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**Rapid thermal conditioning of sewage sludges to improve
digestibility, methane production, and metals solubilization**

Pierides, Kyriacos Michael, Ph.D.

City University of New York, 1994

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**RAPID THERMAL CONDITIONING OF SEWAGE SLUDGES TO IMPROVE
DIGESTIBILITY, METHANE PRODUCTION, AND METALS SOLUBILIZATION**

By

KYRIACOS M. PIERIDES

A dissertation submitted to the Graduate Faculty in Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1994

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirements for the degree of Doctor of Philosophy.

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ABSTRACT

RAPID THERMAL CONDITIONING OF SEWAGE SLUDGES TO IMPROVE DIGESTIBILITY, METHANE PRODUCTION, AND METALS SOLUBILIZATION

By

KYRIACOS M. PIERIDES

Advisor: Professor John Fillos

Sludge was conditioned in a continuous-flow Rapid Thermal Conditioning Reactor (RTCR) by mixing sludge with steam. Operating temperatures were varied between 25°C and 220°C, the hydraulic retention times (HRT) between 10 and 180 seconds, and pH values between 1 and 12.

Most experiments were done on digested sludge, referred to in this study as partially digested sludge (PDS). Optimum conditions were achieved at an RTCR temperature of 220°C. At unmodified pH, 220°C, and 10 seconds, the COD solubilization increased from 3.4% (25°C) to 13% (220°C) and the volatile solids (VS) solubilization increased from 8.1% (25°) to 60% (220°C).

Batch anaerobic digestion experiments showed improvement in the kinetic biodegradation rates and in the ultimate biodegradation. At 220°C, ultimate biodegradation improved by 50% at an RTC retention time of 10 seconds, and by 100% at 60 seconds. No additional improvement was obtained at 120 seconds and 180 seconds.

PDS conditioning at various pH levels resulted in the same biodegradation improvement

as the pH-unmodified PDS but at lower temperatures. For example, the PDS improvement at pH4 and 100°C was the same as at unmodified pH and 220°C.

Waste activated sludge (WAS) solids and COD solubilization reached 50% and 40%, respectively, which may be caused by the high RTC temperatures lysing the bacteria. The anaerobic biodegradation of WAS (220°C, 10 seconds) increased by 80% but there was no improvement in the biodegradation of primary sludge.

The RTC biodegradation results (220°C, 10 seconds) were confirmed in a continuous flow stirred tank reactor, where methane production improved by more than 200% at a 15-day HRT. Biodegradation at a 3-day HRT was equivalent to the biodegradation of unconditioned PDS but at a 15-day HRT, resulting from an improvement in kinetic removal rates.

Thermal conditioning of sludge alone was sufficient to solubilize metals, with equivalent results reached when the pH was lowered to 1.5. Cu and Mo were solubilized by more than 50% in pH-unmodified RTC sludge; Zn and Pb were solubilized by 90% and 70%, respectively, in acidified RTC sludge; and Se, Cd, and Mo were solubilized by 75%, 55%, and 55%, respectively, in alkaline RTC sludge. The choice of pretreatment conditions to solubilize metals depends on the nature of the metal in the sludge and the type of sludge. The concentration of metals remaining in sludge cake after dewatering depends on the solubilization of solids because the metals can only be removed when their solubility exceeds that of solids.

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DEDICATION

I dedicate this report to my mother, Julie, who patiently supported and encouraged me to finish my studies, and to my father, Michael, whose spirit is always with me.

I also dedicate this report to all the graduate students who made this study possible, and to all the researchers who are contributing to a better, safer, and cleaner environment.

NOMENCLATURE

A	=	absorbance
AF	=	anaerobic filter
AGP	=	accumulated gas production, mL
AOR	=	acetate-oxidizing eubacteria rod
ATA	=	anaerobic toxicity assay
ATP	=	adenosine triphosphate
BGP	=	biochemical gas potential
BMP	=	biochemical methane potential
BOD	=	biochemical oxygen demand, mg/L
BOD _i	=	biochemical oxygen demand improvement, %
BOD _r	=	BOD of raw (unconditioned) PDS, mg/L
BOD _T	=	BOD of RTC-sample at temperature T, mg/L
C _f	=	TF concentration, mg/L
CFSTR	=	continuous flow stirred tank reactor
C _{fX}	=	TF concentration per VSS, mg/g
COD	=	chemical oxygen demand, mg/L
DHA	=	dehydrogenase activity
DO	=	dissolved oxygen, mg/L
DS	=	dissolved solids, % or mg/L
DVS	=	dissolved volatile solids, % or mg/L
FDS	=	fixed dissolved solids, % or mg/L
FSS	=	fixed suspended solids, % or mg/L
G ₁	=	ultimate SGP of fast term, mL gas/g TCOD
G ₂	=	ultimate SGP of slow term, mL gas/g TCOD
GPI	=	gas production improvement, %
GPI _N	=	normalized GPI ratio
HAc	=	acetic acid
HRT	=	hydraulic retention time, sec, or hr, or d
INT	=	2-[p-iodophenyl]-3-[p-nitrophenyl]-s-phenyl tetrazolium chloride
k	=	calibration constant from calibration curve, mg/L
k ₁	=	first order reaction rate of fast term, 1/d
k ₂	=	first order reaction rate of slow term, 1/d
MPI	=	methane production improvement, %
MPR	=	methane production rate, mL/d
NC	=	Newtown Creek
NYC	=	New York City

NYCDEP	=	New York City Department of Environmental Protection
OHPA	=	obligate hydrogen-producing acedogenic bacteria
ORP	=	oxidation reduction potential, mV
OUR	=	oxygen uptake rate, mg/L-min
PDS	=	partially digested sludge
pHu	=	unmodified pH
PS	=	primary sludge
RTC	=	rapid thermal conditioning
RTCR	=	rapid thermal conditioning reactor
S_i	=	SCOD improvement, %
SGP	=	specific gas production, mL gas/g TCOD
SCOD	=	soluble COD, mg/L
SCWO	=	supercritical water oxidation
SMP_c	=	specific methane production-TCOD basis, mL CH_4 /g TCOD
SMP_v	=	specific methane production-TVS basis, ft ³ CH_4 /lb TVS
SS	=	suspended solids, % or mg/L
SOUR	=	specific oxygen uptake rate, mg/L-min-g TVS
t	=	incubation time from startup, d
T	=	temperature, °C
TCOD	=	total COD, mg/L
TF	=	triphenyl formazan
TAN	=	total ammonia nitrogen
TKN	=	total Kjeldahl nitrogen, mg/L-N
TOC	=	total organic carbon, mg/L
TS	=	total solids, % or mg/L
TTC	=	triphenyltetrazolium chloride
TVA	=	total volatile acids, mg/L as HAc
TVS	=	total volatile solids, % or mg/L
UAN	=	unionized ammonia nitrogen
V_e	=	extract volume, mL
V_s	=	biomass sample volume, mL
VDS	=	volatile dissolved solids, % or mg/L
VSS	=	volatile suspended solids, % or mg/L
WAO	=	wet-air oxidation
WAS	=	waste activated sludge
WI	=	Wards Island
WPCP	=	water pollution control plant
X	=	VSS of biomass sample, g/L

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1. INTRODUCTION

1.1 Typical Wastewater Treatment Plant

Municipal wastewater treatment plants are designed to reduce biochemical oxygen demand (BOD) and suspended solids (SS) in compliance with discharge permit requirements. The processes used more often by municipal wastewater treatment plants in New York City are shown on Figure 1-1. These processes include (1) primary sedimentation to remove the settleable solids, and (2) biochemical processes, such as the activated sludge process, to partially oxidize and convert both dissolved and colloidal organic matter into settleable solids. The sludge produced is then stabilized in anaerobic digesters and dewatered prior to disposal. Such plants readily comply with the requirements for secondary treatment.

1.2 Sludge Production, Treatment and Disposal

The settled solids removed from the sedimentation tanks as slurry are called "sludge". The slurry from primary sedimentation is called primary sludge (PS), and the slurry from the activated sludge process is called waste activated sludge (WAS) or secondary sludge. Typical compositions of PS and WAS are shown in Table 1-1. In many treatment plants, PS and WAS are combined and thickened to 4-6 % solids in gravity thickeners before stabilization (USEPA, 1979).

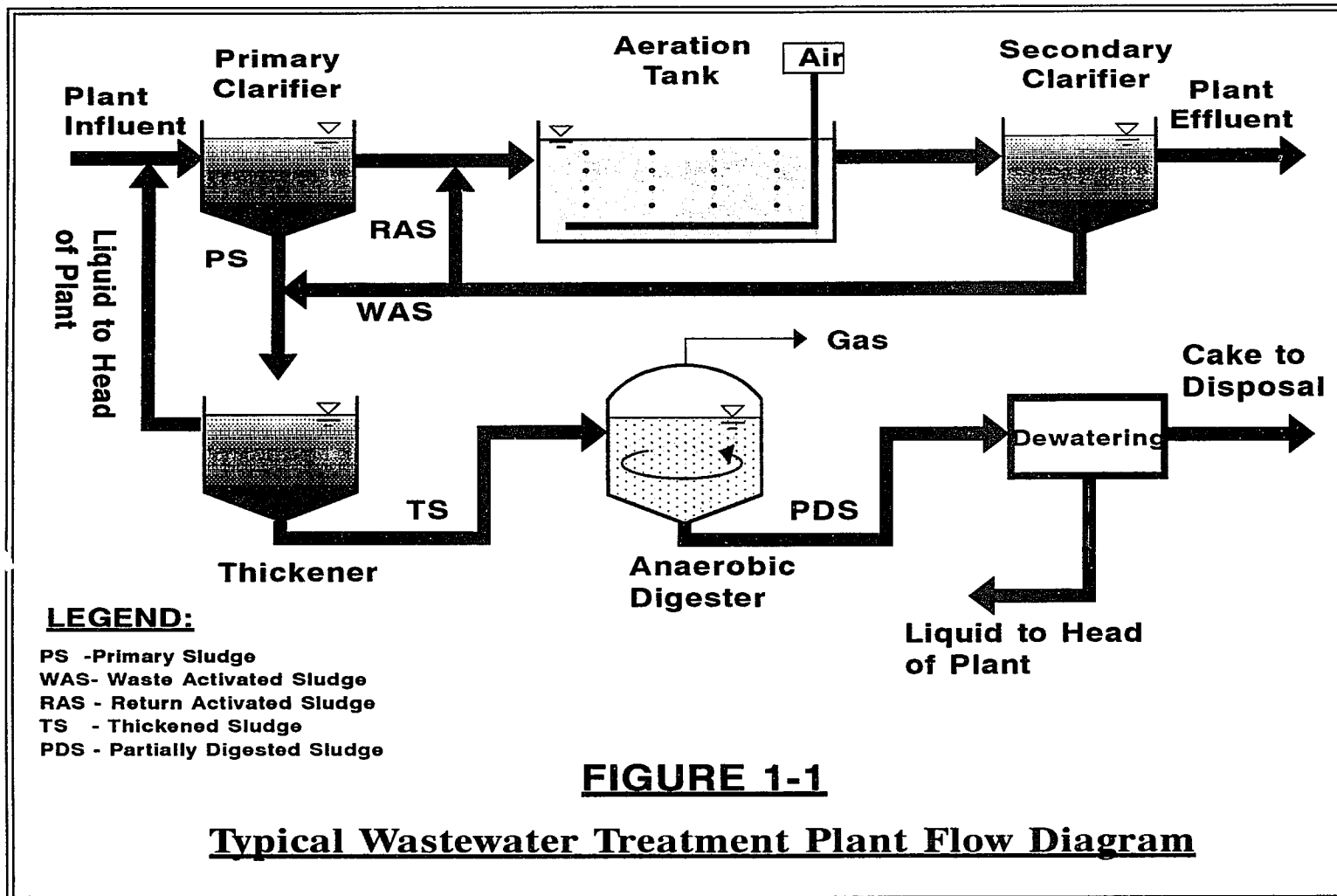


TABLE 1-1

**TYPICAL COMPOSITION OF PRIMARY SLUDGE AND WASTE ACTIVATED
SLUDGE**

Parameter	Primary Sludge		Waste Activated Sludge	
	Range	Typical	Range	Typical
Total Solids(TS), %	2.0-8.0	5.0	0.83-1.16	---
Volatile Solids, % of TS	60-80	65	59-88	---
Volatile Acids, mg/L as HAc	200-2,000	500	1,100-1,700	---
pH	5.0-8.0	6.0	6.5-8.0	---
Alkalinity, mg/L as CaCO ₃	500-1,500	600	580-1,100	---
Specific Gravity of Individual Solids	---	1.4	---	1.08
COD/VSS Ratio	1.2-1.6	---	---	2.17
Org-N/VSS Ratio	0.05-0.06	---	---	---
Protein, % of TS	20-30	25	32-41	---
Nitrogen-N, % of TS	1.5-4	2.5	2.4-6.0	---
Phosphorus-P ₂ O ₅ , % of TS	0.8-2.8	1.6	2.8-11.0	4.0
Potash-K ₂ O, % of TS	0-1	0.4	0.5-0.7	---
Cellulose, % of TS	8.0-15.0	10.0	---	7
Hemicellulose, % of TS	---	3.2	---	---
Lignin, % of TS	---	5.8	---	---
Grease and Fats, % of TS				
Ether Soluble	6-30	---	---	---
Ether Extract	7-35	---	5-12	---
Silica, % of TS	15.0-20.0	---	---	---

Notes:

1. "----" Data not available
[USEPA, 1979]

Anaerobic digestion is the most commonly used stabilization process for municipal wastewater sludges. Under anaerobic conditions, the organic solids, usually measured as volatile solids, are reduced by 50 to 55 % (Metcalf & Eddy, 1991). The reduction of solids involves a complex series of reactions that lead to the production of digester gas which is approximately 65% to 70% methane. The remaining 30 to 35 % of the gas is primarily carbon dioxide with traces of hydrogen sulfide (produced by sulfate reducing bacteria), hydrogen and carbon monoxide. The digested gas has a heating value of 650 to 750 BTU/ft³ (WPCF, 1987). The overall rate of gas production varies between 12 to 18 std ft³ per pound of volatile solids reduction (Metcalf and Eddy, 1991).

New York City operates 14 water pollution control plants (WPCP) to treat approximately 1,680 million gallons of wastewater per day (Hazen and Sawyer, and Stone & Webster, 1990). Figure 1-2 shows the locations and design capacities of the 14 plants. The plants provide gravity thickening for PS and WAS followed by anaerobic digestion of the thickened sludge. Of the 14 plants, 13 operate their anaerobic digesters under mesophilic conditions. Only the Rockaway Beach plant provides a two-stage anaerobic digestion, mesophilic followed by thermophilic conditions. As of June 14, 1992 NYC used a Marine Transportation System (MTS) to dispose the digested sludge at a designated site 106 miles off the coast of the Atlantic Ocean. As a result of the Ocean Dumping Ban Act (ODBA), NYC signed a consent order on August 1, 1989 to cease 20 % of ocean dumping by December 31, 1991 and 100 % by June 14, 1992 (Hazen and Sawyer, and Stone & Webster, 1990).

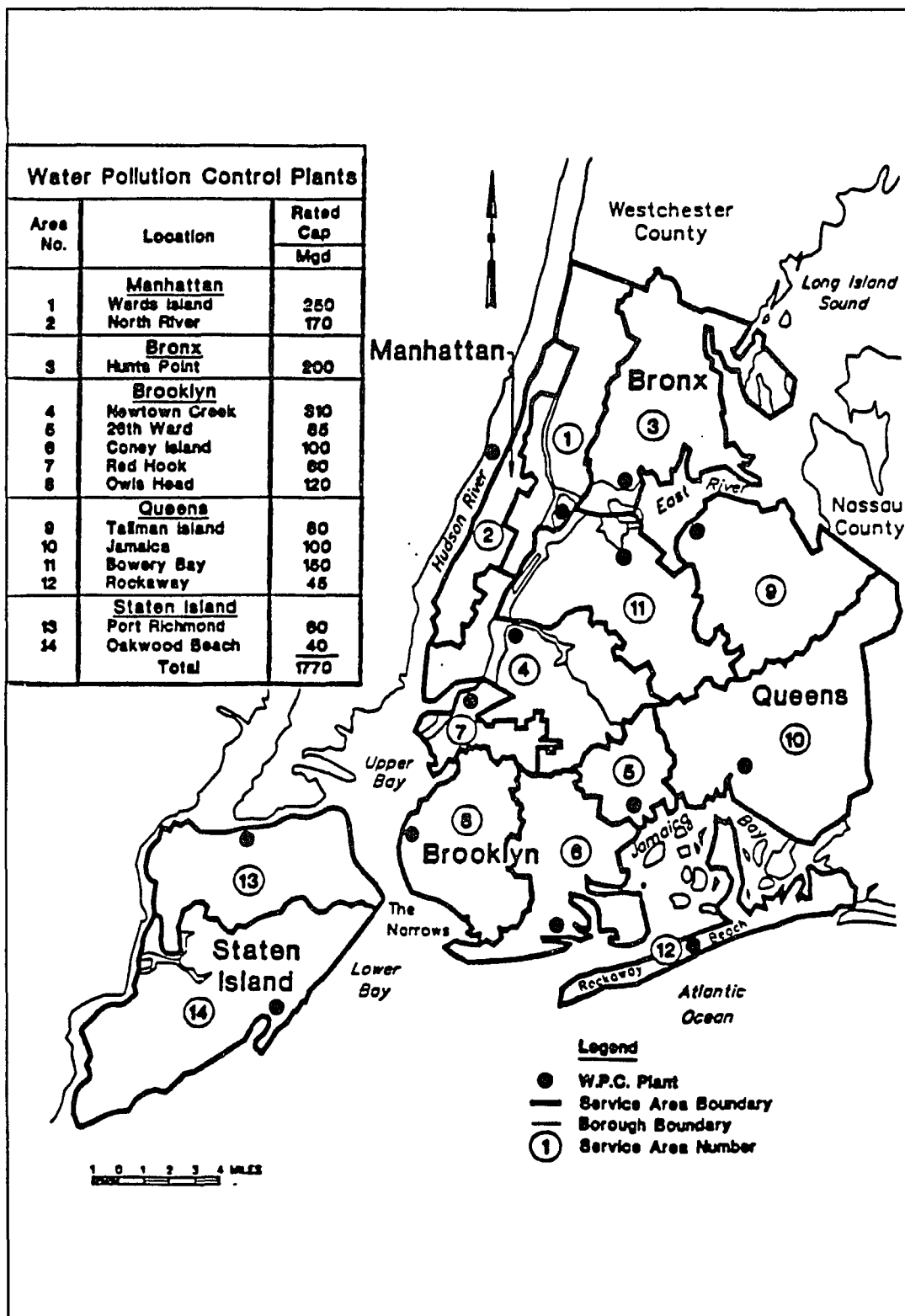


Figure 1-2. Locations and Capacities of NYC Plants [Hazen and Sawyer, and Stone & Webster, 1990]

The termination of ocean dumping forced NYC to design and install dewatering centrifuges to dewater an average of 439 dry tons/day of sludge (Hazen and Sawyer, and Stone & Webster, 1990). Dewatering is provided at eight of the 14 plants, four of which provide centralized dewatering (i.e. dewater sludge from the other six plants). The dewatered sludge is utilized in selected land-application based alternatives. Currently, the dewatered sludge is sealed in containers and shipped by rail or truck to an Arizona composting facility, a Colorado land-spreading site, a Pennsylvania land reclamation site and a Virginia landfill. Three companies are handling the NYC dewatered sludge, New York Fertilizer Company (NYOFCO) at \$215/wet ton, MERCO at \$92/wet ton, and Chambers Service, Inc. at \$127-\$237/wet ton. In the future, a land-spreading program will be developed to apply sludge in the New York State area to replace the remote disposal sites (Lutzic, 1992).

The major cost of sludge processing and disposal is polymer addition cost and transportation fee, which is based on the weight of transported sludge. Only the Wards Island WPCP spends approximately \$1,300,000 per year in polymer and \$9,300,000 to \$23,800,000 per year in disposal costs. The disposal cost range depends on the company processing the sludge. Therefore, if the sludge quantity can be decreased the transportation and polymer cost will correspondingly decrease. Decreasing the sludge volume, plants would contribute to waste minimization and pollution prevention, two USEPA programs (Freeman *et al.*, 1992), resulting to a cleaner and safer environment.

In addition, land-application rates and locations may be limited by the metals content of sludge. For example, sludge from the Newtown Creek plant contain higher metals

concentrations than the other plants and may have to be handled and disposed separately. If metals are removed from the dewatered sludge, disposal options will be increased, resulting to cost decrease.

1.3 Partially Digested Sludge

The anaerobically digested sludge currently produced in municipal wastewater treatment plants is referred to in this study as partially digested sludge (PDS). The term implies that further degradation of the organic content of the sludge is possible. However, the reaction rates are so slow that destruction of volatile solids beyond the 50 to 55 % range is usually not feasible in conventionally designed digesters. Speece (1988) observed the potential of further digestion of digested sludge when he surveyed 30 municipal wastewater treatment plants. Speece obtained the biochemical methane potential (BMP) as the volume of methane produced per volume of sludge after both five days and 30 days of digestion; ranges varied from 0.1-5.4 mL CH₄/mL of sludge for BMP₅ and 0.1-8.7 mL CH₄/mL of sludge for BMP₃₀.

1.4 Study Objectives

The purpose of the study was to evaluate the effect of the relatively new technology, Rapid Thermal Conditioning (RTC), on sewage sludge. The evaluation concerned the ability of RTC to enhance the biodegradation of sewage sludge and solubilize metals in the sludge.

1.4.1 Biodegradability and Methane Production

Rapid thermal conditioning was evaluated on three sludge types: PDS, WAS, and fermented primary sludge. Specific objectives for each sludge type were:

1.4.1.1 Partially Digested Sludge (PDS)

- Use batch digesters to determine the conditions needed to obtain the maximum improvement in biodegradation:

Series 1 Temperature Effect: RTC without pH adjustment at temperatures between 25°C and 220°C, and 10 sec retention time

Series 2 pH Effect: RTC with pH ranging from 1 to 12 at temperatures between 25°C and 220°C, and 10 sec retention times

Series 3 Pressure Effect: Unmodified pH at room temperature (25°C), one cycle at 400 psi

Series 4 HRT Effect: Unmodified pH at temperatures ranging from 25°C to 220°C, and retention times ranging from 10 to 180 sec

Series 5 Thickening Effect: Thicken PDS to about 4.5% TS with unmodified pH, temperatures ranging from 25°C to 220°C, and 10 sec retention time

- Select the optimum condition from the batch reactor experiments, and confirm the biodegradation improvement in continuous flow reactors using suspended growth and attached growth systems

1.4.1.2 Waste Activated Sludge (WAS)

- Use batch digesters to evaluate the improvement in biodegradation with unmodified pH, temperatures ranging from 25° to 220°C, and 10 sec retention time

1.4.1.3 Fermented Primary Sludge

- Ferment primary sludge for six days and use batch digesters to evaluate the improvement in biodegradation with unmodified pH, temperatures ranging from 25°C to 220°C, and 10 sec retention time

1.4.2 Metal Solubilization

Solids in the sludge are solubilized during the thermal conditioning process. Since most heavy metals in sludge are associated with the solids, metals removal during sludge conditioning was investigated under the conditions:

- pH ranging from 1 to 11 without thermal conditioning

- Thermal conditioning with and without pH adjustment at 220°C, at pH ranging from 1.5 to 11, and 10 sec retention time

For each condition tested, the dissolved metals as well as the metals associated with the sludge cake were analyzed.

2. BACKGROUND

2.1 Anaerobic Biological Treatment

2.1.1 Biochemistry of Anaerobic Digestion of Sludge

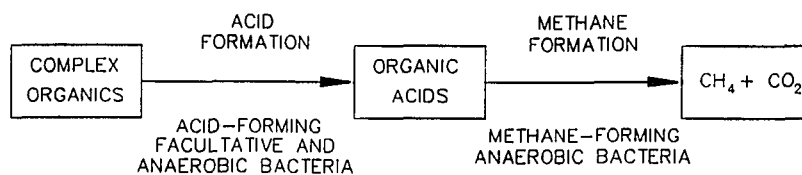
Wastewater treatment plants use a combination of sedimentation and biological processes to treat the influent wastewater. Approximately $\frac{1}{3}$ of the organic load to a municipal treatment plant is removed by primary treatment as primary sludge (PS) with the remaining $\frac{2}{3}$ removed by the activated sludge process. Approximately half the organic load removed by the activated sludge process is converted to biomass as waste activated sludge (WAS). PS and WAS are usually combined and then stabilized in anaerobic digesters. Anaerobic digestion is the process responsible for treating at least $\frac{2}{3}$ of the treatment plant's incoming organic load (Speece, 1981). Nevertheless, less attention has been given to the understanding, design, operation and optimization of the anaerobic process compared to the aerobic process (Speece, 1981).

Anaerobic digestion of sludge usually takes place at a controlled temperature of 35°C and over a period of approximately 15 to 20 days. The overall process (from solubilizing the extracellular polymers to soluble and final conversion to methane gas) proceeds at lower rates than the aerobic treatment processes (used in wastewater treatment plants). The main reason for the slow digestion degradation rates is that the anaerobic bacteria must degrade the more complex organic substrates found in sludge, particularly the difficult to

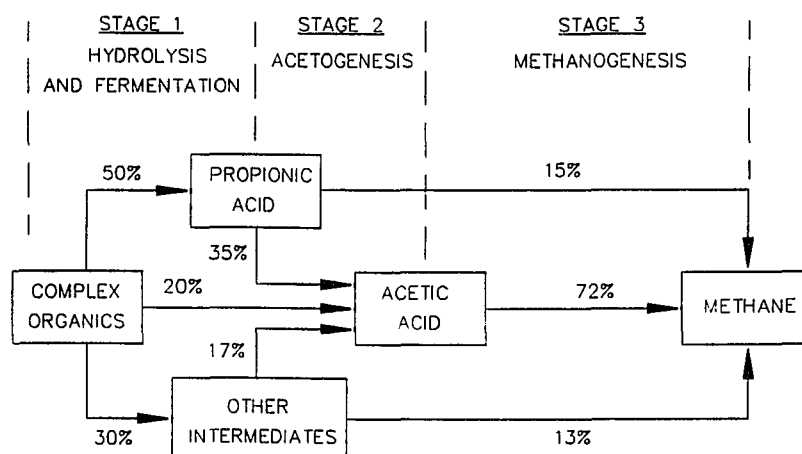
degrade bacterial cells generated by the aerobic treatment (Gossett and Belser, 1982; and Pavlostathis, 1985). In contrast, aerobic treatment handles the simple organic contaminants, mainly soluble or colloidal, found in wastewater. In the treatment of soluble organics, it was found that aerobic and anaerobic processes receiving the same substrate required the same hydraulic retention time and solids retention time to result in comparable COD removal efficiencies (Speece, 1981).

The biochemistry and microbiology of methane production during anaerobic digestion of insoluble organic compounds involve complex processes used by a number of microbial populations linked by their individual substrate and product specificities (Pohland, 1992). Even though all intermediate steps in the process were not fully understood, operating experiences have resulted in design criteria for municipal sludges and high strength wastewaters.

McCarty (1963, 1964) advocated a two-stage concept of anaerobic digestion that includes the **acid fermentation** and **methane fermentation** steps (Figure 2-1a). During the acid fermentation stage, complex organic compounds are degraded to fatty acids, alcohols, hydrogen (bonded to co-enzymes) and CO_2 by acid-forming bacteria. The fermented compounds in turn serve as substrate for methane-forming bacteria in the methanogenic stage. Subsequently, Jeris and McCarty (1965) proposed a three-step process and determined the COD balance around each step (Figure 2-1b). Complex organic compounds are fermented to propionic acid and other intermediate organic compounds subsequently converted to acetic acid. Over 70% of the methane produced in the digestion of complex wastes comes from acetic acid (or acetate).



(a) Two-Stage Methane Fermentation
From Complex Organics (McCarty, 1964)



(b) COD Balance of the Three-Stage
Methane Fermentation (Jeris and McCarty, 1965)

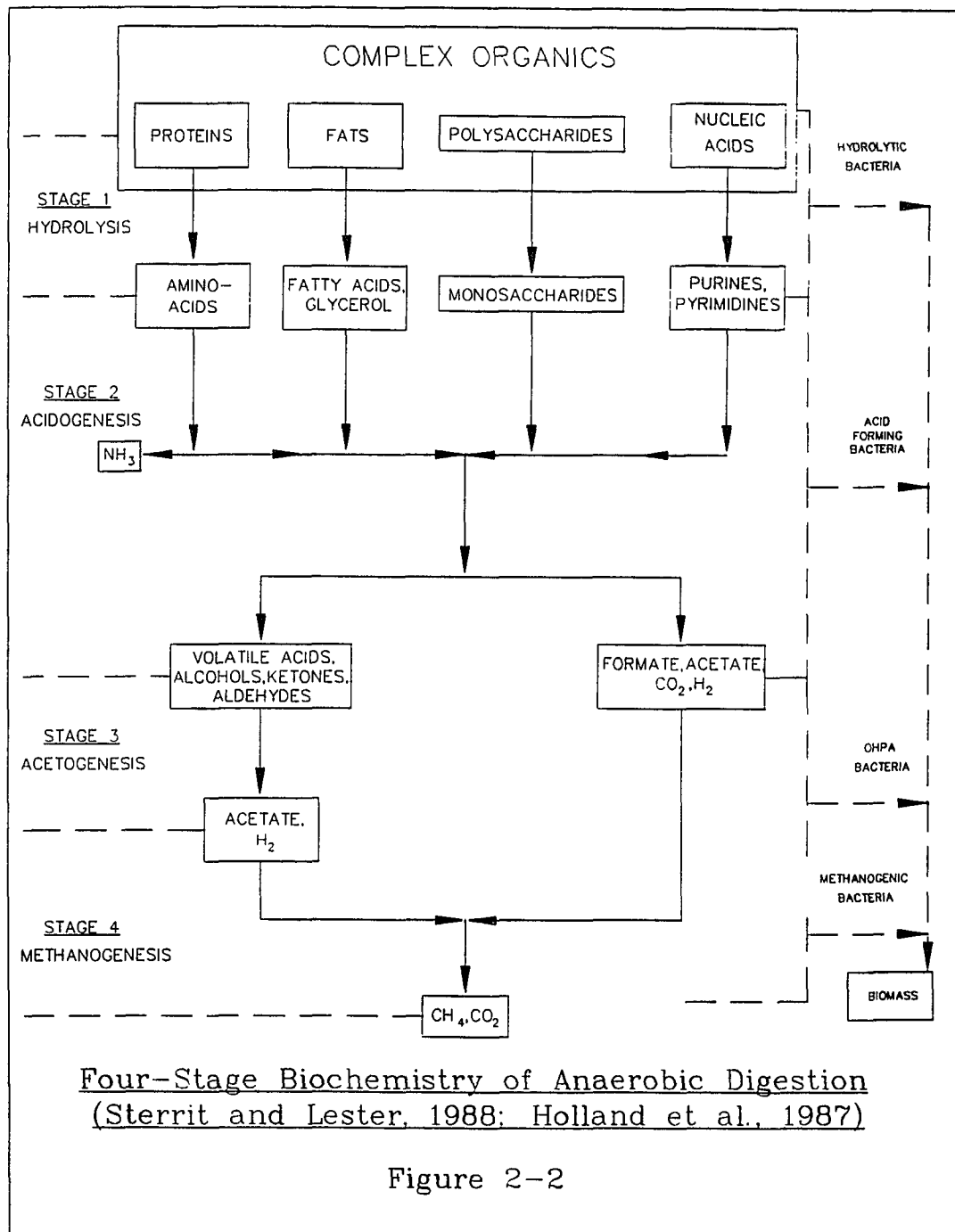
Figure 2-1

During anaerobic digestion, however, more biodegradation pathways are involved, as demonstrated by Bryant *et al.* (1967) (cited in Baily and Ottis, 1987). They found that the ethanol-fermenting methanogen *Methanobacillus omelianskii* was actually a symbiotic association of two species of bacteria, where one fermented ethanol to acetate and hydrogen, and the second used the hydrogen produced to reduce CO₂ to methane. This observation (Bryant *et al.*, 1967), along with the absence of pure methanogen cultures capable of degrading fatty acids to methane, suggested the existence of multi-stage anaerobic processes.

Today, anaerobic digestion is explained in terms of the four distinct stages shown in Figure 2-2 (Sterritt and Lester, 1988; Holland *et al.*, 1987) involving direct and indirect symbiotic associations between different groups of bacteria. The four significant stages are (a) **hydrolysis** of insoluble polymers, (b) **fermentation (acidogenesis)** of monomers produced by hydrolysis, (c) **acetogenesis** of fermentative organics, and (d) **methanogenesis** of acetate and hydrogen. Although other researchers (Harper and Pohland, 1986, 1987; Pohland, 1992) present anaerobic digestion as a nine-stage process, the important intermediate steps are the ones described by the four-stage process.

2.1.1.1 Hydrolysis

The large organic polymers (proteins, carbohydrates, lipids and nucleic acids) present in the sludge cannot be directly utilized by the bacteria since these polymers are too large to diffuse through the cell membrane. The polymers are first hydrolyzed into monomers that are then transported into the cell and metabolized. Polymer hydrolysis is performed



by extracellular enzymes produced by a number of bacteria and fungi. The hydrolysis rate depends on pH, temperature, microbial biomass (hydrolytic enzymes source), particulate substrate type and molecular size, and the remaining concentration of degradable particulate organics (Eastman and Ferguson, 1981). The hydrolysis of each category of compounds found in sludges will be described briefly.

(a) Proteins

Proteins are major components of the internal and external membranes of animal cells, skin and hair, blood and hormones (Gaudy and Gaudy, 1980). Microorganisms also contain large amounts of proteins. The biological catalysts that control the rates of bacterial biochemical reactions, the enzymes, are proteins.

Amino acids are the major building blocks of proteins that are joined together by peptide bonds to form polypeptides. Protein hydrolysis is accomplished by a wide variety of protease enzymes. Some of the proteases are very specific, and others, can degrade a range of proteins and peptides (Sterritt and Lester, 1988). After protein and polypeptide hydrolysis, the resulting products are free amino acids and small peptides that are taken into the cell by several types of transport mechanisms.

O'Rourke (1968) evaluated the effect of detention time on the fermentation of proteinaceous compounds. Proteins were fermented very rapidly, even with a detention time of less than one day, concluding that protein degradation is not the rate-limiting step during anaerobic digestion.

(b) Carbohydrates

Carbohydrates in anaerobic digesters range from simple sugars to complex compounds such as starch, cellulose, and hemicellulose. Carbohydrates can play a central role in bacterial metabolism. Microorganism carbohydrate content may vary from 15% to 35% of the dry weight (Gaudy and Gaudy, 1980). Hunter and Heukelekian (1965) found almost 24% of the suspended solids in treatment plants wastewater consists of carbohydrates. The bacterial capsule and the slime layer, responsible for the flocculation process in activated sludge, consist mainly of polysaccharides (Sterritt and Lester, 1988). The most important polysaccharides found in wastewater treatment plants are cellulose and starch.

Most of the cellulose in wastewater comes from paper, and it is considered one of the most difficult carbohydrates for microorganisms to degrade and metabolize (Edberg and Bengt, 1975; Gaudy and Gaudy, 1980). Edberg and Bengt (1975) studied cellulose degradation under aerobic conditions, concluding that several weeks would be needed to degrade only 50% of the compound. Some microorganisms are able to partially hydrolyze cellulose and make it available either to them or to other microorganisms.

Starch, the second major carbohydrate found in wastewaters, is made and stored in large amounts by plants. Like cellulose, starch consists of glucose subunits but the subunits are connected together by the α -linkage, whereas for cellulose the subunits are connected by the β -linkage (Sawyer and McCarty, 1978). The α -linkage can be easily hydrolyzed into

oligosaccharides and monosaccharides by various microbial enzymes, amylases (Banerji *et al.*, 1968).

Carbohydrates, similar to proteins, are hydrolyzed to simple sugars by extracellular hydrolases produced by various groups of bacteria (Gaudy and Gaudy, 1980). Cellulose is degraded by bacteria (myxobacteria, cytophaga, and species of *Clostridium*) and the fungi *Aspergillus*, *Penicillium*, *Cladosporium*, *Fusarium*, and *Trichoderma* (Gaudy and Gaudy, 1980). After the hydrolysis of starch, glucose, and cellulose, the monomers or oligomers (consisting of glucose units) are readily biodegradable. Carbohydrates are fermented rapidly, even at a detention time of one day (O'Rourke, 1968).

(c) Lipids

Lipids constitute a significant portion of the human diet and, therefore, they can be found in the organic matter in municipal wastewaters. Hunter and Heukelekian (1965) reported that 17% of the SS in wastewaters consists of lipids. Wastewater lipids are also found in bacteria, where their lipid content varies between 10% and 15% of dry weight (Gaudy and Gaudy, 1980). Major lipid constituents are fatty acids and alcohols bonded together with ester linkages.

The extracellular lipases, produced by *Clostridium* and *Micrococcus*, hydrolyze triglycerides (breakage of the ester bond) into fatty acids and glycerol. Glycerol is readily incorporated into the glycolytic pathway. Fatty acids enter metabolic pathways at the

acetyl-CoA level of metabolism. Only the short-chain acids, such as the volatile acids formic, acetic, propionic, and butyric are soluble and, therefore, are easily degraded. Fats, slowly degraded in anaerobic digesters, are easily removed by aerobic treatment (Viswanathan *et al.*, 1962).

Lipid biodegradation is usually the rate-limiting process in anaerobic digestion, especially at low temperatures. As temperature decreases below 20°C, lipid biodegradation ends, although methanogenesis (from other organic compounds) continues at reduced rates (O'Rourke, 1968). Low temperatures affect more the lipid-degrading bacteria than the methanogenic bacteria.

(d) Nucleic Acids and Nucleotides

Nucleic acids and nucleotides are major constituents of microorganisms and all living cells (Gaudy and Gaudy, 1980). Approximately 5% to 30% of the dry weight of microorganisms is in various forms of nucleic acids. Similar amounts are contained in animal and vegetable cells. As a result, wastewater and anaerobic digesters also contain nucleic acids. Similar to proteins, the nitrogen content of nucleic acids is about 16%. But unlike proteins, nucleic acids contain also about 10% phosphorous. Their general function is in cell energetics, replication, and protein synthesis.

Hydrolysis of nucleic acids produces purines and pyrimidines (Holland *et al.*, 1987). Some species of *Bacillus* and *Streptococcus* are responsible for the extracellular degradation of nucleic acids (Gaudy and Gaudy, 1980). DNA is hydrolyzed

extracellularly by the enzyme deoxyribonucleases (DNases), and RNA by ribonucleases (RNases). Hydrolysis breaks the phosphodiester bonds, releasing nucleotides. The highly ionized phosphate group of the nucleotides must be removed further by phosphatase in order for the nucleoside be transported within the cell.

To summarize, all large polymers must be hydrolyzed to their simpler constituents by extracellular enzymes before entering the cell. If extracellular enzymes are not available, biodegradation may not take place. Once the simple-molecules produced enter the cell, they may need further hydrolysis by intracellular enzymes before the molecules enter the catabolic pathways. The first stage of anaerobic digestion, hydrolysis, takes place extracellularly whereas the other three stages, fermentation, acetogenesis, and methanogenesis, take place intracellularly.

2.1.1.2 Fermentation (Acidogenesis)

The second stage in anaerobic digestion is the fermentation of the end-products of hydrolysis. Fermentation is the oxidation of an organic compound with another organic compound being the final hydrogen acceptor. Fermentation takes place within the cell after the hydrolyzed products are transported through the cell membrane. The most readily fermentable organics are sugars and amino acids. Some anaerobic bacteria can also ferment alkanolic acids, purines and pyrimidines (Holland *et al.*, 1987).

Sugars (monosaccharides) are used as an energy source by most of the fermentative microorganisms. Monosaccharides are first fermented to pyruvate via the Embden-

Meyerhof-Parnas (EMP) pathway. Pyruvate is then fermented by most of the microorganisms into alcohols and volatile acids. Carbon dioxide and hydrogen (bonded to coenzymes) are also formed during this stage. Table 2-1 shows some of the fermentative microorganisms and the various compounds produced from one simple substrate, glucose (Gaudy and Gaudy, 1980). Some other fermentation products are produced by a single microorganism, such as propionic acid from *Propionibacterium arabinosum*.

Amino acids are fermented mainly by two microbial groups, the anaerobic spore-formers (*Clostridium*) and the anaerobic cocci (*Micrococcus* and *Diplococcus*). Only one non-sporulating, rod-shaped bacterium is known to ferment amino acids, *Fusobacterium nucleatum* (Barker, 1961, cited in Kotze *et al.*, 1969). Species of the *Bacteriaceae* and the facultative species *E. coli* also can ferment certain amino acids. Table 2-2 presents the end-products from the fermentation of amino acids as produced by the various microbial species (Barker, 1961).

