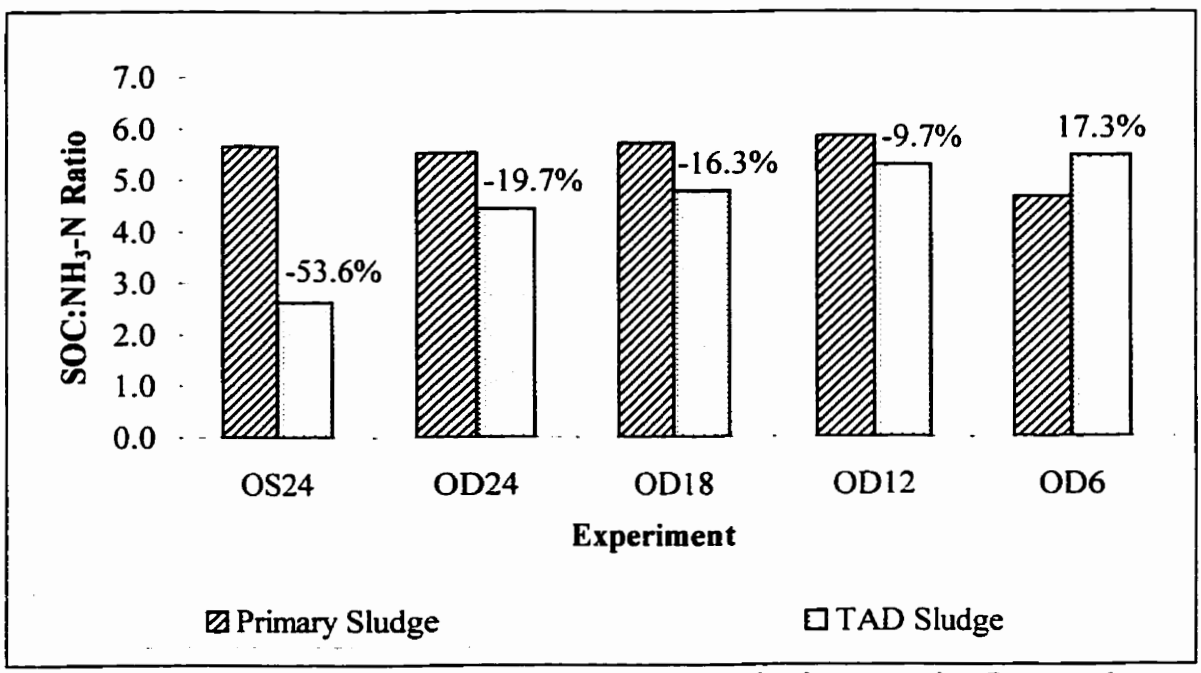


Figure 33. Comparison of soluble organic carbon to ammonia nitrogen ratios. Percent change in SOC:NH_3-N ratio shown above respective experiment.

The influent soluble organic carbon to ammonia nitrogen ratio (SOC: NH_3-N) ranged only slightly from 4.67 to 5.86. The SOC:NH_3 ratio in the TADs varied largely depending on the oxygenation state and retention time. It was observed that the SOC:NH_3-N ratio decreased with an increasing oxygen supply and increasing SRT/HRT. Only during the OD6 experiment did the SOC:NH_3-N increase to greater than that of the influent sludge. This is due to the low level of accumulation of NH_3-N at the short residence time. Although the SOC:NH_3-N ratio decreased under most conditions studied, it is important to remember that after thermophilic aerobic digestion the carbon is in a more readily assimilable form.

5.3.4 Settleability / Dewaterability

Dewaterability as determined by solids capture utilising a centrifuge increased with increasing centrifugation time but with varying degrees depending on the type of sludge (thermophilically digested, mesophilically digested, or primary). Both the primary sludge and mesophilically digested sludge (obtained from the North End Water Pollution Control Centre) exhibited better dewaterability characteristics than did the thermophilically aerobic digested sludge from the first stage TAD reactor (Figure 34). In addition, there appeared to be no relationship between the TAD reactor oxygenation state and residence time to dewaterability. These results are in agreement with those reported by Prakasam *et al.* (1990) and Jewell *et al.* (1978). These results however are questionable since centrifuge results did not correlate directly with CST measurements for Salmon Arm or with the actual observed dewaterability (Kelly, 1990).

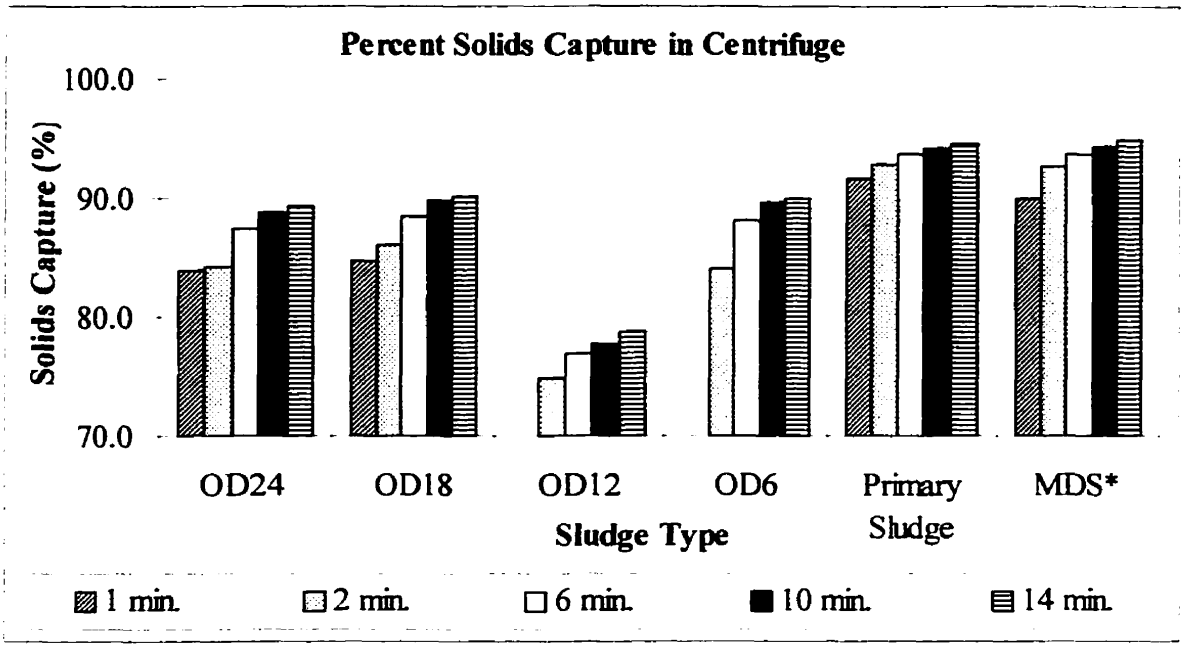


Figure 34. Percent solids capture in centrifuge. Digested sludge from TAD reactor exhibited poorer dewatering characteristics than did mesophilically digested or primary sludge. *Mesophilically digested sludge

5.3.5 Summary

Volatile solids removal appeared to increase with increasing oxygen supply. The percent reduction was 17% in the OS experiment and ranged from 6.7% to 12.4% in the OD reactors. The solids removal appears to increase with an increasing solids loading (decreasing HRT). However, at the 6 hour SRT/HRT, removal dropped and it appears as though the hydrolysis mechanisms or the production of extracellular metabolic intermediates are limited at such a lower residence time. The VS reductions exhibited during this research exceeded those predicted by the EPA design curve under all conditions studied indicating that the TAD process is very proficient with respect to solids removal.

The percent SCOD increased under the OD conditions and decreased under the OS conditions. The percent increase for the OD experiment increased with increasing residence time from 65.9% (6 hours) to 95.1% (24 hours). Beyond the 12 hour SRT/HRT, however the increase was insignificant. This large increase is attributed to volatile fatty acid production. It appears as though the 6 hour SRT/HRT is too short and the micro-organisms are not remaining in the system long enough to reach their optimum soluble substrate production efficiency.

The specific solubilization rates were greatly influenced by the oxygenation state. During the OS experiment the rate of oxidation of dissolved substrate was much higher than the solubilization rate resulting in what appears as a negative COD specific solubilization rate. During the OD experiments, the solubilization rates were much higher and increased with increasing retention time from 0.075 mg COD/mg VS·d at 6 hours to 0.123 mg COD/mg VS·d at 24 hours. Once again there was a stress on the system at the 6 hour SRT/HRT and little increase between the 12 and 24 hour SRT/HRT.

VFA concentrations were high as long as the oxygen deprived conditions existed. Under the OS conditions, volatile fatty acids were consumed. The change in VFA production during each experiment followed closely the same pattern observed for the solubilization process. VFAs accumulated under all OD experiments studied with the production rate increasing with increasing retention time from 0.029 mg HAc/mg VS·d at 6 hours to 0.057 mg HAc/mg VS·d at 24 hours.

The acetic acid concentrations in the OS and OD experiments were comparable and always the highest of all VFAs (59.6% - 64.3%). The OS condition exhibited a much higher

propionic acid concentration (30.3%) then did the OD experiments (average of 17.2%). This higher propionic acid concentration found in the OS experiment was balanced by a lower concentration of butyric and valeric acids. In the range studied the percent VFA distribution was not affected by retention time. The majority of the acid producing bacteria are therefore mostly likely equally influenced by the retention time variation between 6 and 24 hours.

The SCOD content of the OD supernatants are easily biodegradable due to the high percentage of SCOD due to VFAs. The percentage of SCOD due to VFAs increased with increasing retention time during the OD experiments however beyond the 12 hour SRT/HRT the change was not substantial.

TKN was metabolised to ammonia nitrogen which accumulated in the reactors under all conditions studied, but more so with a decreasing oxygen supply and increasing retention time. Due to the pH, the ammonia nitrogen concentration would have been mostly comprised of ionized ammonia.

The SOC:NH_3-N ratio decreased with an increasing oxygen supply and increasing retention time. Albeit the SOC:NH_3-N ratio decreased under most conditions, the TAD carbon is still more readily assimilable.

TAD sludge from the first stage reactor exhibited slower dewaterability rates than mesophilically digested sludge or primary sludge. However, the solids could still be separated out leaving a VFA rich supernatant.

CHAPTER 6

ENGINEERING SIGNIFICANCE

6.1 FULL SCALE IMPLICATIONS OF EXPERIMENTAL RESULTS

6.1.1 Comparison of TAD Results with Conventional Fermentation Processes

This section compares the supernatant quality determined in this laboratory scale study with results from other studies (lab, pilot and full scale). The kinetics of fermentation depend on temperature, SRT, HRT, and type of primary sludge. Table 15 compares the VFA production between the TAD process and the performance of more conventional anaerobic pre-fermenters at ambient temperatures. Comparatively, the results from this study indicate that the TAD process is capable of producing greater quantities of VFAs at lower SRTs.

Table 16 compares the composition of volatile acids produced in various full scale and pilot projects with the results of this study. Under microaerobic conditions, the characteristic VFA pattern is quite different than that typical of the fermentation processes. In the TAD studies, the percent acetate was between 61.5% to 80% of the total VFAs produced. During the fermentation-type processes, there was a relatively even distribution between acetate and propionate accumulation. Seeing as how propionate when used as a carbon source for denitrification possesses a lower denitrification and carbon consumption rate than acetate, butyrate, or valerate, it seems that the TAD process is a more appropriate process for this application.