Some of the amino acid end-products are similar to those of carbohydrates, such as fermentation to pyruvate, from which lactate, propionate, butyrate, formate, and acetate are formed. Therefore, both carbohydrates and amino acids produce common end-products which are degraded further by common pathways (Kotze *et al.*, 1969). The major end-products of the fermented amino acids (from Table 2-2) are volatile acids (such as acetic, propionic, formic and valeric acids) and ammonia (by deamination). Jeris and McCarty (1965) reported that the predominant end-products are the short chain volatile

TABLE 2-1

FERMENTATION PRODUCTS OF GLUCOSE BY VARIOUS MICROBIAL SPECIES
(RESULTS IN mmol PRODUCT/100 mmol GLUCOSE)

Products	Yeast	<i>Streptococcus faecalis</i>	<i>Escherichia coli</i>	<i>Propionibacterium arabinosum</i>	<i>Butyribacterium rettgeri</i>	<i>Clostridium butylicum</i>	<i>Clostridium acetobutylicum</i>
Butyric acid	0.21	---	---	---	29	17.2	4.3
Lactic acid	1.37	146	79.5	---	107	---	---
Acetic acid	15.1	18.8	36.5	10.0	88	17.2	14.2
Formic acid	0.49	33.6	2.43	---	---	---	---
Succinic acid	0.68	---	10.7	7.8	---	---	---
Butanol	---	---	---	---	---	58.6	56
Ethanol	129.9	14.6	49.8	---	---	---	7.2
Acetone	---	---	---	---	---	---	22.4
Isopropanol	---	---	---	---	---	12.1	---
Carbon dioxide	148.5	---	88.0	63.6	48	203.5	221
Hydrogen	---	---	75.0	---	74	77.6	135
Glycerol	32.3	---	1.42	---	---	---	---
Acetoin	0.19	---	0.059	---	---	---	6.4
Propionic acid	---	---	---	148.8	---	---	---

Notes:

1. "----" None or Minimal Production
2. [Table Cited in Gaudy and Gaudy, 1980]

TABLE 2-2

FERMENTATION PRODUCTS OF AMINO ACIDS
BY VARIOUS MICROBIAL SPECIES

Amino Acid	Fermentation Products
Alanine	Ammonia, carbon dioxide, acetic acid, propionic acids
δ -amino valerate	Ammonia, acetic, propionic and valeric acids
Arginine	Ammonia, acetic, propionic and valeric acids, ornithine and citrulline
Citrulline+ADP+inorganic phosphate	Ammonia, carbon dioxide, acetic, propionic and valeric acids, ATP and ornithine
Ornithine	Ammonia, acetic, propionic and valeric acids
Asparagine	Ammonia, carbon dioxide, acetic and succinic acids
Aspartic acid	Ammonia, carbon dioxide, acetic, butyric, lactic, fumaric, and malic acids, ethanol, butanol
Cystine and cysteine	Ammonia, carbon dioxide, hydrogen sulfide, formic, acetic, propionic butyric, valeric and pyruvic acids
Homocysteine	Ammonia, hydrogen sulfide and α -ketobutyric acid
Methionine	Ammonia, methylmercaptan and α -ketobutyric acid
Glutamic acid	Ammonia, carbon dioxide, hydrogen, acetic, butyric, and lactic acids (intermediates mesaconate and citramalate)
Glycine	Ammonia, carbon dioxide, hydrogen, acetic and pyruvic acids
Histidine	Ammonia, carbon dioxide, hydrogen, formic, acetic, butyric, lactic and glutamic acids and formamide
Leucine	Can undergo the Stickland reaction to the branched chain fatty acid β -methyl butyric acid (N.B. leucine not easily fermented)
Isoleucine	Can undergo the Stickland reaction to the branched chain fatty acid α -methyl butyric acid (N.B. isoleucine not easily fermented)
Valine	Can undergo the Stickland reaction to the branched chain fatty acid α -methyl propionic acid
Lysine	Ammonia, carbon dioxide, acetic, propionic and butyric acids
Proline	Can undergo the Stickland reaction to δ -aminovalerate and can be further fermented (See δ -aminovalerate)
Hydroxy-proline	The degradation products are unknown
Serine	Ammonia, carbon dioxide, hydrogen, formic, acetic, propionic, butyric, valeric and lactic acids, alanine and ethanol
Threonine	Ammonia, carbon dioxide, hydrogen, formic, acetic, propionic, butyric, valeric and α -ketobutyric acids, acetaldehyde and glycine
Tryptophan	Ammonia, carbon dioxide, pyruvic acid, indole propionic acid, indole pyruvic acid and indole
Tyrosine and phenylalanine	Ammonia, carbon dioxide, hydrogen, phenol, p-cresol, p-hydroxy phenylacetate, p-hydroxy phenylacrylic, and p-hydroxy-phenyllactic acids

[Adapted from Winfrey, 1984]

acids especially acetic acid. For this reason, this stage is also referred to as the acidogenic stage. The fermentation products long-chained acids and volatile acids (short-chained) were found to control the anaerobic digestion of complex wastes (O'Rourke, 1968).

In addition to volatile acids, two additional fermentative end-products are formed, namely carbon dioxide and hydrogen bonded to coenzymes. These products result from a number of reactions such as the degradation of pyruvate via formate and from intermediate stages of some of the other fermentative pathways (Sterritt and Lester, 1988). For example, one mole of acetate and two moles of hydrogen (bonded to coenzymes) are produced during the degradation of ethanol. Some amino acid degradation also result to hydrogen production (Table 2-2). Amino acids that may contribute to hydrogen production are glutamic acid, glycine, histidine, and serine.

Type and relative quantities of fermentation end-products depend on the medium pH, the temperature, the relative fractions of fats, carbohydrates, and proteins in the feed, the presence or absence of specific trace nutrients, the character of the microbial flora, the solids retention times (Kugelman and Jeris, 1988), and the redox potential (Winfrey, 1984; Wolfe, 1985). One of the most important factors is the character of the microbial culture. Fermentative bacteria and methanogenic bacteria interactions were found to shift by-products to acetate and methane (Winfrey, 1984; Lee, 1987). For example, the final conversion of cellulose to fermented by-products and finally to methane, required the cooperative interactions between methanogens and fermentative microbial species (Lee, 1987).

Lee (1987) studied the conversion of cellulose under thermophilic conditions (58°C) using mixed cultures of *Clostridium thermocellum* (strain CALS-1) and *Methanobacterium thermoautotrophicum* (strain CALS-1). A monoculture of *C. thermocellum* grown on cellulose produced the fermented products ethanol, acetate, and lactate. Addition of *M. thermoautotrophicum* resulted in a shift towards acetate and methane. Finally, adding the acetotrophic *Methanosarcina* sp. strain to the bi-culture didn't increase methanogenesis and didn't decrease acetate levels. The lack of increase in methanogenesis in the tri-culture was attributed to inhibition of *Methanosarcina* by the *C. thermocellum* culture. Table 2-3 summarizes the shift to fermentation products of cellulose by various cultures (Lee, 1987). Several other researchers also have reached the same conclusions about methanogenic interspecies hydrogen-transfer with fermentative bacteria (summarized in Table 2-4; Mah, 1982).

2.1.1.3 Acetogenesis

Acetogenesis is the most important intermediate stage of anaerobic digestion. It is during this stage that acetogenic bacteria metabolize some of the products of fermentation into acetic acid. Jeris and McCarty (1965), using radioactive tracers, found that about 70% of methane produced in anaerobic digestion results from acetate degradation (Figure 2-1b). Most of the remaining methane results from the reduction of carbon dioxide.

Acetate, the major intermediate compound, is generated (1) during the fermentation stage by the degradation of sugars (Table 2-1) and amino acids (see Table 2-2), and (2) during

TABLE 2-3

FERMENTATION PRODUCTS FROM 10 mmol CELLULOSE
BY VARIOUS THERMOPHILIC MICROORGANISMS

Organism	Product, mmol/L as Glucose			
	Acetate	Ethanol	Lactate	Methane
<i>Clostridium thermocellum</i> (Cl.)	9.1	5.2	4.0	0.0
Cl. + <i>Methanobacterium thermoautotrophicum</i> (Mb.)	15.3	0.7	0.6	12.8
Cl. + Mb. + <i>Methanosarcina</i> strain CALS-1	17.5	0.7	0.4	11.8

[Lee, 1987]

TABLE 2-4

METHANOGENIC INTERSPECIES H₂ TRANSFER WITH
FERMENTATIVE H₂-PRODUCING BACTERIA^a

Heterotrophic H ₂ -Producer	Substrate	Monoculture Products	Methanogen	Mixed-Culture Products
S organism	Pyruvate	Ethanol, acetate, H ₂	<i>M. smithii</i>	Acetate (↑), CH ₄
<i>Selenomonas ruminantium</i>	Glucose Lactate	Lactate, acetate, propionate Acetate, propionate	<i>M. smithii</i> <i>M. smithii</i>	Acetate (↑), lactate (↓), propionate, CH ₄ Acetate (↑), propionate (↓), CH ₄
<i>Clostridium cellulosum</i>	Glucose	Acetate, formate, ethanol, H ₂	<i>M. smithii</i>	Acetate (↑), ethanol (↓), formate (↓), CH ₄
<i>Thermoanaerobium brockii</i>	Glucose	Acetate, ethanol, lactate, H ₂	<i>M. thermoautotrophicum</i>	Acetate (↑), ethanol (↓), lactate (↓), CH ₄
<i>Anaeroplasmia sp.</i>	Glucose	Butyrate, propionate, H ₂	<i>M. elizabethi</i>	Acetate (↑), butyrate (↓), propionate (↓), CH ₄
<i>Acetobacterium woodii</i>	Fructose	Acetate Acetate	<i>M. arbophilus</i> AZ ^b <i>M. barkeri</i>	Acetate (↓), CH ₄ CH ₄
<i>Ruminococcus flaveciens</i>	Cellulose	Acetate, succinate, formate, H ₂	<i>M. smithii</i>	Acetate (↑), succinate (↓), CH ₄
<i>Clostridium thermocellum</i>	Cellulose	Acetate, butyrate, ethanol, lactate, H ₂	<i>M. thermoautotrophicum</i>	Acetate (↑), butyrate, ethanol (↓), CH ₄
<i>Acetivibrio cellulolyticus</i>	Cellulose	Acetate, ethanol, H ₂	<i>M. barkeri</i> ± <i>Desulfovibrio sp.</i>	Acetate, (↑), ethanol (↓), CH ₄
Anaerobic fungus	Cellulose	Acetate, formate, ethanol, lactate, H ₂	<i>Methanobrevibacter sp.</i> ^c	Acetate (↑), formate (↓), ethanol (↓), lactate (↓), CH ₄
<i>Clostridium butyricum</i>	Pectin	Methanol, acetate, ethanol, butyrate, H ₂	<i>M. barkeri</i>	Methanol (↓), acetate (↓), CH ₄

NOTES:

- a The fermentation products listed are the major products detected. CO₂ is not shown, but was a major product in all cases. Arrows represent significant increases (↑) or decreases (↓) in the concentration of mixed culture products. The appearance of CH₄ in the coculture represents a significant increase in H₂ production by the fermentative organism. (Mah, 1982, cited in Winfrey, 1984)
- b *M. formicicum*, *M. bryantii*, and *M. barkeri* (nonacetate adapted) gave similar results.
- c A triculture containing *Methanobrevibacter* and *M. barkeri* gave similar results, with the exception that acetate was not detected.

the acetogenic stage by the breakdown of long chain alkanolic acids, and alcohols (Sterritt and Lester, 1988; Holland *et al.*, 1987; and Jeris and McCarty, 1965). Jeris and McCarty (1965) and Novak and Carlson (1970) reported that the main mechanism of the long chain acids breakdown to acetic acids is by beta-oxidation. In beta-oxidation the beta carbon is oxidized, followed by cleavage to acetic acid. The process continues until all the acid is oxidized. Unsaturated fatty acids are degraded more rapidly than saturated fatty acids (Novak and Carlson, 1970).

Obligate hydrogen-producing acetogenic bacteria (OHPA) are responsible for most of the acetate and hydrogen production during the acetogenic stage (Figure 2-2). In addition, as it was mentioned before, methanogenic interactions with fermentative bacteria lead to a shift of the fermented products to acetate (see Tables 2-3 and 2-4).

Besides interacting with fermentative bacteria, methanogens also interact with the OHPA bacteria, shifting thermodynamically unfavorable reactions to favorable reactions. The shift is made possible when methanogens consume hydrogen and keep hydrogen's partial pressure at low levels (Winfrey, 1984; and Fukuzaki *et al.*, 1989). For example, ethanol degradation to acetate and hydrogen becomes favorable when the hydrogen partial pressure is below 0.15 atm (15 kPa); butyrate and propionate degradation become favorable at pressures below 2×10^{-3} atm (200 Pa) and 9×10^{-5} atm (9 Pa), respectively. The effect of the methanogenic-OHPA interaction on the end-products from fermentable substrates, summarized by Mah (1982) in Winfrey (1984), are shown in Table 2-5.

TABLE 2-5

METHANOGENIC INTERSPECIES H₂ TRANSFER WITH
OBLIGATE H₂-PRODUCING ACETOGENIC BACTERIA^a

H ₂ -Producing Acetogen	Substrate Monoculture	Monoculture Products	Methanogen or Other H ₂ -Consumer	Mixed-Culture Products
<i>Thermoanaerobium brockii</i>	Ethanol	Acetate (tr.), H ₂ (tr.)	<i>M. thermoautotrophicum</i>	Acetate (↑), CH ₄
S organism	Ethanol Other alcohols ^b	Acetate (tr.), H ₂ (tr.) None	<i>M. bryantii</i> <i>M. smithii</i>	Acetate (↑), CH ₄ Corresponding acid ^c , CH ₄
<i>Desulfovibrio desulfuricans</i> or <i>D. vulgaris</i>	Ethanol Lactate Lactate	Acetate, (tr.), H ₂ (tr.) Trace products Trace products	<i>M. bryantii</i> <i>M. bryantii</i> <i>M. barkeri</i>	Acetate (↑), CH ₄ Acetate (↑), CH ₄ CH ₄
<i>Syntrophomonas wolfei</i>	Butyrate Valerate	None None	<i>M. hungatei</i> <i>M. hungatei</i>	Acetate, CH ₄ Acetate, propionate, CH ₄
<i>Syntrophobacter wolnii</i>	Propionate Propionate	None None	<i>Desulfovibrio</i> sp. + sulfate <i>Desulfovibrio</i> sp. + <i>M. hungatei</i>	Acetate, H ₂ S Acetate, CH ₄
Benzoate degrading bacterium	Benzoate Benzoate	None None	<i>Desulfovibrio</i> sp. + sulfate <i>Desulfovibrio</i> sp. + <i>M. hungatei</i>	Acetate, H ₂ S Acetate, CH ₄

NOTES:

- a The fermentation products listed are the major products detected. CO₂ is not shown, but was a major product in all cases. Tr. indicates that only a trace of the given product was detected. Arrows represent significant increases (↑) or decreases (↓) in the concentration of mixed culture products. The appearance of CH₄ in the coculture represents a significant increase in H₂ production by the acetogenic organism. (Mah, 1982, cited in Winfrey, 1984)
- b Other alcohols are n-propanol, n-butanol, isobutanol, n-pentanol.
- c The corresponding acid of the above alcohols was presumed to have been formed.

Lee (1987) did also a study on a thermophilic (60°C) anaerobic coculture consisting of an acetate-oxidizing eubacterial rod (AOR), and the hydrogen-using methanogen *Methanobacterium* sp. strain THF. When the AOR grew on ethylene glycol, 1,2-propanediol, formate, pyruvate, glycine-betaine, and H_2 - CO_2 , it formed acetate as the main product. Acetate was formed in stoichiometric amounts during AOR's growth on H_2 - CO_2 , a reversal of acetate oxidation, when the organism was grown in pure cultures and high hydrogen partial pressures. When the coculture grew on ethanol, the ethanol conversion to acetate depended on the hydrogen partial pressure. Lee (1987) found that ethanol was oxidized to acetate when hydrogen partial pressure reached 300 Pa; acetate was used when the hydrogen partial pressure was lowered by the methanogens below 60 Pa; hydrogen was not used below 10 Pa even at prolonged incubation times.

2.1.1.4 Methanogenesis

Waste stabilization by anaerobic digestion is accomplished only during methanogenesis. The three stages preceding methanogenesis convert insoluble, or particulate COD into soluble intermediate compounds. Therefore, in order for a waste to be stabilized anaerobically it must be converted to methane gas. Methane gas is highly insoluble in water and its removal from solution establishes actual waste stabilization. At 35°C, a headspace pressure of one atm with 70% methane in the gas phase, methane's solubility in water is about 15 mg/L.

Table 2-6 lists the methanogenic bacteria that have been isolated and studied in pure cultures. They are strict anaerobes, requiring an oxidation reduction potential of less than

TABLE 2-6

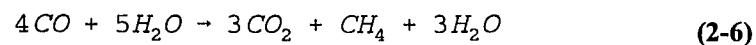
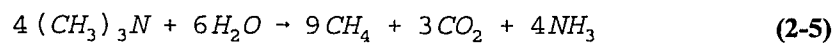
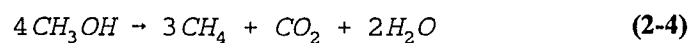
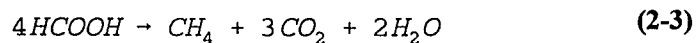
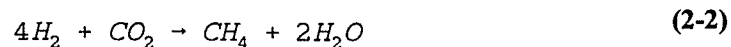
METHANOGENIC BACTERIA AND THEIR SUBSTRATES

Genus	Species	Substrate Utilized
<i>Methanobacterium</i>	<i>M. formicum</i> <i>M. bryantii</i> <i>M. thermoautrophicum</i> <i>M. propionicum</i> <i>M. soehngenii</i>	Formate, CO ₂ + H ₂ CO ₂ + H ₂ Acetate, CO, CO ₂ + H ₂ Propionate Acetate, butyrate
<i>Methanobrevibacter</i>	<i>M. ruminantium</i> <i>M. arboriphilus</i> <i>M. smithii</i>	Acetate, CO ₂ + H ₂ , formate Acetate, CO ₂ + H ₂ Formate, CO ₂ + H ₂
<i>Methanococcus</i>	<i>M. mazei</i> <i>M. vannielii</i> <i>M. voltae</i>	Acetate, formate, butyrate, CO ₂ + H ₂ Formate, CO ₂ + H ₂ Formate, CO ₂ + H ₂
<i>Methanomicrobium</i>	<i>M. mobile</i>	Formate, CO ₂ + H ₂
<i>Methanogenium</i>	<i>M. cariaci</i> <i>M. marisnigri</i>	Formate, acetate, CO ₂ + H ₂ Formate, CO ₂ + H ₂
<i>Methanospirillum</i>	<i>M. hungatei</i>	Formate, CO ₂ + H ₂
<i>Methanosarcina</i>	<i>M. barkeri</i> <i>M. methanica</i>	Methylamines, acetate, methanol, CO, CO ₂ + H ₂ Acetate
<i>Methanothrix</i>	<i>M. soehngenii</i>	Acetate
<i>Syntrophobactor</i>	<i>S. wolinii</i>	Propionate
<i>Methanobacillus</i>	<i>M. omelianski</i>	Primary and secondary alcohols, CO ₂ + H ₂
<i>Methanoplanus</i>	All species	Formate, CO ₂ + H ₂
<i>Methanococcoides</i>	All species	Methylamines, methanol

[McCarty, 1964; Winfrey 1984; and from summary in Montgomery 1984]

-320 mV (Wolfe, 1985) to function, and they are similar to methanogenic organisms found in the stomachs of ruminant animals and in organic sediments from lakes and rivers (Winfrey, 1984).

Methane gas in anaerobic digesters is produced mainly by (1) the cleavage of acetate to methane and carbon dioxide and (2) the reduction of carbon dioxide with hydrogen to produce methane and water. Some methane can also be produced by the conversion of formate, methanol, methylamines, and carbon monoxide (Winfrey, 1984). The aforementioned conversions, beginning with the most prevalent pathway, are presented in Equations 2-1 to 2-6.



Acetate (Equation 2-1) produces about 70% of the methane found in anaerobic digesters (Jeris and McCarty, 1965). Bhadra *et al.* (1984) found that Equation 2-1 is much more complex than presented here, involving various series of enzymatic reactions. Their findings showed that of the total methane produced (using acetate as a sole substrate), 72% comes from acetate **directly** and 28% via the CO_2 reduction. Acetate conversion requires a low hydrogen partial pressure (Lee, 1987; Winfrey, 1984), sustained by the hydrogen-utilizing bacteria (Equation 2-2). Studies by Ferguson and Mah (1983) showed

that from $\text{CO}_2 + \text{H}_2 + \text{acetate}$ substrate *Methanosarcina* sp. strain 227 used acetate after hydrogen was depleted. In the absence of hydrogen, Ferguson and Mah (1983) found by radionuclide labeling techniques that no CO_2 was reduced to methane, and methanogenesis proceeded from acetate.

Equations 2-2 to 2-6 provide the remaining 30% of the methane produced in anaerobic digestion, where as much as 20% (of the total methane gas) is attributed to reduction by hydrogen (Sykes, 1970). Hydrogen and CO are intermediate products that at high concentrations can inhibit methane production. Under normal loading conditions they are at low concentrations. They accumulate rapidly when methanogenesis is severely inhibited by organic toxicants, such as chloroform and formaldehyde (Hickey, 1987). However, studies on methanogenic cultures enriched with glucose found carbon monoxide did not appear to be a reliable monitoring tool to detect and control reactor upset conditions (Bae and McCarty, 1993).

Recent studies showed that methanogens can use directly only acetate and formate from the volatile fatty acids (Dinopoulou *et al.*, 1988). Butyric and propionic acids must be converted to acetate and formate by the OHPA bacteria. Propionate degradation to acetate can be inhibited by high hydrogen partial pressures. Hydrogen is produced by the butyrate-converting bacteria. If the hydrogen-utilizing bacteria remove hydrogen at a slower rate than it is produced, propionate will not be degraded.

To summarize, anaerobic fermentation of complex substrates to methane gas involves several biodegradation pathways, and requires the symbiotic interactions of various groups

of bacteria. The most common interactions are methanogens with fermentative bacteria, and methanogens with OHPA bacteria.

2.1.2 Anaerobic Treatment Processes

The PDS is essentially a dilute slurry (2% to 3% TS) of anaerobically digested solids. Once the PDS is thermally conditioned, the slurry becomes more dilute because of the condensed steam introduced to heat the sludge and the solubilization of suspended solids. Biodegradability is due to both the newly solubilized organic compounds and the remaining suspended solids. Therefore, the biological reactor selected should handle both the soluble and the particulate organic matter remaining after RTC.

Many types of reactors have been used to anaerobically treat high strength wastewaters or slurries. Figure 2-3 shows flow diagrams for most types of reactors that have been evaluated in pilot or full scale applications (Speece, 1983). These reactors can be placed in either of two broad categories, suspended-growth, and fixed-film reactors. In suspended-growth reactors the biomass and other solids are held in suspension. When the process operates without post clarification and returned sludge, as in NYC anaerobic digesters, the hydraulic retention time (HRT) equals the solids retention time (SRT) resulting in relatively large reactors. However, in fixed-film reactors, the solids are retained within the reactor resulting in HRTs lower than the SRTs. Thus these reactors can be smaller and operate at much higher organic loading rates.

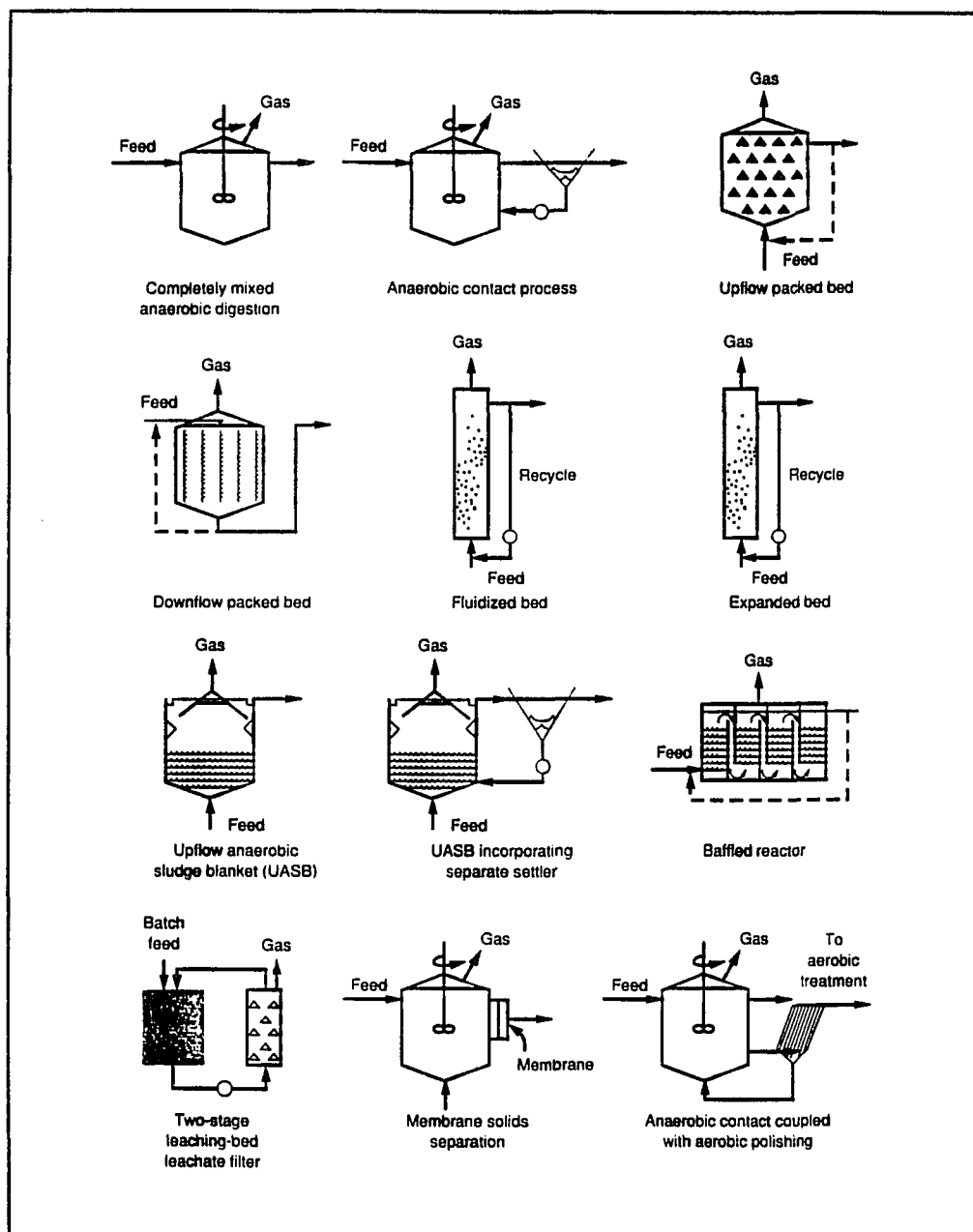


Figure 2-3. Typical Anaerobic Reactor Configurations (Speece, 1983).

Hall and Jovanovic (1982) evaluated the treatability of liquor from thermally-conditioned sludge by fixed-film and suspended-growth process. These processes were a downflow stationary fixed-film system (DSFF), an anaerobic fluidized-bed system (Anitron), an upflow anaerobic sludge blanket system (UASB), and an upflow anaerobic filter (Anfill). Thermally conditioned liquor was supplied by the Lakeview WPCP, Ontario, Canada. COD removal efficiencies ranged from 50% to 76%, indicating that thermally conditioned liquors can be treated by any system. The Anfill system had the highest performance based on organic loading conditions. The UASB system was not very successful in treating the liquor at loadings comparable to the fixed-bed reactors. Solids were lost from the UASB effluent because of poor biomass settling.

In this study both categories of reactors were considered, and a typical reactor from each category, suspended-growth and fixed-growth, was used.

2.1.2.1 Anaerobic Suspended-Growth Processes

Traditionally, organic sludges have been stabilized in anaerobic digesters designed either as continuous flow non-mixed reactors (standard-rate) or continuous flow completely mixed reactors (high-rate). The high-rate digester is more widely used than the standard-rate digester because of the shorter hydraulic retention time (HRT) required. At the mesophilic range (35°C) the HRT of the high-rate digester ranges from 10 days to 20 days, whereas the HRT of the standard-rate digester ranges from 30 days to 60 days (Metcalf and Eddy, 1991; Reynolds, 1982).

Proper mixing is an important requirement for optimum process performance. EPA (1987) summarizes the following reasons of proper anaerobic digester mixing:

- Provide contact between the active biomass and feed sludge
- Provide physical, chemical, and biological uniformity within the digester
- Distribute organics and dilute inhibitory substances
- Utilize the digester volume effectively
- Prevent stratification and temperature gradient
- Minimize formation of scum layer and deposition of solids

The limitation of a completely mixed reactor is that the system operates at a fixed solids retention time, and fixed environmental conditions such as pH and ORP. Under these conditions, only a certain group of bacteria (i.e., methanogens) operate at optimum conditions, whereas other groups (i.e., acetogens) do not. A two-phase anaerobic process, operating at optimum conditions for each of the two major bacterial groups, was evaluated by Ghosh (Ghosh, 1987; and USEPA, 1987). The first phase involved hydrolysis and acetogenesis of organic compounds, and the second phase involved methanogenesis. The process offered better buffering capacity than the single-stage digestion. Digestion HRTs as low as three days gave better gas production and biodegradabilities than the 15-day single-stage digestion system. Two-phase digestion results were also demonstrated by a large-scale pilot plant at the Woodridge wastewater treatment plant, DuPage County, Illinois (Ghosh, 1990).

Mixing in full scale operations is achieved by the devices shown on Figure 2-4 (EPA, 1987). In bench scale studies, mechanical mixing is preferred as it is more practical and easier to control.

High-rate digestion operates either as a single-stage or a two-stage process. In a single-stage operation the raw sludge is pumped into the high-rate digester and the digested sludge is then discharged into downstream sludge handling processes. In a two-stage operation the high-rate digester is followed by a standard-rate digester which is more commonly known as a secondary digester. The secondary digester is used to store and concentrate the digested sludge and to capture any additional gas produced during storage.

In the 1950s, a modified two-stage high-rate digestion process was employed by Schroepfer *et al.* (1955) to treat meat packing wastes. During this process, which operates analogous to the activated sludge process, sludge settles in the secondary digester and then is recycled to the primary digester as needed (Figure 2-3). This process, called the anaerobic contact process, was operated at an HRT as low as 12 hours, and treated organic wastes as low as 1,500 mg/L BOD₅. Solids residence time, the controlling parameter, remained high resulting to similar and even better solids destruction than the high rate digestion, but at much lower HRT values (Pfeffer *et al.*, 1967; and Pfeffer, 1968). The anaerobic contact process, however, is limited by the settling characteristics of the sludge solids in the secondary digester.

Another modification of a suspended growth system is the upflow anaerobic sludge-blanket (UASB) process. The high strength wastewater flows upward through a sludge

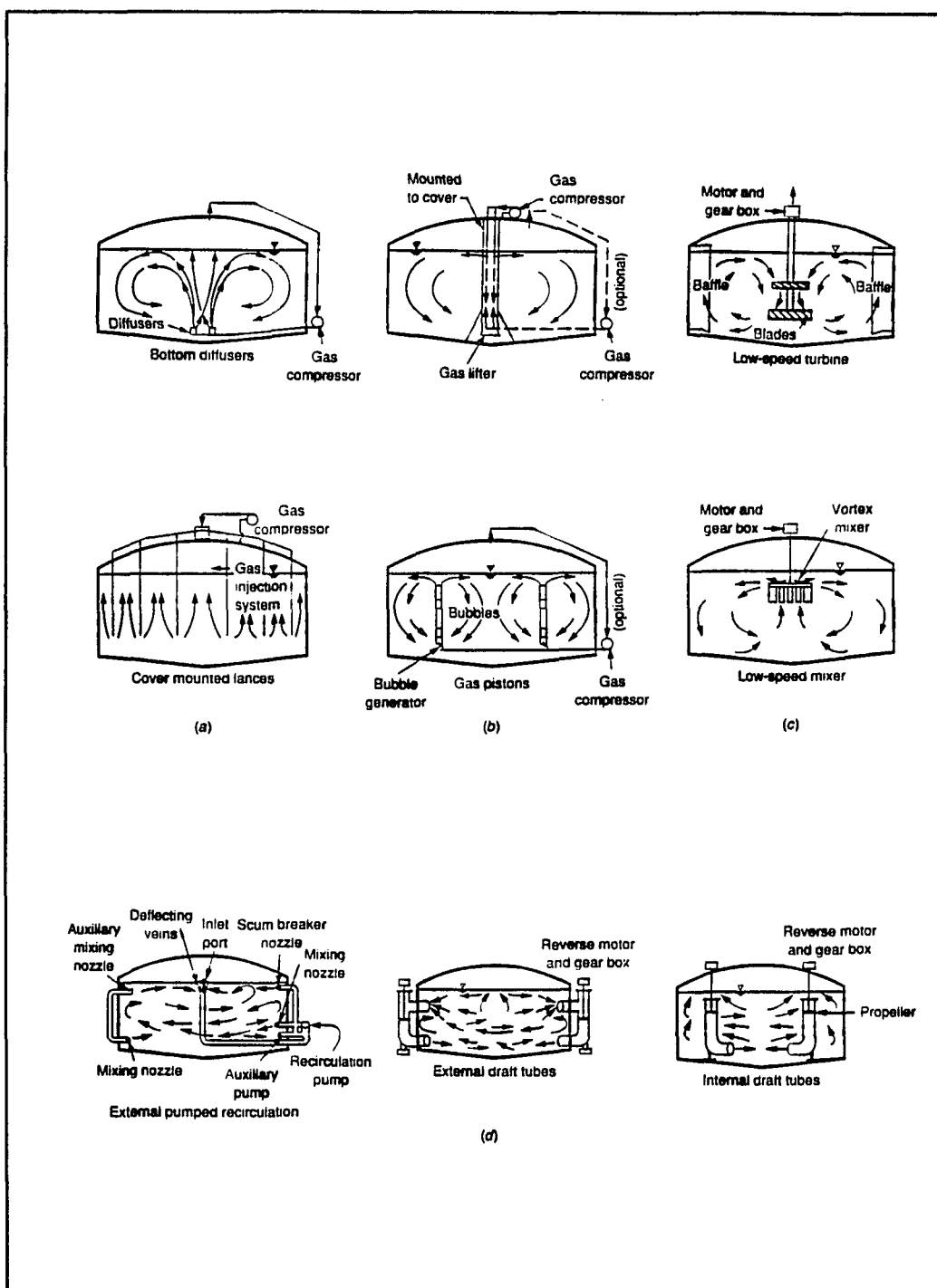


Figure 2-4. Anaerobic Digestion Mixing Systems: (a) Unconfined Gas Injection, (b) Confined Gas Injection, (c) Mechanical Stirring, and (d) Mechanical Pumping (EPA, 1987).

blanket composed primarily of biologically active solids. Treatment occurs as the wastewater contacts the solids. The upflow velocity is controlled within the range of 2 to 3 ft/hr to maintain the sludge blanket in suspension. The process has proven effective with some wastewaters (Lettinga, 1992; and Lettinga and Hulshoff, 1992), and its loadings and efficiencies are compared to other anaerobic processes in Table 2-7.

2.1.2.2 Anaerobic Fixed-Film Biological Process

All of the anaerobic suspended-growth processes, except the anaerobic contact process, require a high HRT (usually greater than 10 days) in order to obtain acceptable digestion. In addition, they are proven uneconomical in treating wastes containing less than 1% biodegradable solids (Young and McCarty, 1969). For these reasons, during the past 20 to 30 years new processes called the "fixed-film" anaerobic biological processes have been developed. These processes operate at very high solids retention times (SRT), beyond 100 days, but at low HRTs, less than 2 to 3 days. The advantages of the fixed-film anaerobic processes over the suspended-growth processes are (Young and McCarty, 1969):

- High treatment efficiencies at low HRTs
- Economical treatment of low strength wastes. Acceptable removals may be obtained at lower temperatures
- Low sludge production. Effluent suspended solids may be within the acceptable range while sludge wasting may not be required for long periods of time

TABLE 2-7

TYPICAL PERFORMANCE DATA OF ANAEROBIC PROCESSES

Process	Input COD (mg/L)	Hydraulic Retention Time (Hours)	Organic Loading (lb COD/ft³-d)	COD Removal (%)
Anaerobic Contact Process	1,500-5,000	2-10	0.03-0.15	75-90
Upflow Anaerobic Sludge-blanket (UASB)	5,000-15,000	4-12	0.25-0.75	75-85
Fixed-bed	10,000-20,000	24-48	0.06-0.30	75-85
Expanded-bed	5,000-10,000	5-10	0.30-0.60	80-85

[Metcalf and Eddy, 1991]

- Biological solids recycling is not required because they remain in the filter and are not lost with the effluent
- More resistant to shock loading conditions
- Less sensitive to temperature fluctuations
- No mechanical mixing required

Some of the disadvantages of the fixed-film anaerobic processes are (Hall, 1992):

- Not suitable for high suspended solids wastewaters
- Suspended solids accumulation may impact reactor hydraulic and internal mass-transfer characteristics
- Provisions may be required for periodic biomass removal
- Limited access to reactor interior for monitoring and inspection of biomass accumulation

Most of the concepts of the anaerobic fixed-film processes were obtained from the aerobic fixed-film processes where trickling filters, biological towers, and rotating biological contactors (RBC) are used in full scale applications with great success. Anaerobic fixed-film processes which were tested successfully in laboratory, pilot, and full scale applications include the following:

- Anaerobic filters
- Anaerobic fluidized bed reactors
- Anaerobic trickling filters

- Anaerobic rotating biological contactors

The anaerobic filter is usually a column filled with submerged media. Biomass attaches to the media surface and biomass flocs are also entrapped between the media and contribute further to the substrate biodegradation (Young and McCarty, 1969). Floc sizes from 1 to 4 mm have been reported.

Two of the first researchers to realize the importance of the anaerobic filter were Young and McCarty (1969). Their anaerobic filter was constructed of a 6-inch diameter by 6-foot high plexiglass column filled with 1 to 1.5 in. diameter rocks. The filter had a porosity of 0.42 and a liquid volume of 12 liters and was operated from 4.5 to 72 hours HRT and loadings of 26.5 to 212 lb COD/day/1000 cf.

Young and McCarty's (1969) promising findings led other researchers to use and modify the anaerobic filter to treat various kinds of loadings and wastes. Modifications included changes in: (1) packing media to increase contact surface area and filter porosity (Mueller and Mancini, 1975); (2) addition of recirculation systems; (3) downflow feeding instead of upflow; (4) downflow feeding with partially submerged media instead of completely submerged media, similar to a trickling filter; and (5) low-strength wastewater feeding with COD concentrations less than 350 mg/L (Houssein, 1989; and Montgomery, 1984).

Dohanyos *et al.* (1985) compared the efficiencies of an upflow anaerobic filter, a downflow anaerobic filter, and an upflow anaerobic sludge-blanket. The upflow anaerobic filter was the least sensitive to volatile fatty acids inhibition, and the least sensitive to

temperature and load fluctuations than the other two reactors. The substrates used were wastewaters from the production of pectin and yeast.

2.1.3 Environmental and Operational Conditions

Anaerobic digestion, like any other biological process, is greatly affected by the environment conditions surrounding the bacteria. Parkin and Owen (1986) presented a review on anaerobic digestion fundamentals and described the factors affecting the process operation. Some important environmental and operational factors affecting the anaerobic bacteria, and that are also important for this study, are:

- Solids retention time (SRT)
- pH-alkalinity
- Temperature
- Nutrients
- Toxic compounds
- Feed characteristics
- Redox potential

Other secondary factors affecting anaerobic digestion are foaming (Niekerk *et al.*, 1987), suspended solids, and incrustation and formation of inorganic precipitates (Dohanyos and Zabranska, 1991a).

2.1.3.1 Solids Retention Time (SRT)

Anaerobic digestion is a difficult process to design and control because of all the interconnected complex reactions and bacterial symbiotic reactions involved. All possible reactions and conversion rates are related to microbial growth rates, and growth rates are related to dilution rates. Distinct dilution rates would select a preferential bacterial species, resulting to different conversion patterns, end-products, and conversion rates. Solid retention time (SRT or θ_c) is the most important operational factor, whose choice would determine the system's efficiency, successful operation, and system's resistance to shock loading and toxic conditions.

To ensure sufficient conversion of complex organic matter to methane, the bacteria population must be of sufficient quantity and concentration, and the bacteria must have enough retention time to allow substrate-metabolism and prevent their washout from the system (WEF and ASCE, 1992). The challenge for designing an anaerobic treatment system is to maximize conversion rates and minimize SRTs, resulting to minimum reactor volume and minimum capital and operating costs.

For a completely mixed system and without recycle, SRTs and HRTs are the same. At the mesophilic range (35°C) the HRT ranges from 10 days to 20 days (Metcalf and Eddy, 1991; Reynolds, 1982), whereas for an attached growth system, HRTs can be less than 12 hours, but SRTs can be higher than 100 days (Young and McCarty, 1969; and Mueller

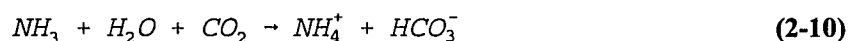
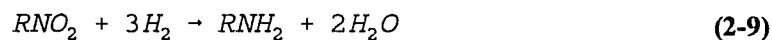
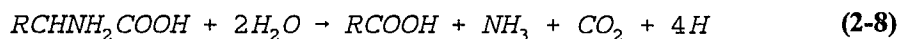
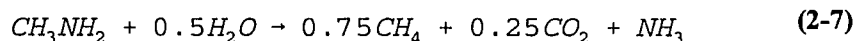
and Mancini, 1975). The generation times for methanogenic bacteria range from less than two days to more than 20 days at a temperature of 35°C, requiring the high SRT values to prevent their washout from the system (Malina, 1992).

2.1.3.2 pH-Alkalinity

As it was mentioned before, anaerobic digestion involves complex reactions that lead to volatile acids production and then to methane gas production. Volatile acids production tends to reduce the pH. Methane gas production counteracts the pH drop by removing the volatile acids from the system and by producing bicarbonate. Because methane-producing bacteria are very sensitive to small deviations of pH, close pH-control is necessary to ensure a good operating system (USEPA, 1979).

Most anaerobic conversion processes operate satisfactorily within the pH range of 6.5 to 7.5, but operate best at neutral pH (Jeris and Kugelman, 1986; and McCarty, 1964). Deviations from the optimum pH value are usually the result of excess production and accumulation of acidic or basic conversion products such as volatile acids or ammonia, respectively (Pohland, 1992). Methanogenic bacteria are more sensitive to low pH than acetogenic bacteria. During upset conditions the acetogenic bacteria will continue to produce volatile acids, despite the pH depression, aggravating the environmental conditions further, and resulting to complete digestion failure.

Low pH can be prevented by providing enough buffering capacity. A minimum bicarbonate alkalinity of 1,000 mg/L is required to maintain the pH within the optimum range (Jeris and Kugelman, 1986). Most of the alkalinity in anaerobic digestion is provided by ammonia that is released during fermentation of amino acids and proteins (McInerney, 1988), methanization of methylamine (Metcalf and Eddy, 1992), and breakdown of other nitrogenous organic compounds (McCormick *et al.*, 1976 in Anderson and Yang, 1992a). Some ammonia-release-consumption reactions are presented below:



The ammonia released, in the presence of excess carbon dioxide, is converted to ammonium ion and bicarbonate alkalinity, shown by the last reaction. It is the interaction of ammonia with the carbonic acid (or CO_2) that controls the pH (Capri and Marais, 1975). Therefore, the biodegradability of nitrogenous organic compounds during anaerobic digestion results in an alkalinity increase equal to the amount of ammonia release (except for the ammonia used for cell synthesis). Wastes containing low protein but high carbohydrate concentrations are prone to low-pH upset-conditions since not enough ammonia would be produced to counteract the volatile acids production.

2.1.3.3 Temperature

Temperature is an environmental factor that greatly affects the anaerobic digestion. It affects bacterial growth rates and metabolic activities (Pfeffer *et al.*, 1967), enzymatic reaction rates and, since enzymes are also proteins, protein denaturation rates (Gaudy and Gaudy, 1980).