Table 15. Comparison of SCVFA Production in TAD with other Conventional Fermentation Processes at Ambient Temperatures

Location & Type of Process	VFA Produced per Sludge COD (gHAc/gCOD)	SRT (d)	Source
Lab scale: 55°C	0.87 (SCOD)	1.0	THIS STUDY (TAD-OD24)
Lab scale: 55°C	0.112 (per g VS)		THIS STUDY (TAD-OD24)
Pilot scale: 18-22°C	0.09	2-10	Rabinowitz (1985)*
Pilot scale: 12-14°C	0.07	2-10	Rabinowitz (1985)*
Batch lab scale: 20°C	0.125	6-9	Wentzel *et al.* (1989)*
Lab scale: 20°C	0.17		Lilley *et al.* (1990)*
Full scale: 14-23°C	0.45	1.7	Skalsky & Daigger (1995)*
Full scale: 14-23°C	0.45	2.1	
Lab scale: 18-22°C	0.05 (per g VSS)	5	Elefsiniotis (1993)*
Lab scale: 18-22°C	0.1-0.13	10-20	Elefsiniotis (1993)*
Pilot scale: 25°C	0.18	2.2	Daigger *et al.* (1993)*
	0.05 per VS	0.9	

*Source: Oleszkiewicz and Barnard, 1995

Table 16. Comparison of Volatile Fatty Acids Composition Produced in Various Full Scale and Pilot Projects

Variables	Salmon Arm♥ (ATAD)	THIS STUDY (OD24-TAD)	UBC Pilot♥ (TAD)	Penticton♥ (Fermenter)	Kelowna♥ (Fermenter)
VFA♦ (mg/L)	2130	1620	950	394	228
TSS♣ %	5.5	4.3 (TS)	1.8	1.4	1.8
SRT (d)	5	1.0	3	12.6	18.8
HRT (h)	120	24	72	32.1	7.7
gHAc/gTSS·d	0.008	0.038	0.018	0.002	0.001
Acetic %	70	61.5	81	48	43
Propionic♦ %	14	18.5	11	42	43
Butyric♦ %	6.9	11.6	7	6.6	10.4
Valeric♦ %	7.2	8.4	0	3.4	3.6

♦All values expressed as acetic acid equivalence

♣Solids expressed as % dry weight

♥ Source: Chu *et al.*, 1994

6.1.2 Impact of Supernatant Recycle to Treatment Plant

The quality of supernatant returned from a sludge digester to the head of a wastewater treatment plant greatly affects the various loads to the plant. Although the return volume is generally low, it often contains high concentrations of suspended solids, COD and ammonia nitrogen.

The impact of plant recycle flows on secondary treatment was calculated by a simple mass balance. The amount of flow to be returned was based upon maintaining a total solids concentration of 7% in the mesophilic feed to avoid mixing problems. The flow to the TAD reactor was assumed to be 1% of the total influent flow. In these calculations, the average NEWPCC raw characteristics as obtained from studies conducted by George (1996) were used (Table 17). Calculations are contained in Appendix D.

Table 17. Average Composition of NEWPCC Wastewater

Parameter	Typical Concentration
COD (mg/l)	108
TKN (mg/l)	32
NH_3-N (mg/l)	28
SOC (mg/l)	38
Alkalinity (mg/l as CaCO3)	322
pH	7.13

Source: George, 1996

Mass balance results indicate load increases of 7% to 25% for COD, and 2% to 8% for NH_3-N depending on the solids loadings to the TAD reactor. In addition, SS loads to the plant would be increased. The estimates in Table 18 are rough since they do not incorporate an iterative method. The greater COD loading would cause an increase in biological sludge production and a subsequent increase in recycle load.

The denitrification process would be increased due to the high concentration of readily assimilable carbon. In addition, aeration requirements in the aeration basins would be increased due to the higher carbon and nitrogen loadings.

Table 18. Estimated Effect of TAD Supernatant Recycle on Influent Flow Concentrations

Exp.	Parameter	Influent (mg/L)	Altered Influent (mg/L)	Load Change (%)
OD24	COD	108	135.2	25
	NH_3-N	28	30.2	8
	COD/NH_3-N	3.9	4.5	
OD18	COD	108	122.2	13
	NH_3-N	28	29.1	4
	COD/NH_3-N	3.9	4.2	
OD12	COD	108	115.7	7
	NH_3-N	28	28.5	2
	COD/NH_3-N	3.9	4.1	
OD6	COD	108	126.9	18
	NH_3-N	28	29.2	4
	COD/NH_3-N	3.9	4.3	

6.1.3 Applicability of Lab Scale Results to Full Scale Results

The lab scale reactors were very well mixed systems, which is not always the case in full scale installations. This difference is common when comparing lab and pilot scale reactors with full scale reactors. Consequently, tank and equipment sizing would be somewhat larger (by a safety factor) than is suggested by these smaller scale results.

6.1.4 Summary

The TAD process is capable of producing greater quantities of VFAs at lower retention times than are the more conventional anaerobic pre-fermenters at ambient temperatures. Also, when compared to conventional fermenters, the TAD process is capable of producing a lower concentration of propionic acid, thereby resulting in a greater percentage of VFAs which possess a higher denitrification and carbon consumption rate. By returning supernatant to the plant influent the COD concentration (in particular the VFA concentration) would increase resulting in a higher COD/NH_3-N concentration to aid in the denitrification process.

6.2 BENEFITS OF DUAL DIGESTION PROCESS

6.2.1 Particulate Organic Carbon Transformation

Baier and Zwiefelhofer (1991) indicate that the dual-digestion process enhanced VS degradation by 25% as compared with mesophilic digestion alone and therefore dual treatment plants produce a sludge with less organic material and a higher degree of stabilisation. Results

of Baier's and Zwiefelhofer's studies are located in Table 19. Likewise, Pagilla, *et al.* (1996), measured a greater volatile solids reduction in the ATP system over the mesophilic anaerobic digested sludge by 6%.

Kelly (1990) concluded that the dual-digestion process is a better stabilisation method than long periods of thermophilic digestion. For example, at Ladysmith for detention times of up to 30 days and a degree-day product of 1400°C-days, VS reduction ranged between about 38 to 53 percent and COD reductions ranged between 35 and 64 percent. For similar overall detention times, the dual digestion process at Gibsons had VS reductions of between 52 and 80 percent and COD reductions between 54 and 79 percent. The overall degree-day products were similar for the two facilities.

Table 19. Volatile Solids Degradation in Dual Digestion Process

Treatment Plant	Retention Time		Biological Degradation (VS)			
	HRT (d) Reactor	HRT (d) Digester	With Aerobic Thermophilic Pre-treatment			Without Pre-treatment
			Reactor ΔVS (%)	Digester ΔVS (%)	Total ΔVS (%)	
Broc♦	1.4	80	10	47	57	N.A.
Ebersdorf♦	1.0	25	10	81	83	N.A.
Furthof♦	1.4	43	6	51	56	48
Lachen♦	1.4	28	12	45	56	N.A.
Märstellen♦	2.0	30	24	31	48	48
Milnerton♣	1.25	20.4	4.1	51.5	55.6	N.A.
Thun♦	1.6	27	14	45	53	47
Sacramento Regional♥	1.0	14	-	-	59	53

♦ Baier and Zwiefelhofer (1991) (Values in % of sludge fed to the respective step)
♣ Messengers (1989)
♥ Pagilla *et al.* (1996)

Likewise, Pagilla *et al.* (1996), found that the dual-digestion supernatant COD was consistently less than the mesophilic anaerobic control supernatant COD. The average supernatant COD concentration in the dual-digested sludge was 12340 mg/L compared to the average supernatant COD concentration of 19080 mg/L found in the full scale control.

6.2.2 Pathogen Reduction

Land application of sludge creates a potential for human and animal exposure to pathogens both through direct and indirect contact. In some countries (e.g. Switzerland, the United Kingdom, and the USA), concern regarding the hygienic quality of treated sludge has resulted in legislation that requires waste sewage sludge that is to be disposed of on land, to be virtually free of pathogenic organisms (pathogen indicator) (Bruce, 1990; Kelly, 1990; Baier, 1991; Federal Register, 1993).

Heat inactivation, a process which is non-specific and irreversible, has been used wherever there was a need to convert sludge into a product free of potentially pathogenic organisms. The pathogenic organisms present in the process feed are subjected to a marked temperature shock that deactivates them (pathogens are irreversibly damaged above 50°C).

Heat treated sludge is classified by the USEPA Sewage Sludge Use and Disposal Regulations (Part 503 Standards) as Class A sludge. Class A pathogen reduction alternatives render the sewage sludge virtually pathogen-free after treatment. Treated sludge can then be applied to the land. ATP systems are also classified by the Swiss and Germans as a process that meets the criteria for the production of a disinfected sludge. Recent regulation in the United Kingdom also includes ATP systems as a means of pasteurisation, providing that the domestic

sludge is digested for 7 days and providing that it has reached 55°C for at least 4 hours (Bruce, 1990; Kelly, 1990).

Studies undertaken concerning the destruction of pathogens through high temperature digestion have been numerous and report the destruction of pathogenic organisms such as *Salmonella* sp., *Ascaris* ova, enteric viruses, viable helminth ova, taenidae eggs, fecal coliforms, etc. Investigators reporting high temperature sludge pasteurisation include Kennedy *et al.* 1994; Baier and Zwiefelhofer, 1991; Messenger *et al.* (1989); Pagilla *et al.* (1996) and Ponti *et al.* (1995b) among others.

Swiss and German regulations concentrate on three groups of organisms regarded as indicator organisms for hygienized sludge: enterobacteriaceae (EBC), salmonellae, and ascaridae and taenidae eggs (Baier, 1991). Over 500 samples of raw, thermophilic, digested, and stored sludge across Europe were analyzed for EBC. Raw sludge usually contains 10^4 to 10^7 counts of EBC/g, and in the thermophilic reactor they are reduced by a factor of about 10^7 to 10^8. In the following mesophilic digester the level of EBC is detected between 1 to 50 EBC/g which meets the stringent Swiss legislative requirements of a maximum of 100 EBC/g of wet, stabilised sludge. This concentration stayed stable in consolidated and cold-stored sludge for up to 1 year. In dual-treated sludge, salmonella counts remain below detection levels and have never been found regardless of the concentration in the raw sludge. Parasitological investigations of pre-treated and digested sludge have failed to find any viable worm eggs (Baier, 1991).

Messenger *et al.*(1989) investigated the disinfection capacity of the dual-digestion process at Milnerton. This 45 m^3/d facility, which treats a blend of primary and humus sludge

from a biofilter works, is batch fed with each batch interval being at least 2 hours (the minimum required time for disinfection at 55°C). Messenger's results indicate that the reactor completely destroys Ascaris ova and Faecal coliforms are reduced by about 8 orders of magnitude although slight regrowth occurs in the digester.

6.2.3 Digester Foaming Control

Mixed sludge containing Nocardia laden WAS, when fed to anaerobic digesters may cause severe surface foam build-up leading to solids profile inversion, tipping of digester floating covers, blockage of gas mixing devices, and clogging of gas collection systems (Pitt and Jenkins, 1990). Pagilla *et al.* (1996), studied the ability of aerobic thermophilic pre-treatment to control the *Nocardia* present in the waste activated sludge, and hence prevent foaming in the subsequent anaerobic digestion. ATP was able to control Nocardia to below detectable levels, whereas the Nocardia levels in the control (mesophilic digestion alone) were $\geq 10^5$ intersection/g VSS when both were fed mixed sludge containing *Nocardia* filament counts in excess of 10^5 intersections/g VSS.

6.2.4 Digester Gas Yield

Biogas is a mixture of colourless, flammable gases produced by anaerobic digestion of organic waste materials (Garba, 1996). The composition of biogas is: methane (CH_4) 50-70%, carbon dioxide (CO_2) 30-40% and minor quantities of hydrogen (H_2), hydrogen sulphide (H_2S), nitrogen (N_2), and oxygen (O_2) (Garba, 1994). It is also saturated with water vapour (EPA). Biogas when generated can be used to supply energy for lighting, water heating,

electricity generation, water pumping etc.

Varying results have been found with respect to digester gas production rate in an ATP digester versus a conventional mesophilic anaerobic digester. Messenger *et al.* (1989) found that in the ATP digester at Milnerton the specific gas yield was 0.92 m^3/kg VS removed. This shows the ATP digester methane yield is slightly higher than what one would expect from a conventional mesophilic anaerobic digester (specific gas yield: 0.75 m^3/kg VS removed).

Similarly, Baier and Zwiefelhofer (1991) investigated 4 plants in which mesophilic digesters were operated identically before and after introduction of pre-treatment into the sludge treatment scheme. Their studies indicate that although there was significant VS reduction in the thermophilic reactor, in none of the four investigated digesters was a reduction of the volume of specific biogas production found. The amount of biogas produced was stable or enhanced as compared with digestion alone. According to Baier and Zwiefelhofer (1991), sludge pre-treatment by aerobic thermophilic hydrolisation alters the amount and composition of organic material fed into the digester. Only part of these products is metabolised by thermophilic bacteria, and the majority is left in the sludge as a substrate for anaerobic digester organisms.

Pagilla *et al.* (1996), on the other hand found that the average gas production rate from their ATP digester was 0.761 m^3/kg VSS destroy and the average gas production from the mesophilic digester was 0.918 m^3/kg VSS destroyed. Pagilla *et al.* (1996) did however find that the CH_4 content of the ATP digester was consistently higher than its counterpart's, while it's H_2S concentration was considerably lower. The lower H_2S concentrations may be due to air stripping of H_2S in the aerobic thermophilic stage. If so, this could be beneficial since the

large volume of anaerobic digester sludge gas produced would not require scrubbing to remove H_2S before beneficial use or flaring and the small volumes of ATP reactor gas could be treated for H_2S removal before atmospheric release. High concentrations of H_2S in the reactor gas makes it less suitable for flaring or reuse because of the SO_2 formation potential resulting in air pollution (Pagilla *et al.*, 1996).

6.2.5 Dewaterability

Pagilla *et al.* (1996) compared the dewaterability of dual digested sludge (TAD pre-treatment plus mesophilic digestion) to mesophilic digested sludge (control) using a centrifuge under the same operating conditions. When 1.2% TS mesophilic digested sludge was centrifuged, a 30% TS sludge cake was produced. Similar experiments with 0.8% TS dual-digested sludge provided sludge cake with solids concentration of 32-36% TS. These observations are in agreement with Baier and Zwiefelhofer (1991), who found that dual-digested sludge produced a 15-40% increase in TS concentration compared with the mesophilic anaerobically digested sludge, when both were statically thickened for the same time periods. The increase in dewaterability was attributed to the more uniform particle size distribution in dual-digested sludge.

6.2.6 Summary

In addition to aiding in the denitrification process, thermophilic aerobic digestion would serve other purposes. Improved pathogen kill and dewatering, enhanced sludge stabilisation and control of filamentous foaming in the anaerobic digester are some of the advantages of the

sequential process. Since the sludge is conditioned and solubilized during the aerobic treatment phase, this should enhance anaerobic digestion and act as an absorber for shock loadings which might be detrimental to the more sensitive anaerobic digester.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The feasibility of a thermophilic aerobic digestion pre-treatment reactor to produce volatile fatty acids to act as a carbon source for denitrification was investigated in this study. The parameters examined in the 55°C reactor fed with primary solids obtained from the NEWPCC were oxygenation state, SRT/HRT, and influent solids characteristics. Based on the results of this research, the following conclusions could be made:

1) The aerobic thermophilic pre-treatment process was found to be capable of producing large quantities of short chain volatile fatty acids as long as oxygen-deprived conditions existed. VFA concentrations decreased under the OS conditions and accumulated under all OD conditions studied. Under the OD conditions, the production rate increased with increasing retention time from 0.029 mg HAc/mg VS·d at 6 hours to 0.057 mg HAc/mg VS·d at 24 hours.

2) Acetic acid concentrations in the OS and OD experiments were comparable and always the highest of all VFAs (59.6% - 64.3%). The OS condition exhibited higher propionic acid concentrations (30.3%) then did the OD experiments (average of 17.2%). This higher propionic acid concentration in the OS experiment was balanced by a lower

concentration of butyric and valeric acids. In the range studied (6 to 24 hours) the percent VFA distribution was not affected by retention time. The majority of the acid producing bacteria are therefore mostly likely equally influenced by the retention time variation.

3) Organic nitrogen was metabolised to ammonia nitrogen which accumulated in the reactors under all conditions studied, but more so with a decreasing oxygen supply and increasing retention time. The OS experiment exhibited a 8.6% increase in ammonia nitrogen concentration while the OD experiments exhibited a 41.6% increase at 6 hours SRT/HRT which increased to 142.8% at a 24 hour SRT/HRT.

4) The VFA specific production rate did not appear to vary with the influent solids concentration

5) The SOC:NH_3-N ratio of the TAD effluent decreased with an increasing oxygen supply and increasing retention time. Although the SOC:NH_3-N ratio decreased under most conditions, the carbon is more readily assimilable.

6) The TAD process is capable of producing greater quantities of VFAs at lower SRTs than are the more conventional anaerobic pre-fermenters at ambient temperatures. For example, OD24 produced 0.112 g HAc/g VS while a conventional fermenter operating at 25°C with a 0.9 day SRT produced 0.05 g HAc/g VS. The TAD process is capable of producing lower concentrations of propionic acid as compared to the more conventional fermenters.

7) Returning TAD supernatant to the plant influent would increase the influent COD/NH_3-N concentration to aid in the denitrification process.

8) The specific solubilization rates were greatly influenced by the oxygenation state. During the OS experiment the COD specific solubilization rate decreased and during the OD experiments, the solubilization rates increased with increasing retention time from 0.075 mg COD/mg VS·d at 6 hours to 0.123 mg COD/mg VS·d at 24 hours. The SCOD content of the OD supernatants are easily biodegradable due to the high percentage of SCOD due to VFAs (60% - 71.3%).

9) Volatile solids removal appeared to increase with increasing oxygen supply. The percent reduction was 17% in the OS experiment and ranged from 6.7% to 12.4% in the OD reactors. As with COD solubilization and VFA production, there was a stress on the system at the 6 hour SRT/HRT and little increase between the 12 and 24 hour SRT/HRT.

10) The alkalinity increased under all conditions studied and was found to increase with increasing oxygen supply and retention time. The total alkalinity increased by 1137 mg/L as $CaCO_3$ during the OS experiment and ranged from 385 mg/L as $CaCO_3$ during OD6 to 975 mg/L as $CaCO_3$ during OD24. The alkalinity increase during the oxygen-deprived experiments was most likely due to metabolism-generated alkalinity from the nitrogenous organic compounds. Alkalinity was also formed from the salts of organic acids however, this alkalinity is not available to neutralize additional VFA. The bicarbonate alkalinity was high enough to buffer the system pH in the neutral range and still have additional alkalinity available for a future mesophilic anaerobic digestion step.

In addition to aiding in the denitrification process, there are many other advantages to

employing thermophilic aerobic digestion as the first step in a two-step process. By adding an aerobic thermophilic pre-treatment step to existing anaerobic sludge treatment facilities, the treatment capacity can be increased as a result of improved performance and a shorter retention time for anaerobic digestion. In addition, improved dewatering, enhanced sludge stabilization, sludge pasteurization and control of filamentous foaming in the anaerobic digester are some of the other advantages of the sequential process.

7.2 RECOMMENDATIONS

This research has proved that a thermophilic aerobic pre-treatment reactor is capable of producing large quantities of VFA and would increase the COD/NH_3-N ratio of the influent wastewater, creating more amiable conditions for denitrification. Many questions however still remain which require additional research. Recommended future areas of research are as follows:

1) Confirm the results of this study in a full scale system, subjected to a greater flow variability.
2) Determine the effect of TAD supernatant of full scale denitrifying plant (including a nitrogen mass balance around whole system).
3) Perform a cost analysis to compare the TAD process with the more conventional fermenters and chemical addition.
4) Perform a heat balance around the system to determine energy requirements.

5) Assess the TAD reactor performance at different operational temperatures ranging from 50°C to 65°C.

6) Investigate of the dewaterability characteristics of the dual digested sludge.

BIBLIOGRAPHY

Abufayed, A.A. and E.D. Schroeder (1986) "Kinetics and Stoichiometry of SBR/Denitrification with a Primary Sludge Carbon Source". *Journal of Water Pollution Control Federation*, Vol. 59, No. 5, pp. 398-405.

Æsøy. A and H. Ødegaard (1994) "Denitrification in Biofilms with Biologically Hydrolysed Sludge as Carbon Source". *Water Science Technology*, Vol. 29, No. 10-11, pp. 93-100.

Anon. (1996) "Dual Digestion of Sludge: Evaluation Report". *International Water and Irrigation Review*, Vol. 16, No. 1, pp. 36-38.

APHA (1992) *Standard Methods for the Examination of Water and Wastewater*. 18th ed. American Public Health Association, Washington D.C.

Baier, U. (1989) "Einfluss der aerob-thermophilen Vorstufe auf die Behandlung von Klarschlamm". *Korrespondenz Abwasser*, 36. Jahrgang, 5, pp.609-616.

Baier, U., and H.P. Zwiefelhofer (1991) "Sludge Stabilisation Effects of Aerobic Thermophilic Pre-treatment". *Water Environment and Technology*, January.

Beaudet, R, C. Gagnon, J.G. Bisaillon and M. Ishaque (1990) "Microbiological Aspects of Aerobic Thermophilic Treatment of Swine Waste". *Applied and Environmental Microbiology*, Vol. 56, No. 4, pp. 971-976.

Bomio, M. (1990) "Bioprocess Development for Aerobic Thermophilic Sludge Treatment". *Diss. ETH Zurich*, No. 9159.

Boulanger, M.L. (1995) "The Effect of Varying Air Supply upon Supernatant Quality in Autoheated Thermophilic Aerobic Digesters Treating Waste Sludge from a Biological Phosphorus Removal Process". *M.Sc. Thesis*, The University of British Columbia.

Bruce, A.M., E.B. Pike and W.J. Fisher (1990) "A Review of Treatment Process Options to Meet EC Sludge Directive". *J. IWEM*, Vol. 4, pp. 1-13.

Caponetto S. and J.A. Oleszkiewicz (1994) "SRT and SSRT Control in Single-Sludge Oxygen Activated Sludge System Removing Nitrogen". *Proc. CSCE Conf. Envir. Eng.*, Winnipeg, Manitoba, pp. 298-307.

Chu, A., D.S. Mavinic, H.G. Kelly, and W.D. Ramey (1994) "Volatile Fatty Acid Production in Thermophilic Aerobic Digestion of Sludge". *Water Resources*, Vol. 28, No. 7, pp. 1513-1522.

Chu, A., D.S. Mavinic, W.D. Ramey, and H.G. Kelly (1996) "A Biochemical Model Describing Volatile Fatty Acid Metabolism in Thermophilic Aerobic Digestion of Wastewater Sludge". *Water Resources*, Vol. 30, No. 8, pp. 1759-1770.

Chu A., D.S. Mavinic, H.G. Kelly and C. Guarnaschelli (1997) "The influence of Aeration and Solids Retention Time on Volatile Fatty Acid Accumulation in Thermophilic Aerobic Digestion of Sludge". *Environmental Technology*, Vol. 18, pp. 731-738.

Comeau, Y., W.K. Oldham and K.J. Hall (1987) "Dynamics of Carbon Reserves in Biological Dephosphatation of Wastewater". *Proceedings of the IAWPRC Specialised Conference on Phosphate Removal form Wastewaters*, Rome, September.

Danesh, S. (1997) "Enhancement of Nutrient Removal in SBR Systems Through Acid Fermentation of Raw Wastewater". *Ph.D. Thesis*, The University of Manitoba.

Deeny, K., H. Hahn, D. Leonhard, and J. Heidman (1991) "Autoheated Thermophilic Aerobic Digestion" *Water Environment and Technology*, Vol. 3, No.10, pp 65-72.

Deeny, K., J. Heidman, and J. Smith (1985) "Autothermal Thermophilic Aerobic Digestion in the Federal Republic of Germany". *40th Industrial Waste Conference*, Perdue University, An Arbor Science Butterworths, Boston, pp. 959-968.