(a) Bacteria Growth

Basically, bacteria are divided into three groups based on their temperature ranges, psychrophilic, mesophilic, and thermophilic (Viessman and Hammer, 1985; Metcalf and Eddy, 1991; and Winfrey, 1984). The maximum growth rate is between the temperature-range of each group. For every 10°C temperature increase the growth rate almost doubles till the maximum rate is reached. Psychrophilic methanogens were found in lake, river, and ocean sediments. They grow best at temperatures slightly above freezing, 4°C-10°C (Viessman and Hammer, 1985).

Anaerobic digestion usually operates at the mesophilic temperature range of 30°C to 38°C with an optimum at 35°C $\pm$ 3°C (Jeris and Kugelman, 1986; and Buhr and Andrews, 1977). Psychrophilic and mesophilic digestion are found in natural habitats. The third digestion type, thermophilic, is rarely found in nature except thermal-spring algal-mats and anaerobic digesters (Winfrey, 1984; and Buhr and Andrews, 1977). Some anaerobic

digestion processes operate at the thermophilic range to take advantage of the higher rates, resulting to lower digestion times (Buhr and Andrews, 1977). Thermophilic digestion temperature is between 50°C and 60°C (Jeris and Kugelman, 1986; and Buhr and Andrews, 1977) with an optimum at 55°C (WEF and ASCE, 1992).

Buhr and Andrews (1977) summarized the following advantages and disadvantages of thermophilic digestion over mesophilic digestion.

Advantages

- Increased reaction rates with respect to volatile solids destruction, thus yielding same digestion as mesophilic but at lower retention time
- Increased efficiency with respect to the fraction of volatile solids destroyed, thus yielding more methane gas
- Improved solid-liquid separation, improving sludge dewaterability
- Increased pathogenic organisms' destruction

Disadvantages

- High energy requirement for heating, thus additional fuel may be required
- Poor supernatant quality due to higher soluble and colloidal organics

- Poor process stability because bacterial cultures are less diverse in thermophilic digestion than mesophilic digestion
- More expensive construction material and more maintenance requirements because of the corrosive nature of digested liquid and the cake formation on heat-exchangers (Jeris and Kugelman, 1986)
- More ammonia production (Maly and Fadrus, 1971)

Methanogens were also found at hot springs and geysers where water temperatures exceeded 100°C. Some methanogens were even found at temperatures as high as 300°C (Winfrey, 1984). The high temperature methanogens are chemotrophs requiring inorganic chemicals for growth and energy. The high temperature-pressure tolerance of the methanogens indicates that they are not "delicate" microorganisms as originally thought to be.

Miller *et al.* (1988) studied the growth of *Methanococcus jannaschii*, an extremely thermophilic methanogen, in a high-pressure-temperature bioreactor. *M. jannaschii* was obtained from a white smoker chimney at a depth of 8,500 feet on the East Pacific Rise. Optimum growth conditions were achieved at 100 atm and 88°C.

(b) Enzymatic Reaction Rates

Enzymatic reaction rates follow the classical Arrhenius reaction equation (Gaudy and Gaudy, 1980) where rates increase with increasing temperatures.

$$K = A e^{-\frac{E^*}{RT}} \quad (2-11)$$

where,

K = specific rate constant, moles/L

A = constant, moles/L

E* = activation energy, cal/mole

R = gas constant

= 1.987 cal/°K-mole

T = reaction temperature, °K

But the rates cannot increase indefinitely. Increasing temperatures denature the proteinaceous enzymes, resulting in loss of activation and decreasing rates (Pelczar and Chan, 1981). Therefore, there is a certain temperature range at which the increased enzymatic rates would be counterbalanced by the decreased activities, and the overall rate would decrease.

2.1.3.4 Nutrients

The inability of many anaerobic bacteria to synthesize some essential vitamins or amino acids requires that they be supplied in the culture medium (Pohland, 1992). Nitrogen and phosphorus are the primary macro nutrients. COD:N ratios between 400:7 and 1000:7 are required for high and low substrate loadings, respectively (Henze and Harremoes, 1983). An N:P ratio of 7:1 has been reported by Stronach *et al.* (1986), with the most broadly accepted ratio being 15:1 (Lee, 1994).

Necessary trace elements include iron, zinc, sodium, potassium, calcium, chloride, nickel, magnesium, calcium, sodium, barium, tungstate, molybdate, selenium, and cobalt. Selenium, tungsten and nickel are used in the enzyme systems of the acetogenic and methanogenic bacteria (Stronach *et al.*, 1986). For example, selenium and tungsten are used by the enzyme formate dehydrogenase, and nickel for the carbon monoxide dehydrogenase enzyme.

Some B vitamins were reported as stimulants of methane fermentation from acetate. Vitamin B₁₂, a methyl-group carrier, has been found in significant quantities in sewage sludge (Jeris and Kugelman, 1986). Municipal sewage sludge, besides nitrogen and phosphorus, contains all the other trace nutrients required for the metabolism and growth of anaerobic bacteria. Industrial wastewater, however, may require addition of these nutrients (WPCF, 1987).

2.1.3.5 Toxic Compounds

Anaerobic digestion must be free from toxic compounds for proper treatment. Substances are considered non-toxic or toxic at specific concentrations. The most common toxic compounds are: organic compounds (i.e., volatile acids at high concentrations), heavy metals, ammonia, sulfide (WPCF, 1987; Jeris and Kugelman, 1986; Kugelman and McCarty, 1965; McCartney and Oleszkiewicz, 1991; and Parkin *et al.*, 1983). Other toxic compounds, usually associated with industrial discharges, include the organic chemicals chloroform, bromoethanosulfonic acid, trichloroacetic acid, and formaldehyde (Hickey *et al.*, 1987).

Literature review on toxic-compound concentrations (WPCF, 1987; Jeris and Kugelman, 1986; and Pohland, 1992) indicated a range of values among researchers. The discrepancies are due to the complexity of the anaerobic system where toxic concentrations depend not only on the factors mentioned in the previous paragraph, but also on various other phenomena. These phenomena include the effect of precipitation complex reactions, antagonism and synergism, multiple cation effects, and acclimation of the microorganisms to the toxic compounds (Jeris and Kugelman, 1986; and Kugelman and McCarty, 1965). Table 2-8 gives an estimate of some compound concentrations that may be toxic to anaerobic microorganism. Again, the concentrations are approximate values and should not be used literally for every anaerobic digestion system.

TABLE 2-8

CONCENTRATIONS OF COMPOUNDS TOXIC TO ANAEROBIC BACTERIA

Compound	Non-acclimated Concentration (mg/L)	Acclimated Concentration (mg/L)
Sodium	4,500	8,000
Potassium	4,000	5,500
Calcium	2,800	5,500
Magnesium	1,200	1,500
Ammonium	1,700	---
Ammonia	30-60	50-100
Iron	> 200	> 200
Sulfide	100	200
Long-chain Fatty Acids	---	500
Heavy Metals	< 1	< 1

Notes:

1. "---" Not available
[Jeris and Kugelman, 1986]

Unionized ammonia-nitrogen concentration (UAN) was reported being the most toxic species of ammonia with total ammonia nitrogen (TAN) the least (Jeris and Kugelman, 1986; Heinrichs *et al.*, 1990; and McCarty and McKinney, 1961). UAN toxic-limit depends on media pH, temperature, and on microbial types. Heinrichs *et al.* (1990) and Bhattacharya and Parkin (1989) found that UAN affected the acetate-utilizing bacteria to a greater extend than propionate-utilizing bacteria in acetate-propionate mixed culture. The pH value affects the dissociation of TAN into UAN. As the pH rises, ammonia shifts in favor of UAN.

Volatile acids toxicity is also affected by the medium pH. Originally it was thought that total acid concentration was the cause of acid toxicity (cited by Jeris and Kugelman, 1986), or that volatile acids toxicity was due to salt toxicity, the cation of the volatile acid salt (McCarty and McKinney, 1961). Now it is believed that it is the unionized form of the volatile acids that is toxic (Andrews, 1969; Fukuzaki *et al.*, 1990; and Graef and Andrews, 1973). As the pH decreases, volatile acids shift in favor of unionized acids. Heavy metals also affect the volatile acid degradation and utilization, where some metals were found to be more toxic to volatile acid degrading acetogens, and some metals to HAc-utilizing methanogens (Lin, 1992).

2.1.3.6 Feed Characteristics

Sludge anaerobic digestion applies to primary sludge, waste activated sludge, or mixture of the two. Primary sludge contains more readily degradable organic matter than WAS, resulting to higher total volatile solids destruction efficiencies (WEF and ASCE, 1992). Literature indicates that as much as 70% of primary sludge is biodegradable (Parkin and Owen, 1986). However, WAS is generally reported to be "half as digestible as primary sludge" (Parkin and Owen, 1986).

The biodegradability of WAS depends on the active anaerobic biomass present, and the characteristics of the biomass greatly depends on solids retention time (SRT) of the aerobic activated sludge process (Gossett and Belser, 1982; and Pavlostathis, 1985). High SRTs result in biomass more resistant to lysis and, consequently, to decreased anaerobic degradation rates. Gossett and Belser (1982) reported that the ultimate WAS biodegradability ranged between 30-50%. Even at long SRTs the reduction of COD or VS will not exceed 50% destruction efficiencies (Parkin and Owen, 1986). More than 50% of the WAS's COD escapes anaerobic digestion, resulting in digester effluents high in COD and VS, and having the potential of further biodegradation and more gas production.

Typically, municipal wastewater treatment plants combine and thicken primary sludge with WAS before digestion. The amount of volatile solids destruction falls somewhere

between the characteristics of either sludge alone. Still, more than 50% of the WAS's COD escapes treatment and remains in the effluent.

2.1.3.7 Redox Potential

Methanogenic bacteria require not only anaerobic conditions but also low redox conditions. They require an oxidation reduction potential (ORP) of less than -330 mV to convert fermented organic compounds to methane (Chen and Lin, 1993; and Wolfe, 1985). Chen and Lin (1993) incubated methanogens in a batch reactor at an initial ORP of -100 mV. Some methane production started when the ORP decreased to -300 mV, and significant production started when the ORP fell below -330 mV.

Although methanogenic bacteria require low redox conditions for activity, a few can survive under oxygen exposure (Winfrey, 1984). Cultures of *Methanobacterium* strain AZ tolerated exposure to up to 100% oxygen for four days and produced methane after reducing conditions were reestablished (Zehnder and Wuhrmann, 1977; cited in Winfrey, 1984).

2.2 Thermal Conditioning

Thermal conditioning of sludge, or heat treatment, dates back to the beginning of this century. The late Dr. Ekenberg from Sweden (from Discussion of J.H. Garner in Lumb and Barnes, 1944) invented heat treatment. Ekenberg used heat treatment to convert liquid peat into fuel priquettes. Although between 1902 and 1911 the Government of Sweden granted a large amount of money to develop the system on a commercial basis, the goal was never achieved and the process was abandoned. Ekenberg died in 1910, but his death did not put an end to his invention.

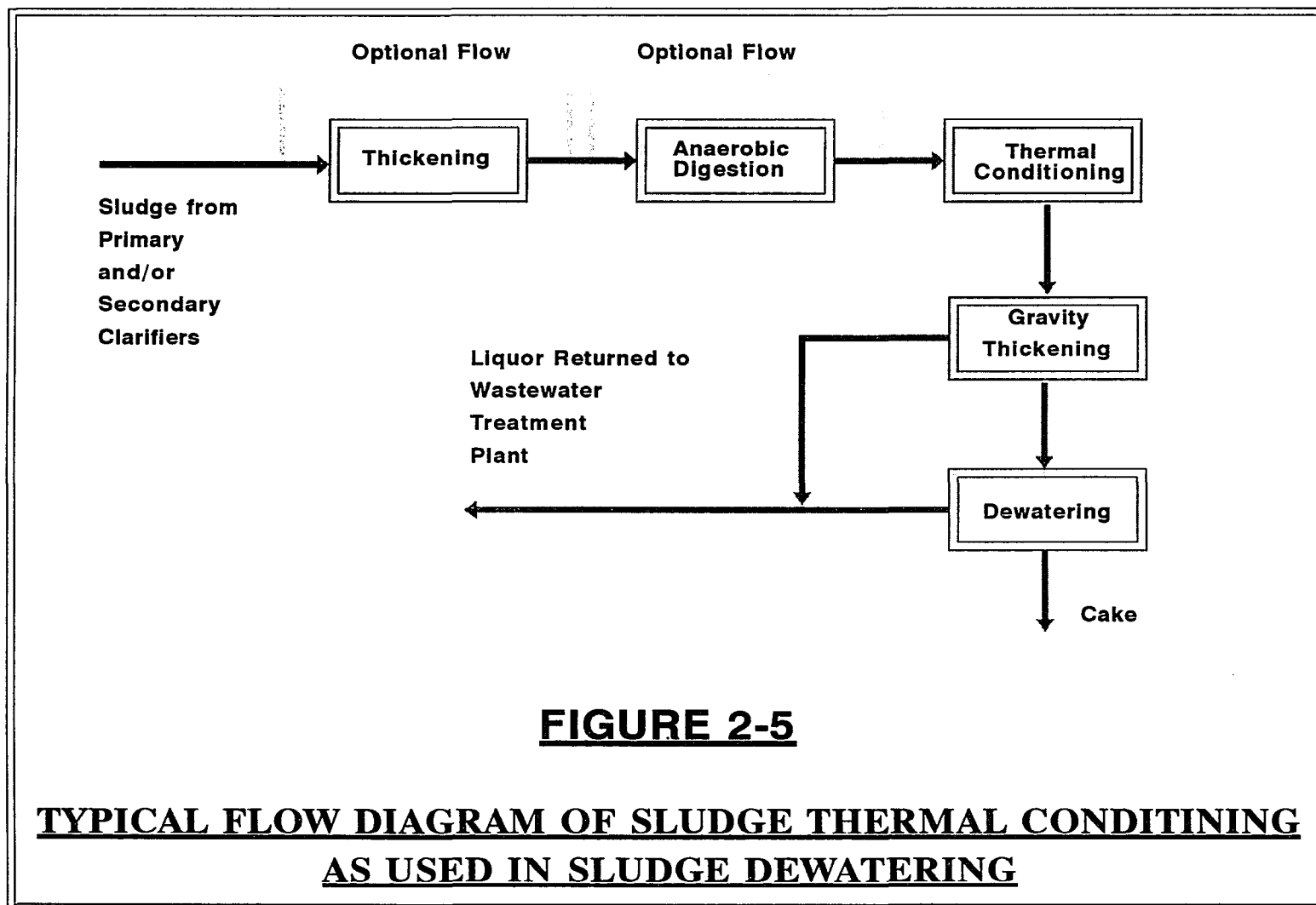
In 1911 Nils Testrup, assistant to Ekenberg, patented the heat treatment process on sludge (from Discussion of J.H. Garner in Lumb and Barnes, 1944); his process was developed to improve sludge filterability by heating the sludge at a temperature of 130°C under a pressure of 25 psi. The first heat-treatment reactor consisted of two concentric tubes where the outer tube was closed at one end and opened at the other end. The sludge entered between the two tubes and exited through the inner tube. The apparatus was placed in a furnace and the required temperatures and pressures were achieved by adjusting the sludge flowrate.

Some treatment plants adopted the Testrup method but, because they were experiencing financial problems and mechanical problems, especially with primary sludge, abandoned the process in 1914. The Halifax plant in England installed an improved version of the

Testrup heat treatment process in 1939 to treat secondary sludge. The improvement was performed by W.K. Porteous, whose technical abilities enabled him to redesign and revive the original process. Porteous' improvements included short and vertical heat exchange tubes, reaction time vessels to increase sludge residence time, and settling tanks to decant the liquid before filtration of the heat-treated sludge.

Traditionally, thermal conditioning is used to enhance the **dewatering characteristics** of sludge in a continuous flow process. This was utilized by the Testrup and Porteous methods. The process is applied either to raw or digested sludge prior to dewatering as shown on Figure 2-5. During this process, sludge is heated to a temperature range of 177°C (350°F) to 204°C (400°F) in a reactor under pressures of 250 to 400 psig for 15 to 40 minutes (USEPA, 1979). The process improves sludge dewatering and eliminates the need for chemical conditioning or polymer addition. However, the produced liquids have high BOD concentrations and impart a significant load to the plant when they are returned for treatment.

Thermal conditioning breaks down the gel-like structure of the sludge, allowing the bound water to separate from the solid particles. Since the bound water is released, sludge dewateres better. In addition, the particulate organic matter, which is composed mainly of proteins, carbohydrates and lipids, is hydrolysed into soluble organic monomers. These monomers may be readily available to microorganisms since they can now transport through the cell membrane and be metabolized within the cell cytoplasm. Therefore,



thermal conditioning may improve both biodegradability and dewaterability of the organic solids.

2.2.1 Sludge Biodegradability

2.2.1.1 Conventional Thermal Conditioning

Modifications of thermal conditioning processes of sludge include addition of air to oxidize organic compounds (wet air oxidation) and addition of chemicals such as acids or bases. The three potential thermal conditioning processes are (a) auto-hydrolysis, (b) oxidative-hydrolysis, and (c) thermochemical-hydrolysis.

(a) Auto-Hydrolysis

Auto-hydrolysis involves the thermal conditioning of sludge without the addition of air or chemicals. William K. Porteous was the first person to successfully use auto-hydrolysis as a thermal conditioning of sludge in England in the 1930s (USEPA, 1979; Lumb and Barnes, 1944). In 1969, the first auto-hydrolysis thermal conditioning facility in the United States was installed at Colorado Springs, Colorado.

Haug (1977) evaluated the biodegradability of thermally conditioned primary sludge (PS) and waste activated sludge (WAS) conditioned for 30 minutes at 177°C. His results indicated that mesophilic digestion of thermally conditioned WAS produced 70 percent more gas than unconditioned sludge. Thermally conditioned PS did not show any increase in gas production. Haug *et al.* (1978) reevaluated the biodegradability of thermally conditioned WAS at temperatures of 100, 135, 175, 200 and 225°C for 30 minutes. Biodegradation results (obtained by completely mixed reactors) indicated an increase in biodegradation from 100°C to 175°C and a decrease from 200°C to 225°C. The decrease in biodegradation at the high thermal conditioning temperatures was attributed to the production of inhibitory substances. COD solubilization increased with thermal conditioning temperatures but the solubilization at 225°C was less than the predicted value extrapolated by the lower temperature results. This effect was attributed to the formation of insoluble humic substances or to the presence of organics which could not be solubilized at any condition.

Stuckey and McCarty (1984) also evaluated the biodegradability of thermally conditioned WAS and reported an optimum thermal conditioning temperature of 175°C at a conditioning time of 60 minutes. They evaluated temperatures from 150 to 275°C at 25°C increment (all at a thermal conditioning time of 60 minutes) and used the serum bottles biodegradation test to assess biodegradability. Methane production of WAS thermally conditioned at 175°C was increased by 27% over the control. The decrease in

biodegradation at the higher than 175°C temperature was attributed to the production of toxic compounds.

In addition to WAS, Stuckey and McCarty (1984) evaluated thermal conditioning (200°C, 60 minutes) on four nitrogenous organic chemical mixtures (amino acids, RNA, DNA, and collagen). Biodegradability of all mixtures decreased with thermal conditioning at both mesophilic and thermophilic conditions, with thermophilic being the worst. Decrease of biodegradability was attributed to toxicity. Stuckey and McCarty performed the test to understand better as to why thermal conditioning increases WAS biodegradability, since WAS consists of the four nitrogenous organic chemical mixtures (within the bacterial cell). However, because of the contradictory results (higher biodegradability of WAS and lower of nitrogenous mixtures) there was no clear understanding to the process. It is possible that the results from the four nitrogenous compounds (especially the amino acids) can be used to understand the thermal conditioning effect on primary sludge (PS). For example, Haug (1977) found that thermal conditioning of PS did not improve the sludge's biodegradability, probably because amino acids degradation decreases after thermal conditioning, described by Stuckey and McCarty (1984).

Li and Noike (1992) thermally conditioned WAS from 62 to 175°C at retention times 15, 30, 60, 90 and 120 minutes. Thermal conditioning was performed in a batch reactor, where for temperatures less than 100°C conditioning was performed in a temperature-controlled water-bath; for temperatures higher than 100°C, conditioning was performed

in an autoclave. Their continuous-flow results indicated an optimum condition of 170°C and 60 minutes, where COD reached a maximum removal of 60% and gas production ranged from 223 to 235 mL/g COD, approximately twice those of the control.

Hiraoka *et al.* (1984) evaluated the effect of a low-temperature thermal conditioning process on waste activated sludge. Thermal conditioning was performed by batch reactors placed in an autoclave. Investigated temperatures were 60°C, 80°C and 100°C and holding times were more than 60 minutes at 60°C and 80°C, and 30 minutes at 100°C. As much as 30% improvement in gas production yield was obtained at 60°C and 80°C for a digester loading of 3 kg VS/m³-d. More than 50% improvement could be attained at 100°C at a loading less than 3 kg VS/m³-d.

A successful **field demonstration** of WAS autohydrolysis was performed by Haug (Haug *et al.*, 1983) at the Joint Water Pollution Control Plant in Los Angeles. WAS was thermally conditioned at 205°C and then anaerobically-digested (49°C) in a 12,000 gal single-stage well- mixed digester. No inhibition was encountered at the temperature of 205°C; inhibition was encountered at high temperatures in the laboratory studies (Haug *et al.*, 1978).

(b) Oxidative Hydrolysis

Oxidative-hydrolysis includes the Zimpro process (low-pressure system) and the Wet-Air Oxidation process (higher pressures and temperatures than the Zimpro process). During the oxidative-hydrolysis process, air is injected in the sludge stream before thermal conditioning. Air or oxygen oxidizes organic matter to CO₂ and water, thus decreasing the volatile content of the conditioned sludge. Sludge biodegradability should be decreased because of the solids oxidation during the process. Dewatering improvement, not biodegradability improvement, was the objective of sludge oxidative conditioning. In the United States, sludge conditioning received some attention in the 1960s, where the first facility with air addition was built at Levittown, Pennsylvania, in 1967 (USEPA, 1979).

Supercritical water oxidation (SCWO) is another oxidative process whose objective is not to improve biodegradability. SCWO was first used on sludge in 1982 (USEPA, 1992). It operates similarly to the WAO process where oxygen or hydrogen peroxide is injected to the sludge, but at water's supercritical conditions (over 374°C and 221 atm). COD oxidation can reach over 90% (Gloyne and Li, 1993; and Li *et al.*, 1993). SCWO is energy intensive, requires strong and oxidation-resistive reactors, and does not recover energy, such as methane gas, which other conditioning processes do. ECO Waste Technologies (1993) is installing a 5-gpm demonstration plant for a chemical manufacturing facility.

(c) Thermochemical Hydrolysis

Chemical conditioning refers to the addition of acid or base to the sludge prior to thermal conditioning.

Haug *et al.* (1978) thermally conditioned WAS at pH 12 (by adding 250 meq/L of NaOH), pH 1.2 (by adding 180 meq/L HCl) and unmodified pH (auto-hydrolysis) at a conditioning temperature of 175°C for 30 minutes. COD solubilization was much higher with chemical conditioning than without, with values of 68% (pH 12), and 52% (pH 1.2) compared to the 42.7% of the unmodified sample. Biodegradation results indicated a decrease in gas production of reactors fed with the chemically-conditioned WAS as compared to the untreated WAS (control). The inhibition was attributed to the production of inhibitory substances which the reactors were never able to acclimate to. The WAS subjected to the auto-hydrolysis of 175°C showed a 57% increase in gas production over the control.

Stuckey and McCarty (1984) evaluated the biodegradability of thermally conditioned WAS to which 300 meq/L of 15 N NaOH were added. They evaluated temperatures from 150 to 275°C increment (all at a thermal conditioning time of 60 minutes) by using the serum bottles biodegradation test. Gas production was maximum at 200°C and decreased at the higher temperatures. Maximum gas production improvement was 24% (at the 200°C) over the control, compared to the auto-hydrolysis improvement of 27% at a

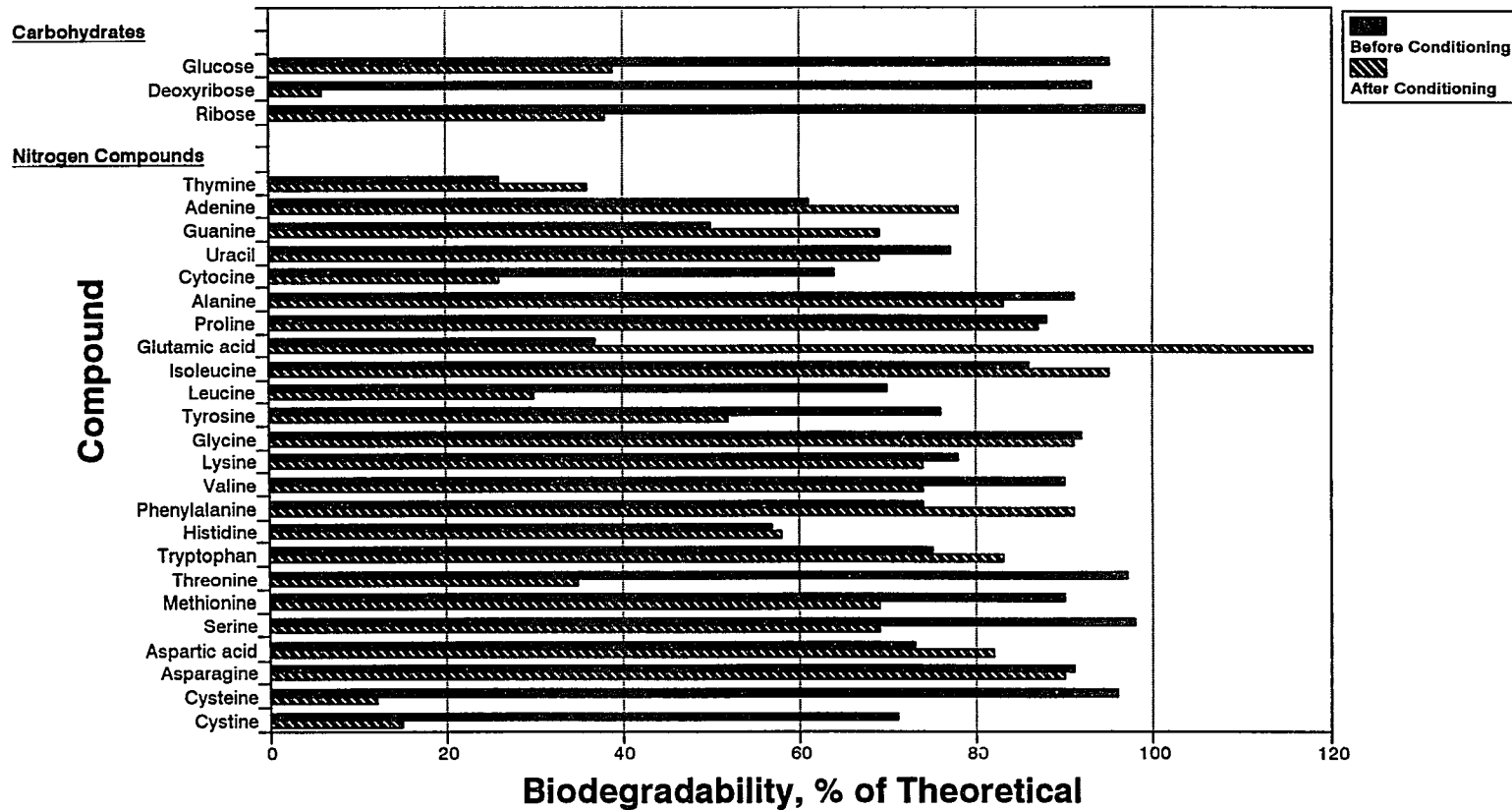
thermally conditioned temperature of 175°C. Decreasing gas production at temperatures higher than 200°C was attributed to toxic or refractory compounds formation.

Besides WAS, Stuckey and McCarty (1984) evaluated thermochemical conditioning (200°C with 300 meq/L NaOH for 60 minutes) on individual nitrogenous compounds (amino acids and proteins) and individual carbohydrates (ribose, deoxyribose, and glucose). These compounds are major constituents of WAS (within the bacterial cell). Thermochemical conditioning, similar to thermal conditioning, decreased the biodegradability of most nitrogenous compounds and all carbohydrates. Percent biodegradabilities without and with thermochemical conditioning are presented on Figure 2-6. The sulfur containing amino acids were amongst the most strongly affected by conditioning. Substitution of sulfur with oxygen led to the considerably less reduction in bioconvertibility after pretreatment. The biodegradability decrease of ribose was also attributed to oxygen substitution on ribose's ring.

Even though Stuckey and McCarty used the aforementioned individual compound to understand the thermochemical conditioning effect on WAS, their results can be also used to understand conditioning on primary sludge (PS). The individual compounds can be found in the PS matrix whereas, for WAS, the cells must be lysed in order for the compounds to be released.

FIGURE 2-6

THERMOCHEMICAL CONDITIONING EFFECT ON N-Compounds & Carbohydrate Biodegrad'n



NITRO-HY

[Stuckey and McCarty, 1984]

2.2.1.2 Rapid Thermal Conditioning

The aforementioned thermal conditioning processes operate at elongated contact times in the order of 30 minutes to 60 minutes. A short residence time reactor, Rapid Thermal Conditioning Reactor (RTCR), was used by McParland *et al.* (1982) to hydrolyze corn stover into glucose. A steam-injection plug flow reactor was operated from six to 21 seconds, hence the term rapid thermal conditioning. Evaluated temperatures ranged from 160 to 245°C. An optimum condition was obtained at 9 seconds in the range of 230 to 240°C, where glucose yield reached 55 to 60%. Provisions were made to add sulfuric acid in the feed slurry to enhance the hydrolysis.

Garzon-Lopez (1987) utilized the aforementioned RTCR to condition partially digested sludge (PDS) and increase methane production by improving the PDS's biodegradation. Thermal conditioning was performed under auto-hydrolysis, acid hydrolysis and alkaline hydrolysis conditions. Retention times varied from one to 30 seconds and temperatures varied from 140 to 260°C. The results indicated an increase in biodegradation at both auto-hydrolysis and mild alkaline hydrolysis at a retention time of 10 seconds and an optimum temperature of 200°C. Retention times greater than 10 seconds did not exhibit significant biodegradation over the 10 seconds. Acid hydrolysis yielded low biodegradability.

2.2.2 Other Substrates

Lignocellulose and other cellulose-related compounds (corn stover, newsprint) are among substrates tested under thermochemical conditions. As it was mentioned before, Grethlein used rapid thermal conditioning at acidic conditions to hydrolyze corn stover into glucose. Kwarteng (1983) used the same plug flow reactor that Grethlein used to hydrolyze hardwood, also at acidic conditions.

Thermal autohydrolysis increased lignocellulose's biodegradability and achieved maximum COD solubilization at 225°C (Owen, 1979). Heat-treatment was done in a 2-liter batch reactor where temperatures ranged from 125°C to 250°C. Reaction times ranged from 30 minutes (at 125°C) to 60 minutes (at 250°C). Lignocellulose biodegradability did not improve with oxygen addition. Owen (1979) also evaluated thermal autohydrolysis on agriculture residues, resulting to low biodegradability. Others evaluating lignocellulose thermochemical conditioning were Baugh and McCarty (1988), and Baugh *et al.* (1988). They obtained high lignocellulose-conversion to simple sugars at acidic conditions and temperatures between 170°C and 230°C.²²

2.3 Chemical Conditioning

Chemical conditioning refers to the addition of organic or inorganic chemicals to sludges to improve their characteristics. Past studies of chemical conditioning were primarily targeted for improving dewaterability. Limited literature was found on improving sludge's biodegradability by chemical conditioning.

Chemical conditioning of sludge is explicitly used to improve dewaterability (Metcalf & Eddy, 1991). Rajan *et al.* (1989) and Ray *et al.* (1990) were the first ones to evaluate chemical conditioning on WAS biodegradability. Chemical conditioning was done at alkaline conditions with NaOH and $\text{Ca}(\text{OH})_2$ at 20°C and 38°C. Even though the 38°C temperature is higher than normal room temperature, still the process cannot be considered thermochemical conditioning since 38°C is on the mesophilic range of anaerobic digestion. Conditioning was performed from 10 meq/L to 60 meq/L of each chemical separately, and conditioning time was 12 hours.

COD solubilization rate was highest within 30 minutes of conditioning and was highest at 60 meq/L of NaOH and 38°C. Solubilization improvement was not very significant from 20°C to 35°C. As much as 46% of COD was solubilized during the study. NaOH conditioning improved the removal of VS by 31%, COD by 34%, TOC by 41%, and overall gas production by 38%. Improvements for $\text{Ca}(\text{OH})_2$ were 16%, 20%, 39%, and 22%, respectively.

An innovative process that was used to disrupt microbial cells and release intact their cytoplasm is by pressurized carbon dioxide (Lin *et al.*, 1992). Although the cell disruption is a physical than a chemical phenomenon, it is mentioned in this section because carbon dioxide, under high pressures, can decrease the media pH resulting to acidic conditioning. Lin *et al.* (1992) performed experiments under various temperatures and pressures. At high pressures, carbon dioxide enters the cell membrane. When the pressure is suddenly released, the carbon dioxide ruptures the cell membrane. Under optimum conditions, over 80% of the cells were ruptured within one-hour contact time. The released cytoplasm could also make the media easy to biodegrade. Unfortunately, biodegradability was not evaluated by Lin *et al.* (1992) since this was not their objective.

2.4 Heavy Metals Solubilization

Heavy metals are common components of sewage sludges because they are removed from dilute wastewaters at a high degree of efficiency. Sources contributing metals to municipal wastewater treatment plants are numerous and highly varied. Industries such as electroplating, steel production, petroleum refining, chemicals manufacturing, non-ferrous metals works and fertilizer production are major contributors (Hayes *et al.*, 1979). However, sewage from essentially domestic wastewater sources, such as runoff, and leaching of lead from drinking water-supply pipes, can also contain substantial amounts of heavy metals. Therefore, metals will still be found in sewage sludges even if industrial pretreatment programs are implemented to eliminate or minimize the metal discharge to municipal treatment plants. For this reason, it is prudent to assume that heavy metals in sludge may continue to be a problem, and metals removal technologies should be considered.

In municipal wastewater treatment plants, heavy metals can be either adsorbed to organic particles and settle out during primary treatment or entrapped in the biological floc of the activated sludge process. Combined efficiencies of heavy metal removal from primary and secondary treatment range from 60% to 90%. These removals result in a sludge with a heavy metal concentration of 10 to 1,000 times greater than the influent concentration (Mytelka *et al.*, 1973; Neufelt and Hermann, 1975; and Jewell and Kabrick, 1978). A

general classification of possible metal species found in anaerobically digested sludges is presented in Table 2-9 (Gould and Genetelli, 1975).

The distribution of a particular heavy metal among various chemical forms in treated sludges largely depends on the physical and chemical properties of the environment established by the sludge treatment process. Upon introduction into the biological treatment system, species of heavy metals would be expected to make adjustments toward a new equilibrium state as defined by certain chemical environmental parameters such as pH, ORP, presence of complexing agents, and concentration of ligands. Adsorption to solid phases and to biomass are also important mechanisms.

Heavy metals in anaerobically digested sludge are usually associated with the suspended solids. Gould and Genetelli (1975) reported that more than 90% of heavy metals concentration in sludge were found in the particulate fraction (greater than 100 micron effective diameter). Therefore, in order for the metals to be removed from sludge they need to be separated from the solids.

Acid extraction has been used by various researchers to solubilize metals. Scott and Horlings (1975) used sulfuric acid to acidify anaerobically digested sludge to pH 1.5 for 15 minutes. The results showed that iron, chromium, copper, and zinc were extracted by 100%, 54%, 26%, and 73%, respectively. Martinkat and Yapijakis (1991) showed that the solubilization of copper, chromium, and lead (from anaerobically-digested sludge)

TABLE 2-9

SPECIES OF HEAVY METALS IN SEWAGE SLUDGE

I.	SOLUBLE
	A. Ionic
	B. Organic Complexes
	C. Inorganic Complexes
II.	COPRECIPITATES IN METAL OXIDES
III.	PRECIPITATES
IV.	ADSORBATES
	A. Physical
	B. Chemisorption
	C. Clay Lattice
V.	ORGANOMETALLIC COMPLEXES
	A. Simple Complexes
	B. Chelation
VI.	BIOLOGICAL RESIDUES

[Gould and Genetelli, 1975]

exceeded 40%, 40%, and 50%, respectively, at pH 1.5 and acidification times between 10 hours and 17 hours.

Wozniak and Huang evaluated metals solubilization from waste activated sludge at pH values 1.5, 2.0 and 3.0 (by adding HCl), and at solids concentration ranging from 0.5% to 2.5%. They found maximum metals solubilization at low pH and low solids concentration. Some metals, such as Zn and Ni were readily solubilized. Metals, such as Cu and Cd, required long pH-contact times to solubilize. Therefore, metals solubilization depends on pH conditions, sludge solids concentration, metal type, and acidification contact time.

McNulty *et al.* (1977) used hot acid-treatment to solubilize metals from thickened activated sludge. Metal solubilization took place at 95°C, with pH from 2.0 to 3.5, and contact times between 10 minutes and 60 minutes. Zinc and nickel solubilized by 91% and 36%, respectively. Chromium, cadmium, and lead, however, showed low solubilization. Alsop and Conway (1982) evaluated metals-removal from WAS under a new-type thermal conditioning process using a combination of base, heat, and acid in the given order. Sludge, enriched with Zn and Cd, passed through a reactor where the pH was increased to 10.5. The alkaline slurry was passed through a thermal conditioning reactor set at 70°C for a one-minute contact time. Finally, the slurry was acidified to pH3.5. Metals removal, based on cake-metals concentration, reached 49% for Zn and 73% for Cd.

An extensive literature review showed that only the solubilization of metals was evaluated (except Alsop and Conway (1982) who tested cake-metals concentrations but not solids solubilization). Metal concentrations in the cake, once the sludge was dewatered, was not considered. It was implied that when metals were solubilized, metal concentrations in the resulting cake should have decreased. However, this expectation may not be true for all metals since acidic conditions can cause the solubilization of solids; if the solids solubilization is greater than metals solubilization, then metals concentration in the sludge cake may actually increase in concentration.

3. RAPID THERMAL CONDITIONING PROCESS

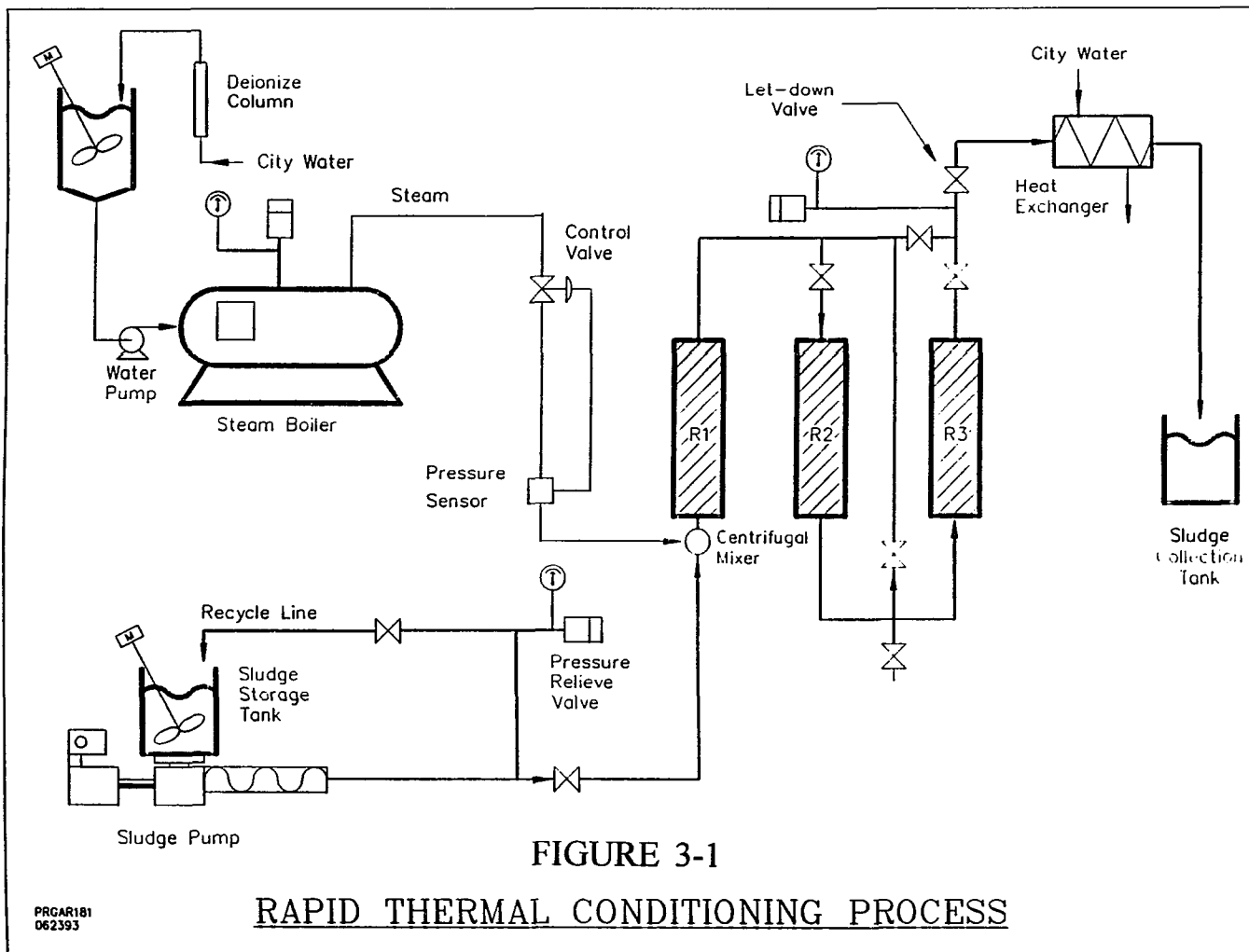
3.1 Rapid Thermal Conditioning System

The rapid thermal conditioning reactor (RTCR) used in this study is equivalent to that previously used by Grethlein (McParland *et al.*, 1982), Garzon-Lopez (1987) and Dynatech (1988). The reactor could handle sludge with up to 8 percent solids, pressures up to 30 atm, retention times up to 180 seconds, and temperatures up to 240°C. Maximum operating temperatures were kept at 220-225°C. Reactor construction, shakedown runs, and operation was done by Jianhong Zheng (Doctoral Dissertation pending), Chemical Engineering Department, CCNY.

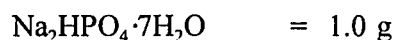
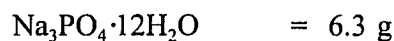
The RTC process flow-diagram is shown in Figure 3-1. Sludge, from a 200 L storage tank equipped with an agitator, was pumped to the reactor via a 12-stage, progressive cavity pump capable of reaching 900 psia. The pump is a Moyno type, model number 12P2SSQAAA. Adjustment of pH was done in the 200 L storage tank.