Doelle, H.W., K.N. Ewing, and N.W. Hollywood (1982) "Regulation of Glucose Metabolism in Bacterial Systems". *Adv. Biochem. Engng.* Vol. 23, pp. 1-35.

Eastman, J. and J. Ferguson (1981) "Solubilization of Particulate Organic Carbon During the Acid Phase of Anaerobic Digestion". *Journal of the Water Pollution Control Federation*, Vol. 53, pp. 352-366.

Elefsiniotis, P.T. (1993) "The Effect of Operational and Environmental Parameters on the Acid-Phase Anaerobic Digestion of Primary Sludge". *Ph.D. Thesis*, The University of British Columbia.

EPA (1979) *Process Design Manual, Sludge Treatment and Disposal*, Cincinnati, Ohio.

EPA (1990) "Environmental Regulations and Technology". *Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge*, Washington, DC.

EPA (1993) *Manual Nitrogen Control*. Office of Research and Development, EPA/625/R-93/010, Washington, DC.

Fass, S., V. Ganaye, V. Urbain, J. Manem, and J.C. Block (1994) "Volatile Fatty Acids as Organic Carbon Sources in Denitrification". *Environmental Technology*, Vol. 15., pp 459-467.

Federal Register (1993) Part 503. Subpart D. February 19.

Garba, B. (1996) "Effect of Temperature and Retention Time on Biogas Production From Lignocellulosic Material". *Renewable Energy*, Vol. 9, No. 1-4, pp. 938-941.

George, R.T. (1996) "Long Term Feasibility of Nitrification and its Effects in a Closed Pure Oxygen Activated Sludge System". *M.Sc. Thesis*, The University of Manitoba.

Grueninger, H. *et al.* (1984) "Bacterial Diversity in Thermophilic Aerobic Sewage Sludge". *Applied Science Biotechnology*, Vol. 19, pp. 414-421.

Hamer G., and J.D. Bryers (1985) "Aerobic Thermophilic Sludge Treatment - Some Technological Concepts". *Proc IWTUS-3 Conservation and Recyc*, Vol. 8. pp. 267-284.

Häner, A, C.A. Mason and G. Hamer (1994) "Death and Lysis During Aerobic Thermophilic Sludge Treatment: Characterisation of Recalcitrant Products". *Water Resources*, Vol. 28, No. 4, 863-869.

Harrison, D.E.F., and S.J. Pirt (1967) "The Influence of Dissolved Oxygen Concentration on the Respiration and Glucose Metabolism of *Klebsiella aerogenes* during Growth" *J. gen. Microbiology*, Vol. 46, pp. 193-211.

Hawash, S., N. El Ibiari, F.H. Aly, G. El Diwani, and M.A. Hamad (1994) "Kinetic Study of Thermophilic Aerobic Stabilisation of Sludge". *Biomass and Bioenergy*, Vol. 6. No. 4, pp. 283-286.

Henze M., G.H. Kristensen, and R. Strube (1994) "Rate-Capacity Characterisation of Wastewater for Nutrient Removal Processes". *Water Science Technology*, Vol. 27. No. 7, pp. 101-107.

Jewell, W.J. and R.M. Kabrick (1978) "Autoheated Aerobic Thermophilic Digestion with Air Aeration". Department of Agricultural Engineering, Cornell University, Ithaca, New York 14850.

Jewell, W.J. and R.M. Kabrick (1980) "Autoheated Aerobic Thermophilic Digestion with Aeration". *J. WPCF*, Vol. 53, No. 3, pp. 512-523.

Jewell, W.J., R.M. Kabrick and J.A. Spada (1982) "Autoheated, Aerobic Thermophilic Digestion with Air Aeration". USEPA-600/S2-82-023, May.

Kambhu, K and J.F. Andrews (1968) "Aerobic Thermophilic Process for the Biological Treatment of Wastes - Simulation Studies". *Journal WPCF*, Vol. 41, No. 5, Part 2, pp. 127-141.

Kelly, H.G. (1990) "Demonstration of an Improved Digestion Process for Municipal Sludges". *Supply and Services Contract KE405-8-6575/01-SE UP-D8-010*, Dayton & Knight Ltd. Consulting Engineers.

Kennedy, M., R. Kondapalli, and L. Johnson (1994) "Reducing Wastewater Sludge Pathogens Using Heat Treatment". *Proceedings of the 1994 National Conference on Environmental Engineering*, pp. 281-288.

Loll, U (1984) "Combined Aerobic, Thermophilic and Anaerobic Digestion of Sewage Sludge". *Abwasser-Abfall-Aquatechnik*, pp. 20-27.

Koch, F., W. Oldham, and H. Wang (1988) "ORP as a Tool for Monitoring and Control in Bio-Nutrient Removal Systems". *Proceedings of the 1988 Joint CSCE-ASCE National Conference on Environmental Engineering*. pp. 162-170, Vancouver, BC.

Koers, D.A., and D.S. Mavinic (1977) "Aerobic Digestion of Waste Activated Sludge at Low Temperatures". *JWPCF*, Vol. 49, March, pp. 460-468.

Lawler, D. and P. Singer (1984) "Return Flows from Sludge Treatment". *Journal of the Water Pollution Control Federation*, Vol. 56, No. 2, pp. 118-126.

Mason, C.A., (1986) "Microbial Death, Lysis and "Cryptic" Growth: Fundamental and Applied Aspects". *Ph.D. Thesis Diss.* ETH No 8150 submitted to the Swiss Federal Institute of Technology Zurich.

Mason, C.A., G. Hamer, T. Fleischmann, and C. Lang (1987) "Aerobic Thermophilic Biodegradation of Microbial Cells Some Effects of Dissolved Oxygen and Temperature". *Applied Microbiology Biotechnology*. Vol. 25, pp. 568-576.

Matsch, L.C. and R.F. Drnevich (1977) "Autothermal Aerobic Digestion". *Journal WPCF*, February, pp. 296-310.

Messenger, J.R., H.A. Villiers, and G.A. Ekama (1989) "Dual Digestion Research at Milnerton - Some Process and Energy Considerations". Department of Civil Engineering, University of Cape Town and CSIR Division of Water Technology Waste Management Programme.

Messenger, J.R., H.A. Villiers, and G. A. Ekama (1990) "Oxygen Utilisation Rate as a Control Parameter for the Aerobic Stage in Dual Digestion". *Water Science Technology*, Vol. 22, No. 12, pp. 217-227.

Metcalf and Eddy, Inc. (1991) *Wastewater Engineering: Treatment/Disposal/Reuse*. McGraw-Hill, USA, pp. 430-433.

Morgan, S.F., H.G. Gunson, M.H. Littlewood, and R. Winstanleg (1984) "Aerobic Thermophilic Digestion of Sludge Using Air". *Sewage Sludge Stabilisation and Disinfection*, WRC published by Ellis, Harwood Ltd, Chichester, Eng., p. 278.

Narkis N., M. Rebhun and C.H. Sheindorf (1979) "Denitrification at Various Carbon to Nitrogen Ratios". *Water Resources*, Vol. 13, pp. 93-98.

Novaes, F.F.V. (1986) "Microbiology of Anaerobic Digestion". *Water Science and Technology*, Vol. 18, No. 12, pp. 1-14.

Oleszkiewicz, J.A. (1995-a) "Nutrient Cycles and Effects on Aquatic Community". *Nutrient Removal Strategies and Techniques Workshop Proceedings*, Western Canada Water and Wastewater Association, November 6-7.

Oleszkiewicz, J.A. (1995-b) "Biological Nitrogen Removal". *Nutrient Removal Strategies and Techniques Workshop Proceedings*, Western Canada Water and Wastewater Association, November 6-7.

Oleszkiewicz, J.A., W. Wilson, and T. Takack (1995) "Example A: Winnipeg Pure Oxygen Treatment Plant". *Nutrient Removal Strategies and Techniques Workshop Proceedings*, Western Canada Water and Wastewater Association, November 6-7.

Pagilla K.R., K.C. Craney, and W.H. Kido (1996) "Aerobic Thermophilic Pre-Treatment of Mixed Sludge for Pathogen Reduction and Nocardia Control". *Water Environment Research*, Vol. 68, No. 7, pp. 1093-1098.

Parkin, G.F. and W.F. Owen (1986) "Fundamental of Anaerobic Digestion of Wastewater Sludges". *Journal of Environmental Engineering, American Society of Civil Engineering*, Vol. 112, p. 867-920.

Peddie, C.C., F.A. Koch, C.J. Jenkins, and D.S. Mavinic (1988) "ORP as a Tool for Monitoring and Control of SBR Systems for Aerobic Sludge Digestion". *Proceedings of the Joint CSCE-ASCE National Conference on Environmental Engineering*, pp 171-178, Vancouver, BC

Pfeffer, J. T. (1981) "Methane Fermentation Engineering Aspects of Reactor Design," *34th International Conference of Cebedeau*, Belgium.

Pitt, P.A., and D. Jenkins, (1990) "Causes and Control of *Nocardia* in Activated Sludge". *J. Water Pollution Control Federation*, Vol. 62, p. 143.

Ponti, C., B. Sonnleitner, and A. Fiechter (1995-a) "Aerobic Thermophilic Treatment of Sewage Sludge at Pilot Plant Scale. 1. Operating Conditions". *Journal of Biotechnology*, Vol. 38, pp. 173-182.

Ponti, C., B. Sonnleitner, and A. Fiechter (1995-b) "Aerobic Thermophilic Treatment of Sewage Sludge at Pilot Plant Scale. 2. Technical Solutions and Process Design". *Journal of Biotechnology*, Vol. 38, pp. 183-192.

Popel, H. and N. Jardin (1993) "Influence of Enhance Biological Phosphorus Removal on Sludge Treatment". *Water Science Technology*, Vol. 28, No. 1, pp. 263-271.

Prakasam, T.B.S., S. Soszynski, D.R. Zenz, C. Lue-Hing, L. Blyth, and G. Sernel (1990) "Effect of Recycling Thermophilic Sludge on the Activated Sludge Process". *EPA Research and Development EPA/600/S2-90/037.*

Prescott, L.M., J.P. Harley, and D.A. Klein (1993) *Microbiology*, 2nd ed., Wm. C. Brown Communications Inc., Dubuque, IA, pp. 155-156.

Qasim, S.R. (1994) *Wastewater Treatment Plants Planning, Design, and Operation.* Technomic Publishing, Lancaster, Pennsylvania, pp. 451-460.

Rabinowitz, B. and W.K. Oldham (1985) "Excess Biological Phosphorus Removal in Activated Sludge Process Using Primary Sludge Fermentation". *Proceedings of the Canadian Society for Civil Engineering Annual Conference*, Saskatoon, May.

Sawyer, C.N. and P.L. McCarty (1967) *Chemistry of Sanitary Engineers*, McGraw-Hill Book Company, 2nd Edition, USA.

Sears, K.J. (1995) "Factors Affecting Nitrification in a Pure Oxygen Activated Sludge System". *M.Sc. Thesis*, University of Manitoba.

Scheibel, E.G. (1954) "Liquid Diffusivities". *Industr Engng Chem.* Vol. 46, pp. 2007-2008.

Schaad, P. (1988) "Aerob-thermophile Schlammstabilisierung mit anschliessender Faulung". *Bericht des 2. Hohenheimer Seminars Entseuchung von Klarschlamm, Deutsche Veterinarmedizinische Gesellschaft* (Hrsg.), pp. 114-133.

Sixt, H. (1987) "Die aerob-thermophile Klarschlammentseuchung mit dem UTB-Verfahren". Berict zum 5. Bochumer Workshop *Entseuchung von Klarschlamm*, Schriftenreihe Siwawi, Bd. 10, Universitat Bochum, pp. 151-163.

Skalsky, D.S. and G. T. Daigger (1995) "Wastewater Solids Fermentation for Volatile Acid Production and Enhanced Biological Phosphorus Removal". *Water Environment Research*, Vol. 67, No. 2, pp. 230-237.

Smith J.M., A.N. Masse, W.A. Feige and L.J. Kamphake (1972) "Nitrogen Removal from Municipal Wastewater by Columnar Denitrification". *Environmental Science Technology*, Vol. 6, pp. 260-267.