3.2 Rapid Thermal Conditioning Steam Production

Treated city-water was used as feed-water for the high pressure boiler. City water was first passed through an ion exchange column to remove dissolved solids that would be harmful to the boiler. The deionized water was then chemically treated to remove the



dissolved oxygen and increase the pH to protect the boiler against corrosion. The following conditioning chemicals were added per 100 liters feed-water:



Lattner Boiler Co., Cedar Rapids Iowa, was the manufacturer of the 3.6 HP electric boiler. The boiler could operate at a maximum pressure of 900 psia and was equipped with a blow-down separator. A steam pressure control system was designed for a source pressure of 900 psia, a temperature of 288°C, and steam flow rates of 20 to 100 lbs/hr. The steam control system consisted of an electronic gauge pressure transmitter with 10 ft of silicone fluid-filled capillary tube between the seal and transmitter, an electronic controller, a current to pneumatic converter, and a pneumatic control valve. Conditioned sample cooling was provided by a pressure let-down valve and by a plate heat-exchanger with a heat transfer area of 8.96 ft², manufactured by Alfa-Laval Inc. City water was used as the cooling media for the heat-exchanger.

3.3 Rapid Thermal Conditioning Reactor

RTC of sludge took place in three identical reactors R1, R2 and R3, constructed of 31-inch length 304 SS tubing with a 0.12-inch wall thickness and 1-inch internal diameter. The three reactors could be operated at HRTs from 10 to 180 seconds by adjusting the

sludge feed flowrate from 1.5 to 0.5 L/min and by using one, two, or three reactors in series. As shown on Figure 3-1, two or three reactors could be operated by just opening and closing control valves.

Steam from the high pressure boiler was combined with the sludge in a centrifugal mixer at the base of R1, providing rapid heating up to the reaction temperatures. Temperatures were monitored via thermocouples that were placed at each end of the reactors. Reaction was terminated when the sludge was forced through a pressure let-down valve which also allowed the steam-sludge mixture to cool down. The mixture was cooled down further to room temperatures by the heat exchanger and was then collected for chemical and biological testing.

The major equipment comprising the rapid thermal conditioning process are summarized in Table 3-1.

TABLE 3-1

MAJOR COMPONENTS OF THE RAPID THERMAL CONDITIONING PROCESS

Equipment (Quantity)	Manufacturer	Model	Description
Boiler (1)	Lattner	36AF	Pmax = 900 psi W = 1.5 hp
Sludge Pump (1)	Moyno	12P2SSQAAA	Pmax = 900 psi Flow = 0-0.6 GPM = 0-2.3 L/min
Water Pump (1)	CAT	SF20E	Pmax = 900 psi
Air Compressor (1)	Relloc-American	---	Pmax = 100 psi W = 0.75 hp
Steam Control Valve (1)	Foxboro	V1SD1S3HOOV	Body Size=1/2 in. Air Supply =20 psi
Controller (1)	Foxboro	760CNA-AT	Self-contained; Single Loop; and Microprocessor Based
Converter (1)	Foxboro	E69F	Input=4-20 mA; Output=3-27 psi
Transmitter (1)	Foxboro	841GM-D11	Input=1-1000 psi; Output=2-20 mA
Thermocouple/ Thermometer (6)	Omega and Cole-Parmer	Type k	T=250°C
Heat-exchanger	Alfa-Laval Inc.	---	Plate type; 8.96 ft ² area
Storage Tanks (2)	---	---	V=200 Liters

Notes:

1. "----" Not available

4. BENCH-SCALE APPARATUS

4.1 Batch Reactors

4.1.1 Introduction

Batch biodegradability was assessed using two separate procedures, namely the **Biochemical Methane Potential** test (BMP), utilized by Owen *et al.* (1979), and toxicity by the **Anaerobic Toxicity Assay** test (ATA), utilized by Stuckey *et al.* (1980). BMP is the anaerobic counterpart of the aerobic biochemical oxygen demand test (BOD). The assay is conducted in septum sealed serum bottles incubated at 35°C (mesophilic) or 50°C (thermophilic) for a total of 60 days. The apparent long incubation time is needed to observe potential acclimation trends. Gas production is measured daily during the first days and then at prolonged intervals thereafter. Cumulative gas production is then plotted.

The ATA is designed to indicate the presence of **toxicity** to methanogens. Thermally-conditioned PDS was incubated with seed duplicate samples, where non-limiting and non-inhibiting concentrations of acetate were added in one of the samples. Since substrate was non-limiting, any toxicity to the methanogens would be manifested by a reduction of the gas production rate. Potential acclimation characteristics of the methanogens to the toxicity would also be reflected in the gas production pattern, monitored over a prolonged incubation period.

Because of the large number of samples required, the serum bottle tests were used first in the initial screening of conditioning alternatives. The selected alternative was then tested in continuous flow studies. The selected alternative was the one that exhibited the greatest gas production.

4.1.2 Sample Preparation

Batch biodegradation of PDS was evaluated using anaerobic 160-mL serum bottles and measuring total gas production with incubation time. The 160-mL serum bottles were cleaned with alconox detergent, rinsed with distilled water and oven-dried at 105°C for periods longer than 12 hours. The cleaned bottles were sealed with butyl rubber stoppers and stored for future usage.

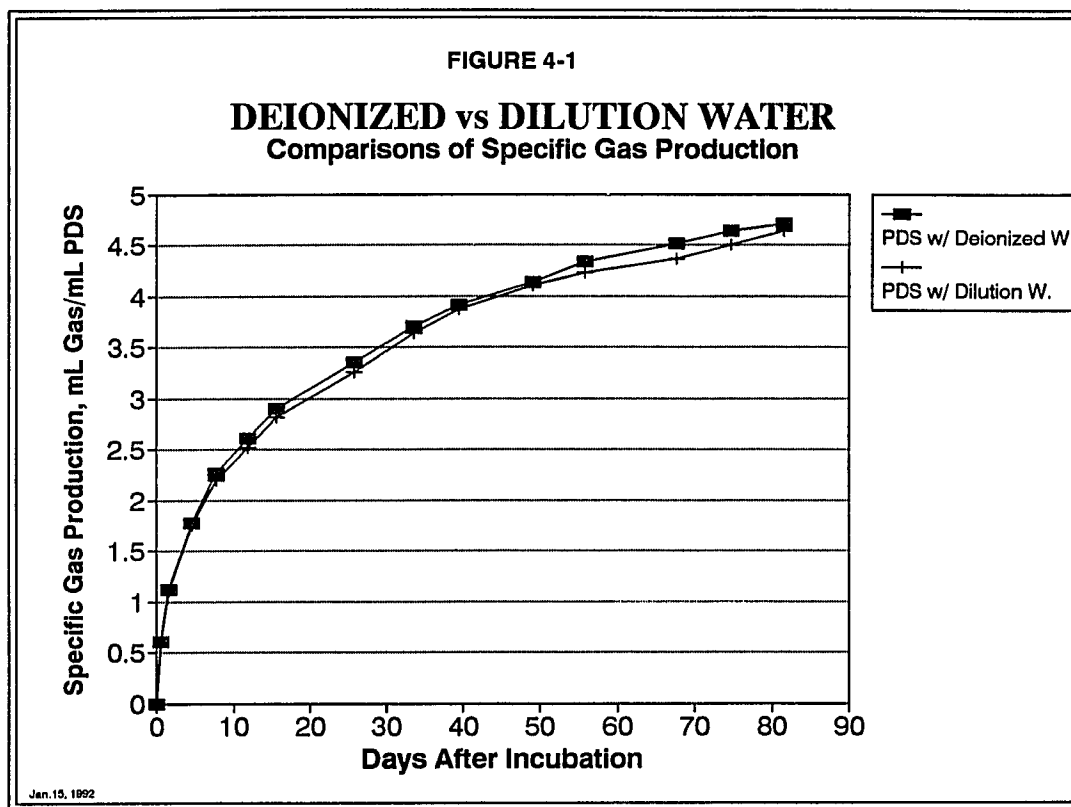
The incubated sample volume consisted of three components namely, **seed**, **feed**, and **dilution water**. Sieved PDS was used as seed for all biodegradation tests. A 50-mL seed was used for all samples.

Dilution water was added to compensate for the various steam dilutions caused by the need for different amounts of steam to achieve the targeted RTC operational temperatures. Since the steam was deionized water, the dilution water was also deionized water. The inherent dilution associated with different operating temperatures was accounted for in all tests. Stuckey *et al.* (1980) utilized a buffered dilution water for his anaerobic studies by adding 5.7 g/L NaHCO₃ and 0.37 g/L FeCl₂ because his samples did not contain enough alkalinity. However, since the PDS contains enough nutrients and has enough

buffering capacity, the dilution water was deionized water. To confirm the validity of this approach, separate seed PDS samples were diluted with deionized water and buffered dilution water and then incubated. Figure 4-1 shows no difference between the two types of dilution water. Therefore, deionized water was used as the dilution water in this study. A total volume of 100 mL sample was kept in each serum bottle. The difference between 100 mL and seed and feed volume was the dilution water added.

The feed was either sieved PDS (control sample) or thermally-conditioned PDS. Preliminary biodegradation tests were done at various seed:feed ratios which indicated that all subsequent tests should be done at a seed:feed ratio of 50:15. The preliminary tests showed that high seed:feed ratios resulted to erratic gas production rates; a ratio 50:15 showed reproducible results. In addition, the lower seed:feed ratio did not indicate any toxicity effect even at the high RTC temperature of 220°C, evaluated by the ATA test and by the lack of a lag-phase in the gas production curve. Because thermally-conditioned PDS was diluted with steam and since feed volume refers to the volume of PDS before dilution, the actual volume added to the serum bottle was adjusted by the respective dilution factor.

The **seed viability** was always confirmed by adding **acetic acid** (HAc) in seeded serum bottles. The additional gas production was compared to the acid's theoretical gas production. An HAc gas production recovery of greater than 90% was an indication of good seed viability. HAc was used for the evaluation of the seed viability because it is the most dominant intermediate volatile acid formed during the fermentation of proteins,



carbohydrates and fats. About 70 percent of the methane produced in anaerobic digestion results from the HAc degradation (Jeris and McCarty, 1965).

During serum bottles preparation, the seed was temporarily stored in a bottle equipped with an automatic dispenser; a magnetic stirrer kept the contents well mixed. Feed, dilution water and HAc were added by syringes. It was found that this technique of supplying seed by automatic dispensing and the rest of samples by syringes was reliable and fast. As many as 50 serum bottles could be prepared in less than one hour.

The following steps were used to prepare the serum bottles for incubation:

- 1 : Add dilution water
- 2 : Add feed
- 3 : Add seed
- 4 : Mix, purge with Nitrogen gas for 4-5 minutes, and seal with a butyl rubber stopper and a crimped metal seal
- 5 : Incubate at 35 °C
- 6 : Relieve pressure of all serum bottles after one hour of incubation; re-incubate and thereafter record gas volume produced
- 7 : Add HAc after step 6 to selected number of serum bottles

All serum bottle tests were done in duplicate.

4.1.3 Gas Production Evaluation

Gas production was measured manometrically by the apparatus shown on Figure 4-2. Gas production data was imputed into the computer for the various calculations. Calculations included the following:

1) Accumulated Gas Production (AGP), mL gas: The accumulated gas production (AGP) is the continuous summation of the gas measured at time.

2) Specific Gas Production (SGP), mL gas/g TCOD applied: Specific Gas Production (SGP) is the AGP divided by the TCOD in each serum bottle. For seed only:

$$SGP_s = \frac{AGP_s}{S_s} \quad (4-1)$$

where "S" is substrate TCOD and subscript "s" is seed. For thermally-conditioned sludge (feed):

$$SGP_f = \frac{AGP_{s+f} - AGP_s}{S_f} \quad (4-2)$$

where subscript "f" is feed.

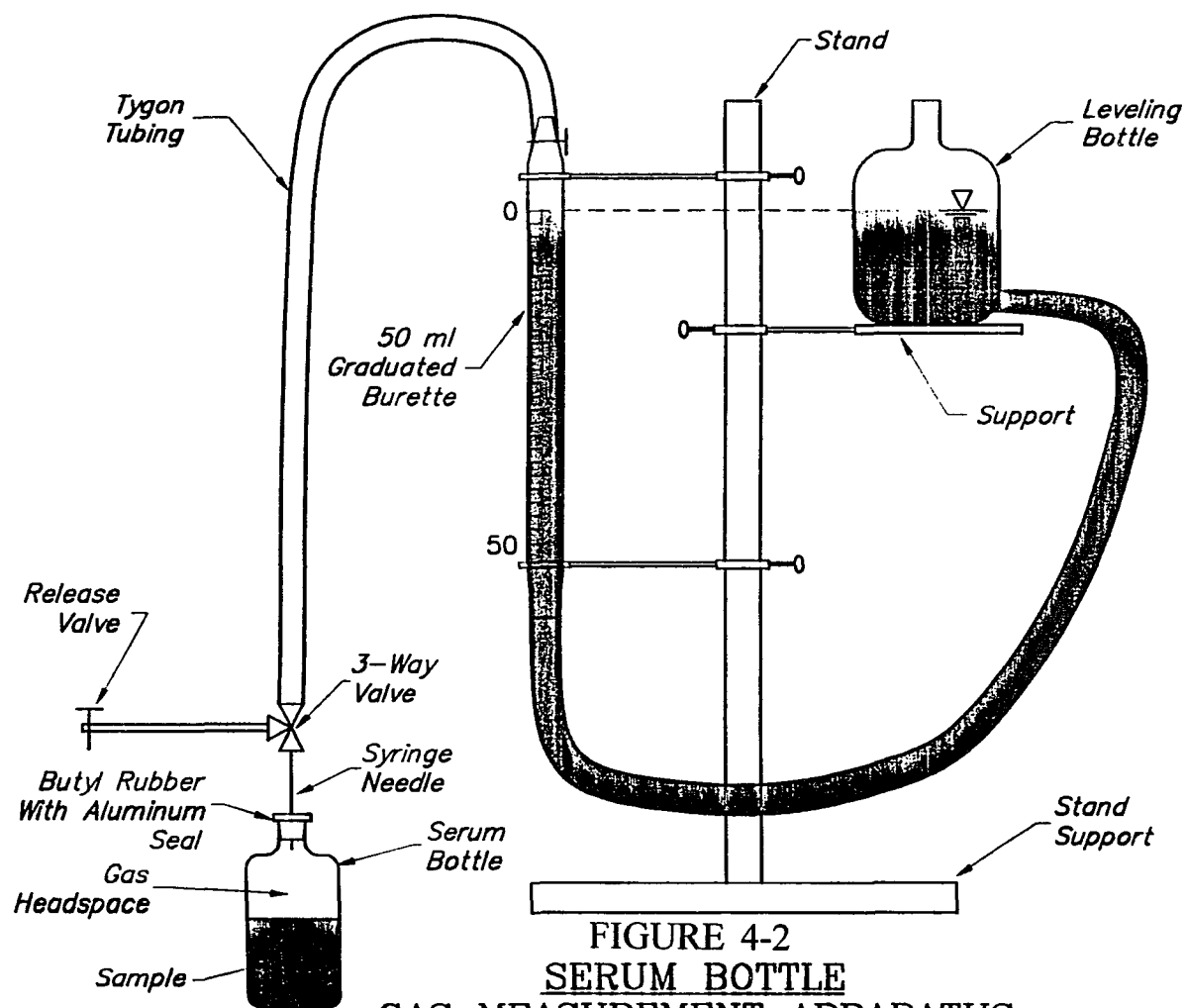


FIGURE 4-2
SERUM BOTTLE
GAS MEASUREMENT APPARATUS

PRGARI84
070893

3) Gas Production Improvement (GPI), % of control:

$$GPI = \frac{(SGP_f - SGP_c) \times 100}{SGP_c} \quad (4-3)$$

where subscript "c" is control. For most of the tests, "control" and "seed" are the same samples.

Because the results demonstrated that gas production improvement (GPI) varied with incubation time, the GPI at one incubation time could not be used for comparison purposes. The BMP test uses a 60-day comparison time. From this study's results, GPI was maximum at the beginning of the incubation period (usually within one day). The GPI then decreased exponentially to an asymptotic value. For this reason, the following incubation times were used to compare GPI: initial incubation; 15-day incubation, typical hydraulic retention time of digesters (Metcalf and Eddy, 1991); 60-day incubation, BMP test; and infinite time for the ultimate biodegradability improvement.

For illustration purposes, Figures 4-3, 4-4 and 4-5, are theoretical graphical representations of the aforementioned parameters, namely AGP, SGP and GPI respectively. Figure 4-3 was generated by assuming that the accumulated gas production curve resembles the conventional, first order biochemical oxygen demand (BOD) curve.

$$SGP = G (1 - e^{-kt}) \quad (4-4)$$

where,

SGP = specific gas production, mL gas/g TCOD applied

FIGURE 4-3
ACCUMULATED GAS PRODUCTION (AGP)
Theoretical Calculations

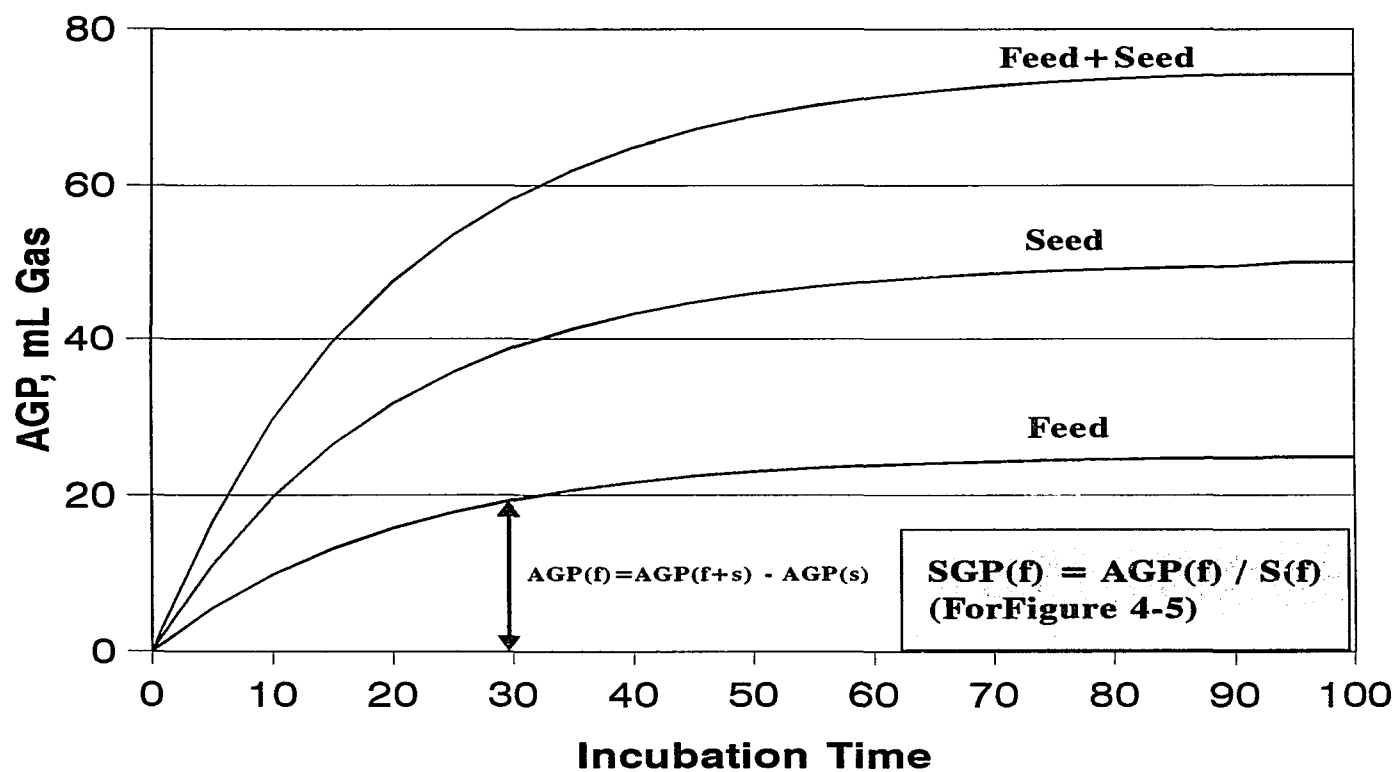


FIGURE 4-4

SPECIFIC GAS PRODUCTION (SGP) Theoretical Calculations

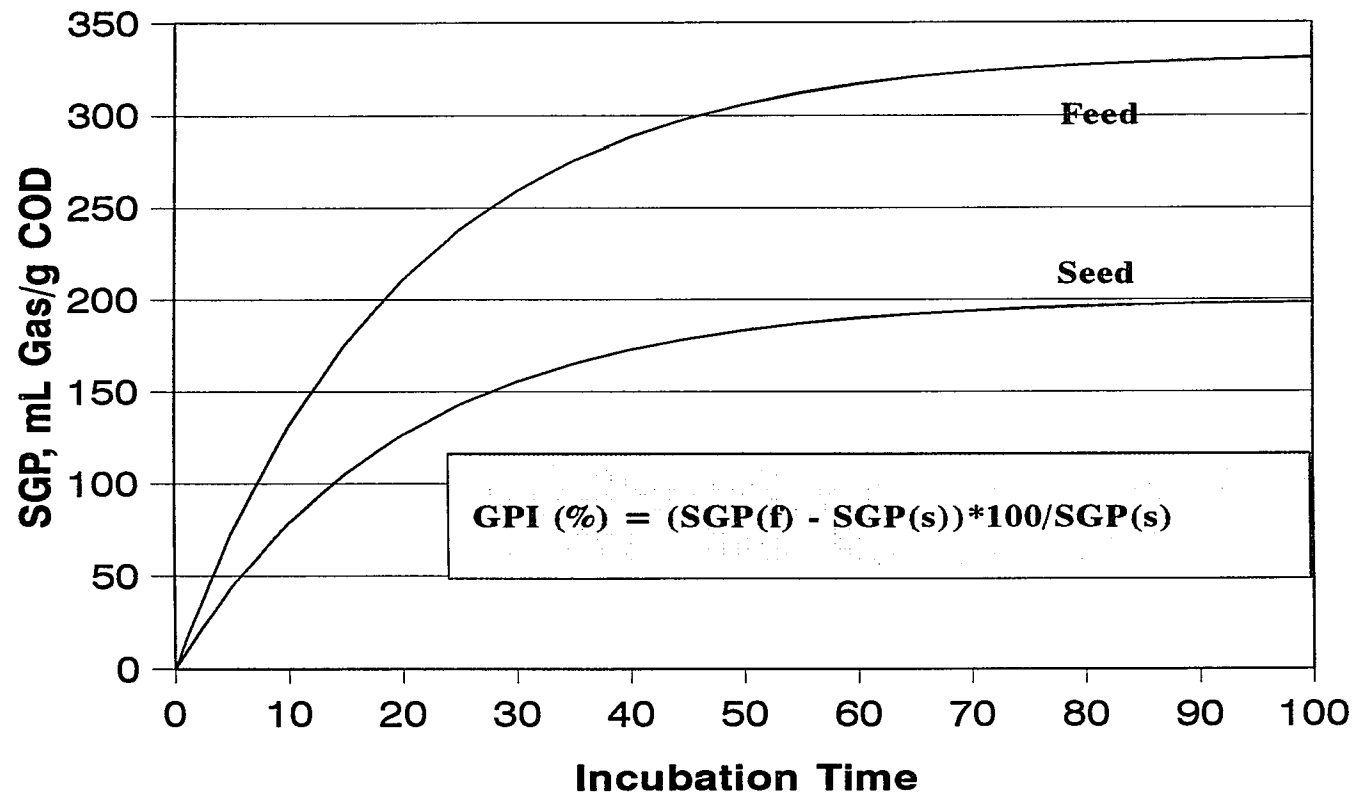
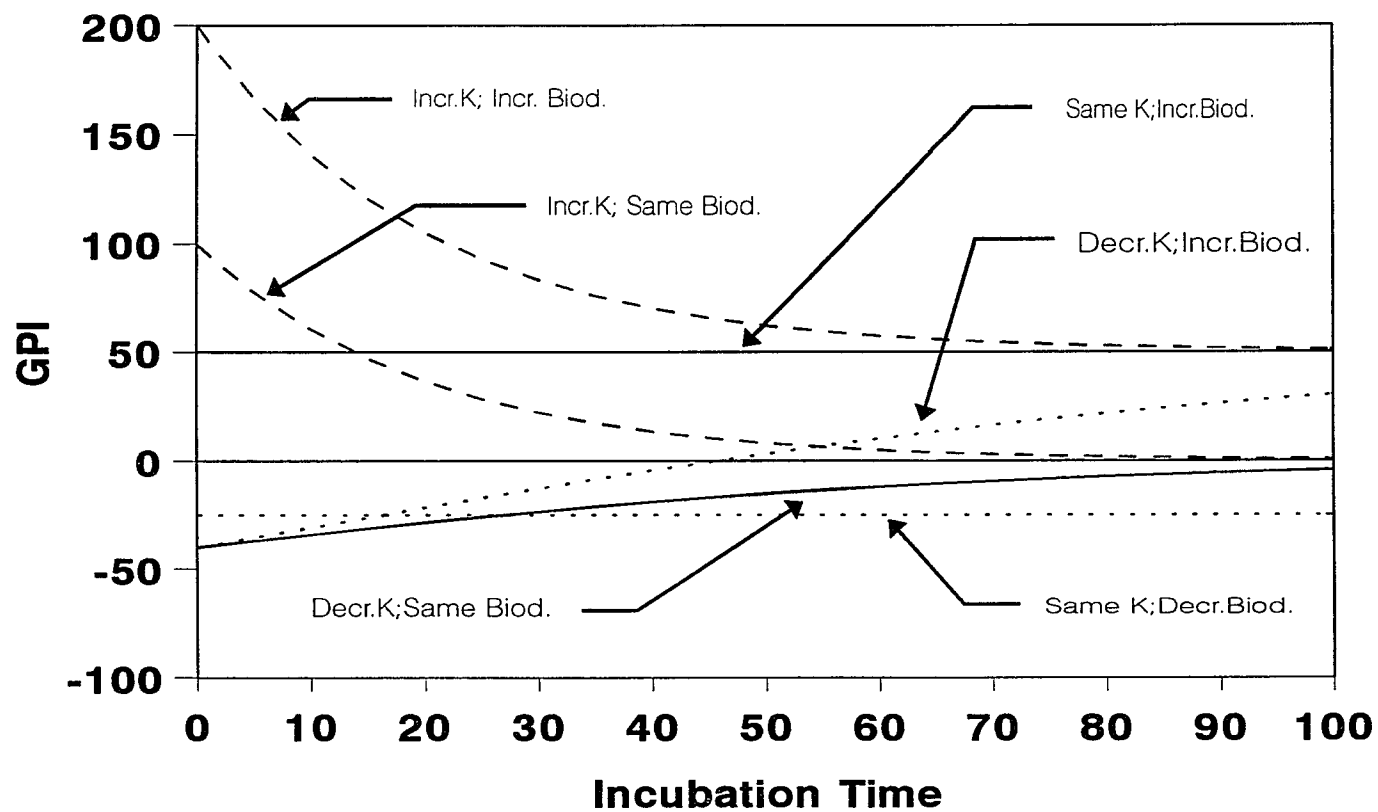


FIGURE 4-5
GAS PRODUCTION IMPROVEMENT (GPI)
Theoretical Calculations



G	=	ultimate SGP of slow term, mL gas/g TCOD applied
k	=	first order reaction rate, 1/d
t	=	incubation time from start-up, d

A further discussion of the actual equation used is presented in Section 6, "Results and Discussion". Figure 4-4 was generated from Figure 4-3, and Figure 4-5 from Figure 4-4 assuming various kinetic rates "k" and various ultimate biodegradations. As Figure 4-5 shows, if there is an increase in the kinetics but no increase in the ultimate biodegradation, GPI will be maximum at the very beginning of incubation period and then will decrease exponentially to zero. If there is both an increase in kinetics and an increase in the ultimate biodegradation, then the curve will shift up by the amount of the biodegradation increase, the kind of curve observed by the experiments.

4.2 Arthur Respirometer

4.2.1 Description

Batch biodegradability was also assessed using a new apparatus made by Tech-Line Instruments, the **Phase III Arthur Respirometer**. The Phase III Arthur Respirometer is a dual-unit system located in a constant-temperature water bath. Figure 4-6 shows the respirometer's configuration, which consists of two reactors operated in parallel and with an operating volume of two liters (each). Reactors are mixed by gas recirculation using a build-in gas circulating pump. The respirometer is typically used for aerobic studies but it was modified by Tech-Line to be used for anaerobic studies.

The main advantage of this system was that the gas produced is monitored continuously by a built-in oil type manometer and the data plotted on a two-channel chart recorder. The chart recorder was calibrated so that the results were given as mL of gas produced. Calibration was performed by injecting a known volume of inert gas (i.e. nitrogen gas) into the respirometer. The deflection on the chart was adjusted so that it represented the volume of gas injected. Sludges with different characteristics can be compared concurrently on the same chart.

The disadvantage of the unit was that because of its plastic hardware it could not be operated at temperatures greater than 35°C. Therefore, only mesophilic conditions could be evaluated with the Arthur Respirometer. Initially, the respirometer was located inside a water bath and the operating temperature was reached by a recirculating immersed-

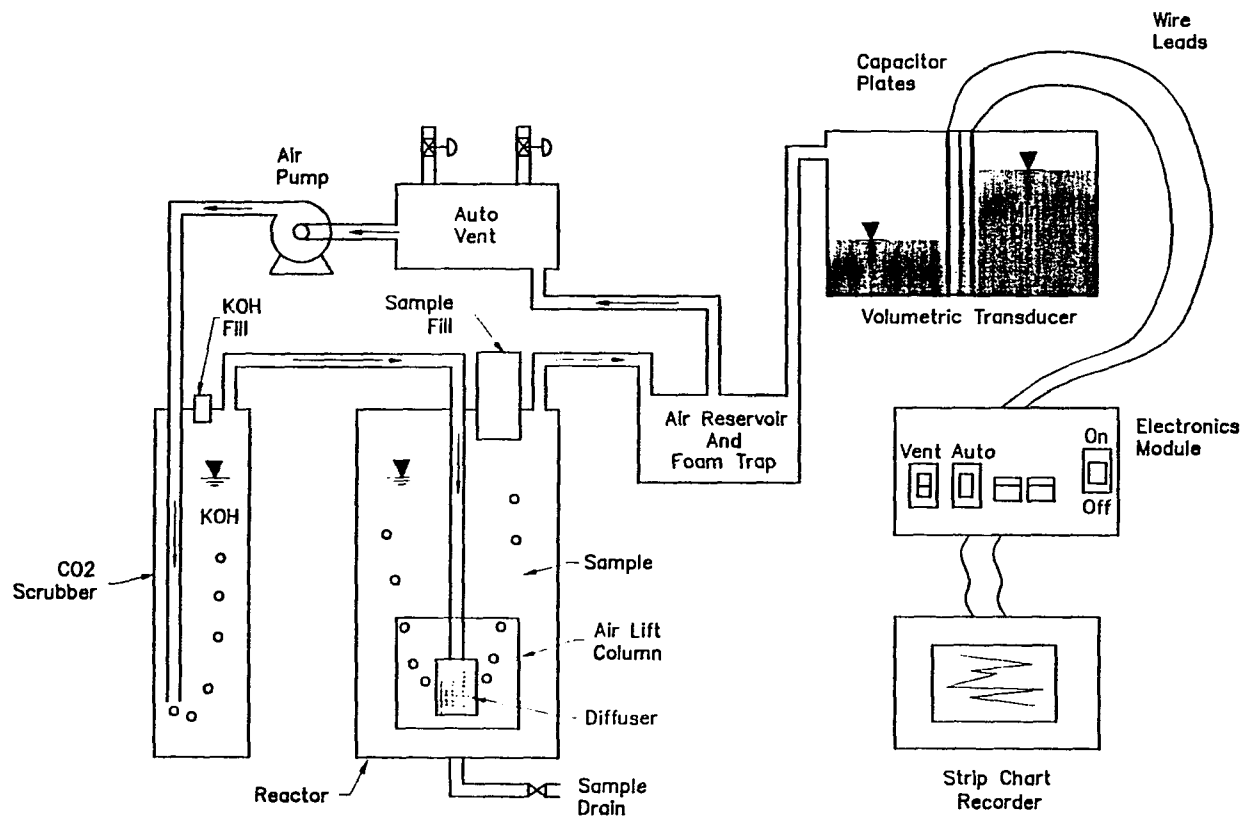


FIGURE 4-6

SCHEMATIC DIAGRAM OF
ARTHUR RESPIROMETER

PRGAR180
052593

heater. To eliminate scaling and slime formation on the respirometer's hardware and tubing, distilled water was used in the water bath. The first experiments were performed using the water bath. Subsequent experiments were carried out in a walk-in constant temperature environmental chamber.

Gas production simulates substrate removal and biological growth in a batch reactor. Therefore, when soluble substrate is plentiful the microorganisms will grow at their maximum rate, which occurs during the logarithmic (log) growth phase. As in the log growth phase, a gas log production phase should be observed. The slope of the curve at this phase would be the maximum gas production rate that could be achieved by the system. This maximum gas production rate would be correlated with the total gas production and, if the correlation is acceptable, this rate could be used to evaluate future anaerobic studies. This would shorten the running time of the tests.

4.2.2 Operation

During preliminary batch-experiments, it was found that foaming in the reactor (due to gas recirculation) and condensation in the tubes (due to high operating temperatures) were taking place preventing long-term operations. Therefore, the respirometer was not used as a batch reactor but was used with the continuous flow studies as a gas-monitoring apparatus. Gas lines from the continuous flow stirred tank reactor (CFSTR) and the anaerobic filter (AF) were connected to the KOH chamber (without any KOH solution inside the chamber) of the respirometer. The KOH chamber is connected to the built-in oil manometer of the respirometer, where gas production was recorded continuously.

Therefore, by slightly modifying the respirometer, it was possible to efficiently measure both the gas production rate and the accumulated gas production from the two continuous flow reactors. Any upset conditions would be seen immediately on the chart recorder.

4.3 Continuous Flow Stirred Tank Reactor (CFSTR)

4.3.1 Reactor Description

Sludge in the New York City Water Pollution Control Plants is stabilized in two-stage digesters operating in the mesophilic range in all plants except the Rockaway Beach plant. Stabilization of sludge takes place in the primary high-rate digester. For this reason, high-rate digestion has been selected to assess the continuous flow suspended growth treatment of the thermally-conditioned PDS.

The bench-scale reactor selected for the study is manufactured by New Brunswick Scientific. The **New Brunswick Bioflo III Benchtop Fermentor** is a 6.5 liter glass vessel equipped with a dished-bottom water jacket for temperature control, mechanical mixing, and several ports for feed, gas measurement, continuous pH monitoring, temperature monitoring, and sludge removal. The reactor, shown on Figure 4-7, was operated at the mesophilic range as an intermittently-fed anaerobic reactor. The reactor's operating liquid volume was 4 liters and the gas volume was 2.5 liters.

4.3.2 Reactor Operation and Monitoring

The reactor was located in a constant-temperature walk-in incubator (Environmental Chamber). The chamber was operated at the mesophilic temperature of 35°C. A refrigerator with the influent sample was also located inside the Environmental Chamber. Initially, the reactor was seeded with 4 liters of screened PDS. This high volume of seed

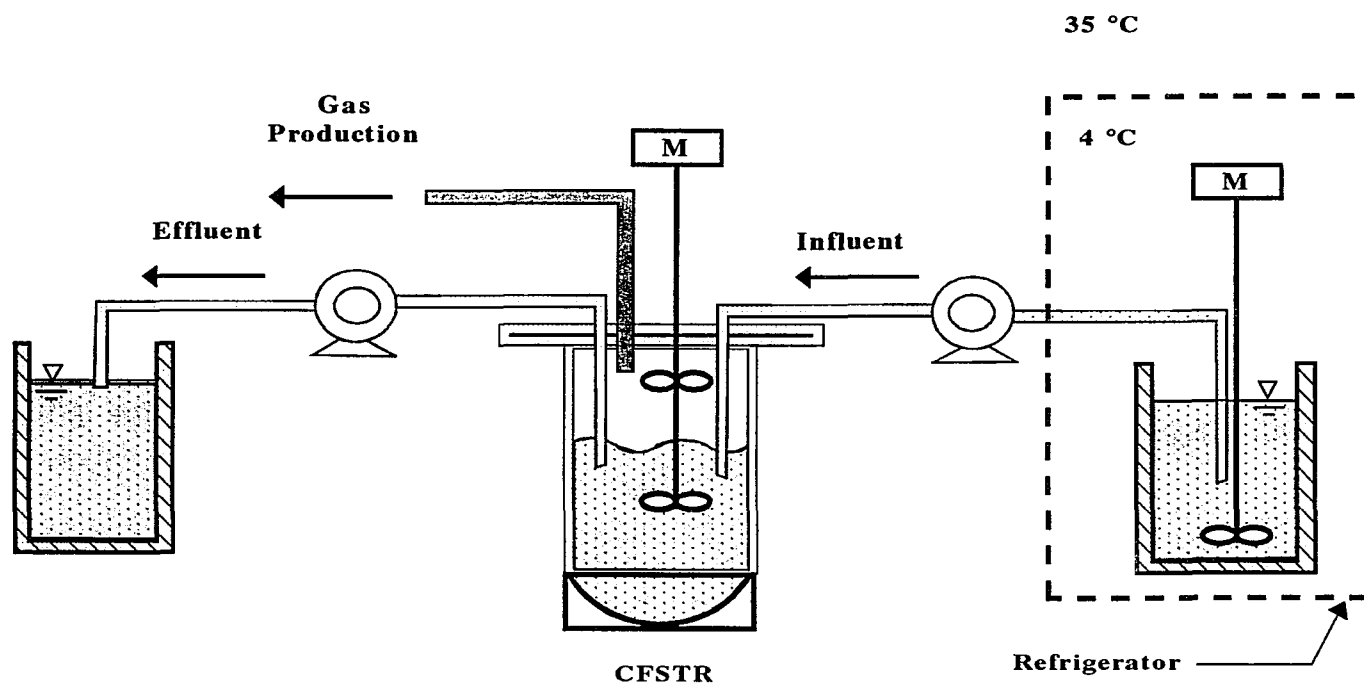


FIGURE 4-7

CONTINUOUS FLOW STIRRED TANK REACTOR
(CFSTR)

insured a high population of acetogenic and methanogenic bacteria. The feed to the CFSTR was kept well-mixed in a vessel stored in the refrigerator. Holes were made at the side of the refrigerator to accommodate electricity for the mixer and facilitate passage for effluent line. Any short-term temperature variations caused by the cold feed would not affect gas production results. A short-term temperature variation effect was evaluated by Speece and Kem (1970); a slight lag in gas production was noted after the digestion temperature was decreased to 10°C for two hours and then restored to 35°C. The study's temperature changes were negligible.

The feed storage-vessel was a 20-L carboy equipped with a rubber stopper in its mouth. The stopper had four holes, one for the mechanical mixing using an electric stirred, two holes for effluent lines, and one hole for venting. Initially, the feed was mixed by a large magnetic stirrer, but the high solids concentration and the high viscosity precluded its continuous operation. The system was changed to an electric mixer that proved to be reliable.

The influent was pumped to the CFSTR **intermittently** by a Cole-Parmer peristaltic pump. The pump's controller was operated by a timer and was adjusted to supply 44 mL of feed in one minute every four hours to give a 15-day HRT. The treated effluent was pumped out by the same technique as the influent. The influent/effluent flow rates were easily checked by the gas-monitoring apparatus, which displayed on a chart recorder a continuous gas production curve. During feeding and emptying, the instantaneous displacement on the chart recorder represented the volume fed to or removed from the reactor.

Tygon tubing, 1/4-inch ID and 5-feet long, transported the feed from the refrigerator to the reactor. The tubing's volume of 0.048 L, 1.2% the CFSTR's operating volume of 4 L, was insignificantly small to affect feed's characteristics during travel time.

The gas produced was monitored continuously by the built-in oil manometer of the Arthur Respirometer and was recorded on a strip chart. The strip chart recorder was calibrated so that the volume of gas production could be read directly in mL. Gas composition was determined using the Perkin-Elmer 2000 Gas Chromatograph.

Until the system reached steady state, pH, alkalinity, volatile acids, oxidation reduction potential (ORP), COD, $\text{NH}_3\text{-N}$, and gas production and composition were monitored so that any drastic changes would reveal upset conditions of the system. The monitoring parameters and minimum frequency of testing performed are summarized in Table 4-1.

Process efficiency is generally satisfactory within a pH range of 6.5 to 7.5 with an optimum pH close to 7.0. Methane bacteria are very sensitive to small deviations of pH from neutrality. To maintain the pH close to 7.0 sufficient buffer should be present. As a result of the fermentation of organic compounds to volatile organic acids, the buffer present is destroyed. The destroyed alkalinity is reformed when methane production takes place and the volatile acids are removed. For this reason, total volatile acids (TVA) were monitored as well because they contribute to the alkalinity destruction of

TABLE 4-1

ANALYSIS SCHEDULE FOR 15-DAY ANAEROBIC DIGESTION

Parameter	Influent	Effluent
Flowrate	Daily	1/d
pH	Biweekly	1/d
ORP	Biweekly	1/d
Alkalinity	Biweekly	Biweekly
TVA	Weekly	Biweekly
TS, TVS, SS, VSS	Weekly	Biweekly
COD; Total & Soluble	Weekly	Biweekly
CST	Weekly	Biweekly
Gas • Production Rate • Composition	GAS PHASE	
	Continuous (Rate) Weekly (Gas Composition)	

the system. Ammonia also contributes to the system's alkalinity, released during hydrolysis of organic nitrogen and deamination of the amino acids (McInerney, 1988).

The desirable alkalinity range is 2,000 to 4,000 mg/l as CaCO_3 . A minimum bicarbonate alkalinity of 1,000 mg/l as CaCO_3 should be able to maintain the pH in the optimum range (Jeris *et al.*, 1986). Total alkalinity measures both the bicarbonate and a portion of the volatile acids alkalinity. Therefore, to determine the bicarbonate alkalinity, the alkalinity due to volatile acids is subtracted from total alkalinity, as shown in the following equation:

$$\text{Bicarbonate Alk.} = \text{Total Alk.} - 0.833 \times \text{TVA} \quad (4-5)$$

The factor 0.833 is to convert mg/L of TVA as acetic acid to mg/L as CaCO_3 (Jeris *et al.*, 1986).

The ratio of TVA to alkalinity (TVA:Alk) was also monitored. This ratio is an early indicator of system upset. When an increase of TVA is associated with a decrease in alkalinity, the TVA:Alk ratio increases rapidly warning a potential imbalance in the system. If the TVA:Alk ratio exceeds 0.8, methane production ceases and the system fails. At 0.4 the system is in upset condition. The appropriate ratio is between 0.1 and 0.2 (WPCF, 1987).

Methane bacteria are also very sensitive to the ORP of the system, requiring a low value for their survival. They require an ORP less than -320 mV to convert fermented organics

to methane (Wolfe, 1985).

The system was assumed to be at steady state when the aforementioned parameters (Table 4-1) remain constant (i.e. variation $\pm 10\%$). The most convenient parameter used to indicate steady state conditions was the gas production rate.

4.3.3 Determination of Optimum HRT

Initially, the completely mixed reactor was operated with screened and untreated PDS at an HRT of 15 days. When steady state conditions were attained, the feed was changed to thermally-conditioned PDS. The parameters used to evaluate the improvement in biodegradability due to RTC and the effect of HRT were:

- Gas production rate
- Gas production per VS applied and per COD applied
- Gas composition ($\%CH_4$, $\%CO_2$)
- COD and VS removal

When steady state conditions were reached with thermally-conditioned PDS, the reactor's HRT was reduced stepwise to 10 days, 7.5 days, etc. by increasing the feed rate until the system failed. The variation in HRT was performed in order to provide additional data to determine the optimum operating conditions of the system. Generation times of methanogenic bacteria treating acetic, propionic and butyric acid were estimated by Lawrence (1967) to be about two days. A 5-day HRT was found as optimum by Li and

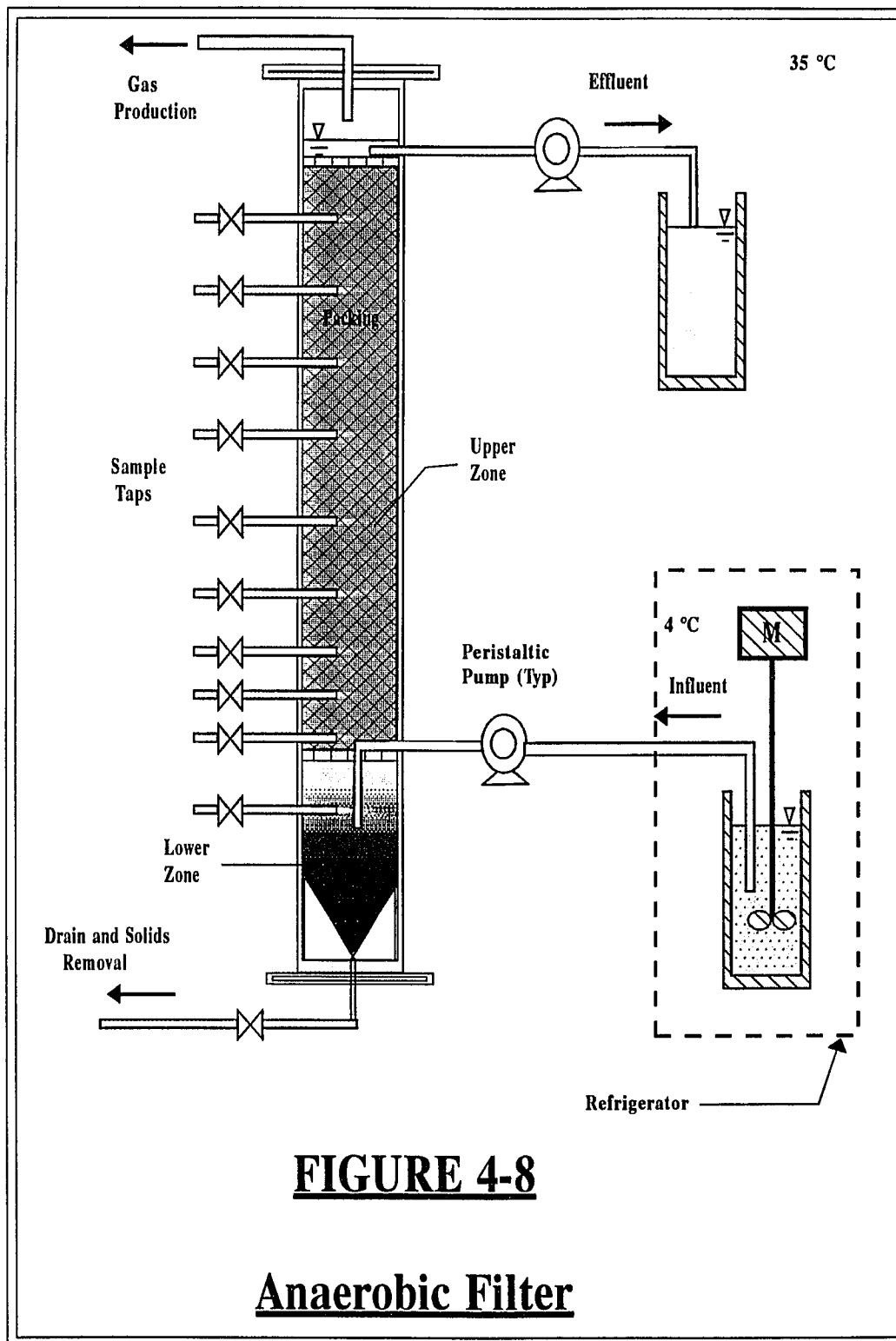
Noike (1992) who obtained comparable COD removals at both 5 and 10 days HRT for a waste activated sludge (WAS) that was heat-treated at 170°C for 30 minutes; as much as 65% COD removal was obtained by the 170°C heat-treated WAS whereas 28% COD removal was obtained by the control at the same 5 days HRT.

4.4 Anaerobic Filter

4.4.1 Reactor Description

A modified upflow completely submerged anaerobic filter (AF) was chosen for the study because of extensive literature available, the filter's ability to treat high strength wastes, and the filter's ease of operation. Because thermally-conditioned PDS still contained some biodegradable SS, the AF contained a section where solids hydrolysis and settling would take place. Hussein (1989) used a similar configuration to treat low-strength wastewater, with COD concentrations varying from 250 mg/L to 350 mg/L. Kimata *et al.* (1993) used a hybrid reactor (part of the reactor was completely mixed and part attached growth system) to treat liquor from thermally-conditioned sludge. As much as 70% of COD was removed at a loading rate of 30 kg COD/m³·d.

The AF, shown on Figure 4-8, was constructed of a plexiglass column, of 4.5 inches inside diameter and 6 feet tall. The column was divided into two zones, the lower zone and the upper zone. The lower zone did not contain any media and functioned as an influent distribution zone, a hydrolysis/fermentation zone, and a clarification zone for the influent settleable solids. The upper zone functioned as the fixed-film anaerobic zone and was filled with 4 ft of plastic media. The plastic media are the pall-ring actifill media manufactured by Norton Co., Parsippany, New Jersey. The 5/8-inch diameter pall-ring media have a specific gravity of 1.15, surface area of 104 ft²/ft³, weight of 7 lb/ft³, and porosity of 0.87. The empty volume of the 4-ft upper zone was 12.5 L with an active liquid volume of 10.9 L. The total active AF volume (including the lower influent zone)



was 14.3 L.

Distribution rings were located at 1-foot intervals in the upper zone to prevent wall-effect and short-circuiting of the wastewater through the large void space formed by the media on the column boundaries. Sampling tabs were located at 6-inch intervals throughout the upper zone with an additional tap 3 inches from the bottom.

4.4.2 Reactor Operation and Monitoring

The AF was located in the same walk-in incubator (Environmental Chamber) where the CFSTR was located. The influent thermally conditioned PDS, located inside the refrigerator, served as the feed for both the AF and the CFSTR. The results, therefore, from the two types of processes can be compared directly since both are using the same feed PDS and are incubated at the same temperature.

The AF was operated at a fixed loading until it reached steady state. The feed, kept in the same mixing vessel used for the CFSTR, was added continuously to the AF by a double-head Cole-Parmer peristaltic pump. The treated effluent was pumped out by the same double-headed pump as the influent so that both influent and effluent flowrates were exactly equal. Initially, the influent flowrate was maintained at the minimum rate of 1.6 mL/min that could be supplied by the pump. At this rate, and for the upper-zone active liquid volume of 10.9 L, the HRT was 4.7 days. If the lower-zone volume is included, the HRT was 6.2 days. Calculations were based on the total active AF volume.

The gas produced was monitored continuously by the build-in oil manometer of the Arthur Respirometer and recorded on a strip chart. Gas composition was determined using a Perkin-Elmer 2000 Gas Chromatograph.

Before and during steady state conditions the same parameters were monitored as for the suspended-growth process shown in Table 4-1. However, the sampling frequency were shorter because of the AF's shorter HRT. Steady state conditions were reached when the monitored parameters remained constant with time.

4.4.3 Determination of Optimum HRT

The optimum HRT of the AF was determined by the same procedure used for the suspended-growth process. Initially the AF was operated with screened and untreated PDS. However, because of the high SS concentration, the filter's lower zoned was filled with solids at a short time and then the solids were transported to the upper zone, plugging the filter. Thus the run with unconditioned PDS was terminated well before the filter reached steady state conditions. The next experiment was performed with conditioned PDS at the maximum HRT of 6.2 days. When steady state was reached, the filter's HRT was reduced stepwise down to the HRT of one day. At this HRT, a large volume of PDS had to be conditioned, since 14 liters were required every day.

Crawford *et al.* (1982) treated, in a similar anaerobic filter, thermally-conditioned liquor from the Lakeview Water Pollution Plant, Ontario, Canada. BOD and volatile acids were reduced by 80% at hydraulic retention times between 12 and 18 hours. No toxicity

problems were reported at the treated COD concentrations of 6,300 mg/L, $\text{NH}_3\text{-N}$ of 300 mg/L, and volatile acids of 1,600 mg/L.

5. SAMPLING AND ANALYTICAL PROCEDURES

5.1 Sludge Sampling, Handling and Storage

5.1.1 Treatment Plant Selection

Partially digested sludge (PDS) from three NYC wastewater pollution control plants was utilized for the study. These treatment plants were the Wards Island plant in Manhattan, the Newtown Creek plant in Brooklyn, and the Rockaway Beach plant in Queens (see Chapter 1, Figure 1-1).

The Wards Island plant was chosen because it was also used for a similar study conducted by Dynatech Scientific, Inc. (1988), and Garzon-Lopez (1987). The plant treats mostly residential wastewater, and its anaerobic digesters operate under mesophilic conditions. Because of the plant's proximity to City College, PDS from Wards Island was used for most of the experiments. The Newtown Creek plant has mesophilic anaerobic digesters but treats a higher proportion of industrial and commercial wastewater. The Rockaway Beach plant operates mesophilic-thermophilic anaerobic digesters and treats mostly residential wastewater. Design flows, sludge quantities and sludge metal concentrations for the three plants are summarized in Table 5-1. The high metal concentrations in Newtown Creek sludge reflect the higher percentage of industrial discharges. Consequently, the chosen plants provided different types of PDS and the results will have a wider application.

TABLE 5-1

**PARAMETERS AND CHARACTERISTICS OF THE SELECTED WASTEWATER
TREATMENT PLANTS**

Parameter	Wards Island	Newtown Creek	Rockaway Beach
Design Flow, MGD	250	310	45
<u>Present Digested Sludge Quantities:</u>			
Wet, ft ³ /d	64,400	45,800	3,400
Dry, Ton/d	54.6	50	2.9
<u>Metal Concentrations in Dry Sludge (mg/kg):</u>			
April/89 - March/90			
Cadmium	12	33	11
Chromium	227	835	60
Copper	1,354	1,858	1,171
Mercury	3	4.6	2.6
Nickel	34	125	25
Lead	269	532	170
Zinc	958	1735	750

[Hazen and Sawyer, and Stone & Webster, 1990]

5.1.2 PDS Collection and Storage

PDS samples were collected from the respective plants as needed. Due to the close proximity to all plants there was no reason to maintain primary anaerobic digesters in the laboratory. The respective plant digesters served as sources of both PDS samples and seed during the study.

PDS was collected in 20-L heavy-duty polypropylene carboys. Carboys were washed with Alkonox and rinsed with tap water before use. PDS was collected from the pump that recirculates the digesters' content through the heat exchanger.

The short exposure of PDS to the atmosphere during sample collection did not affect the viability of the anaerobic organisms. This was tested by intentionally aerating a PDS sample for 20 to 30 minutes prior to setting up the biodegradation testing. Such aeration, representing the worst-case sample collection and handling procedure, was performed on PDS from Wards Island and Newtown Creek. For Wards Island, the PDS oxidation reduction potential (ORP) during aeration increased from -205 mV to -24 mV. For Newtown Creek the ORP increased from -340 mV to -80 mV. However, the ORP of the PDS decreased to -200 mV and -292 mV after nitrogen purging for the Wards Island PDS and Newtown Creek PDS, respectively. The purged PDS was then anaerobically digested in serum bottles. Aerated PDS prior to nitrogen purging was even incubated to evaluate the effect of purging on anaerobic digestion.

The findings of the above "stress" sampling conditions, summarized on Table 5-2, indicate that the short contact time of sludge with the atmosphere during routine collection and handling is not critical. The Wards Island results demonstrated that: (1) a 30 minute aeration **with** subsequent purging with nitrogen gas before incubation decreased gas production by only 8%, and (2) a 20 minute aeration period **without** purging with nitrogen gas before incubation decreased gas production by 4%. Newtown Creek results were comparable to Wards Island results. Figure 5-1 compares the accumulated gas production per volume of PDS used for Wards Island and Newtown Creek. Because no lag phase was observed for the Wards Island results, incubation was terminated after 20 days. Newtown Creek results, however, exhibited a lag phase, requiring longer incubation times for gas production results to be comparable. The lag phase was more apparent for the non-purged sample; gas production rates started increasing after 20 days incubation and reached similar results to the purged sample after 45 days.

The Wards Island results indicate that methanogenic bacteria, the more sensitive ones among the bacteria found in anaerobic digesters, are not affected by short exposures to air. Any oxygen from air contamination is consumed by the facultative bacteria before it affects the methanogenic bacteria. Even nitrogen purging would not be required for samples obtained from anaerobic digesters, due to the complex microorganism nature of the system. Nitrogen purging, however, would be definitely required for studies involving pure cultures of methanogenic bacteria since facultative bacteria are not present to remove any oxygen contamination. The Newtown Creek lag phase observed on the

TABLE 5-2

EFFECT OF AIR EXPOSURE ON SLUDGE VIABILITY

Sample Type	PDS Volume Used (mL)	Total Gas Production (mL)	Gas per PDS Volume (mL/mL)	% Difference
Wards Island; 20-Day Incubation				
Raw PDS	100	186	1.86	---
30-min Aerated PDS Purged with N ₂ Gas	75	129	1.72	-8
20-min Aerated PDS not- Purged with N ₂ Gas	100	179	1.79	-4
Newtown Creek; 61-Day Incubation				
Raw PDS	100	347	3.47	---
30-min Aerated PDS Purged with N ₂ Gas	100	267	2.67	-23
30-min Aerated PDS not- Purged with N ₂ Gas	100	292	2.92	-16

Notes:

1. "----" Calculation not appropriate
2. % Difference calculated using as baseline the raw PDS

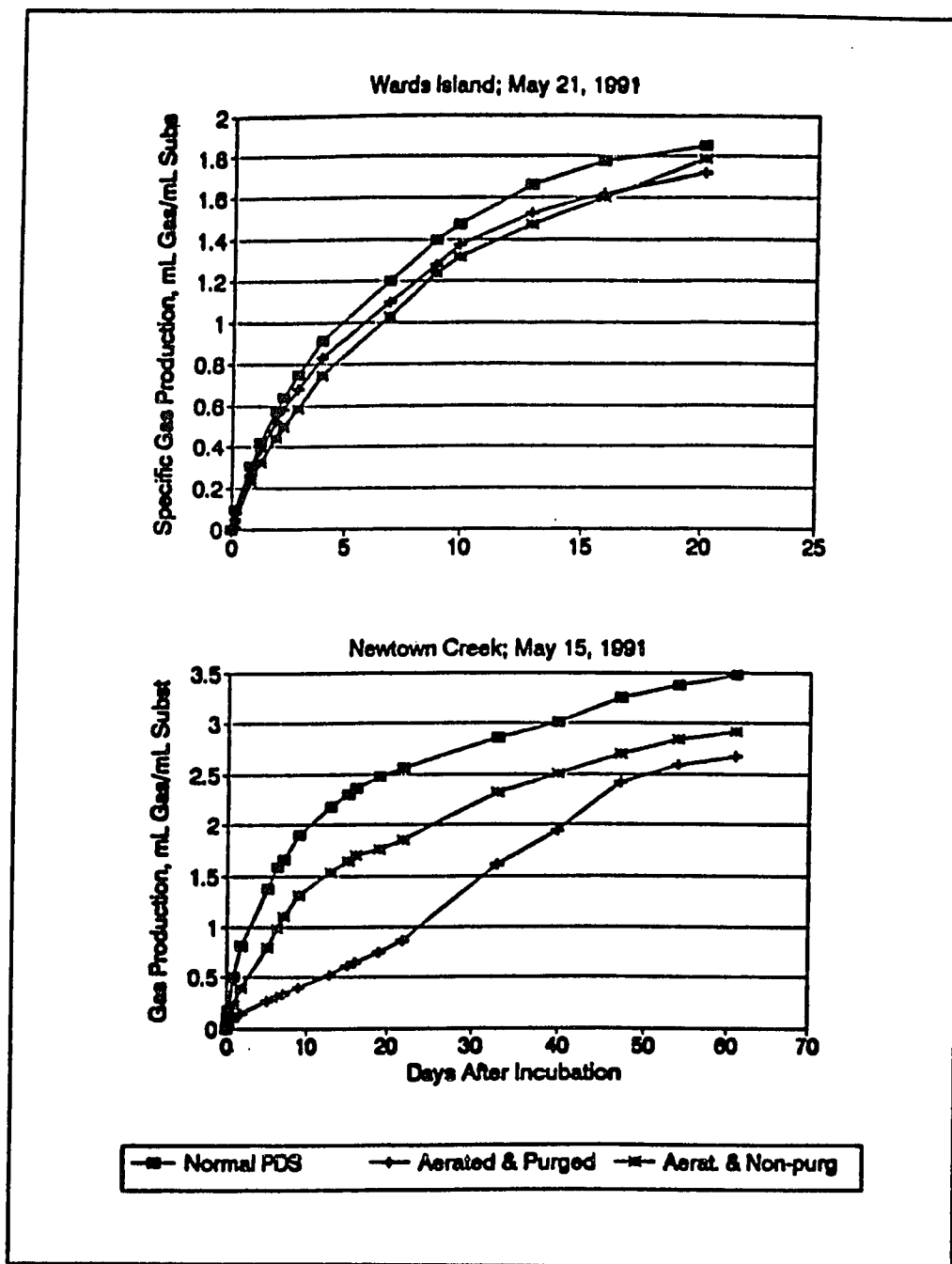
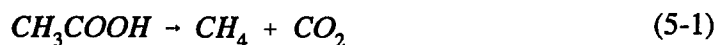


Figure S-1. Comparison of Gas Production from Aerated and Non-aerated PDS

non-purged sample could be due to low facultative bacteria concentrations or due to the longer aeration time of 30 minutes, compared to the Wards Island of 20 minutes.

As a result of the aforementioned findings, no special sampling methods were used to collect and handle PDS samples. As a precaution, though, the PDS viability was always confirmed by adding a certain amount of acetic acid (HAc). The acid is readily biodegradable by methanogenic bacteria and produces a predetermined specific gas volume. Comparison of gas volume produced to the theoretical volume would determine the seed viability. HAc is converted to equal volumes of methane gas and carbon dioxide:



One mole of HAc (60.05 g) produces 44.8 L of gas at standard conditions. The HAc solution used for the study was 99.7 % pure HAc with a specific gravity of 1.05. A volume of 0.1 mL of the solution added to a serum bottle should produce 88 mL of gas at 35°C.

5.1.3 Rapid Thermal Conditioning Sample Preparation

PDS was transported to the Environmental Engineering Laboratory of City College of New York for thermal conditioning and subsequent biodegradation. Preliminary testing of the RTCR samples showed that hair and fiber in PDS were plugging the reactor's let-down valve. This resulted in excessive pressure build-up in the reactor, activation of the

pressure relief valves, and shut-down of the system. To prevent such a pressure build-up the hair and fibers had to be removed from PDS or be mechanically sheared to prevent plugging of the valve. An attempt made to shear the fibers and hair by a dispenser failed and instead the dispenser itself began to plug. Alternately, the PDS was sieved through a 20-mesh sieve to remove the hair and fibers. Though plugging was not eliminated, the let-down valve was manually adjusted to let through any fibers that could cause intermittent plugging.

The sieving apparatus, constructed in the laboratory, consisted of an 8-inch diameter 20-mesh size sieve placed inside a 10-inch diameter plastic funnel, a 20-liter carboy, and a vacuum pump. The funnel was affixed at the carboy through a rubber stopper and sieving was facilitated by applying vacuum as needed.

The effect of sieving on PDS biodegradation was determined using Wards Island PDS. The biodegradation testing showed comparable results of the sieved PDS with the unsieved PDS. The results at the end of the 20-day incubation period are summarized in Table 5-3. The accumulated gas production throughout the incubation period of sieved and unsieved PDS are compared on Figure 5-2. Results were obtained using 50 mL of sample and 50 mL of dilution water in each serum bottle. Sieved PDS was not seeded with raw PDS. From the results, it was concluded that removing hair and fibers did not alter the PDS biodegradation properties. In addition, the results indicated that even though the PDS was exposed to air during sieving, the exposure did not affect the viability of the anaerobic organisms. Therefore, all future samples were sieved prior to thermal conditioning. Sieving a sufficient volume to run the RTCR required

TABLE 5-3

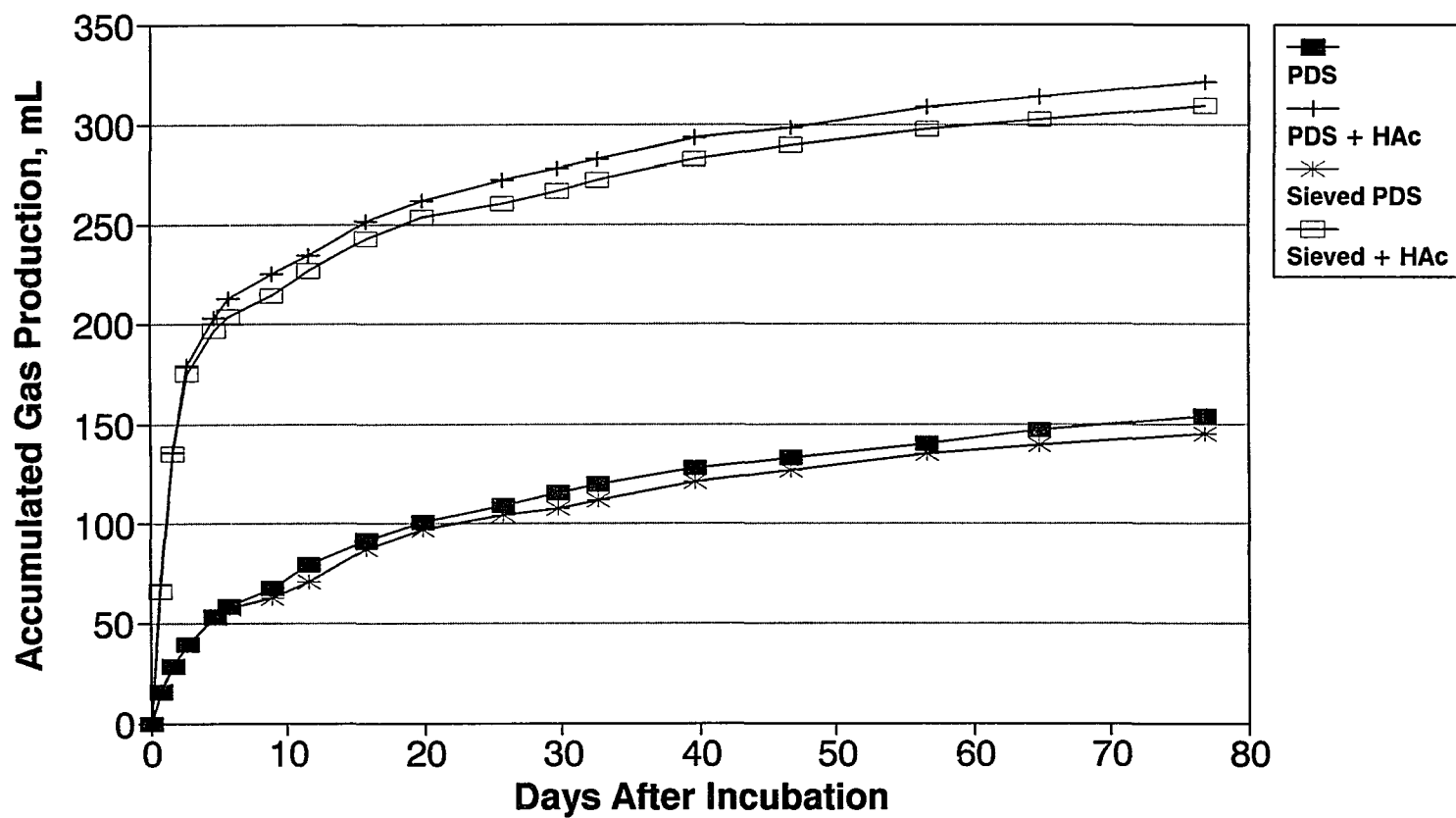
BIODEGRADATION RESULTS OF UNSIEVED AND SIEVED PDS

Sample	Total Gas Production (mL)	% HAc Gas Recovery	% Difference
Unsieved PDS	101	--	--
Unsieved PDS with 0.2 mL HAc	262	92	--
Sieved PDS	97	--	-4
Sieved PDS with 0.2 mL HAc	254	89	-3

Notes:

1. "---" Data not available, or calculation not appropriate
2. % Difference calculated using as baseline the unsieved PDS samples

FIGURE 5-2
ACCUMULATED GAS PRODUCTION
20-Mesh Sieved PDS; June 12, 1991 (WI)



approximately half a day. Thus the PDS was sieved the first day of sampling and thermally-conditioned the following day. The seed for the biodegradation testing was taken from the sieved PDS prior to thermal conditioning. Thus, both the seed and the thermally-conditioned PDS were taken from the same PDS sample.

Initial RTC tests were conducted on unmodified PDS. Afterwards the pH of the PDS was modified prior to thermal conditioning. The PDS was acidified by adding concentrated HCl while alkaline pH was obtained by adding 12.6 N NaOH. The pH modification took place in the 200 L sludge storage tank just before the RTC process started. For all the samples the pH-modified PDS without thermal conditioning was digested separately to determine the effect of pH alone on biodegradability.

Conditioned PDS for the batch biodegradation testing was collected in 1-L Pyrex autoclavable media bottles and in 1-gal autoclavable plastic bottles. Before usage, the bottles were cleaned with Alconox detergent, rinsed with distilled water, and oven-dried at 105°C for periods longer than 12 hours.

PDS for the continuous flow studies was collected in 20-L carboys. To ensure that conditioned samples would have the same characteristics, the carboys (usually eight for every test day) were emptied in a 50-gal tank, mixed well, and transferred back to the carboys. The carboys were then refrigerated at 4°C until utilization.

5.2 Baseline Determination and Sample Analysis

5.2.1 Standard Tests

The characteristics of the unconditioned PDS were the baselines on which all tested conditions were evaluated. Characteristics included biodegradability, physical-chemical characteristics, and metals.

The biodegradability improvement of PDS by the RTC process was evaluated by measuring the biodegradation of the sample. Biodegradation was assessed in terms of gas production rates using batch reactors that were incubated in the mesophilic range (34-38°C) for the Wards Island and Newtown Creek plants, and thermophilic range (50-60°C) for the Rockaway Beach plant. Gas constituents, such as methane gas (CH₄) and carbon dioxide (CO₂), were measured to characterize the gas composition.

The following tests were used to characterize the samples characteristics:

- Solids: Total Solids (TS), Total Volatile Solids (TVS), Dissolved Solids (DS), Dissolved Volatile Solids (DVS), Suspended Solids (SS), and Volatile Suspended Solids (VSS).
- Total and Soluble Chemical Oxygen Demand (TCOD and SCOD)
- Nitrogen: Total Kjeldahl Nitrogen (TKN), Organic Nitrogen (Org-N) and Ammonia Nitrogen.
- Total Volatile Acids (TVA)

- pH
- Alkalinity
- Biochemical Oxygen Demand (BOD)
- Dehydrogenase Activity (DHA)

Most of the analyses conformed to Standard Methods (1992) and the rest of the analyses conformed to published or vendors' recommended methods. All analytical methods are summarized in Table 5-4, and modified or specialized analyses are described in the Appendices. The titrimetric TVA analysis, as presented by Anderson and Yang (1992b), involved measuring volumes of acid consumed at the pH values of 5.1 and 3.5. The test was done on the same sample that alkalinity was measured, saving time and sample volume.

The aforementioned parameters were also used to monitor the chemical changes that took place during the sludge conditioning process. BOD and DHA analyses were done on a few samples only. BOD was analyzed to determine whether anaerobic degradation can be measured by an aerobic test, such as the BOD test, since organic substances that are aerobically degraded can also be degraded anaerobically (Speece, 1983).

5.2.2 DHA Measurement

The DHA test measures microbial activity. Only lately the test has been used to measure the activities of anaerobic microorganisms (Chung, 1988; and Zabranska *et al.*). ATP (adenosine triphosphate) is also used to measure microbial activities (Chung and

TABLE 5-4

METHODS USED FOR SAMPLE ANALYSES

Parameter	Method	Comments
Solids	Standard Methods	TS and DS were dried over-night
Chemical Oxygen Demand (COD)	HACH Procedure Code O.10	EPA Accepted
Nitrogen: • TKN • NH ₃ -N	HACH Procedure Code N.10 Standard Methods; Ammonia-Selective Electrode Method	Modified from Standard Methods Measured Ammonia in Gas Phase to Eliminate Interferences (Electrode-manufacturer Recommendation); Appendix A
Volatile Acids: • Individual Acids • Total	Gas Chromatography 1) Standard Methods, or 2) Titration	See Appendix B Anderson and Yang, 1992b
pH	Standard Methods; Electrometrically	
Alkalinity	Standard Methods; Potentiometric Titration	End-point pH = 4.3
Oxidation Reduction Potential (ORP)	ORP Electrode	
BOD	Standard Methods	
Gas Composition: CH ₄ and CO ₂	Gas Chromatography	See Appendix C
DHA	Tetrazolium salt	See Appendix D

Notes:

1. Standard Methods refers to Standard Methods for The Examination of Water and Wastewater, 1992
2. HACH refers to HACH Company, 1990

Neethling, 1990). The major benefit of DHA and ATP measurements is that they measure activities of viable bacteria, whereas other tests, such as the VSS determination, do not differentiate between dead and viable bacteria.

DHA is an indirect measurement of the hydrogen transfer during organic substrate oxidation. During the metabolic pathways, taking place within the cell, organic compounds are broken down through a series of oxidation-reduction reactions. Oxidation reactions involve removal of electrons, equivalent to the removal of hydrogen atoms (called dehydrogenation). The activity measurement of the various dehydrogenases, enzymes catalyzing dehydrogenation, is associated with the microbial activity responsible for the substrate degradation.

DHA measures the dehydrogenases activity by using tetrazolium salt [triphenyltetrazolium chloride (TTC), or 2-[p-iodophenyl]-3-[p-nitrophenyl]-5-phenyl tetrazolium chloride (INT)] as the terminal hydrogen acceptor (Chung, 1988). The reduction of the colorless tetrazolium salt produces the red and insoluble triphenyl formazan crystals (TF) inside the bacterial cell. Extracting, solubilizing, and measuring the red-color intensity is a measure of the microbial activity. The intensity of the color is proportional to TF yield and the hydrogen transfer. Color intensity is measured by a spectrophotometer at 490 nm wavelength and the results are obtained from a calibration curve as mg/L TF formed. The final results are expressed per g TVS as mg TF/g TVS.

Using substrates utilized solely by a certain bacterial group, can measure the activity of that particular group. For example, glucose can measure the activity of the fermentative

microorganisms, and acetate the activity of acetate-utilizing methanogens. Appendix D presents the DHA test-procedure as modified from Chung and Neethling (1988) by Zabranska (1993).

The DHA method offers the following advantages (Zabranska, 1993):

- Confirmation of viable bacteria
- Differentiation of activities of various bacterial groups by adding a specific substrate for each group
- Requires little sample volume
- Evaluation of toxic, inhibitory, or stimulating effects
- Determination of actual environmental conditions of biomass, i.e. under overloading or starvation, based on "endogenous" and "substrate" activities
- Simple and accurate procedure without requiring sophisticated equipment
- Fast response, comparing to other activity-measurement methods

5.3 Metal Analyses

Analyses for total and soluble metals were performed by the New York City Department of Environmental Protection laboratory, a New York State certified laboratory, located at the Wards Island Water Pollution Control Plant, and using EPA analytical methods. Soluble metals are those present in the filtrate passed through a 0.45 μm filter, or in the supernatant after a 10-minute centrifugation at 3,000 rpm. A laboratory-type bench-top centrifuge was used for the solids separation.

6. RESULTS AND DISCUSSION

6.1 Biodegradability and Solubilization

The first set of experiments evaluated the effect of RTC on PDS. Once the optimum RTC operating parameters were determined in terms of improved biodegradability, they were repeated on waste activated sludge and primary sludge.

The initial thermal conditioning of PDS involved combinations of different temperatures, pH levels, and hydraulic retention times. To assess the impact on biodegradability, 160 mL serum bottles were used and the gas produced was measured with a manometer. The conditions giving the optimum biodegradability were then confirmed in continuous flow reactors.

6.1.1 Serum Bottles Results

GPI Kinetic Equation Evaluation

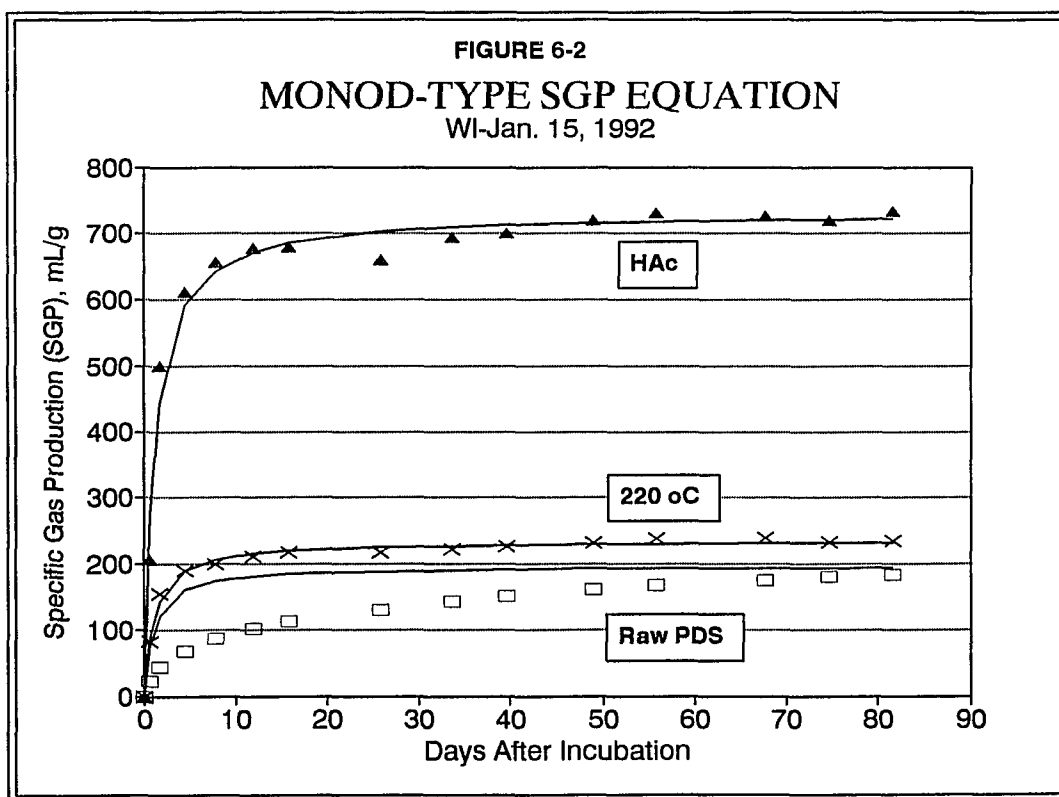
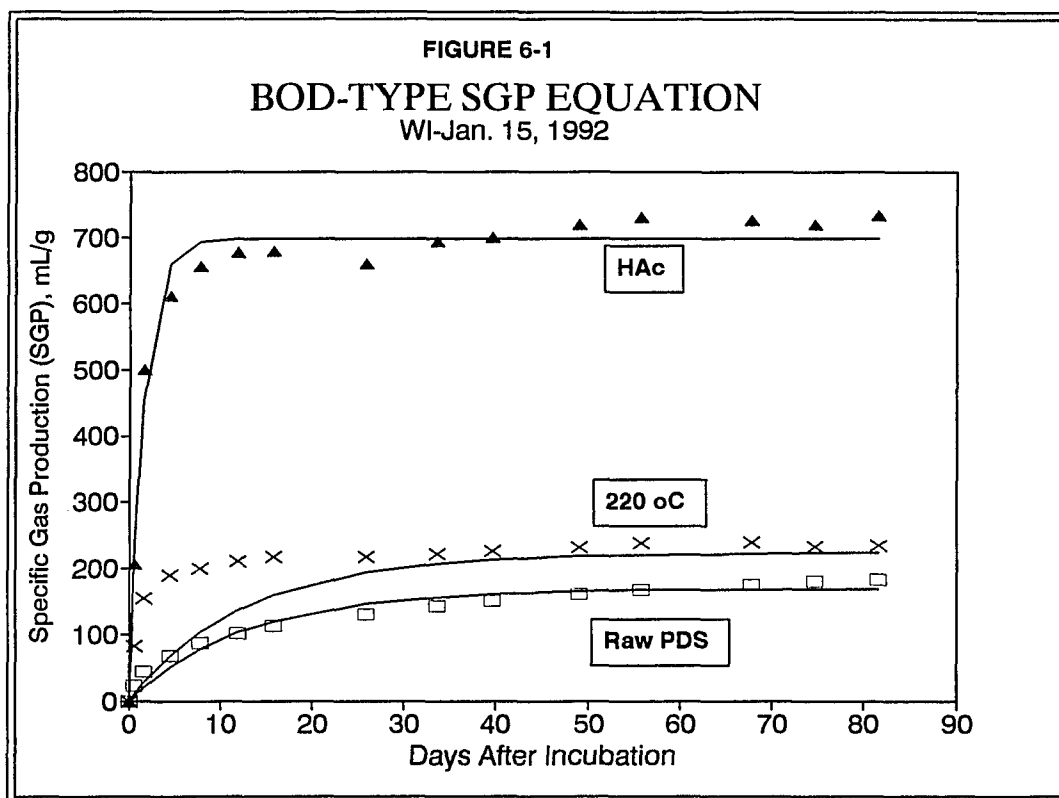
Gas production from the serum bottles was measured daily during the first week of incubation, when gas production was high. Afterwards, only periodic gas measurement was needed. The specific gas production (SGP) was then calculated from the accumulated gas production (AGP) and the COD of the feed sludge to the bottles. To expand the usefulness

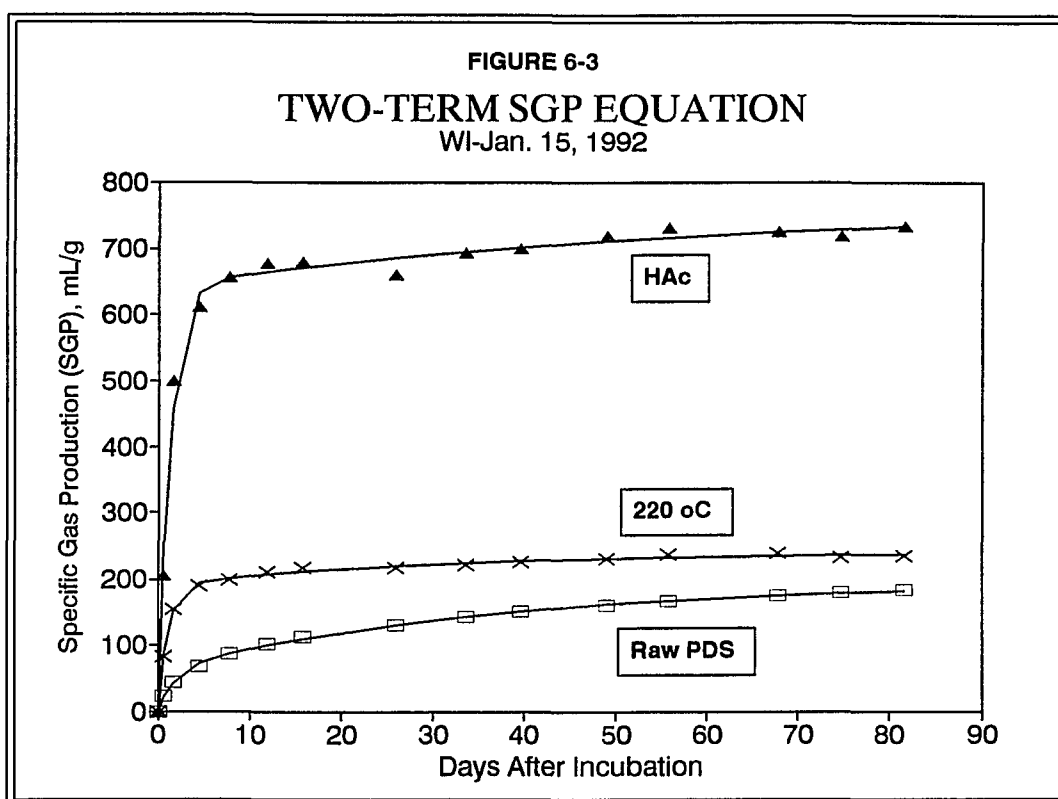
of the information on SGP, it was necessary to fit a mathematical model to the SGP data. Additional benefits of the model included the calculation of SGP at time intervals that did not coincide with actual data collection and the ability to perform mathematical operations which could predict optimum conditions or be used to estimate SGP for parameters beyond those tested.