Speece, R.E. (1996) *Anaerobic Biotechnology for Industrial Wastewaters*. Archae Press, Nashville, Tennessee.

Surueu, G.A., E.S.K. Chain and R.S. Engelbercht (1976) "Aerobic Thermophilic Treatment of High Strength Wastewaters". *J. Water Pollution Control Federation*, Vol. 48, No. 4, pp. 669.

Surueu, G.A., and C. Dilek (1990) "Effects of Temperature, pH and DO Concentrations on Settleability of Activated Sludge". Middle East Technical University, Environmental Engineering Department, Ankara, Turkey.

Sonnleitner, B. (1983) "Biotechnology of Thermophilic Bacteria - Growth Production, and Application". *Advances in Biochemical Engineering/Biotechnology, Microbiol Activities Volzo*, pp. 68-138, Springer-Verlag, Berlin Heidelberg, New York, Tokyo.

Sonnleitner, B. and A. Fiechter (1983-a) "Bacterial Diversity in Thermophilic Aerobic Sludge I. Active Biomass and its Fluctuations". *European Journal of Applied Microbiol. Biotechnol.*, Vol. 18, p. 47-51.

Sonnleitner, B. and A. Fiechter (1983-b) "Bacterial Diversity in Thermophilic Aerobic Sludge II. Types of Organisms and Their Capacities". *European Journal of Applied Microbiol. Biotechnol.*, Vol. 18, p. 174-180.

Timmermans P. and A. Van Haute (1983) "Denitrification with Methanol". *Water Resources*, Vol. 17, pp. 1249-1255.

Varma A., B.W. Boesch and B.O. Palsson (1993) "Stoichiometric Interpretation of *Escherichia coli* Glucose Catabolism Under Various Oxygenation Rates". *Applied Environmental Microbiology*, Vol. 59, pp. 2465-2473.

Vismara, R. (1985) "A Model for Autothermic Aerobic Digestion, Effects of Scale Depending on Aeration Efficiency and Sludge Concentration". *Water Resources*, Vol. 19, No. 4, pp. 441-447.

Williamson, D.A. (1988) *Manitoba Surface Water Quality Objective, a Water Standards and Studies Report*, Manitoba Environment and Workplace Safety and Health, Manitoba.

Wolf, P. (1982) "Aerobic, thermophilic Stabilisation of Sludge Versus Anaerobic Digestion and other kinds of Sludge Treatment at Middle-Sized Plants with Respect to Power Conservation and Economy". *Water Science Technology*, Vol. 14, pp. 727-738.

Wolinski, W.K. and I. Postings (1984) *Effluent and Water Treatment Journal*, Vol. 24, February, p.49.

Woodley, R.A. (1961) "A Study of Aerobic Biochemical Oxidation of Primary Sewage Sludge at Mesophilic and Thermophilic Temperatures". *M. Sc. Thesis*, Purdue University.

Zeikus, J.G. (1979) "Thermophilic bacteria: Ecology, Physiology, and Technology". *Enzyme Microbiology Technology*, Vol. 1, pp. 243-252.

APPENDIX A

PATHWAYS

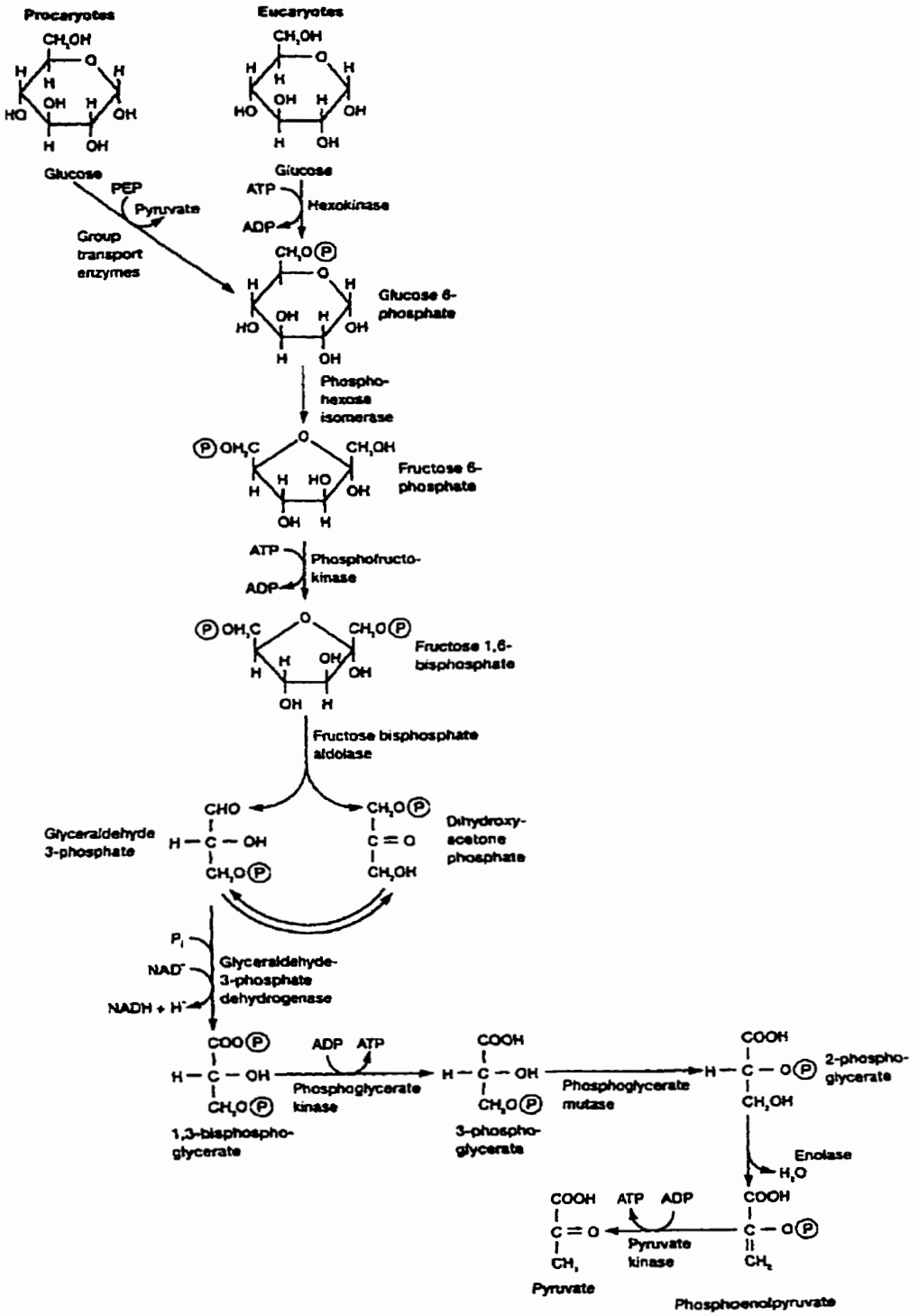


Figure A1. Glycolysis. The Embden-Meyerhof pathway for the conversion of glucose and sugurs to pyruvate.

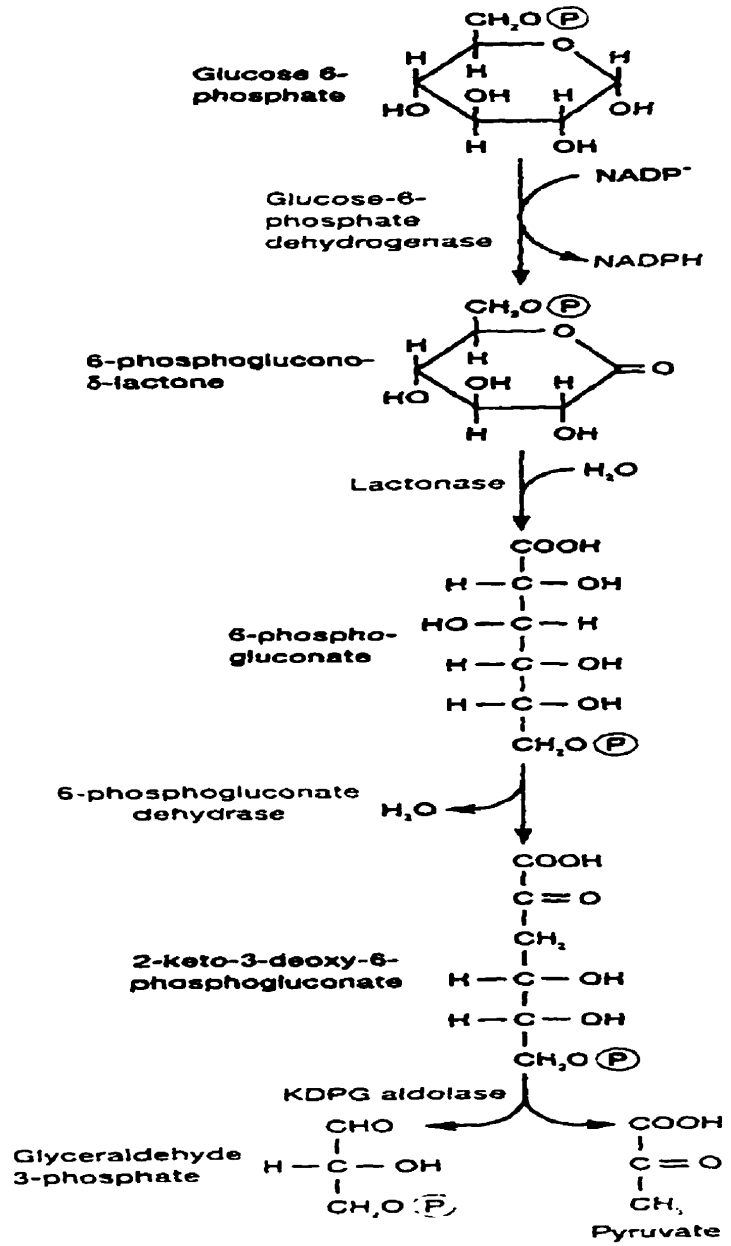


Figure A2. The Entner-Doudoroff Pathway.