Three different types of equations were evaluated to determine which one provided the best fit to the SGP data, (1) a BOD-type, (2) a Monod-type, and (3) a BOD two-term type. The two-term type was originally used by NCASI (1982) to estimate the ultimate BOD of pulp and paper effluent. Incubation times were over 100 days in this study. The following conclusions were made from applying three different equations to the gas production results:

- The BOD-type equation fitted the raw PDS's SGP relatively well but fitted the thermally conditioned PDS at 220°C poorly, Figure 6-1
- The Monod-type fitted the 220°C PDS very well, but not the raw PDS data, Figure 6-2
- The two-term equation fitted all data well, Figure 6-3

In the two-term exponential equation, the first exponential component represents the fast term of the equation, and the second component represents the slow term. Though anaerobic biodegradation involves the complex reactions described on Figure 2-2, it appears that the





overall reaction can be defined by a two-term equation, Equation 6-1. Appendix E presents the model and the equation derivation. Best-fit results were obtained by the computer software SIGMAPLOT Ver. 5.0. SIGMAPLOT uses a nonlinear regression method to minimize the sum of the squares of the residuals. The solution is found by iteration.

$$SGP = G_1 (1 - e^{-k_1 t}) + G_2 (1 - e^{-k_2 t}) \quad (6-1)$$

where,

- SGP = specific gas production, mL gas/g COD applied
- G_1 = ultimate SGP of fast term, mL gas/g COD applied
- k_1 = first order reaction rate of fast term, 1/d
- G_2 = ultimate SGP of slow term, mL gas/g COD applied
- k_2 = first order reaction rate of slow term, 1/d
- t = incubation time from start-up, d

The GPI at any incubation time t is then given by:

$$GPI = \left(\frac{G_1^f (1 - e^{-k_1^f t}) + G_2^f (1 - e^{-k_2^f t})}{G_1^r (1 - e^{-k_1^r t}) + G_2^r (1 - e^{-k_2^r t})} - 1 \right) 100 \quad (6-2)$$

where,

- GPI = gas production improvement, %
- f = conditioned PDS feed sludge

r = raw PDS

Figure 6-4 compares the GPI values of the data to the three aforementioned equations, namely the BOD-type, the Monod-type, and the two-term type. Again, the results indicate that the two-term equation fits the data very well.

The GPI at $t=0$ is calculated by taking the $\lim_{t \rightarrow 0}$ of Equation 6-2 and applying L'Hopital's rule:

$$GPI_o = \left(\frac{G_1^f k_1^f + G_2^f k_2^f}{G_1^r k_1^r + G_2^r k_2^r} - 1 \right) 100 \quad (6-3)$$

The ultimate GPI at $t=\infty$ (GPI_u) is calculated by:

$$GPI_u = \left(\frac{G_1^f + G_2^f}{G_1^r + G_2^r} - 1 \right) 100 \quad (6-4)$$

Normalized GPI Ratio - GPI_N

Though the source of sludges were large and relatively stable, slight changes in sludge characteristics were noted during the study period. Table 6-1 is a summary of the sludge characteristics experienced during the study period. To compare data obtained from different

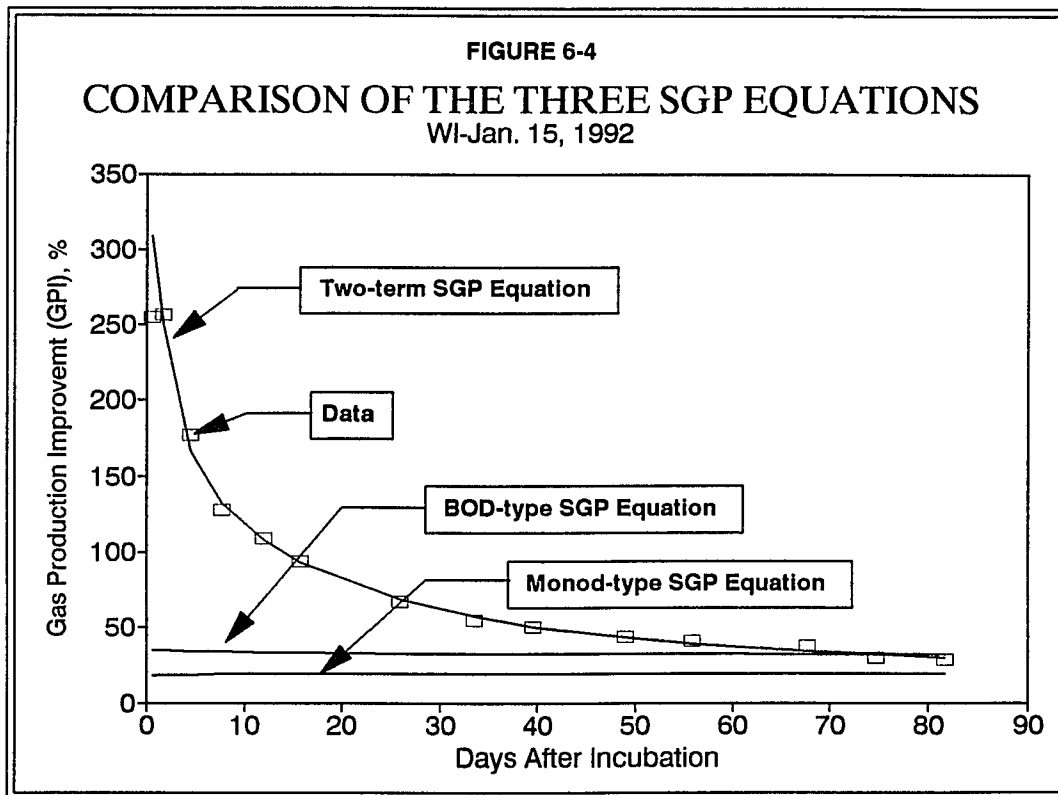


TABLE 6-1

SUMMARY TABLE OF PDS CHARACTERISTICS
WARDS ISLAND TREATMENT PLANT

Parameter	4/15/91	5/21/91	6/12/91	7/3/91	7/17/91	7/25/91	8/17/91	1/15/92	3/25/92	7/21/92	8/5/92	9/23/92	11/18/92	1/28/93	Average
TS, %	2.05	2.00	2.75	2.00	1.85	1.82	2.01	2.00	2.07	2.84	2.57	1.95	2.12	2.50	2.18
TVS, % of TS	69.2	65	65.4	64.2	65.2	64.8	68.3	69.5	67.8	64.9	64.6	67.2	65.6	64.8	66.1
DS, %	0.27	0.29	0.29	0.28	0.21	0.13	0.14	0.24	0.29	0.23	0.24	0.31	0.25	0.27	0.25
VDS, % of DS	55.1	55.0	49.4	53.4	43.5	26.2	22.6	46.9	48.0	41.0	43.0	60.3	43.4	48.8	47.5
TSS, %	1.78	1.71	2.46	1.72	1.64	1.69	1.87	1.76	1.78	2.61	2.33	1.64	1.87	2.23	1.94
VSS, % of TSS	71.3	66.7	67.3	66.0	68.0	67.8	71.7	72.6	71.0	67.0	66.8	68.5	68.6	66.7	68.4
Total TOC, mg/L	2,510	1,500	1,060	2,020	4,340	4,850	4,660	---	---	---	---	---	---	---	2,991
Soluble TOC, mg/L	148	201	113	148	104	106	160	---	156	---	---	---	---	---	142
Total COD, mg/L	20,170	17,750	24,990	18,020	21,500	35,000	19,800	25,770	29,080	24,200	27,240	25,800	35,440	31,140	25,421
Soluble COD, mg/L	220	316	623	500	167	151	550	1,394	1,325	770	1,260	368	740	1,440	702
TKN-N, mg/L	2,880	1,980	1,980	2,050	1,750	1,710	3,810	---	---	---	---	---	3,650	---	2,476
NH3-N, mg/L	1,270	1,240	804	990	780	820	730	360	580	---	---	---	1,100	850	866
TVA, mg/L as Ac. Acid	59	18	---	---	67	---	---	---	578	---	1,170	---	---	---	378
pH	7.21	7.34	7.83	7.61	7.44	7.39	7.47	---	7.43	7.35	7.24	7.23	7.28	7.46	7.41
Alkalinity, mg/L as CaCO3	4,470	4,050	4,510	3,930	3,760	3,530	3,120	---	4,280	3,210	3,430	3,290	2,920	3,340	3,680
Phosphates, mg/L	498	420	628	---	---	---	---	---	---	---	---	---	---	---	515
Sulfates, mg/L	1,520	51	---	---	---	---	---	---	---	---	---	---	---	---	786
Chlorides, mg/L	234	403	468	---	402	---	---	---	---	---	---	---	---	---	377
Carbohydrates, mg/L															
- Total	---	---	---	---	---	---	---	---	---	---	---	---	2,290	---	2,290
- Dissolved	---	---	---	---	---	---	---	---	---	---	---	---	1,460	---	1,460
BOD ₅ , mg/L	---	---	---	---	---	---	---	---	---	---	---	---	1,380	2,720	2,050

Notes:

1. "----" Data not available

collection days, the **normalized GPI ratio (GPI_N)** was developed. The GPI_N ratio is the GPI of a sample under a certain condition i (GPI_i) divided by the GPI of a sample thermally conditioned at 220°C and at unmodified pH (GPI_{U220}).

$$GPI_N = \frac{GPI_i}{GPI_{U220}} \quad (6-5)$$

The GPI_N ratio was calculated using the GPI_{U220} because it was found that during the pH-unmodified experiments, the 220°C RTC temperature gave the best biodegradation results. A ratio greater than unity would represent a condition where GPI is greater than the GPI of pH-unmodified, 220°C PDS. To be able to normalize the GPI results, especially during thermochemical conditioning, the GPI_{U220} was obtained during all runs by conditioning PDS at 220°C and at unmodified pH.

6.1.1.1 Partially Digested Sludge (PDS) Results

Most of the RTC experiments with serum bottles were conducted on Wards Island PDS. Limited testing was conducted on Newtown Creek PDS and one test was conducted on Rockaway Beach PDS which utilizes a mesophilic/thermophilic process.

The research effort for PDS was divided into five test series based on the respective conditioning as shown in Table 6-2. The effect of temperature, pH, pressure, and hydraulic retention time on unthickened PDS (as collected), and the effect of temperature on thickened PDS was evaluated during the first phase of the study.

TABLE 6-2

EXPERIMENTS PERFORMED ON PDS

Series	pH (s.u.)	RTC HRT (sec)	Temperature Range (°C)	Other
Series 1	Unmodified - pH7.5	10	Room-220	Temperature Effect
Series 2	pH1 - pH12	10	Room-220	pH Effect
Series 3	Unmodified	None	Room	Pressure Only
Series 4	Unmodified	10 - 180	Room-220	HRT Effect
Series 5	Unmodified	10	Room-220	Thickened PDS

(a) Series 1 - Unmodified pH

Series 1 experiments were performed to evaluate only the effect of temperature on PDS. Five experiments were performed on Wards Island PDS at unmodified pH and 10 seconds HRT, with temperatures varying from 25°C (room temperature) up to 220°C. Table 6-3 lists the Series 1 test dates, RTC temperatures, and kinetic results of the two-term SGP equation. The terms G_1 , G_2 , k_1 , and k_2 kinetic results were calculated by fitting Equation 6-1 to the collected SGP data. Some of the RTC temperatures were repeated at every test (e.g. 100°C, 160°C, and 220°C), whereas intermediate temperatures were tested occasionally. On February 5, 1992, the 70°C temperature was also tested to evaluate the biodegradability at low temperatures. In general, G_1 , k_1 and k_2 increased with rising temperatures whereas G_2 decreased.

GPI results at initial, 15-days, 60-days, and infinite (ultimate) incubation times are presented on Figures 6-5, 6-6, 6-7, and 6-8, respectively. Table 6-4 tabulates the GPIs at the calculated SGPs, using Equations 6-2 to 6-4 and the kinetic results from Table 6-3. All the results, fitted using a second-degree polynomial, indicate that GPIs increase with increasing RTC temperatures, reaching a maximum value at 220°C. The second-degree polynomials at each incubation time are summarized in Table 6-5.

The initial GPI values (Figures 6-5) represent the extent of kinetics improvement in gas production. GPI reached a maximum range at 220°C, where it ranged from a minimum of 330% to a maximum of 920%, and averaged 570%. The 15-day GPI values (Figure 6-6)

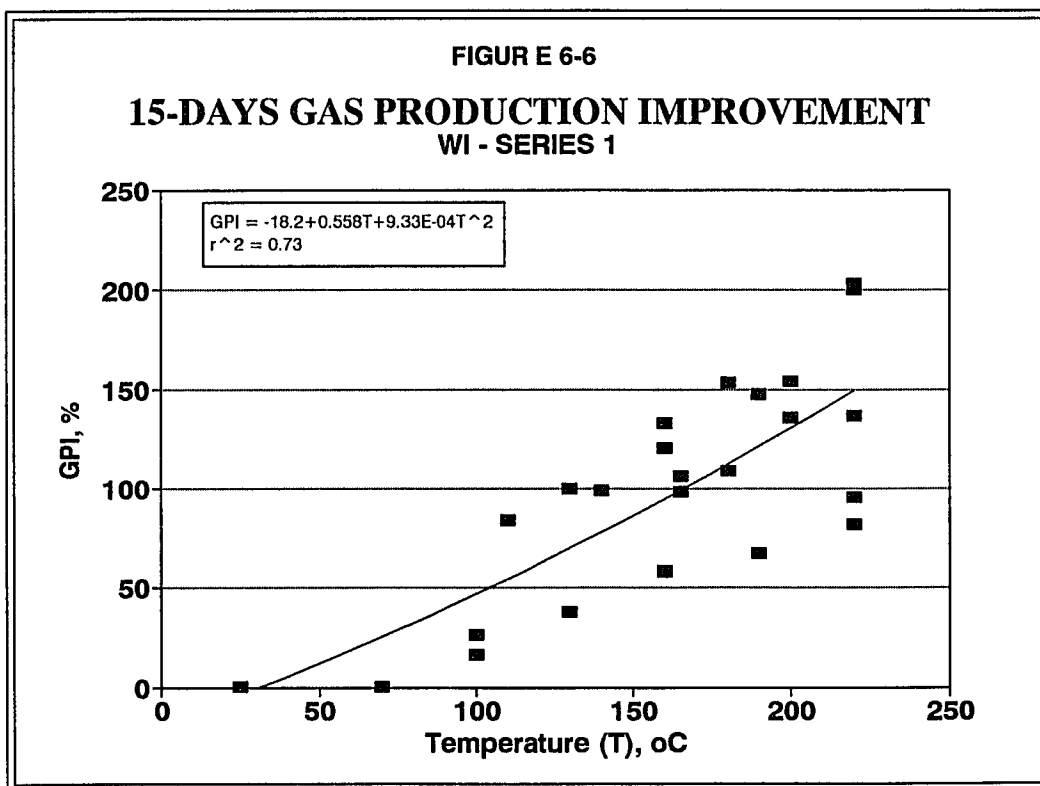
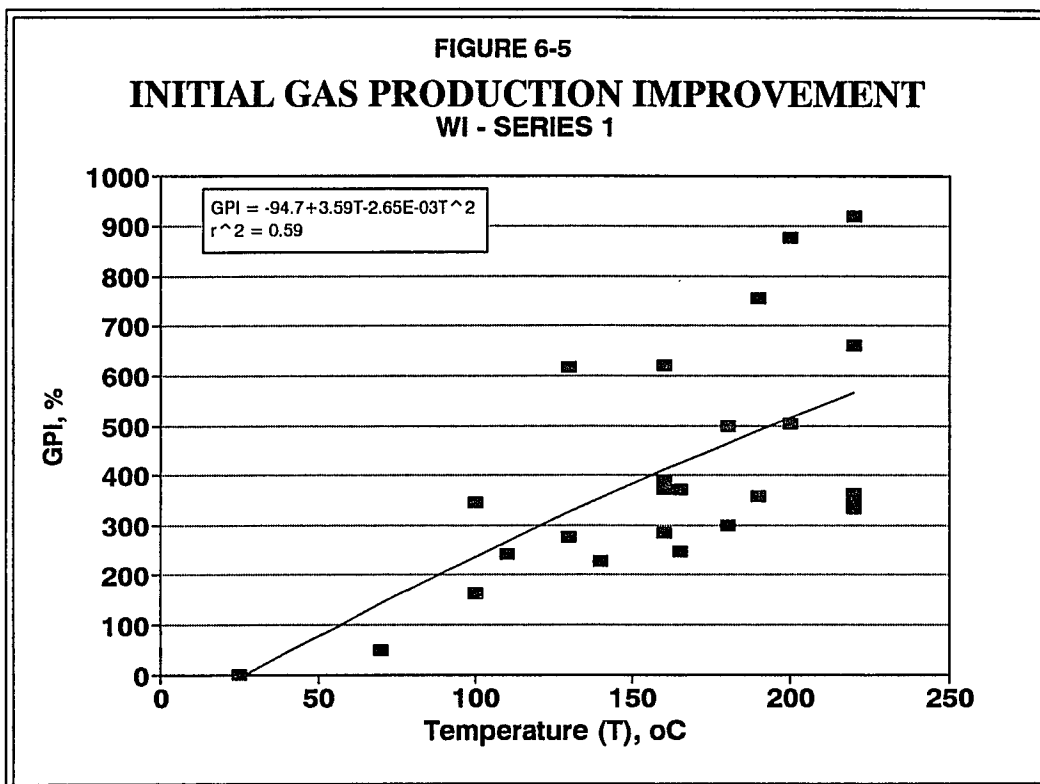
TABLE 6-3

SPECIFIC GAS PRODUCTION (SGP) KINETIC RESULTS
SERIES 1 (UNMODIFIED pH), WARDS ISLAND

Test Date	RTC Temperature T (°C)	SGP Coefficients				G ₁ +G ₂ (mL/g)	G ₁ k ₁ +G ₂ k ₂ (mL/g-d)
		G ₁ (mL/g)	G ₂ (mL/g)	k ₁ (1/d)	k ₂ (1/d)		
July 3, 1991	25	48.6	135.0	0.455	0.0262	183.6	25.7
	110	124.1	88.1	0.673	0.0494	212.2	87.9
	140	158.9	74.7	0.515	0.0275	233.6	83.9
	165	154.2	90.9	0.762	0.034	245.1	120.6
	165	139.6	88.3	0.61	0.046	227.9	89.2
	180	174.4	107.0	0.846	0.055	281.4	153.4
	180	160.7	71.5	0.62	0.04	232.2	102.5
	200	151.1	113.8	1.592	0.089	264.9	250.7
	200	163.4	83.5	0.911	0.071	246.9	154.8
	220	169.7	81.8	0.646	0.061	251.5	114.6
Sept. 17, 1991	25	37.6	127.2	0.546	0.0308	164.8	24.4
	160	87.4	115.1	1.191	0.132	202.5	119.3
	220	209.0	90.4	0.869	0.0497	299.4	186.1
Jan. 15, 1992	25	61.1	133.8	0.564	0.0287	194.9	38.3
	160	144.0	80.8	1.01	0.0272	224.8	147.6
	220	188.7	49.8	0.927	0.0404	238.5	176.9
Feb. 5, 1992	25	48.5	115.4	0.617	0.0366	163.9	34.1
	70	64.1	109.0	0.758	0.024	173.1	51.2
	100	92.3	101.6	0.954	0.0153	193.9	89.6
	130	113.2	110.6	1.124	0.0142	223.8	128.8
	160	124.2	89.6	1.279	0.0266	213.8	161.2
	190	132.6	75.1	1.163	0.0346	207.7	156.8
	220	137.3	92.5	1.051	0.0379	229.8	147.8
Nov. 18, 1992	25	26.7	64.9	0.254	0.0219	91.6	8.2
	100	23.7	70.1	1.42	0.0411	93.8	36.5
	130	53.3	65.0	1.04	0.0524	118.3	58.8
	160	69.2	71.1	0.809	0.0435	140.3	59.1
	190	71.1	72.1	0.935	0.051	143.2	70.2
	220	97.5	64.7	0.823	0.0532	162.2	83.7

Notes:

1. $SGP = G_1(1 - \exp(-k_1 t)) + G_2(1 - \exp(-k_2 t))$



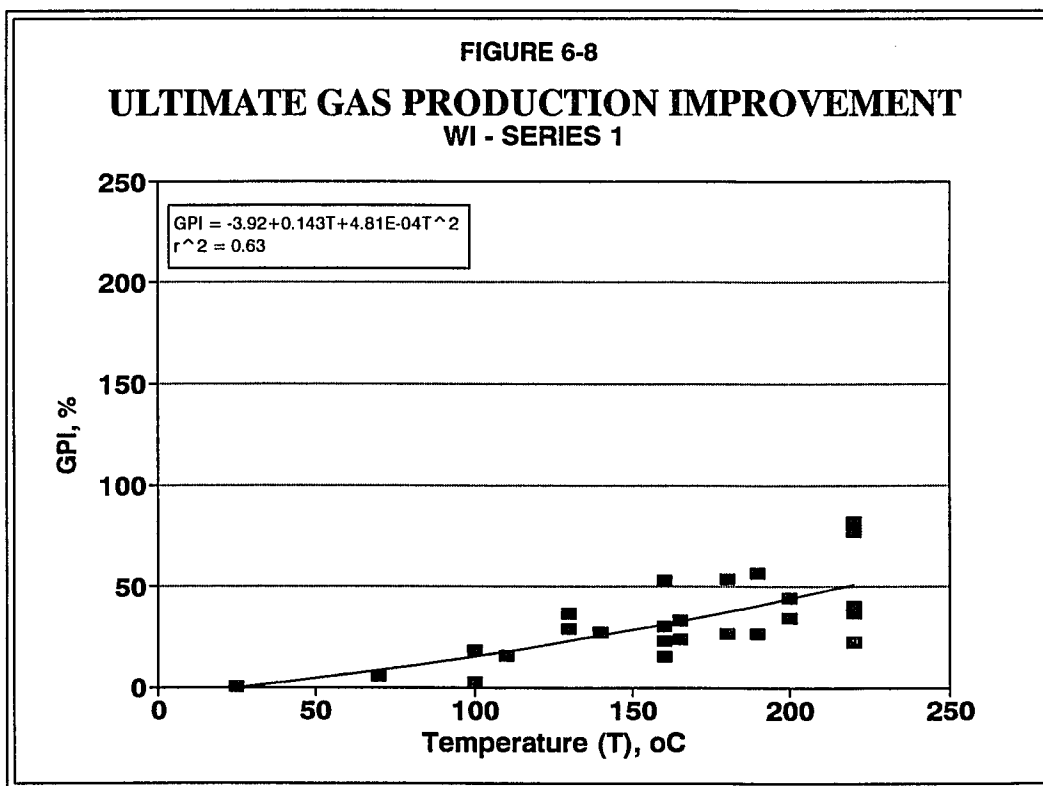
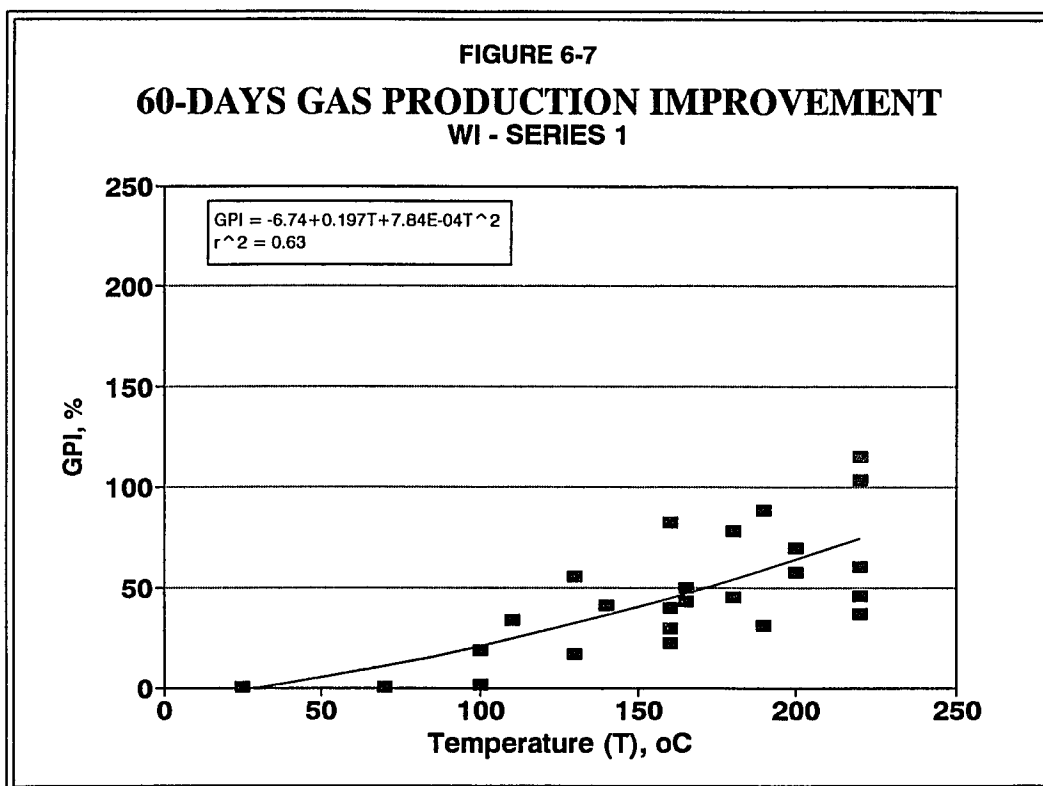


TABLE 6-4

GAS PRODUCTION IMPROVEMENT (GPI), IN PERCENT, AT VARIOUS
INCUBATION TIMES, SERIES 1 (UNMODIFIED pH), WARDS ISLAND

Test Date	RTC Temperature T (°C)	Incubation Time (t), Days			
		0	15	60	Infinite
July 3, 1991	25	0	0	0	0
	110	243	84	33	16
	140	227	99	41	27
	165	370	106	50	33
	165	248	99	43	24
	180	498	154	78	53
	180	300	109	45	26
	200	877	154	70	44
	200	503	136	58	34
	220	347	137	60	37
Sept. 17, 1991	25	0	0	0	0
	160	388	120	40	23
	220	661	203	104	82
Jan. 15, 1992	25	0	0	0	0
	160	285	59	22	15
	220	362	96	37	22
Feb. 5, 1992	25	0	0	0	0
	70	50	0	0	6
	100	162	16	2	18
	130	277	38	17	37
	160	372	58	30	30
	190	359	68	31	27
	220	333	82	46	40
Nov. 18, 1992	25	0	0	0	0
	100	345	26	18	2
	130	617	100	56	29
	160	620	133	82	53
	190	755	148	89	56
	220	920	201	115	77

TABLE 6-5

GPI-TEMPERATURE EQUATIONS AT VARIOUS INCUBATION TIMES

Incubation Time	GPI (%)
Initial	$-94.7+3.59T-2.65E-3T^2$
15-Days	$-18.2+0.558T+9.33E-4T^2$
60-Days	$-6.74+0.197T+7.84E-4T^2$
Infinite	$-3.92+0.143T+4.81E-4T^2$

Notes:

1. Temperature, T, in °C

represent typical anaerobic digestion HRTs. Maximum values were reached at 220°C, where GPI ranged from 80% to 200%, and averaged 150%. The 60-days GPI values (Figure 6-7) represent the recommended BMP incubation time. At 220°C, GPI ranged from 40% to 115% and averaged 75%. Finally, the ultimate GPI (infinite time) represents the improvement in ultimate biodegradability (Figure 6-8). Ultimate GPI reached maximum at 220°C, where it ranged from 20% to 80% and averaged 50%. Clearly, the BMP test does not reflect the ultimate gas production due to the exponential GPI decrease over time, and because the GPI_{60} overestimated the ultimate GPI by 50%.

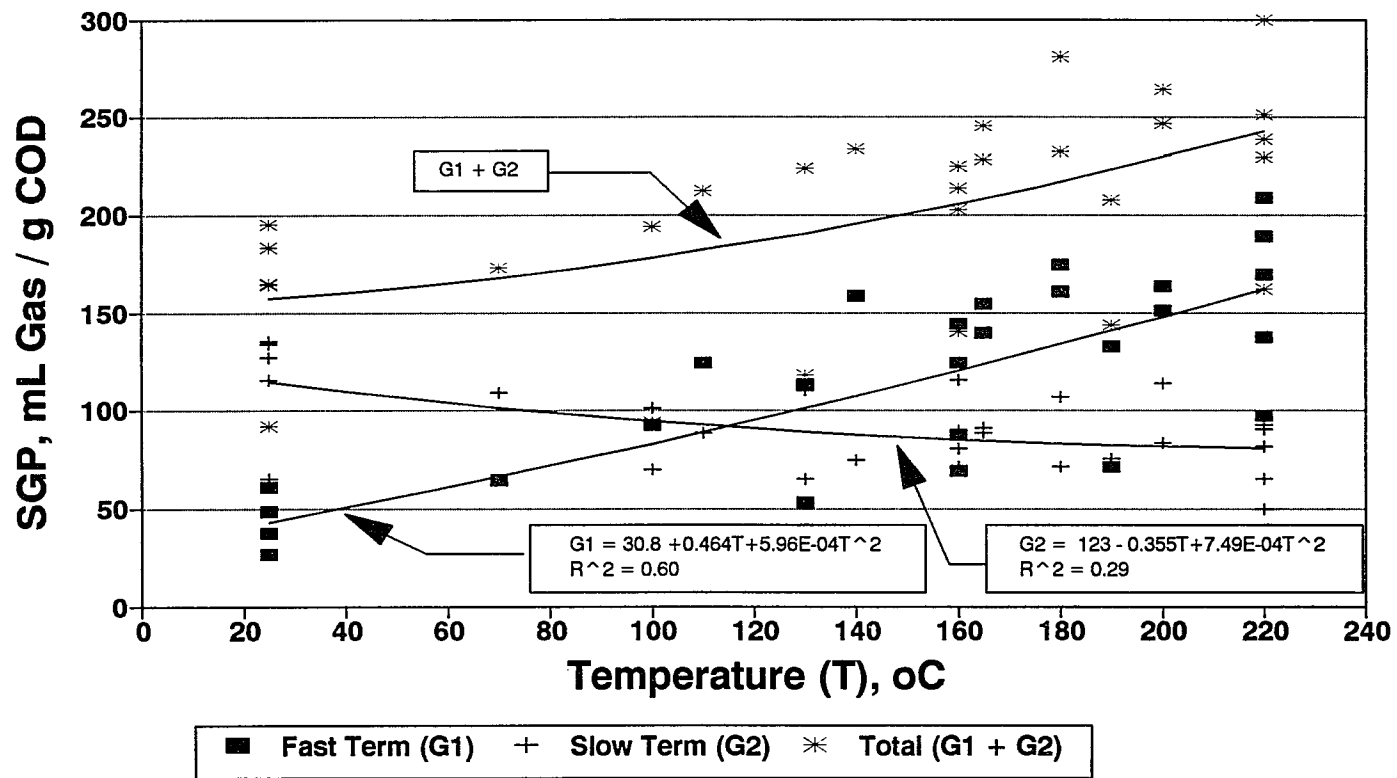
From Equation 6-4, the ultimate GPI is related to the ultimate SGP, $(G_1 + G_2)$. Therefore, the ultimate SGP of the fast term (G_1) and the slow term (G_2) of the equation were plotted on Figure 6-9 to justify the ultimate biodegradability improvement. The important observation is that G_1 increases and G_2 decreases with RTC temperature, indicating that slowly degraded organics were converted into fast degraded organics. If the slowly degraded organics are represented by the particulate fraction of PDS, the RTC converted the particulate part, via physico-chemical hydrolysis, into soluble.

As with GPI, the two terms G_1 and G_2 were fitted with a second-degree polynomial. The best-fit results, as a function of temperature T , are:

$$G_1 = 30.8 + 0.464T + 5.96E-4T^2 \quad (6-6)$$

$$G_2 = 123 - 0.355T + 7.49E-4T^2 \quad (6-7)$$

FIGURE 6-9
ULTIMATE SPECIFIC GAS PRODUCTION
SERIES 1 (UNMODIFIED pH)



G1G2

For a one-to-one conversion, i.e., a decrease of a certain particulate amount to an equal increase of soluble amount, the absolute value rates of G_1 and G_2 should be the same. Differentiating the terms and calculating the temperature at which the rate is zero, yields:

$$dG_1/dT = 0.464 + 0.0012T; dG_1/dT = 0 @ T = -387^\circ C \quad (6-8)$$

$$dG_2/dT = -0.355 + 0.0015T; dG_2/dT = 0 @ T = +237^\circ C \quad (6-9)$$

Since the second derivatives of G_1 and G_2 are positive, the associated temperatures at which the first derivatives diminish are where the minimum G s occur. In addition, G_1 is minimum at $T=-387^\circ C$ and G_2 is minimum at $T=+237^\circ C$. For a one-to-one conversion, G_1 should be at maximum where G_2 is at minimum. The results, that both G_1 and G_2 have only minimums which occur at different temperatures, indicate that there is not a one-to-one conversion and that G_1 increases at a faster rate than G_2 decreases. This is shown on Figure 6-10, where the rates dG_1/dT and $-dG_2/dT$ are plotted over the tested temperature range. Therefore, the above results demonstrate that (1) the slowly degraded organic matter is converted into rapidly degraded organic matter, and (2) organic matter that was not degraded before thermal conditioning is converted into degradable organic matter, as indicated by the increase of G_1 at a faster rate than the decrease of G_2 . This is also shown on Figure 6-9 where the ultimate SGP ($G_1 + G_2$) increases with increasing temperatures. For a one-to-one conversion, the ultimate SGP should remain constant. It is the conversion of the nondegradable organic substances that improves the ultimate biodegradability of PDS after RTC.

FIGURE 6-10

dG1/dT AND dG2/dT vs TEMPERATURE
WI - Series 1 (Unmodified pH)

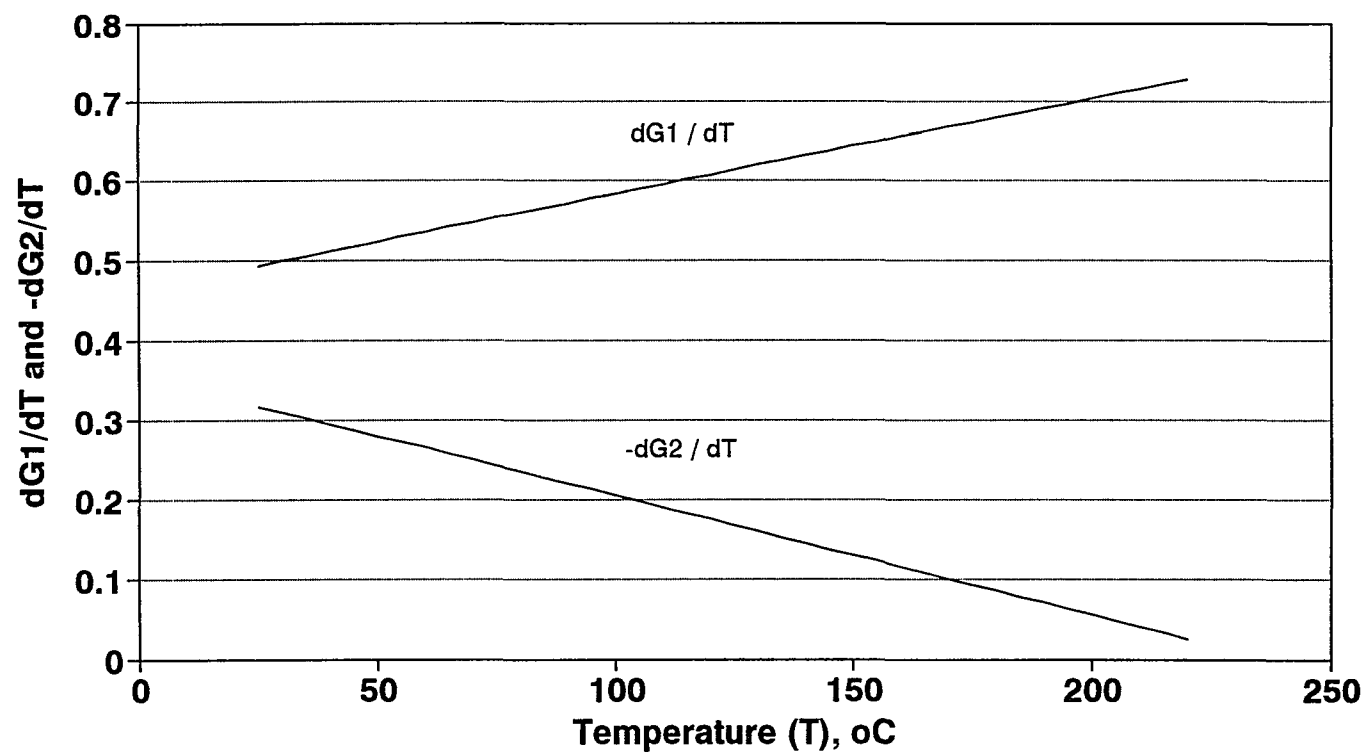


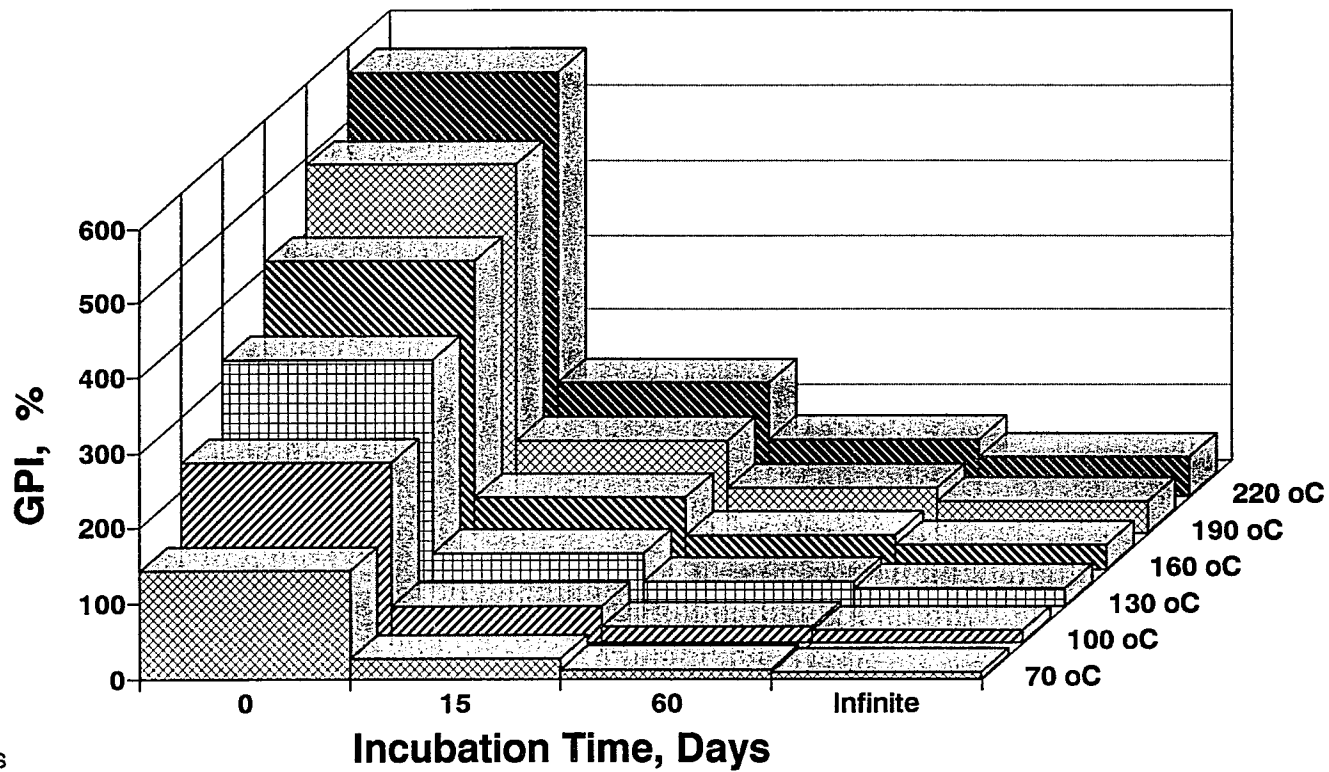
Figure 6-11 summarizes the GPI results that were calculated by the second-degree polynomials, and clearly shows the ultimate biodegradability improvement and the kinetics improvement. GPI values start with maximum values at time $t=0$ and then drop exponentially to asymptotic values. The highest GPI values at the beginning of the incubation period clearly represent the improvement to the ultimate biodegradation. The higher the conditioning temperature the greater the kinetics improvement and the greater the ultimate biodegradation. As much as 50% of additional biodegradation could be obtained from PDS thermally conditioned at 220°C, resulting in additional methane production and less sludge for disposal. In addition, the kinetic rates improvement indicates that biodegradation could take place in shorter time periods than the 15 days to 20 days currently used by conventional anaerobic digesters.

Solids and COD solubilization occurred throughout the PDS conditioning as the data of Table 6-6 demonstrates. Figure 6-12 presents COD solubilization results, where the higher the temperature the greater the solubilization. At 220°C COD solubilization ranged from 9% to 21% with an average of 13%, compared to the untreated (25°C) of 3.4%, an increase of 280%. COD solubilization was fitted with a second-degree polynomial equation, resulting to:

$$SCOD/TCOD (\%) = 3.5 - 0.011 T + 2.53 E-4 T^2 \quad (6-10)$$

where SCOD and TCOD represent the soluble and total COD, respectively, in mg/L.

FIGURE 6-11
GAS PRODUCTION IMPROVEMENT
SERIES 1 (UNMODIFIED pH)



GPIU-S

TABLE 6-6

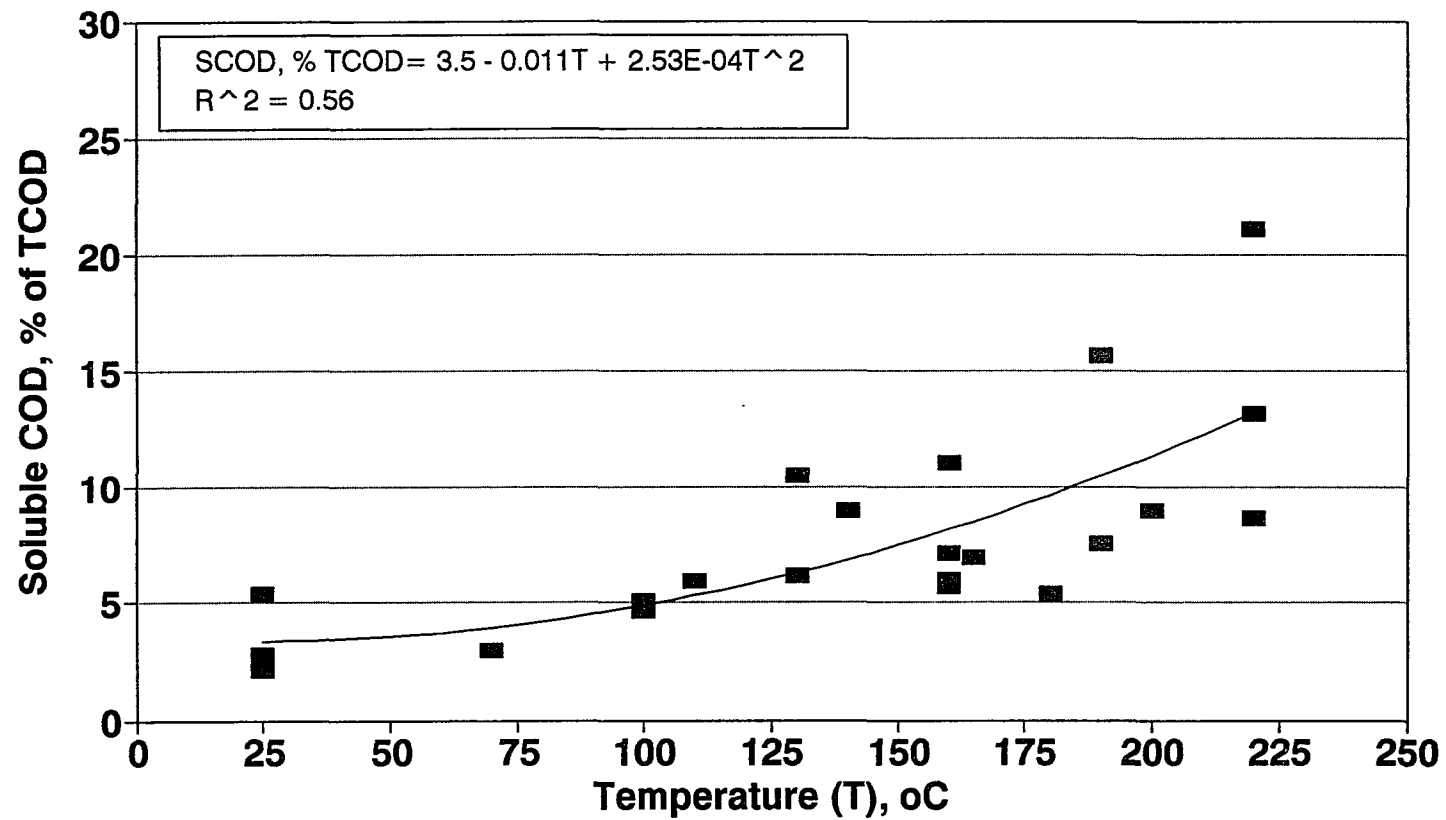
SOLIDS AND COD SOLUBILIZATION RESULTS FOR SERIES 1 (UNMODIFIED pH), WARDS ISLAND

Test Date	Temp. T (°C)	TS (%)	TVS % of TS	DS (%)	VDS % of DS	VDS (%)	DS/TS (%)	DVS/TVS (%)	TCOD (mg/L)	SCOD (mg/L)	SCOD/ TCOD (%)
July 3, 1991	25	2.00	64.2	0.28	53.4	0.15	0.14	11.6	18,025	500	2.8
	110	2.03	65.1	0.440	69.5	0.31	0.22	23.1	17,093	1,019	6.0
	140	1.85	65.5	0.460	74.2	0.34	0.25	28.2	16,154	1,452	9.0
	165	1.88	65.7	0.630	77.3	0.49	0.34	39.4	18,546	1,293	7.0
	180	1.75	65.7	0.6	79.9	0.50	0.36	43.8	16,531	894	5.4
	200	1.67	65.4	0.680	78.0	0.53	0.41	48.6	13,954	1,250	9.0
	220	1.87	66.5	0.950	78.0	0.74	0.51	59.6	16,072	1,394	8.7
Sept. 17, 1991	25	2.01	68.3	0.14	22.6	0.03	0.07	2.3	19,800	550	2.8
	160	1.88	68.4	0.28	64.1	0.18	0.15	14.0	20,395	1,159	5.7
Jan 15, 1992	25	2	69.5	0.245	46.9	0.11	0.12	8.3	25,770	1,390	5.4
	160	2.09	69.9	0.785	79.3	0.62	0.38	42.6	27,910	2,000	7.2
	220	2.05	70.6	1.04	83.5	0.87	0.51	60.0	24,870	3,270	13.1
Feb 5, 1992	70	2.2	69.8	0.398	66.4	0.26	0.18	17.2	31,770	944	3.0
	100	2.2	70.5	0.439	72.5	0.32	0.20	20.5	31,830	1,480	4.6
	130	2.2	70.1	0.563	77.9	0.44	0.26	28.4	33,560	2,070	6.2
	160	2.2	70.4	0.658	81	0.53	0.30	34.4	32,980	1,970	6.0
	190	2.2	70.4	0.967	84	0.81	0.44	52.4	33,210	2,510	7.6
Nov 18, 1992	25	2.12	64.8	0.25	43.4	0.11	0.12	7.9	35,440	740	2.1
	100	1.88	65.6	0.34	37	0.13	0.18	10.2	32,460	1,650	5.1
	130	1.65	65.2	0.38	69.7	0.26	0.23	24.6	29,460	3,100	10.5
	160	1.57	66.11	0.48	76.6	0.37	0.31	35.4	26,240	2,900	11.1
	190	1.49	65.4	0.63	75.4	0.48	0.42	48.7	24,960	3,905	15.6
	220	1.32	66.8	0.71	73.2	0.52	0.54	58.9	20,900	4,405	21.1

FIGURE 6-12

COD SOLUBILIZATION vs TEMPERATURE

Unmodified pH; Wards Island



SOLUB'N.WQI/COD-Best

Similar to COD, comparable results are obtained for volatile solids solubilization, presented on Figure 6-13. Solids data is not as scattered as COD, resulting to a better 2nd-degree polynomial fit with a correlation of 0.9:

$$DVS/TVS (\%) = 7.8 - 0.016T + 11.5E-4T^2 \quad (6-11)$$

Soluble solids increased from 8.1% (25°C) to 60% (220°C), an increase of 640%. Therefore, RTC greatly affected solids solubilization, especially their volatile portion. These results are reinforced in Figure 6-14, where the total solids distribution is shown. Only marginal fixed solids solubilization took place at the high temperatures.

(b) Series 2 - Modified pH

The Series 2 experiments refer to the thermochemical hydrolysis process where the PDS pH is adjusted to acidic or basic conditions by adding HCl or NaOH, respectively. PDS pH was modified in the sludge storage tank before the beginning of each experiment.

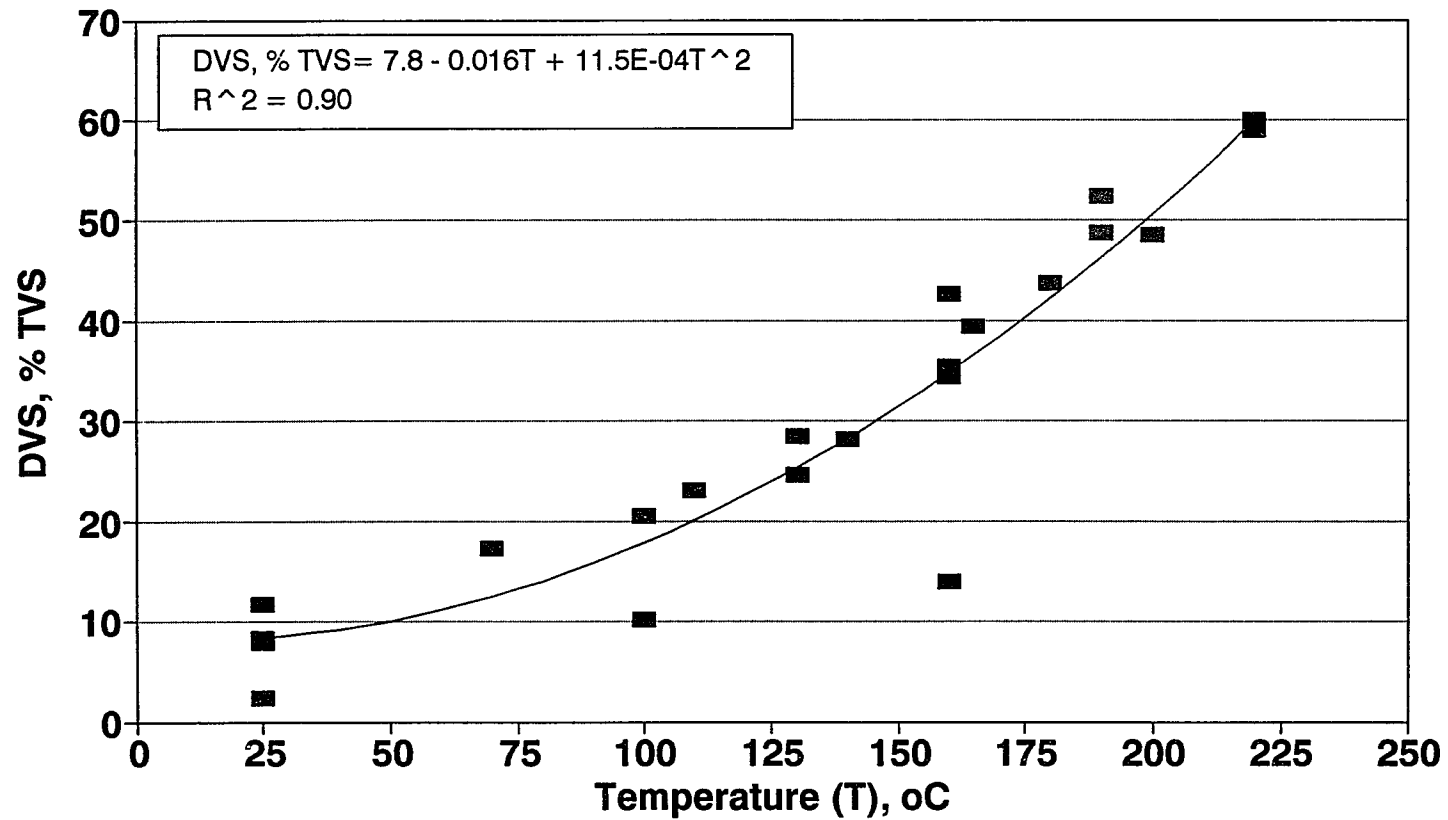
I. Wards Island Results

Table 6-7 presents Wards Island SGP results ranging from pH1 to pH12. All SGPs, except July 18 and 25, 1991, were based on substrate COD. Because of inaccurate COD

FIGURE 6-13

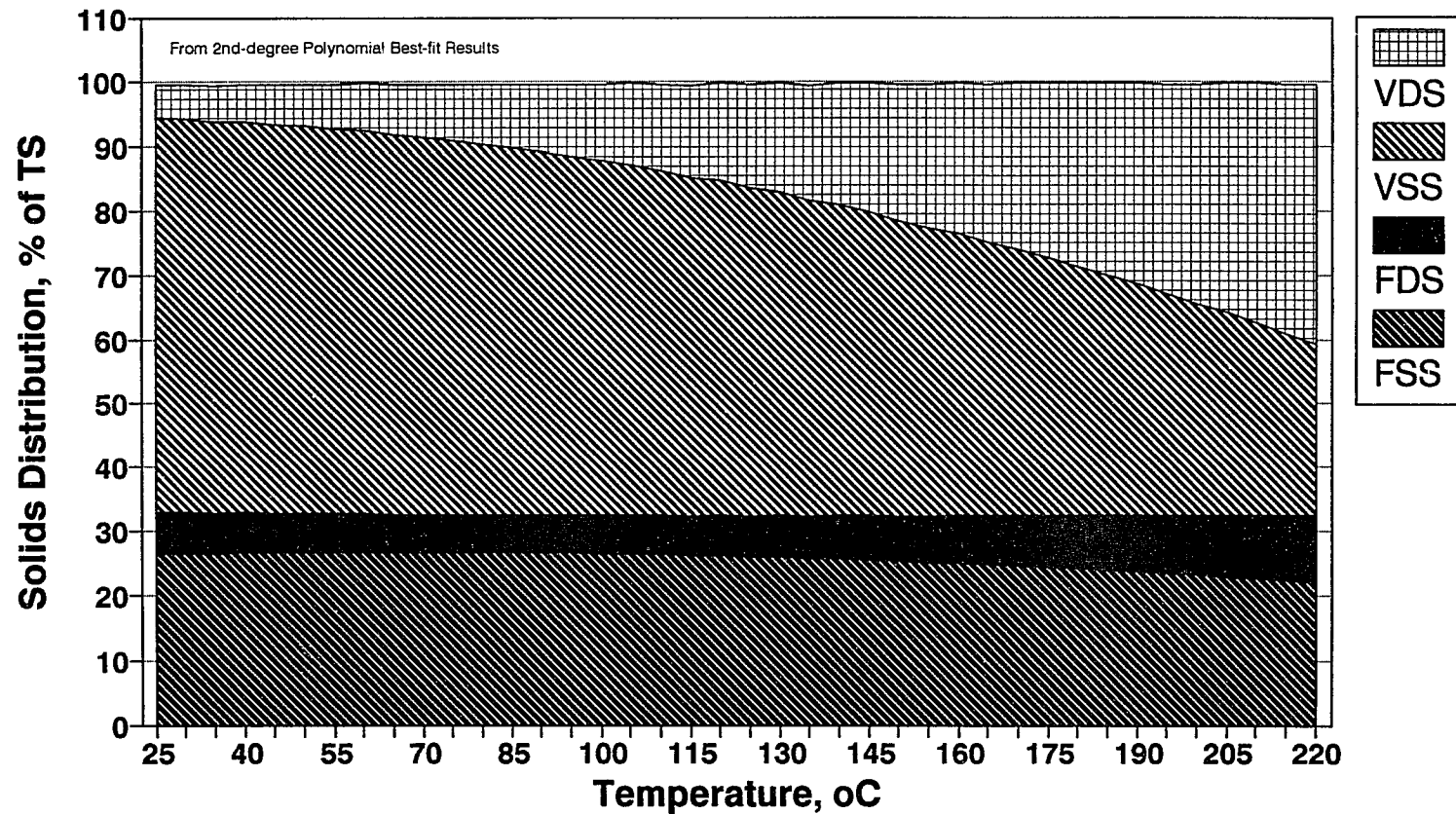
DVS SOLUBILIZATION vs TEMPERATURE

Unmodified pH; Wards Island



SOLUB'N WQI/COD-Best

FIGURE 6-14
SOLIDS DISTRIBUTION FOR SERIES 1
Unmodified pH Conditions - Wards Island



SOLUB/N/SOLIDS

TABLE 6-7

SPECIFIC GAS PRODUCTION (SGP) KINETIC RESULTS, SERIES 2 (MODIFIED pH), WARDS ISLAND

Date	pH	RTC Temperature (°C)	SGP Coefficients				G ₁ + G ₂ (mL/g)	G ₁ k ₁ + G ₂ k ₂ (mL/g-d)
			G ₁ (mL/g)	G ₂ (mL/g)	k ₁ (1/d)	k ₂ (1/d)		
July 18, 1991	7.5	25 (Raw)	0.604	2.19	0.498	0.0293	2.8	0.36
		100	1.92	1.2	0.509	0.0327	3.1	1.0
		160	2.45	3.56	1.26	0.0422	6.0	3.2
		220	2.99	2.14	0.992	0.357	5.1	3.0
	8	100	1.66	1.86	1.19	0.0249	4.0	1.2
		160	2.93	1.84	0.967	0.0379	3.8	1.8
		220	3.18	1.30	1.11	0.0388	5.1	2.1
	9	100	2.46	1.57	0.466	0.00784	3.5	2.0
		160	2.53	1.27	0.724	0.00752	4.8	2.9
		220	4.42	0.639	0.465	0.0163	4.5	3.6
July 25, 1991	7.5	25 (Raw)	0.356	1.05	0.578	0.0256	1.4	0.23
		100	1.89	3.1	0.585	0.0279	5.0	1.2
		160	4.02	6.76	0.775	0.0256	11.0	3.3
		220	4.58	6.85	0.997	0.0302	11.0	4.8
	6	100	3.07	7.31	0.626	0.0264	10.0	2.1
		160	3.66	7.58	0.751	0.0323	11.0	3.0
		220	3.92	7.46	1.01	0.0312	11.0	4.2
	4	100	3.09	8.1	0.648	0.0299	11.0	2.2
		160	2.89	8.64	0.927	0.0323	12.0	3.0
		220	4.17	7.71	1.022	0.0308	12.0	4.5
Sept. 17, 1991	7.5	25 (Raw)	37.6	127.2	0.546	0.0308	165.0	24.0
		160	87.4	115.1	1.191	0.132	202.0	119.0
		220	209.0	90.4	0.869	0.0497	299.0	186.0
	2	25	120.0	118.0	0.858	0.0308	238.0	106.0
		160	145.0	78.3	1.14	0.0565	223.0	170.0
		220	222.0	53.1	1.06	0.0568	275.0	238.0

Table 6-7 Continued . . .

Date	pH	RTC Temperature (°C)	SGP Coefficients				$G_1 + G_2$ (mL/g)	$G_1 k_1 + G_2 k_2$ (mL/g-d)
			G_1 (mL/g)	G_2 (mL/g)	k_1 (1/d)	k_2 (1/d)		
Jan. 15, 1992	7.5	25 (Raw)	61.1	134.0	0.564	0.0287	195.0	38.0
		160	144.0	81.0	1.01	0.0272	225.0	148.0
		220	189.0	49.8	0.927	0.0404	238.0	177.0
	3	25	44.2	79.5	0.854	0.0366	124.0	40.0
		160	136.0	72.5	0.974	0.0450	209.0	136.0
		220	164.0	96.5	1.22	0.0498	260.0	205.0
	1	25	56.2	10.7	0.250	0.00991	67.0	14.0
		160	119.0	5.31	1.18	0.0983	125.0	141.0
		220	158.0	81.9	1.24	0.0576	240.0	201.0
Feb. 5, 1992	7.5	25 (Raw)	48.5	115.0	0.617	0.0366	164.0	34.0
		160	124.0	90.0	1.28	0.0266	214.0	161.0
		220	137.0	92.5	1.05	0.0379	230.0	148.0
	12	25	94.9	81.7	1.14	0.0433	177.0	112.0
		160	144.0	78.9	0.951	0.0439	223.0	141.0
		220	97.7	0.0	0.705	--	97.7	69.0
Sept. 23, 1992	7.5	25 (Raw)	23.6	88.3	0.266	0.0247	112.0	8.0
		220	162.0	69.7	0.642	0.0259	231.0	105.0
	12	25	124.0	109.0	0.877	0.0407	233.0	113.0
		110	141.0	93.6	0.716	0.0395	234.0	105.0
		130	130.0	77.5	0.738	0.0437	208.0	99.0
		160	143.0	77.0	0.558	0.0362	220.0	83.0
		190	141.0	85.0	0.557	0.0391	226.0	82.0

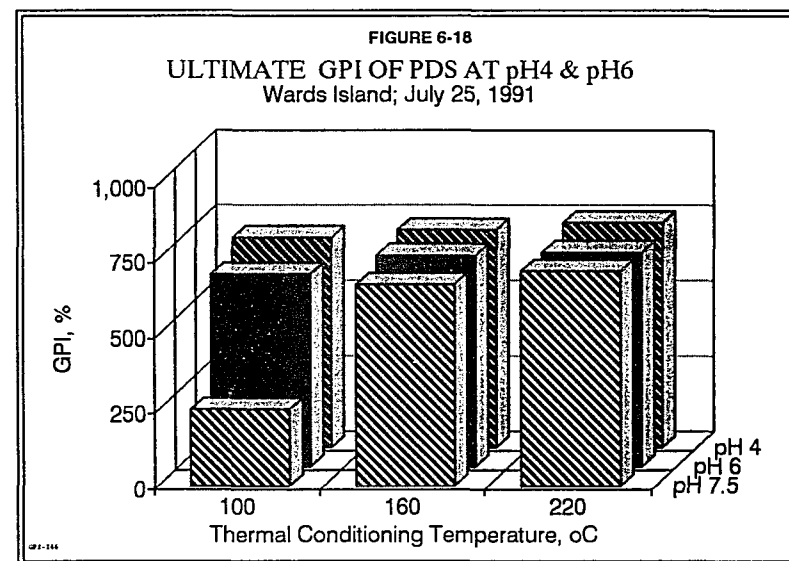
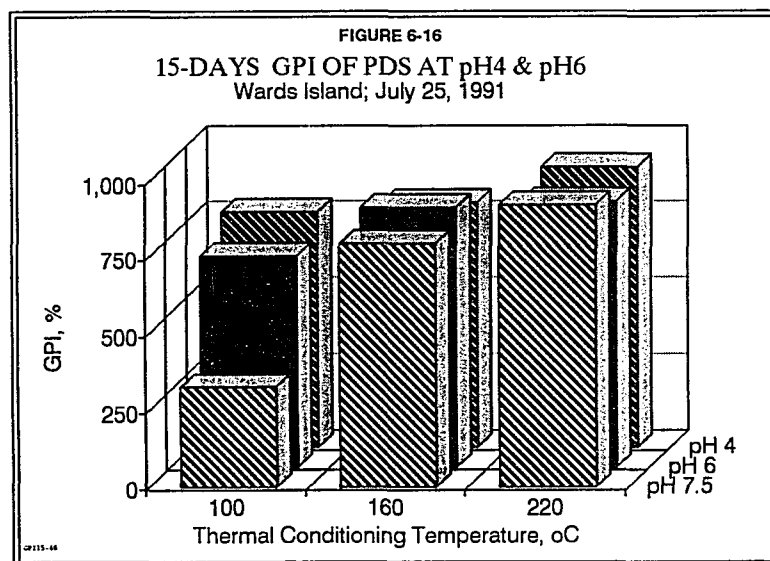
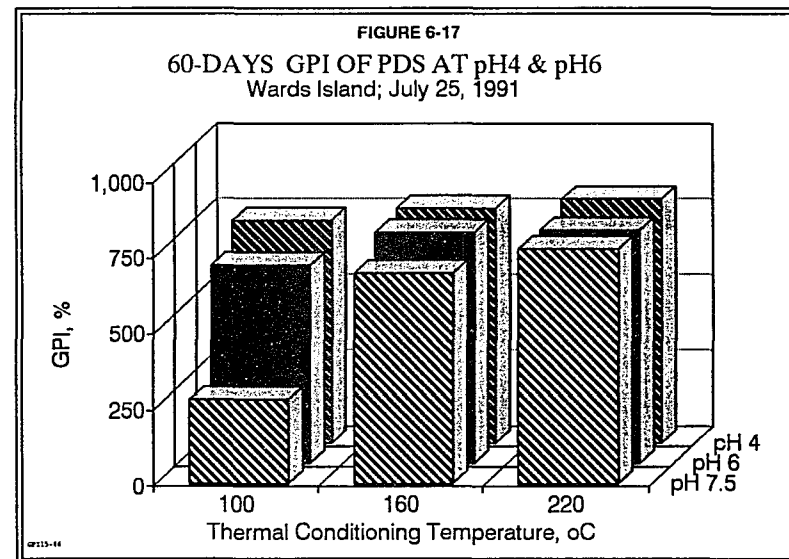
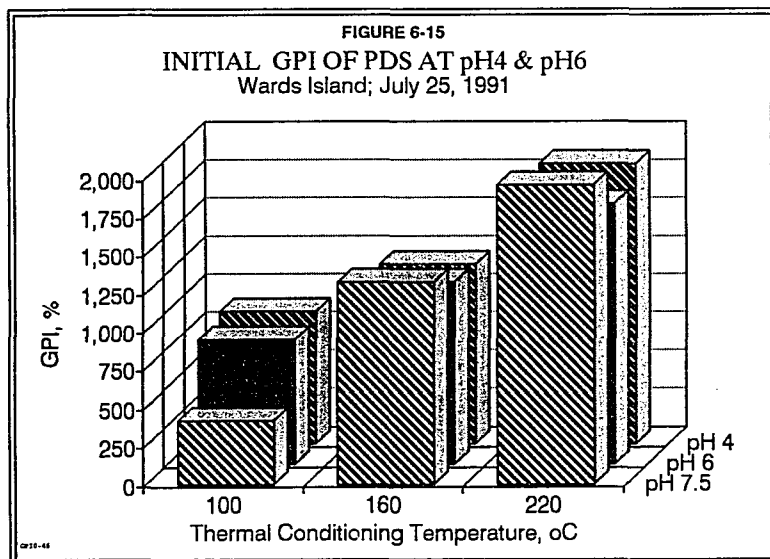
NOTES:

1. $SGP = G_1(1 - \exp(-k_1 t)) + G_2(1 - \exp(-k_2 t))$
2. July 18 and 25, 1991 were based on feed volume, thus G_1 and G_2 are in mL/mL

measurements, the July 1991 results were based on feed volume and are represented as mL gas/mL feed. However, GPI results are not affected by the basis of calculating SGP.

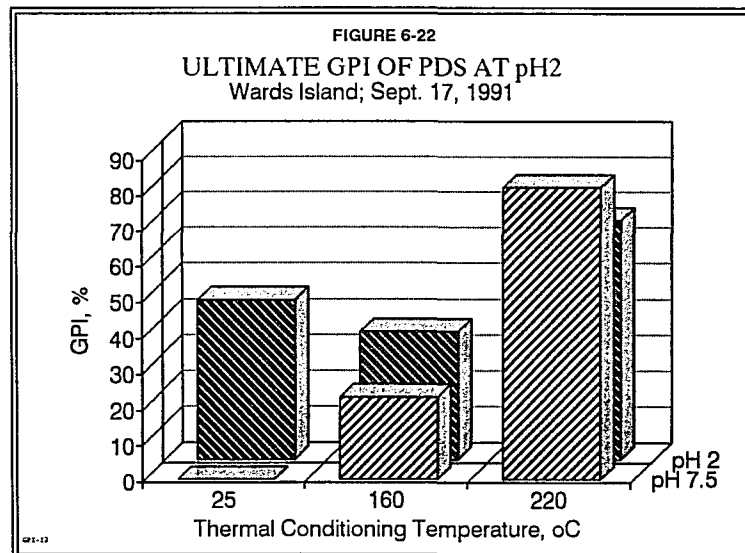
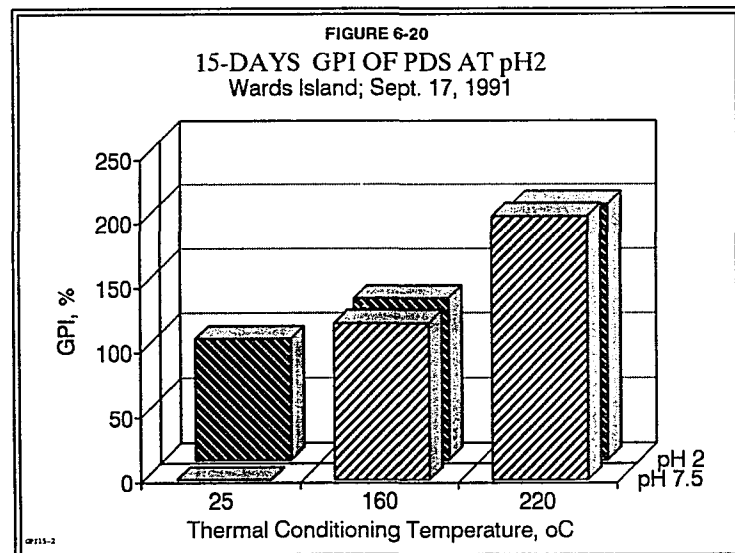
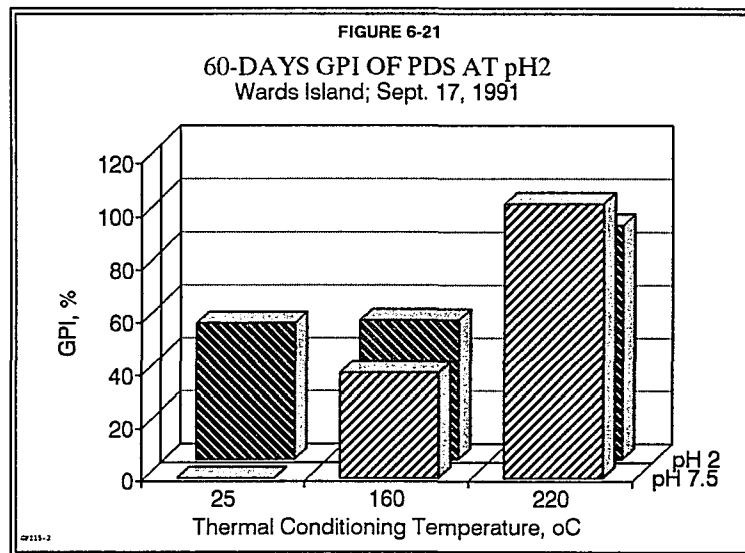
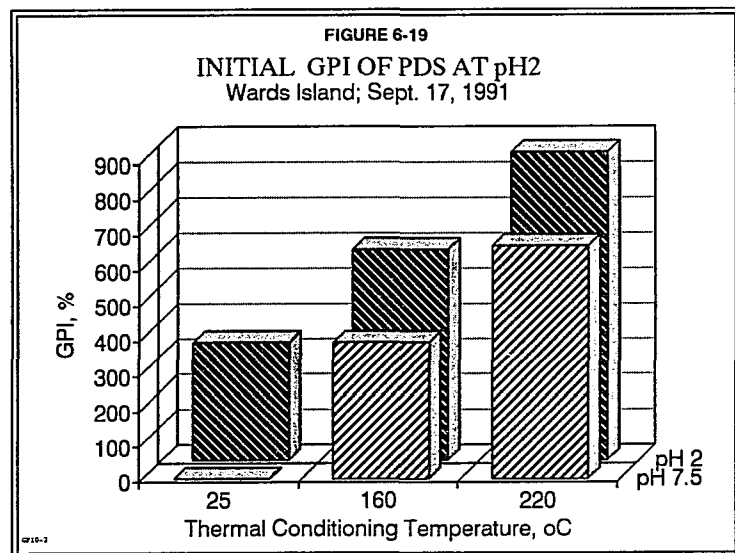
i. Acidic Conditions (pH1, pH2, pH3, pH4, pH6)

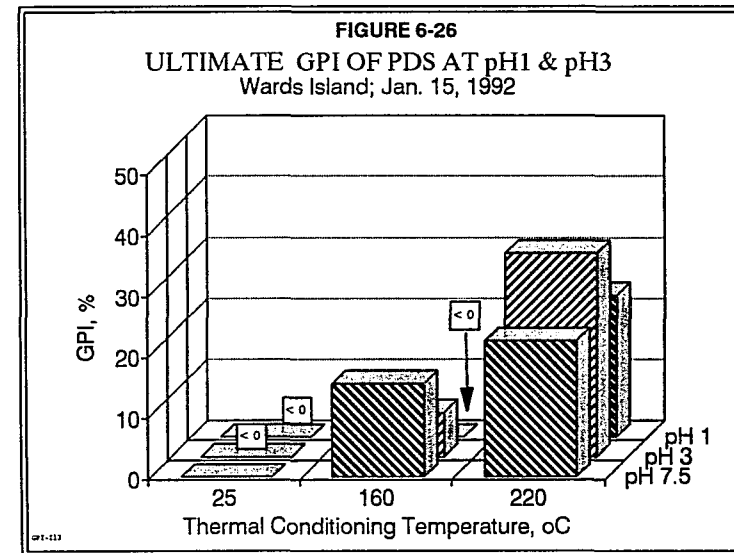
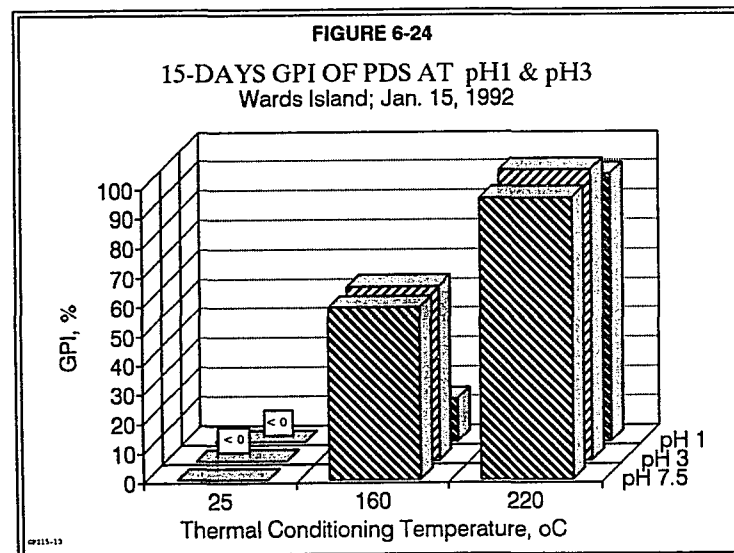
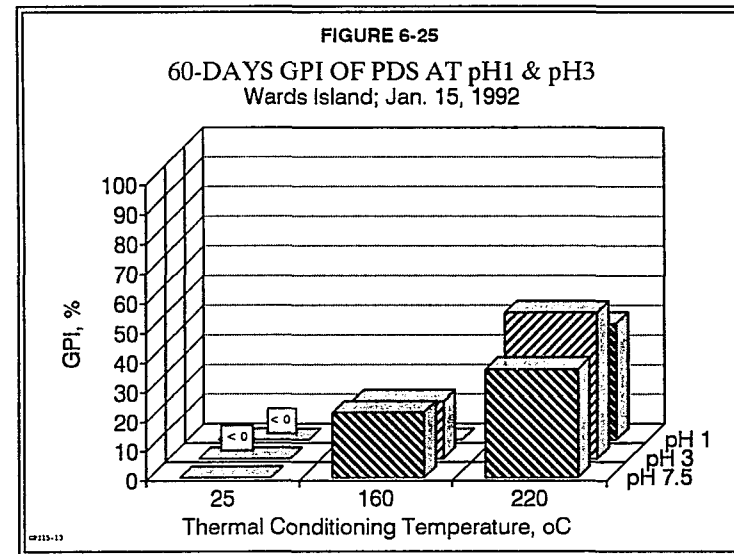
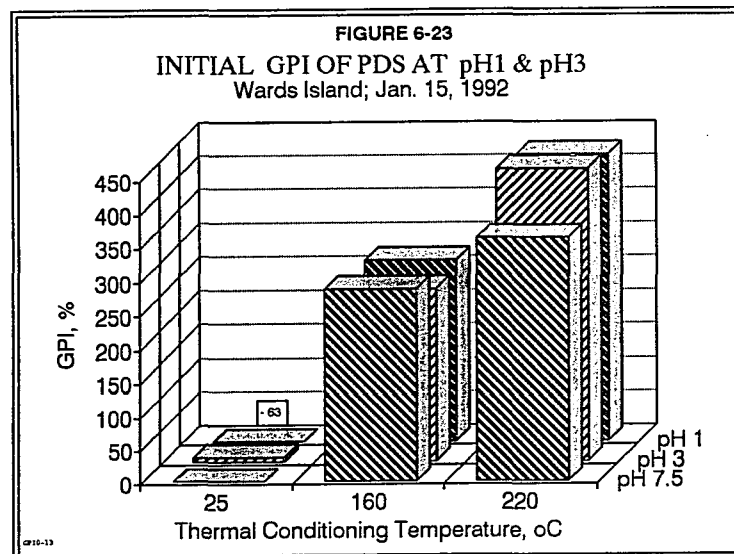
July 25, 1991 - pH4 and pH6: PDS collected on July 24, 1991 was adjusted to pH4 and pH6 using hydrochloric acid. The pH adjustment, RTC, and anaerobic digestion were performed on July 25. RTC was performed at 100°C, 160°C, and 220°C. Because of inaccurate COD measurements, SGP calculations were based on the feed volume used in the serum bottles for digestion. Since the SGP of the unmodified PDS was also based on PDS volume, the GPI values should be comparable to results that were based on substrate COD. Figures 6-15 to 6-18 present GPIs at initial, 15-days, 60-days, and infinite (ultimate) incubation times, respectively. Even though the GPI of unmodified PDS was much higher than the GPIs reported under Series 1, the July results are still comparable to each other since they were obtained from the same sample. The results show that RTC at 160 and 220°C does not increase the GPI beyond the improvement observed for the unmodified PDS. However, RTC at 100°C showed significant improvement over the unmodified PDS and at the same RTC temperature, but less than the 220°C, where GPI was maximum. After comparing the initial GPIs to the ultimate GPIs it was observed that at the high temperatures the kinetic rates increased the most. The GPI value of 1,750% at 220°C was reduced to 700% at infinite incubation time. Kinetics improvement was less significant at pH4 and pH6 for an RTC of 100°C, where the initial GPI dropped from approximately 800% to 650%.



September 17, 1991 - pH2: Based on the July 25 results, PDS collected on September 17 was adjusted to pH2. RTC, performed at 160°C and 220°C, and biodegradability were also done on September 17. During this experiment, the effect of pH alone was also evaluated by digesting the pH2 PDS before thermal conditioning. Initial, 15-days, 60-days, and ultimate GPI results are presented on Figures 6-19 to 6-22. Maximum GPI results were obtained within the first day of incubation and dropped exponentially to an asymptotic value indicating the improvement to ultimate biodegradability. The pH2 initial GPI showed higher values at all temperatures, compared to the pH-unmodified PDS. Even without thermal conditioning, the pH2 GPI results were comparable to the pH-unmodified and 160°C GPI results. After 15-days incubation, both GPI results (pH2 and pH-unmodified) at 160°C and 220°C were comparable, indicating that pH2 did not improve further the PDS biodegradability. However, the pH alone (without thermal conditioning) improved biodegradability significantly and is comparable to the pH-unmodified, 160°C PDS. The 60-days and ultimate GPI results (Figures 6-21 and 6-22) showed similar trends to the 15-days results. Therefore, the effect of pH adjustment prior to thermal conditioning appears to be significant at the lower temperatures and insignificant at the higher temperatures. Or, the same GPI can be achieved at lower RTC temperatures if the PDS is acidified prior to thermal conditioning.

January 15, 1992 - pH3 and pH1: Acidic conditions were evaluated again on January 15, 1992. PDS was adjusted to pH1 and pH3. Initial, 15-days, 60-days and ultimate GPI results are presented on Figures 6-23 to 6-26. Maximum GPI was obtained within the first day of incubation and dropped exponentially to an asymptotic value indicating the improvement to

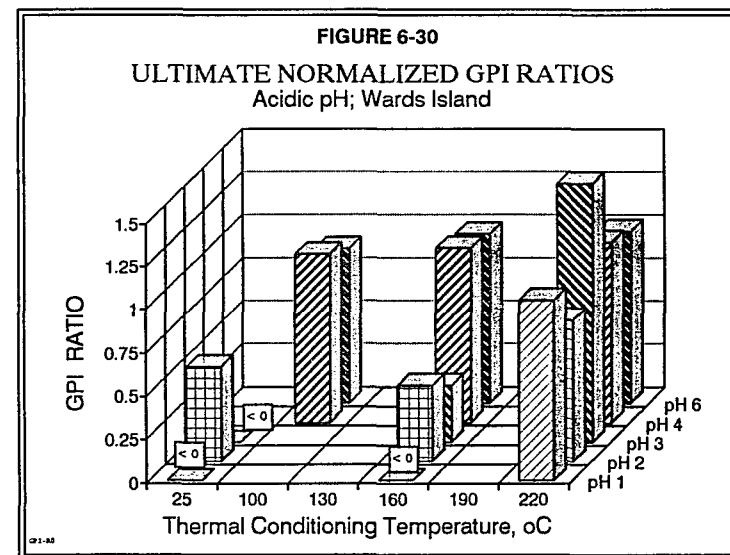
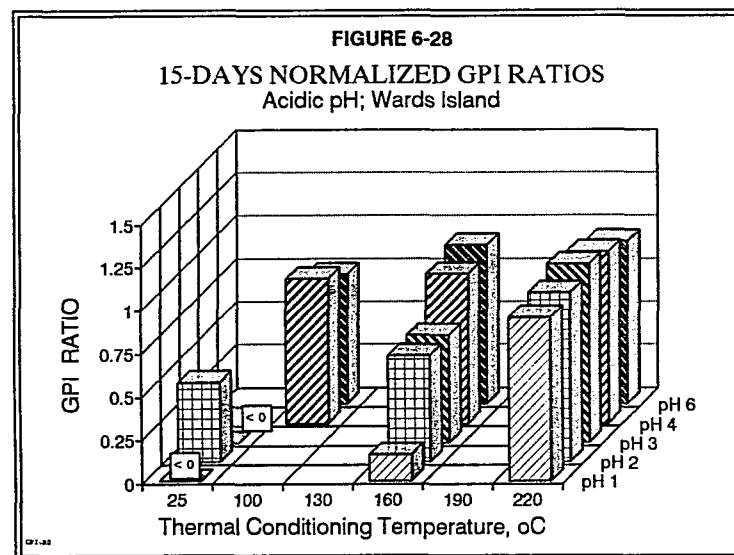
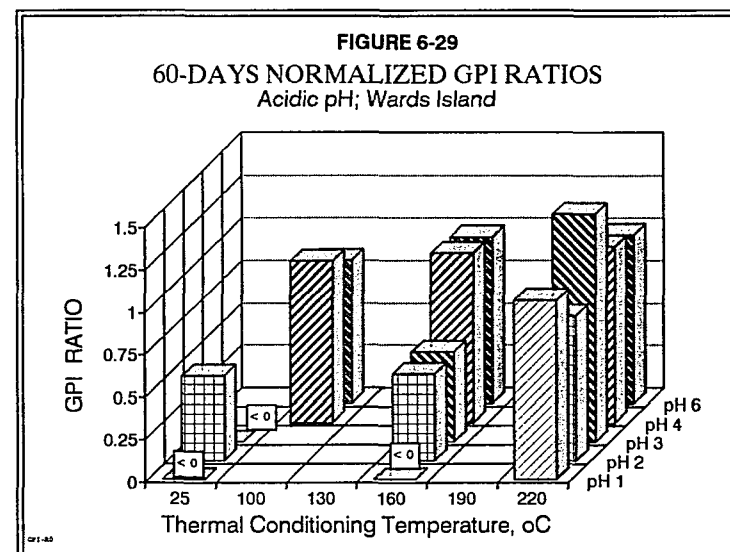
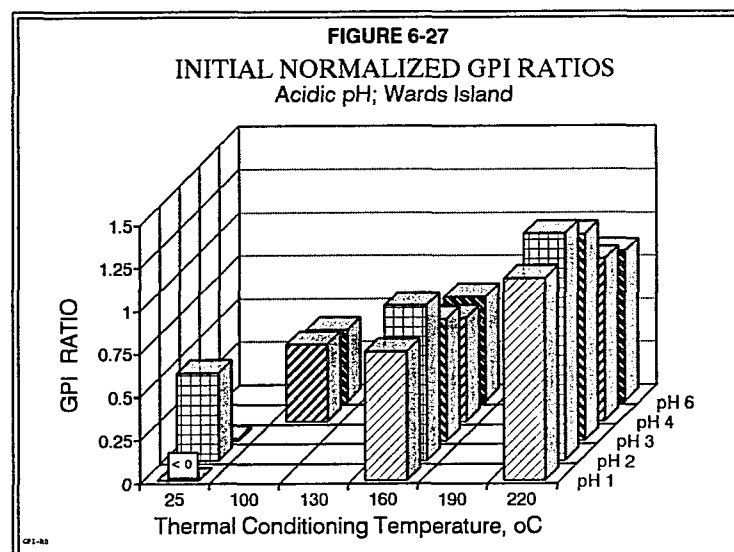




ultimate biodegradability. During this test, pH adjustment (without thermal conditioning) showed negative GPIs since the gas production of treated PDS was less than the one obtained from untreated PDS. At the higher temperatures, however, GPI was comparable and even somewhat higher than the pH-unmodified PDS results. At 220°C, pH3 PDS showed an ultimate biodegradability of 34%, compared to the unmodified PDS of 22%.