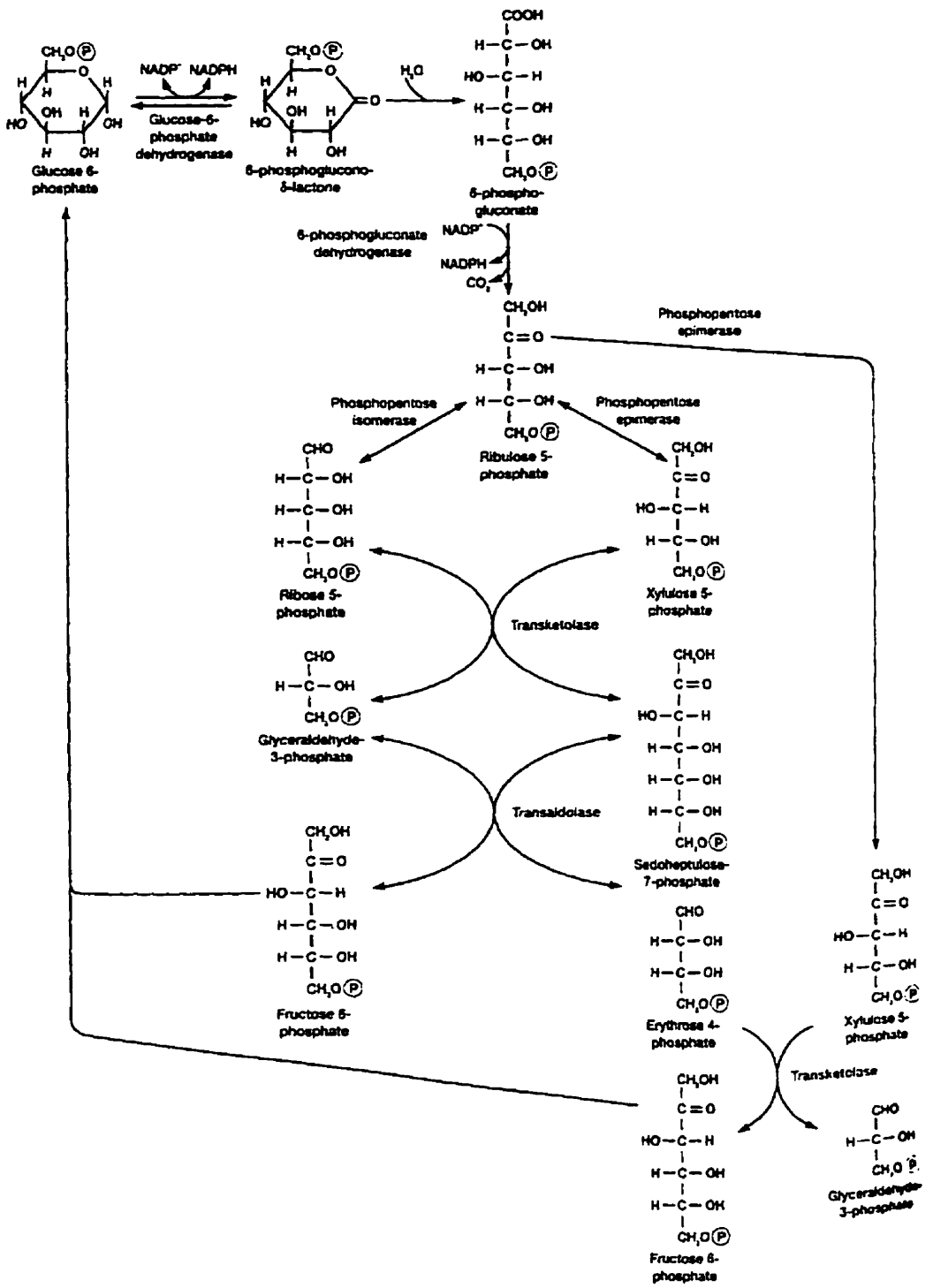


Figure A3. The Pentose Phoshate Pathway.

APPENDIX B

DATA

APPENDIX B: DATA - Solids Measurements

Experiment 1						
Date	**Primary Sludge**		**TAD Sludge: OS24**		**TAD Sludge: OD24**	
	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)
7/6/95	52340	36320			41760	27560
7/7/95	32980	22980	48140	29480	36280	23600
7/10/95	38040	25440	39320	25080	37620	25200
7/12/95	47340	29980	36980	24260	38360	24720
7/14/95	54760	33640	40580	23940	58680	28480
7/17/95	56600	31100	44760	28820	56600	29280
7/19/95	48480	29480	49900	28880	50720	28040
7/21/95	52220	36880				
7/25/95	31340	23260	31440	21380	27700	19940
7/27/95	33300	24800	31000	22440	29720	21720
7/31/95	56580	37740	46280	28240	43240	28320
8/1/95	37760	24200	48580	30300	49420	30700
8/2/95	34140	23280	40220	25020	40120	25320
8/3/95	30780		34440	21500		
8/4/95	34920	25000	29980	18880	34020	23420
8/5/95	33500	24440	29320	20000	32240	22900
8/7/95	36900	27540	30700	21400	33060	23860
8/8/95	40380	30040	32960	22820	34760	25320
8/9/95	41020	30460	33980	24140	35920	26440
Average OS24	38442	27837	36273	23589		

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - Solids Measurements

Experiment 2						
Date	**Primary Sludge**		**TAD Sludge: OD18**		**TAD Sludge: OD24**	
	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)
8/14/95	42750	27860	40130	25550	39720	25410
8/15/95	35180	21570	39420	23350	38180	23750
8/16/95	41400	25200	44300	24230	41960	24880
8/18/95	51780	30610	49140	26860	45080	25430
8/19/95	46280	27460	50770	28010	49070	26750
8/21/95	54400	31740	63070	32350	53810	29230
8/22/95	50830	28680	65950	32000	54640	27680
8/23/95	46620	27240	63170	29600	53890	27330
8/24/95	43100	25370	60720	28780	49230	25690
Average OD24	43061	28234			42531	25807

Experiment 3						
Date	**Primary Sludge**		**TAD Sludge: OD18**		**TAD Sludge: OD12**	
	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)
8/26/95	81010	39230	66510	3157	63900	30900
8/27/95	72550	37800	66580	33490	61880	31960
8/28/95	68030	37750				
8/29/95	64000	35460			64040	33870
8/30/95	64520	36050			64390	32910
8/31/95	63850	34070			64860	32250
Average OD18	51445	29342	55433	26125		
Average OD12	68993	36727			63814	32378

APPENDIX B: DATA - Solids Measurements

Experiment 4				
Date	Primary Sludge		TAD Sludge: OD6	
	Total Solids (mg/L)	Volatile Solids (mg/L)	Total Solids (mg/L)	Volatile Solids (mg/L)
9/12/95	30260	16690	30870	16530
9/13/95	28820	16970	53120	26610
9/14/95	28480	17230	34310	18870
9/15/95	38990	23890	25780	15800
9/16/95	41940	28650	34630	20990
9/17/95	48550	26710	38380	23000
Average OD6	36173	21690	36182	20300

APPENDIX B: DATA - Discharge Gas Measurements

Date	N_2 (mg/L)	CH_4 (mg/L)	CO_2 (mg/L)
	OS24		
8/4/95	85.80	0.00	14.20
	83.10	0.00	16.90
	OD24		
8/4/95	60.10	2.50	37.40
	61.80	1.40	36.80
8/14/95	46.10	4.30	49.60
	49.80	2.40	47.80
8/21/95	44.80	1.30	53.90
	43.90	1.30	54.80
	OD18		
8/21/95	65.30	0.50	34.70
	65.40	1.30	34.60
	OD12		
8/28/95	52.50	1.50	46.00
	53.80	1.50	44.70
	OD6		
9/14/95	68.30	1.00	30.70
	67.50	1.00	31.50

APPENDIX B: DATA - ORP

Experiment 1		
Date	**TAD Sludge: OS24**	**TAD Sludge: OD24**
	ORP (mV)	ORP (mV)
07/06/95	-194.0	-295.5
07/07/95	-195.0	-275.0
07/10/95	-300.6	-242.9
07/12/95	-289.0	-309.0
07/14/95	-248.7	-287.9
07/17/95	-340.0	-340.0
07/19/95	-279.0	-301.0
07/21/95		
07/25/95	-310.0	-265.0
07/27/95	-264.2	-308.5
07/31/95	-77.9	-398.2
08/01/95	-39.7	-381.9
08/02/95	-57.7	-313.0
08/03/95	-57.0	-303.0
08/04/95	-12.7	-285.9
08/05/95	-34.7	-310.7
08/07/95	-43.8	-365.8
08/08/95	-27.7	-384.1
08/09/95	-29.6	-377.2
Average OS24	-42.3	

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - ORP

Experiment 2		
Date	**TAD Sludge: OD18**	**TAD Sludge: OD24**
	ORP (mV)	ORP (mV)
08/14/95	-328.5	-383.4
08/15/95	-387.6	-381.7
08/16/95	-321.8	-334.8
08/18/95	-380.4	-390.5
08/19/95	-323.5	-292.2
08/21/95	-315.0	-310.0
08/22/95	-331.2	-304.5
08/23/95	-331.0	-304.0
08/24/95	-326.0	-325.0
Average OD24		-324.84

Experiment 3		
Date	**TAD Sludge: OD18**	**TAD Sludge: OD12**
	ORP (mV)	ORP (mV)
08/26/95	-317.0	-314.5
08/27/95	-381.4	-378.8
08/28/95		-347.0
8/29/95		-398.0
8/30/95		-398.0
8/31/95		
Average OD18	-340.31	
Average OD12		-367.26

APPENDIX B: DATA - ORP

Experiment 4	
Date	**TAD Sludge: OD6**
	ORP (mV)
9/12/95	-350.0
9/13/95	-361.0
9/14/95	-306.8
9/15/95	-309.1
9/16/95	-314.9
9/17/95	-337.0
Average OD6	-329.8

APPENDIX B: DATA - Alkalinity and pH Measurements

Experiment 1						
Date	**Primary Sludge**		**TAD Sludge: OS24**		**TAD Sludge: OS24**	
	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH
7/6/95	2580	6.10	3540	6.15	2880	6.40
7/7/95	1380	6.45	3528	6.80	2760	6.30
7/10/95	1320	6.40	2640	6.35	2544	6.15
7/12/95	1800	6.00	2664	6.85	2544	6.10
7/14/95	1932	5.80	3144	7.10	2808	6.20
7/17/95	2028	6.20	3360	7.60	3000	6.30
7/19/95	1656	6.20	3420	7.00	2820	6.00
7/21/95	1704	6.20	3060	7.50	2820	6.00
7/25/95	1068	6.25	1920	7.40	1716	6.15
7/27/95	1176	6.25	2100	7.30	1776	6.15
7/31/95	2160	6.00	2136	7.10	2736	6.15
8/1/95	1380	5.80	2400	7.40	2940	6.30
8/2/95	1344	6.00	2004	7.15	2340	6.15
8/3/95	1116	6.00	1644	7.20	1704	5.90
8/4/95	996	6.15	1704	7.20	1920	5.95
8/5/95	924	5.75	1464	7.00	1956	6.05
8/7/95	1080	5.85	1608	7.30	2148	6.15
8/8/95	1320	6.10	1620	7.00	2400	6.10
8/9/95	996	5.70	1524	6.80	2700	6.30
Average OS24	1257	5.93	1789	7.13		

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - Alkalinity and pH Measurements

Experiment 2						
Date	**Primary Sludge**		**TAD Sludge: OD18**		**TAD Sludge: OD24**	
	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH
8/14/95	1380	6.25	2220	6.15	2220	6.20
8/15/95	1224	6.40	2292	6.15	2400	6.10
8/16/95	1356	6.50	2676	6.10	2580	6.30
8/18/95	1848	6.10	2712	6.10	2712	6.30
8/19/95	1680	6.10	2640	6.10	2532	6.10
8/21/95	2028	6.30	3276	6.00	3576	6.15
8/22/95	1824	6.40	2640	5.80	2676	6.20
8/23/95	1908	6.40	2580	5.85	2724	6.10
8/24/95	1524	6.40	2748	5.90	2088	6.00
Average OD24	1526	6.14			2501	6.15

Experiment 3						
Date	**Primary Sludge**		**TAD Sludge: OD18**		**TAD Sludge: OD12**	
	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH
8/26/95	2880	6.00	3000	5.75	2952	5.95
8/27/95	3348	6.00	3312	5.85	3552	6.10
8/28/95	2856	6.30			3360	5.90
8/29/95	2244	6.15			3264	5.90
8/30/95	2580	6.25			3444	5.90
8/31/95	2400	6.05			3084	5.85
Average OD18	1909	6.26	2736	5.98		
Average OD12	2718	6.13			3276	5.93

APPENDIX B: DATA - Alkalinity and pH Measurements

Experiment 4				
Date	**Primary Sludge**		**TAD Sludge: OD6**	
	Alkalinity (mg/L as $CaCO_3$)	pH	Alkalinity (mg/L as $CaCO_3$)	pH
9/12/95	1632	6.95	1596	6.20
9/13/95	1308	6.30	2358	6.15
9/14/95	1368	6.45	1932	5.90
9/15/95	1704	6.10	1452	5.95
9/16/95	1608	6.20	2160	5.90
9/17/95	1716	5.90	2148	6.00
Average OD6	1556	6.32	1941	6.02

APPENDIX B: DATA - COD Measurements

Experiment 1			
Date	**Primary Sludge**	**TAD Sludge: OS24**	**TAD Sludge: OD24**
	Soluble COD (mg/L)	Soluble COD (mg/L)	Soluble COD (mg/L)
7/6/95	5350	4920	4838
7/7/95	4650	7750	8600
7/10/95	4150	7025	7950
7/12/95	4850	6700	8500
7/14/95	5425	6000	9100
7/17/95		6250	9600
7/19/95	3850	5350	8050
7/21/95	3700	4900	7200
7/25/95	3675	3325	5225
7/27/95	3488	3875	6200
7/31/95	4275	2850	8500
8/1/95	3300	2950	8550
8/2/95	3850	1713	7550
8/3/95	3300	1600	6425
8/4/95	3425	1460	6000
8/5/95	3630	1408	6100
8/7/95	4000	1400	7750
8/8/95	4175	1663	8300
8/9/95	3300	1645	7450
Average OS24	3695	1854	

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - COD Measurements

Experiment 2			
Date	**Primary Sludge**	**TAD Sludge: OD18**	**TAD Sludge: OD24**
	Soluble COD (mg/L)	Soluble COD (mg/L)	Soluble COD (mg/L)
8/14/95	2575	6975	6600
8/15/95	2000	5350	5900
8/16/95	1785	6000	6000
8/18/95	3350	6950	6250
8/19/95	2900	7150	6600
8/21/95	3100	6500	6050
8/22/95	3250	7400	6250
8/23/95	3175	6600	6550
8/24/95	3700	7000	6625
Average OD24	3638		7097

Experiment 3			
Date	**Primary Sludge**	**TAD Sludge: OD18**	**TAD Sludge: OD12**
	Soluble COD (mg/L)	Soluble COD (mg/L)	Soluble COD (mg/L)
8/26/95	3900	7200	7150
8/27/95	4025	8350	7950
8/28/95	5400		10075
8/29/95	4675		9175
8/30/95	4610		8800
8/31/95	4330		8950
Average OD18	3069	6861	
Average OD12	4490		8683

APPENDIX B: DATA - COD Measurements

Experiment 4		
Date	**Primary Sludge**	**TAD Sludge: OD6**
	Soluble COD (mg/L)	Soluble COD (mg/L)
9/12/95	1560	2687
9/13/95	2000	3668
9/14/95	1975	3963
9/15/95	2900	4060
9/16/95	2855	4555
9/17/95	3425	5488
Average OD6	2453	4070

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 1							
Date	**Primary Sludge**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
7/6/95	906	418	51	247	81	59	1530
7/7/95	864	378	57	303	82	72	1507
7/10/95	956	513	57	334	82	82	1735
7/12/95	848	472	97	277	69	69	1567
7/14/95	1599	586	0	393	114	11	2416
7/17/95	1080	530	86	381	119	106	1960
7/19/95	906	431	41	173	72	55	1476
7/21/95	1158	413	0	153	61	32	1652
7/25/95	817	319	0	223	82	64	1314
7/27/95	777	369	0	265	98	57	1348
7/31/95	1055	568	0	307	109	95	1845
8/1/95	846	596	0	267	81	102	1619
8/2/95	940	608	50	267	83	96	1754
8/3/95	790	500	0	217	69	77	1429
8/4/95	805	502	30	222	72	75	1470
8/5/95	848	501	80	216	72	68	1538
8/7/95	914	542	90	248	82	73	1675
8/8/95	1015	527	50	249	82	74	1736
8/9/95	850	477	63	225	79	72	1522
Average OS24	896	536	40	246	81	81	1621

*Total VFA expressed as acetic acid equivalence

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 1							
Date	**TAD Sludge: OS24**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
7/6/95	1122	260	130	222	238	66	1752
7/7/95	1333	155	187	350	320	104	2074
7/10/95	1682	152	222	325	369	121	2466
7/12/95	1167	116	209	243	331	118	1833
7/14/95	463	7	213	61	450	57	954
7/17/95	1039	79	216	8	371	11	1480
7/19/95	578	13	202	0	459	10	1002
7/21/95	568	1	138	0	279	0	827
7/25/95	384	2	63	2	136	5	513
7/27/95	387	0	122	1	268	3	630
7/31/95	32	8	10	1	2	1	48
8/1/95	40	27	0	2	4	1	66
8/2/95	14	9	0	0	2	2	24
8/3/95	9	8	0	0	0	0	16
8/4/95	5	3	0	0	0	0	7
8/5/95	17	11	0	1	0	0	26
8/7/95	14	10	0	1	0	0	23
8/8/95	17	13	0	1	0	0	28
8/9/95	16	11	0	1	0	0	25
Average OS24	18	11	1	1	1	1	29

*Total VFA expressed as acetic acid equivalence

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 1

Date	TAD Sludge: OD24						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
7/6/95	1938	806	226	689	438	163	3568
7/7/95	1974	724	203	603	417	139	3438
7/10/95	2207	857	195	569	360	148	3722
7/12/95	1647	818	220	483	311	138	3054
7/14/95	2879	792	0	469	349	155	4137
7/17/95	1981	827	225	627	424	197	3598
7/19/95	2381	837	182	503	360	154	3829
7/21/95	2893	683	0	240	278	100	3833
7/25/95	1368	410	55	226	239	92	2087
7/27/95	1453	567	41	305	298	94	2379
7/31/95	1964	897	207	600	418	158	3580
8/1/95	2045	883	180	605	402	160	3627
8/2/95	1994	880	185	448	330	149	3421
8/3/95	1951	831	200	343	294	145	3253
8/4/95	1885	701	190	216	274	131	2968
8/5/95	1876	730	220	257	272	130	3030
8/7/95	1884	820	220	423	347	147	3278
8/8/95	1973	826	210	504	384	140	3438
8/9/95	1701	807	188	471	342	118	3075

*Total VFA expressed as acetic acid equivalence

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 2							
Date	**Primary Sludge**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/14/95	634	372	10	160	70	40	1116
8/15/95	486	225	50	86	48	23	802
8/16/95	503	211	38	63	48	19	782
8/18/95	873	488	85	238	97	73	1589
8/19/95	919	521	60	209	88	74	1620
8/21/95	998	493	63	178	88	72	1656
8/22/95	740	409	63	190	74	54	1319
8/23/95	810	407	30	172	72	49	1349
8/24/95	729	386	50	208	79	57	1298
Average OD24	881	456	43	231	80	64	1522

*Total VFA expressed as acetic acid equivalence

Experiment 2							
Date	**TAD Sludge: OD24**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/14/95	1631	631	150	254	268	97	2633
8/15/95	1595	544	138	228	273	89	2498
8/16/95	1573	521	140	269	292	106	2508
8/18/95	1603	630	188	414	265	111	2745
8/19/95	2256	689	163	262	320	131	3370
8/21/95	2169	609	200	94	299	90	3092
8/22/95	2017	643	140	132	292	86	2946
8/23/95	2025	687	168	183	309	111	3068
8/24/95	1651	621	137	250	271	121	2649
Average OD24	1947	724	163	381	326	129	3172

*Total VFA expressed as acetic acid equivalence

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 2							
Date	TAD Sludge: OD18						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/14/95	1640	569	138	222	258	87	2550
8/15/95	1484	517	125	253	240	104	2363
8/16/95	1511	472	124	233	233	115	2342
8/18/95	1982	694	158	393	317	138	3188
8/19/95	2029	831	166	412	297	147	3358
8/21/95	2052	716	168	264	295	156	3192
8/22/95	2102	678	138	311	291	155	3220
8/23/95	1921	639	140	284	287	131	2974
8/24/95	1763	638	125	305	266	132	2808

*Total VFA expressed as acetic acid equivalence

Experiment 3							
Date	Primary Sludge						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/26/95	949	528	69	362	87	76	1767
8/27/95	942	530	75	359	102	78	1774
8/28/95	1224	696	100	457	135	111	2313
8/29/95	1107	666	112	401	120	104	2129
8/30/95	1295	705	0	368	111	91	2236
8/31/95	1086	490	0	397	118	99	1882
Average OD18	780	415	54	202	78	56	1370
Average OD12	1101	603	59	391	112	93	2017

*Total VFA expressed as acetic acid equivalence

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 3							
Date	**TAD Sludge: OD18**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/26/95	1828	726	134	424	261	151	3039
8/27/95	1936	846	181	519	319	188	3397
8/28/95							
8/29/95							
8/30/95							
8/31/95							
Average OD18	1841	666	145	329	279	137	2948

*Total VFA expressed as acetic acid equivalence

Experiment 3							
Date	**TAD Sludge: OD12**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
8/26/95	1734	762	140	463	240	112	2970
8/27/95	1802	888	188	623	302	135	3332
8/28/95	2214	942	196	546	320	156	3764
8/29/95	2066	968	183	616	344	168	3697
8/30/95	2657	1136	0	679	321	154	4320
8/31/95	1870	698	200	666	344	152	3318
Average OD12	2057	899	151	599	312	146	3567

*Total VFA expressed as acetic acid equivalence

APPENDIX B: DATA - Volatile Fatty Acids Measurements

Experiment 4							
Date	**Primary Sludge**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
9/12/95	446	207	130	80	43	19	793
9/13/95	350	161	0	117	32	21	591
9/14/95	374	185	0	145	42	26	663
9/15/95	651	324	0	162	43	31	1068
9/16/95	638	336	30	203	56	37	1124
9/17/95	809	462	0	242	70	45	1416
Average OD6	545	279	27	158	48	30	943

*Total VFA expressed as acetic acid equivalence

Experiment 4							
Date	**TAD Sludge: OD6**						
	Acetate (mg/L)	Propionate (mg/L)	Iso-Butyrate (mg/L)	Butyrate (mg/L)	Iso-Valerate (mg/L)	Valerate (mg/L)	Total VFA* (mg/L)
9/12/95	522	142	135	91	74	25	849
9/13/95	824	240	119	143	121	34	1288
9/14/95	918	252	113	214	147	42	1456
9/15/95	965	218	48	109	96	25	1320
9/16/95	1400	489	0	326	139	55	2133
9/17/95	1349	566	83	446	196	66	2323
Average OD6	996	318	83	222	129	41	1562

*Total VFA expressed as acetic acid equivalence

APPENDIX B: DATA - Ammonia Measurements

Experiment 1			
Date	**Primary Sludge**	**TAD Sludge: OS24**	**TAD Sludge: OS24**
	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)
7/6/95	282.4	729.0	735.1
7/7/95	255.1	648.3	686.1
7/10/95	270.4	641.0	650.0
7/12/95	290.0	650.7	679.5
7/14/95	337.9	707.0	712.5
7/17/95	330.1	646.5	746.4
7/19/95	217.0	653.5	631.6
7/21/95	225.3	554.0	555.0
7/25/95	223.8	381.1	463.4
7/27/95			
7/31/95	294.8	241.8	696.3
8/1/95	224.4	318.3	722.6
8/2/95	228.6	308.8	614.0
8/3/95	214.6	252.9	543.4
8/4/95	226.2	240.9	491.0
8/5/95	252.3	213.5	498.0
8/7/95	278.7	261.0	598.2
8/8/95		294.6	695.3
8/9/95	245.7	260.5	583.9
Average OS24	245.7	265.8	

Note: Double line indicates mixer speed increase from 200 RPM to 400 RPM.

APPENDIX B: DATA - Ammonia Measurements

Experiment 2			
Date	**Primary Sludge**	**TAD Sludge: OD18**	**TAD Sludge: OD24**
	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)
8/14/95	212.2	495.9	533.7
8/15/95	153.5	470.7	524.5
8/16/95	159.8	499.3	523.7
8/18/95		583.8	534.0
8/19/95	223.6	545.1	581.8
8/21/95	204.7	512.4	555.2
8/22/95	201.2	568.9	551.6
8/23/95	203.0	544.7	580.0
8/24/95	209.0	524.0	525.0
Average OD24	238.6		600.4

Experiment 3			
Date	**Primary Sludge**	**TAD Sludge: OD18**	**TAD Sludge: OD12**
	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)
8/26/95	262.0	539.0	492.0
8/27/95	283.0	641.0	596.0
8/28/95			638.0
8/29/95	301.0		670.0
8/30/95	316.1		664.7
8/31/95	278.6		644.0
Average OD18	231.4	538.6	
Average OD12	288.1		617.5

APPENDIX B: DATA - Ammonia Measurements

Experiment 4		
Date	**Primary Sludge**	**TAD Sludge: OD6**
	Ammonia Nitrogen (mg/L)	Ammonia Nitrogen (mg/L)
9/12/95	173.0	207.1
9/13/95	120.8	198.2
9/14/95	202.9	307.4
9/15/95	197.7	278.2
9/16/95	206.9	367.8
9/17/95	282.4	317.0
Average OD6	197.3	279.3

APPENDIX C

BALANCE CALCULATIONS

AND

BALANCE ERRORS

APPENDIX C: BALANCES AND BALANCE ERRORS

Sample Calculation OD24

Appendix C2: Liquid Balance

P = 3 L	Volume of thickened primary sludge feed
TADS = 200 mL	Volume of TAD sludge removed by sampling
TF = (4 + 273)°K	Air temperature of refrigerator at feeding time
TTAD = (55 + 273)°K	TAD temperature before feeding
ϕ_4 = 1000 kg/m^3	Density of water at 4°C
ϕ_{55} = 986 kg/m^3	Density of water at 55°C
ϕ_{20} = 988 kg/m^3	Density of water at 20°C
OF24 = 0.417 liters/min	Oxygen flow
AAT = (21 + 273°C)	Average ambient temperature over past 24 hours
ATT24 = (53.9 + 273°C)	Average temperature in TAD over past 24 hours
ATT18 = (52.9 + 273°C)	Average temperature in TAD over past 24 hours
ATT12 = (51.8 + 273°C)	Average temperature in TAD over past 24 hours
ATT6 = (50.8 + 273°C)	Average temperature in TAD over past 24 hours
PPATT24 = 15303 Pa	Partial pressure of water vapour at average TAD24 temp
PPATT18 = 14533 Pa	Partial pressure of water vapour at average TAD18 temp
PPATT12 = 13686 Pa	Partial pressure of water vapour at average TAD12 temp
PPATT6 = 12916 Pa	Partial pressure of water vapour at average TAD6 temp
R = 8.3144 joule/Kmole	

1. Calculation of volume lost with saturated off-gas

$$\text{Gout} = \frac{\text{PPATT24}\cdot\text{OF24}}{\text{R}\cdot\text{ATT24}} \cdot (0.018 \text{ kg/mole})$$

= 0.061 kg/day (Mass of water in air out of TAD24)

$$\text{GTAD24} = \frac{\text{GTAD24}}{\phi_{20}}$$

= 0.062 liter/day (Volume of water lost in off-gas from TAD24)

2. Calculation of sludge volumes in and out at 20°C

$$\text{VIn} = \text{Influent}\ \frac{\phi_4}{\phi_{20}} = 3036 \text{ mL}$$

$$\text{TADS} = \text{TADS}\ \frac{\phi_{55}}{\phi_{20}} = 199.6 \text{ mL}$$

VOut = VIn - GTAD24

= 2974 mL

MeanVIn = 3.036 L

MeanVOut = 2.974L

3. Calculation of Balance Error

$$\text{TAD OD24 Balance Error} = \frac{\text{MeanVOut - MeanVIn}}{\text{MeanVIn}} \cdot 100$$

= -2.0 Percent error in liquid balance around TAD OD24

APPENDIX C: BALANCES AND BALANCE ERRORS

Sample Calculation OD24

Appendix C2: Solids Balance

Volatile solids destruction was determined by calculating the percentage difference between the mean mass of volatile solids entering the digester and the mean mass of volatile solids exit the digester. Example values from OD24.

InVS = 85.7 g/day
OutVS = 76.8 g/day

$$VSD = \frac{OutVS - InVS}{InVS} \cdot 100$$

$$= -10.4\ \%$$

Measurement errors for the solids balance were determined by combining the calculated error in the liquid balance with the coefficient of variance calculated for the solids concentration measurements.

The total solids mass error around the TAD reactor was calculated as the sum of the influent solids concentration coefficient of variance, the TAD solids concentration coefficient of variance and the liquid balance percent error around the TAD reactor.

EMassSystem = 1.2 + 2.0 + 2.0
EMassSystem = 5.2%

APPENDIX D

RECYCLE CALCULATIONS

APPENDIX D: RECYCLE CALCULATIONS

Sample Calculation for OD24

Assumptions:

1) 7% TS to be maintained in TAD sludge to be sent to mesophilic digester.
2) 1% of plant influent flow goes to TAD digester

$$V_T \cdot X_T = V_R \cdot X_R + V_M \cdot X_M$$
$$V_T = V_R + V_M$$

where,

V_T = Total volume of sludge entering TAD reactor (L) = 1 L
V_R = Volume of sludge recycled to plant influent (L)
V_M = Volume of sludge to mesophilic digester (L)
X_T = Concentration of total solids entering TAD reactor (mg/L) = 42531 mg/L
X_R = Concentration of total solids recycled to plant influent (mg/L)
X_M = Concentration of total solids to mesophilic digester (mg/L) = 70000 mg/L

Since V_T is equal to 1L and X_T is equal to 42531 mg/L, it follows that the amount of solids in V_T is equal to 42531 mg.
If X_R is negligible, the volume required to send a concentration of 70000 mg/L to mesophilic digester is $V_M = 42531/X_M = 42531/70000 = 0.61$ L
Since $V_R = V_T - V_M$,
$V_R = 1 - 0.61 = 0.39$ L
If the flow to the TAD reactor is 1% of the total influent flow, and the volume assigned to it is 1 L, then the influent flow is equal to 100 L.

$$COD_T \cdot V_T = V_{INF} \cdot COD_{INF} + V_R \cdot COD_R$$

where,

COD_T = Combined chemical oxygen demand of influent wastewater and TAD recycle
COD_{INF} = Chemical oxygen demand of influent wastewater = 108 mg/L
COD_R = Chemical oxygen demant of TAD supernatant to be recycled to plant influent =7097 mg/L
V_T = Total volume of wastewater (influent + recycle) = 100.39 L
V_{INF} = Volume of influent wastewater (100 L)
V_R = Volume of supernatant recycled to plant influent (0.39 L)

Therefore,

$$COD_T = \frac{(100\ L)\cdot(108\ mg/L) + (0.39\ L)\cdot(7097\ mg/L)}{(100\ L + 0.39\ L)} = 135.2\ mg/L$$

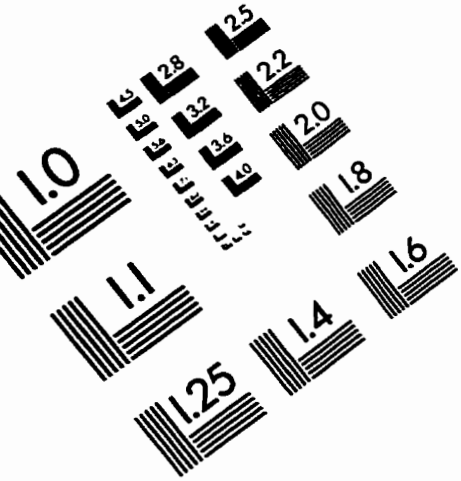
Table D1. Supernatant Recycle Volumes

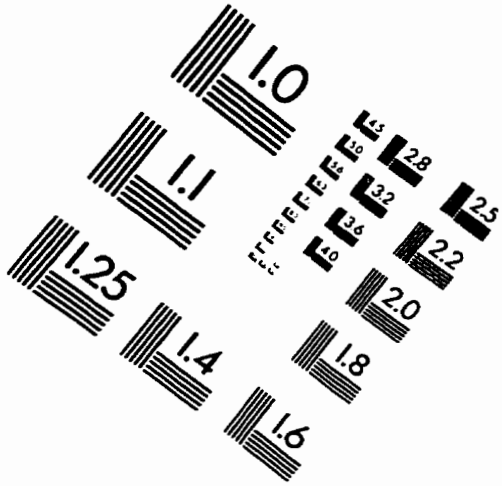
Exp.	V_T (L)	X_T (mg/L)	X_M (mg/L)	V_M (L)	V_R (L)
OD24	1.0	42531	70000	0.61	0.39
OD18	1.0	55433	70000	0.79	0.21
OD12	1.0	63814	70000	0.91	0.09
OD6	1.0	36182	70000	0.52	0.48

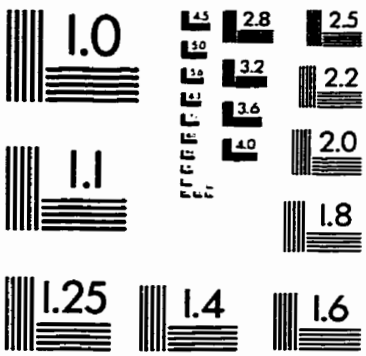
Table D2. Estimated Effect of TAD Supernatant Recycle on Influent Flow Concentrations

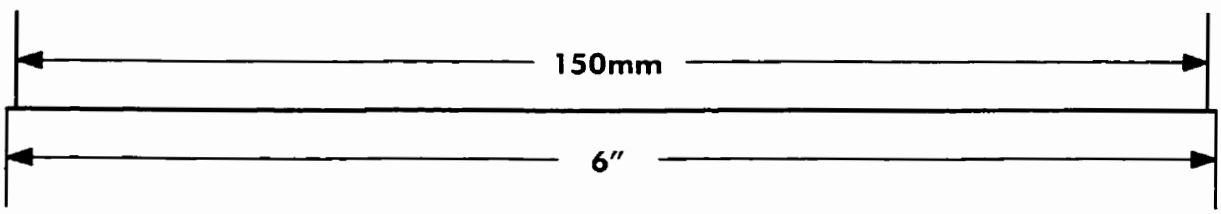
Exp.	Parameter	Influent	TAD Supernatant	Altered Influent	Load Change (%)
OD24	COD (mg/L)	108	7097	135.2	25
	NH_3-N (mg/L)	28	600	30.2	8
	COD/NH_3-N	3.9		4.5	
OD18	COD (mg/L)	108	6861	122.2	13
	NH_3-N (mg/L)	28	539	29.1	4
	COD/NH_3-N	3.9		4.2	
OD12	COD (mg/L)	108	8683	115.7	7
	NH_3-N (mg/L)	28	618	28.5	2
	COD/NH_3-N	3.9		4.1	
OD6	COD (mg/L)	108	4070	126.9	18
	NH_3-N (mg/L)	28	279	29.2	4
	COD/NH_3-N	3.9		4.3	

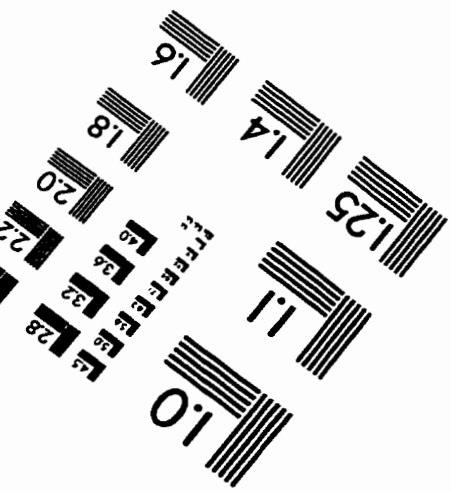
IMAGE EVALUATION TEST TARGET (QA-3)

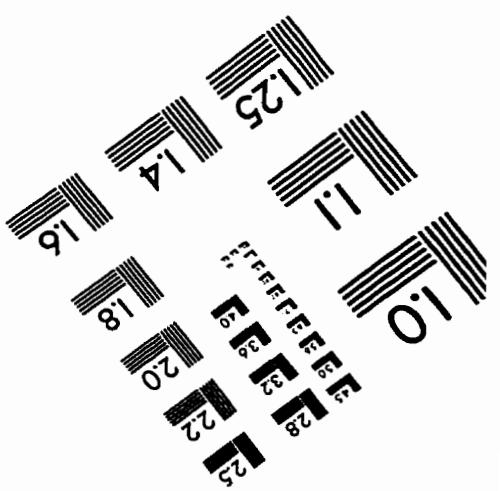












APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989