Acidic pH GPI_N Results

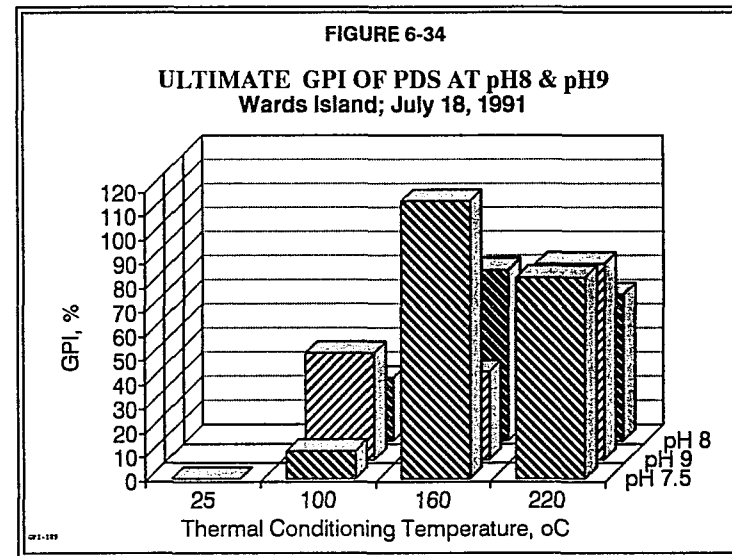
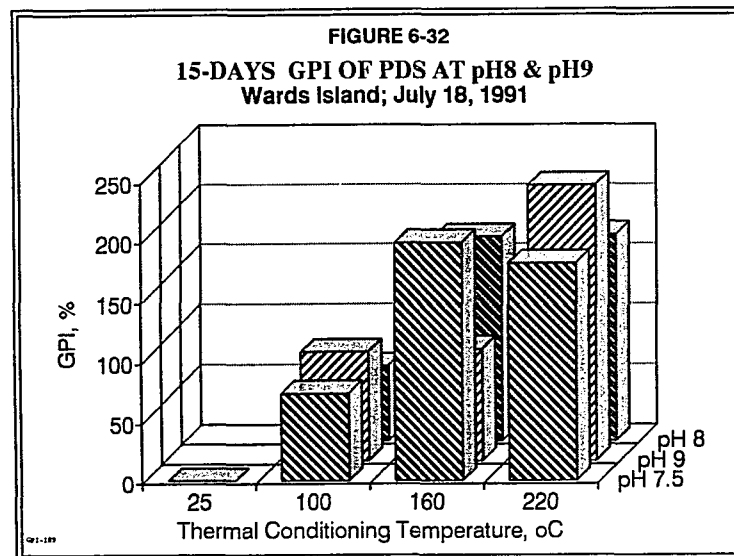
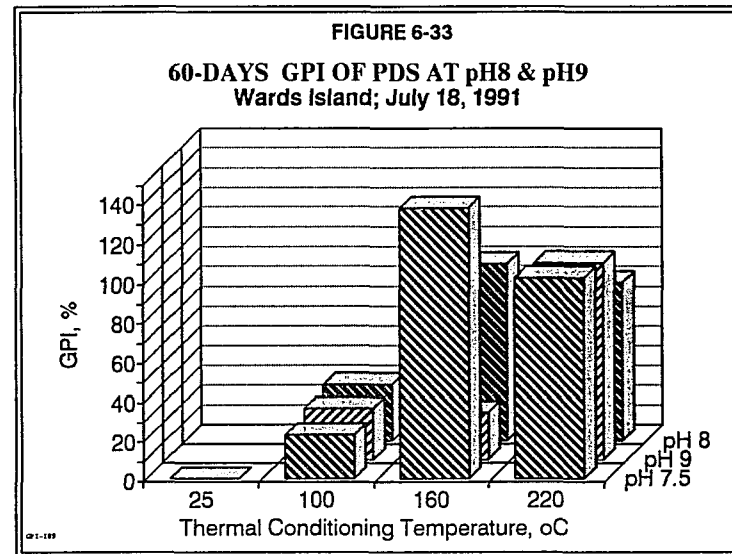
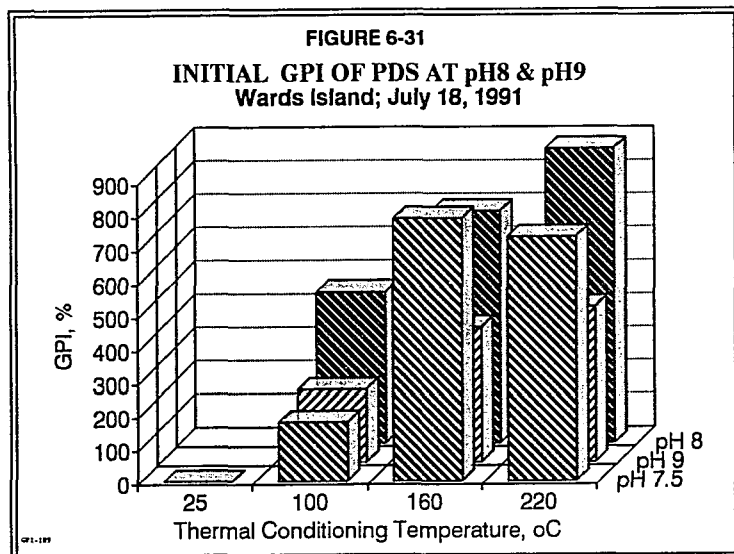
The GPI_N was then calculated so that the acidic-pH effect on PDS can be clarified. Initial, 15-days, 60-days, and ultimate GPI_N ratios are presented on Figures 6-27 to 6-30. The figures show that the GPI_N ratios are a good approach to resolve variability in data caused by sampling PDS on different days. The figures show insignificant improvement in kinetics and ultimate biodegradation if PDS is acidified prior to thermal conditioning. However, for some pH conditions (e.g., pH4 and pH6), the low pHs give GPI_N ratios near unity at lower temperatures, implying that a combination of acid and low temperatures could give the same results as higher temperatures alone. Only pH3 resulted in an ultimate ratio of 1.5 which was obtained during a test where the GPI_{U220} was a low 22%, much lower than the values obtained during Series 1. The cost of acid for lowering the pH and the base to neutralize the pH after thermal conditioning, along with mixing tanks, chemical storage tanks, well-operating pH-control systems, and the corrosive nature of low pH couple to the insignificant improvement in GPI does not warrant any further considerations. If low pH conditions could be associated with other benefits, the process may be justified.

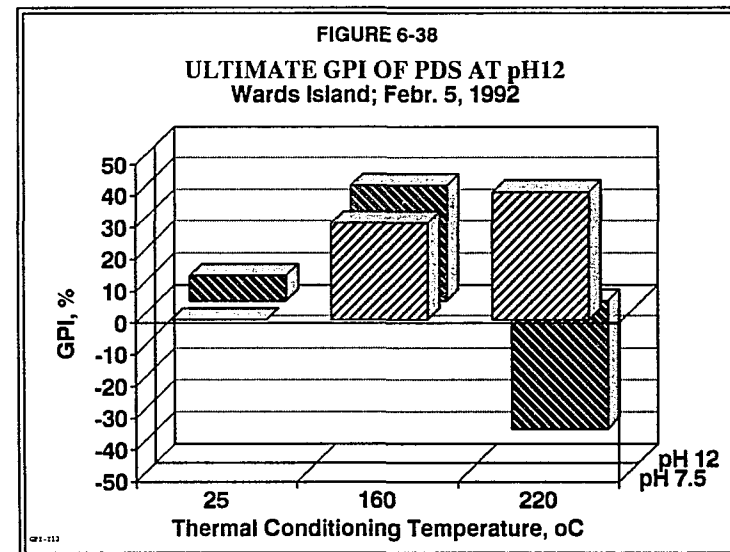
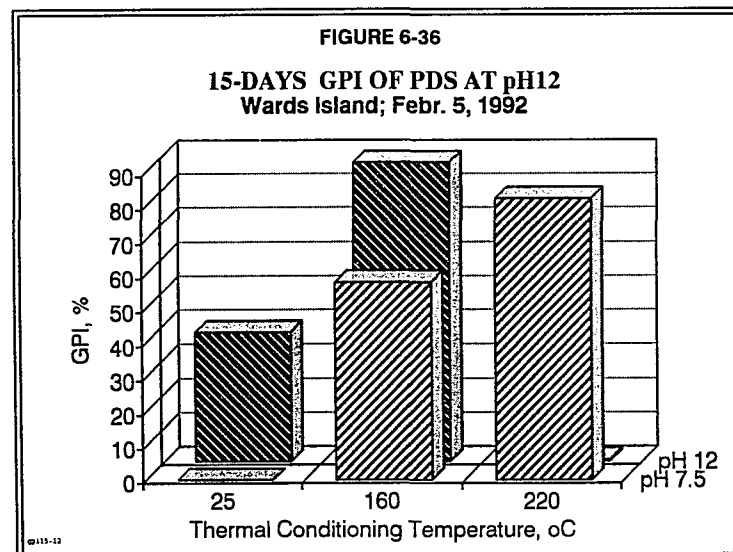
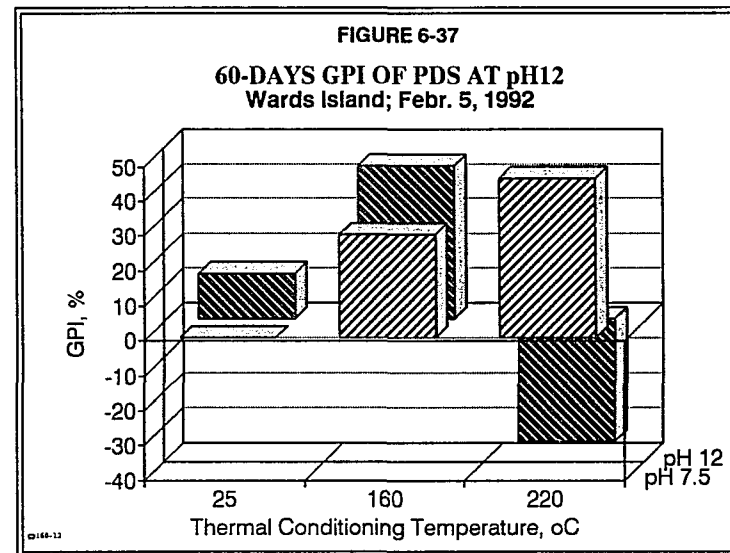
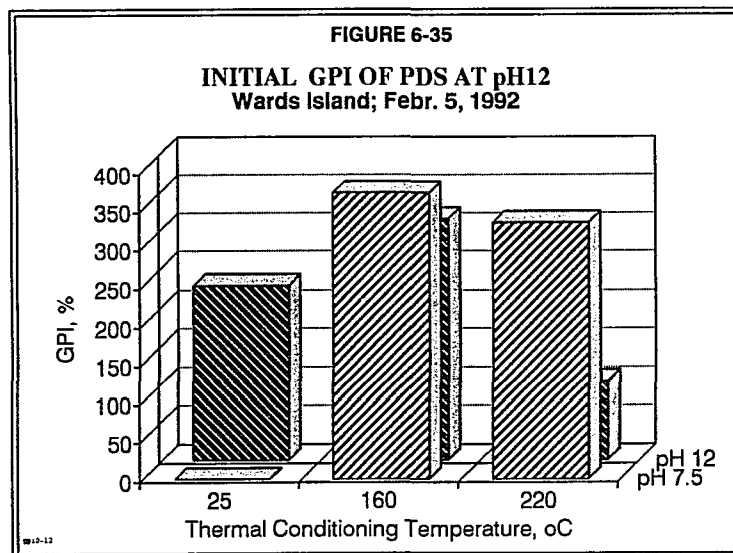


ii. Alkaline Conditions (pH8, pH9, pH12)

July 18, 1991 - pH8 and pH9: PDS collected on July 17, 1991 was adjusted to pH8 and pH9 using sodium hydroxide prior to thermal conditioning at 100°C, 160°C, and 220°C. Anaerobic digestion in serum bottles was performed on July 18. Because of inaccurate COD measurements, SGP calculations were based on the feed volume used in the serum bottles for digestion. Figures 6-31 to 6-34 present GPIs at initial, 15-days, 60-days, and infinite (ultimate) incubation time, respectively. The initial GPI results show marginal increases for pH8, compared to pH7.5. The test incubation periods at pH8 and pH9 did not show GPI increases. In some cases, the GPIs were even lower than the ones obtained at unmodified pH.

February 5 and September 23, 1992 - pH12: The last test was performed on PDS that was modified to pH12. Thermal conditioning was performed at 160°C and 220°C. In order to evaluate the effect of pH alone, the biodegradability of the pH-modified PDS without thermal conditioning was also evaluated during this experiment. Figures 6-35 to 6-38 present GPIs at initial, 15 days, 60 days and infinite (ultimate) incubation times. The results indicate that the pH alone increased the PDS biodegradability, but to a lower level than unmodified pH and 160 and 220°C. Ultimate biodegradability and kinetics improvement of PDS conditioned at 160°C and pH12 were comparable to pH-modified PDS results. However, PDS at pH12 and 220°C showed low GPI results at initial and 15 days incubation and negative results at the rest incubation times. This indicates a marginal kinetics



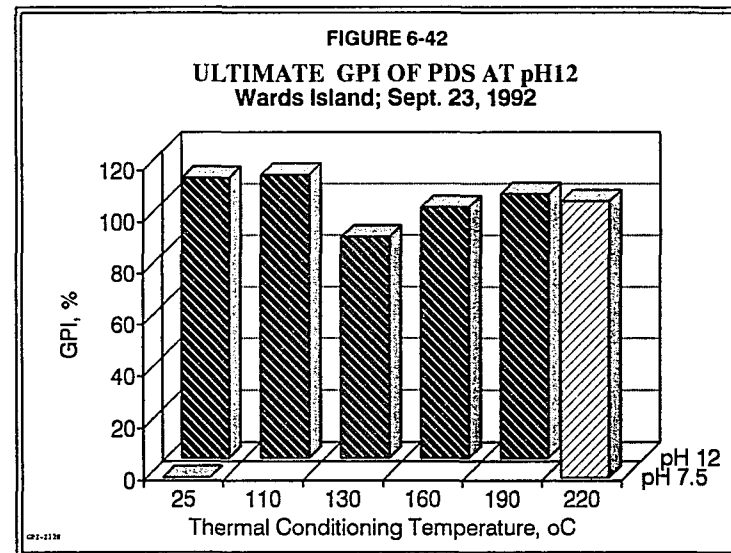
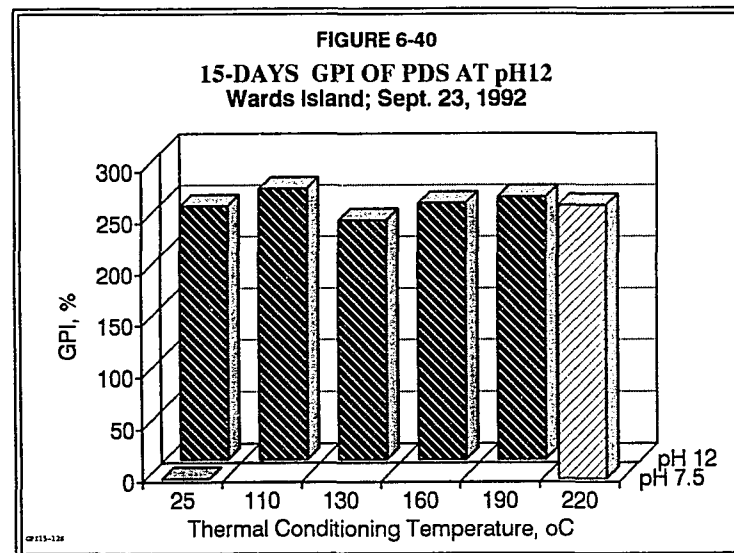
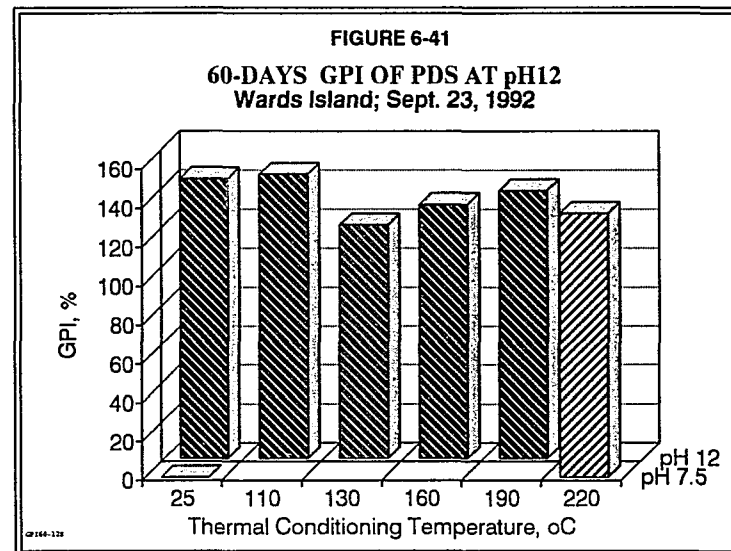
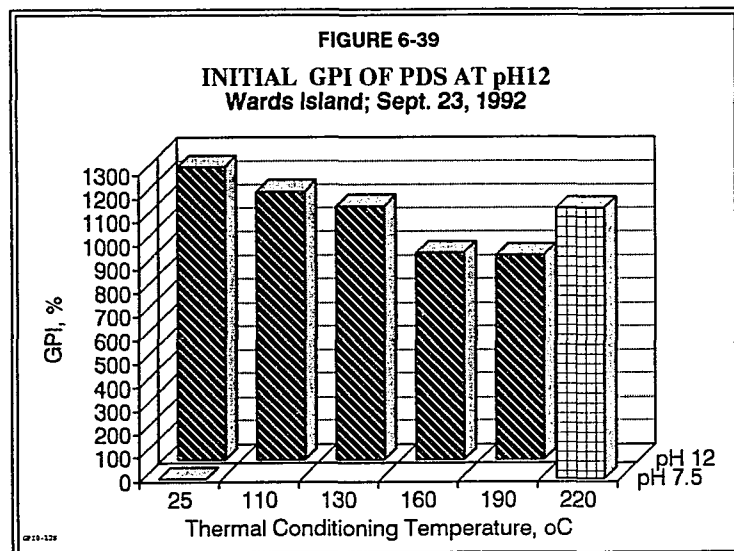


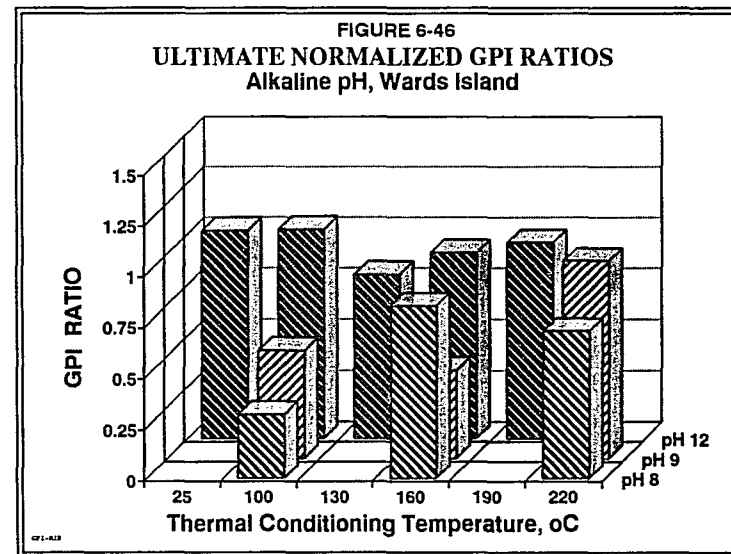
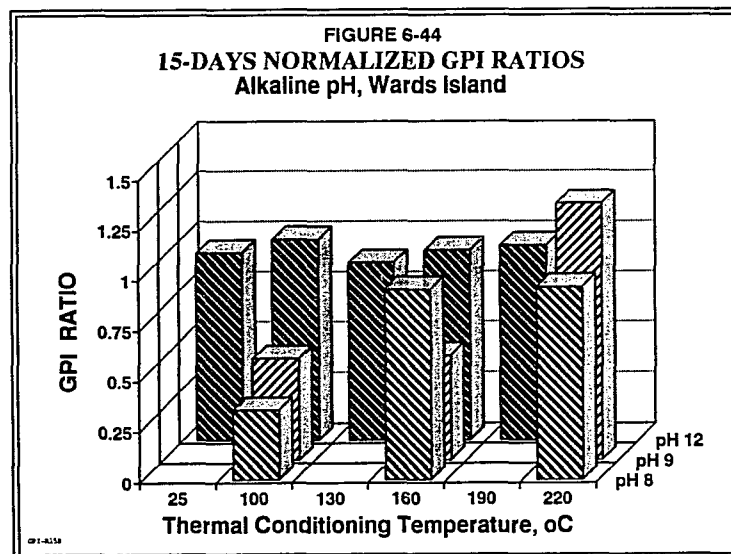
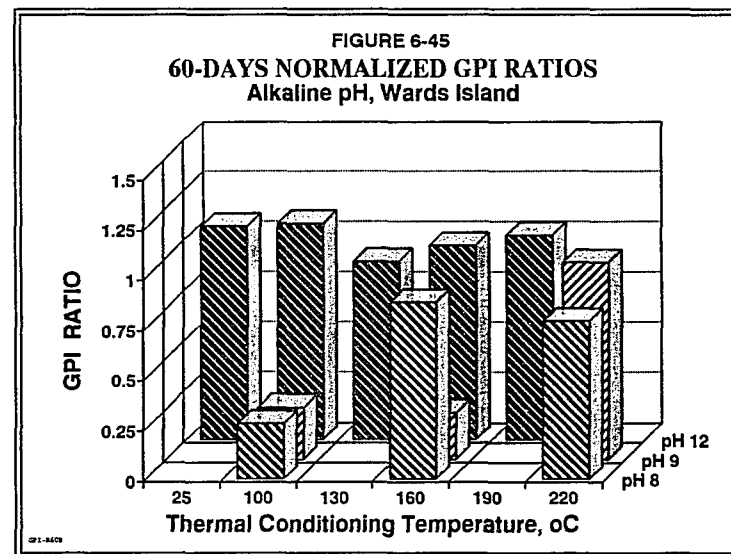
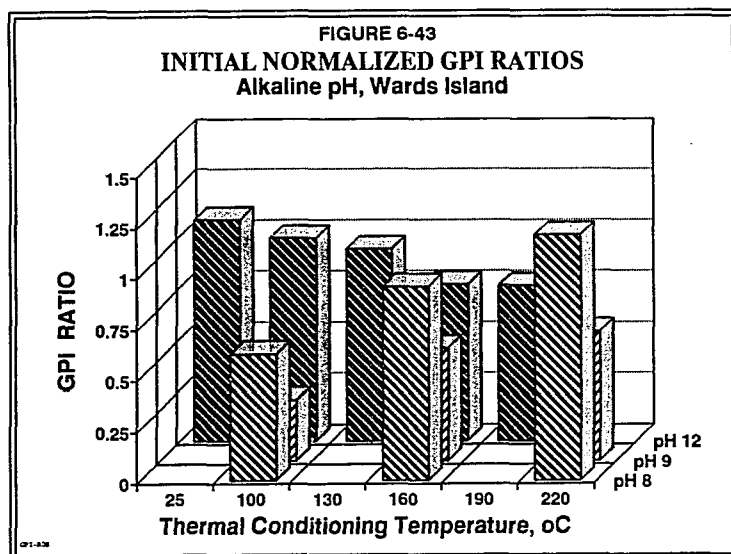
improvement (initial GPI of 230% compared to the 15 days of 40%), and a biodegradability decrease.

The same pH12 test was repeated in September 23, 1992, but RTC was performed at 110°C, 130°C, 160°C and 190°C at pH12, and at 220°C for the pH-unmodified PDS. Figures 6-39 to 6-42 present GPIs at initial, 15 days, 60 days, and infinite incubation periods. These test results, compared to the February results, exhibited high initial GPI without thermal conditioning. The initial GPI reached the value of 1,240% whereas the pH-unmodified and 220°C reached 1,150%. The GPIs at the other incubation periods and at all temperatures were similar to pH-unmodified PDS results.

Alkaline pH GPI_N Results

The GPI_N ratios were then calculated to clarify the effect of alkaline-pH. The initial, 15 days, 60 days and ultimate GPI_N ratios are presented on Figures 6-43 to 6-46. The pH12 results were obtained from the September experiment, where a broader temperature range was evaluated. Even though the GPI is affected by sludge characteristics (that vary from day to day), GPI_N is unaffected and can be used to compare conditions evaluated at different times. Results indicate that not much improvement would be obtained in kinetics and ultimate biodegradability for PDS modified at pH8 and pH9. For pH12, however, it appears that GPI_N ratios greater or closer to unity could be obtained without thermal conditioning, implying that just the high pH by itself could give improvements comparable to unmodified pH and 220°C. But the use of chemicals to raise and drop the pH, mixing tanks,





chemical storage facilities, a well-operating pH-control system, and safety concerns may restrict the alkaline-pH conditioning of PDS. If high pH conditions could be combined with some other processes, such as high pH to remove ammonia by air stripping, then the process could be justifiable.

Acidic and Alkaline Summary Results

Figures 6-47 and 6-48 present the acidic and alkaline GPI_N results at 160°C and 220°C, respectively. Results at 160°C (also presented on Figure 6-49 for clarity) provided ratios less than unity, indicating that pH-unmodified PDS and thermally conditioned at 220°C would give better GPI results. However, for some pH conditions and at the RTC temperature of 220°C, ratios were higher than unity, providing higher improvements than if pH-unmodified PDS was only thermally conditioned at 220°C. Ultimate biodegradation ratios ranged from a minimum of 0.75 (pH8) to a maximum of 1.5 (pH3). But, it may not be justifiable to modify the pH for the sole purpose of improving biodegradability. However, if the pH would be adjusted for some other objective, the PDS biodegradability would be further enhanced.

II. Newtown Creek Results

Results from Wards Island were evaluated and confirmed by performing the RTC on Newtown Creek PDS. Newtown Creek treats mostly industrial wastewater and its PDS is

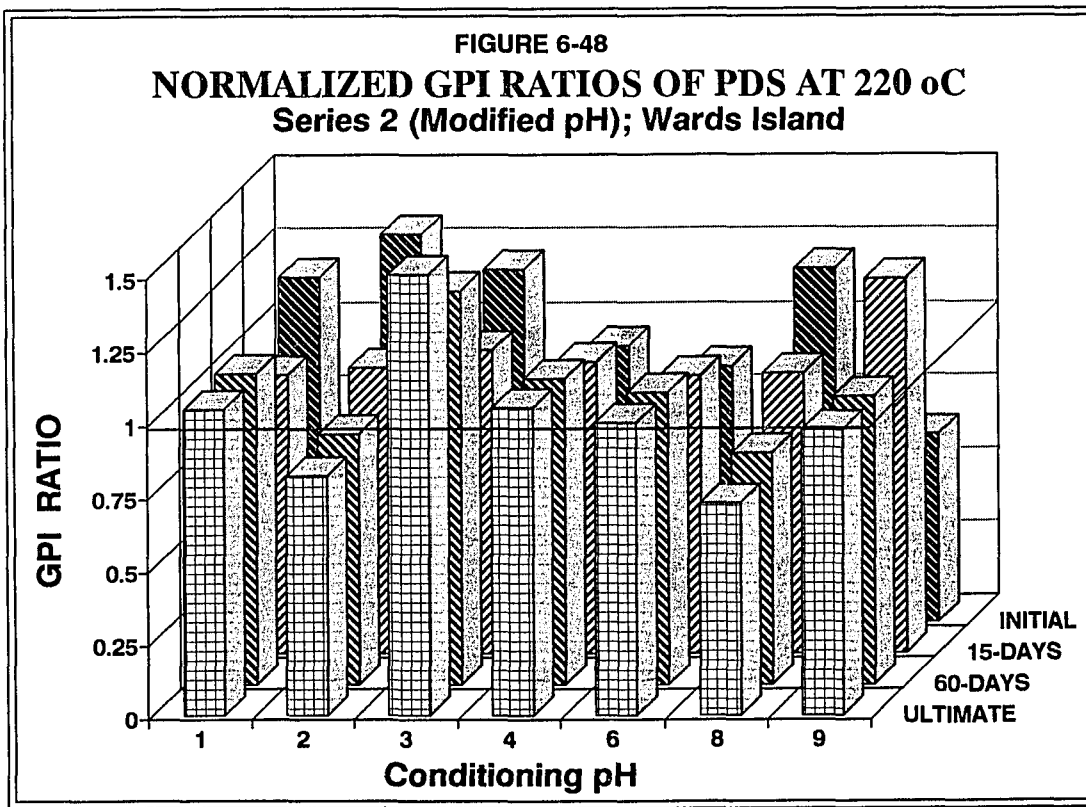
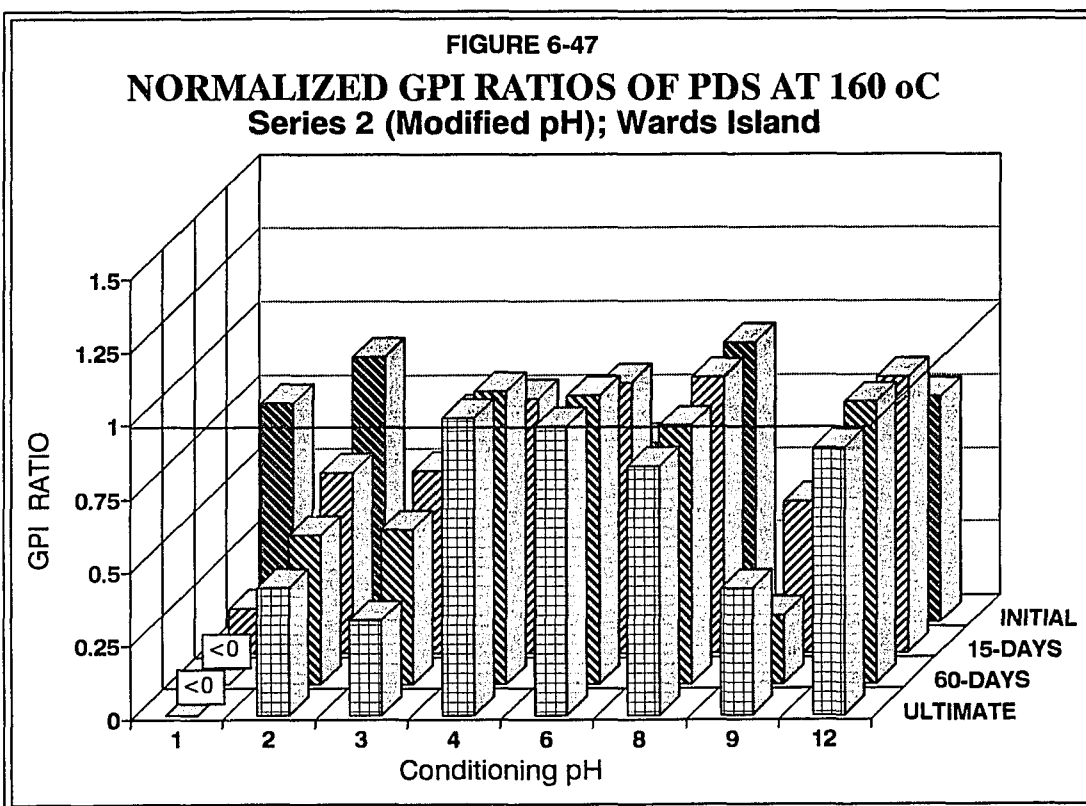
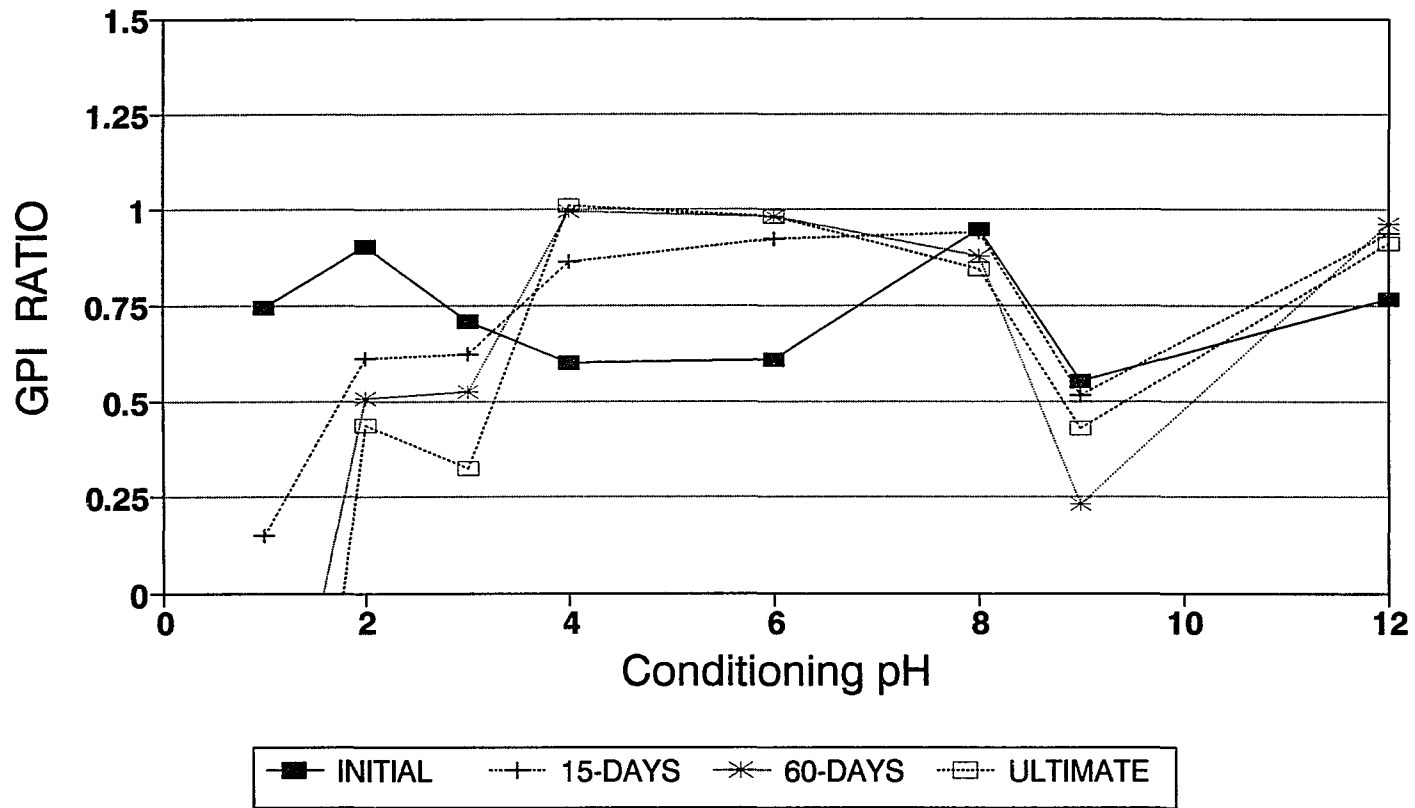


FIGURE 6-49

NORMALIZED GPI RATIOS AT OF PDS 160 oC
Series 2, Wards Island (XY Plot)



high in TS, COD, ammonia, and alkalinity concentrations (Table 6-8). PDS collected on August 19, 1991, was evaluated on August 20 using the following 10-second RTC conditions:

- Unmodified pH (pHu); 100°C, 160°C, and 220°C
- pH6; 25°C, 100°C, 160°C, and 220°C
- pH2; 25°C, 100°C, 160°C, and 220°C

Unmodified pH GPI results, shown on Figure 6-50, indicate similar improvements as obtained from the Wards Island PDS. The highest GPI was obtained at the beginning of the incubation period and decreased to asymptotic values at infinite times. For the 100°C, initial and infinite GPIs were 310% and 40%, respectively; for the 160°C, initial and infinite GPIs were 580% and 50%, and for the 220°C, initial and infinite GPIs were 680% and 70%. These results indicate increases to both kinetics and ultimate biodegradability. The higher the thermal conditioning temperature the higher the kinetics and the ultimate biodegradability improvement.

Similar to the unconditioned pH results, the pH6 and pH2 GPI results, shown on Figures 6-51 and 6-52, respectively, were highest at the beginning of the incubation period. Even at modified pH and without thermal conditioning (25°C), significant GPIs were obtained at both pHs. At pH6 and 25°C, GPI ranged from the maximum of 250% to the ultimate of 40%, and at pH2 ranged from 620% to 60%. The higher the RTC temperatures the higher the respective GPIs.

TABLE 6-8

SUMMARY TABLE OF PDS CHARACTERISTICS, NEWTOWN CREEK

Parameter	2/11/91	4/4/91	4/15/91	8/19/91	3/18/92	Average
TS, %	3.71	5.21	3.45	3.05	2.56	3.60
TVS, % of TS	61.9	58.2	60.6	53.0	58.6	58.6
DS, %	0.21	0.56	0.58	0.19	0.44	0.40
VDS, % of DS	---	61.3	67.9	30.2	61.6	67.3
TSS, %	3.50	4.65	2.87	2.86	2.12	3.20
VSS, % of TSS	---	58.0	59.5	54.5	58.0	57.5
Total TOC, mg/L	---	1,913	2,902	8,520	---	4,445
Soluble TOC, mg/L	724	385	442	151	320	404
Total COD, mg/L	---	18,375	30,400	32,650	33,710	28,784
Soluble COD, mg/L	---	840	1,080	508	1,440	967
TKN-N, mg/L	---	4,134	3,880	2,925	---	3,646
NH3-N, mg/L	---	2,320	2,917	1,950	3,200	2,597
TVA, mg/L as Ac. Acid	266	148	154	62	---	158
pH	7.75	7.91	7.81	7.8	7.79	7.81
Alkalinity, mg/L as CaCO3	9,820	11,046	10,689	6,480	7,560	9,119
Phosphates, mg/L	---	1,450	790	---	---	1,120
Sulfates, mg/L	---	---	854	---	---	854
Chlorides, mg/L	---	---	274	---	---	274

Notes:

1. "----" Data not available

FIGURE 6-50
GPI - NEWTOWN CREEK; UNMODIFIED pH
August 20, 1991

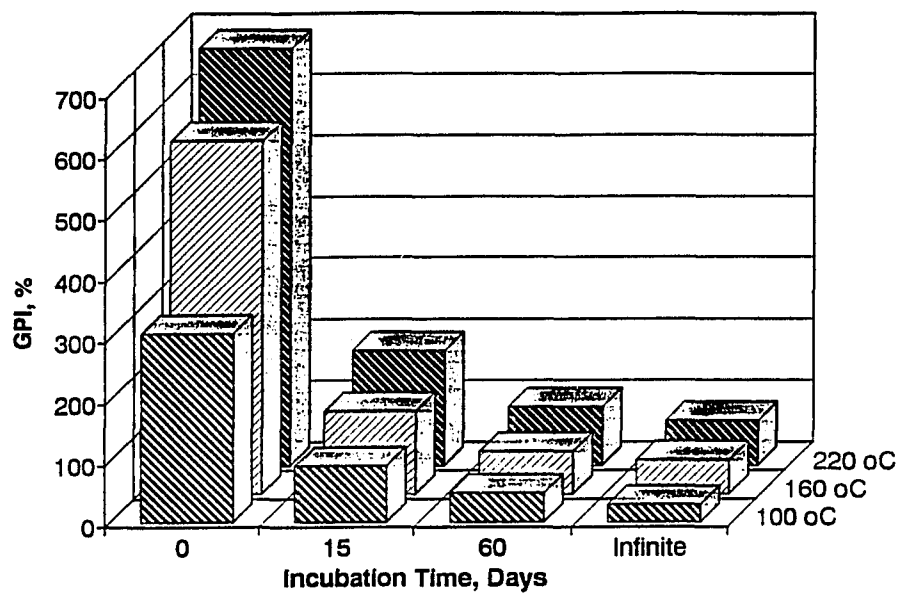


FIGURE 6-51

GPI - NEWTOWN CREEK; pH=6
August 20, 1991

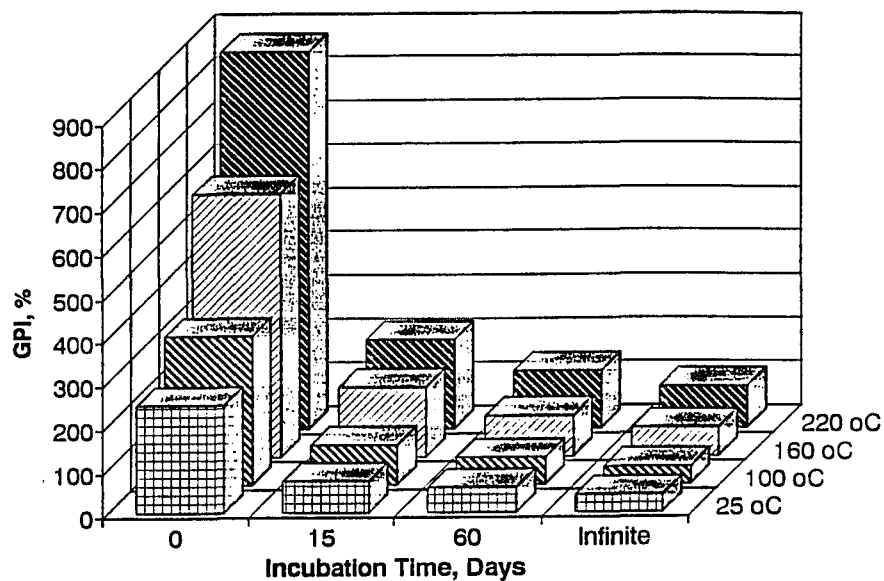


FIGURE 6-52

GPI - NEWTOWN CREEK; pH=2
August 20, 1991

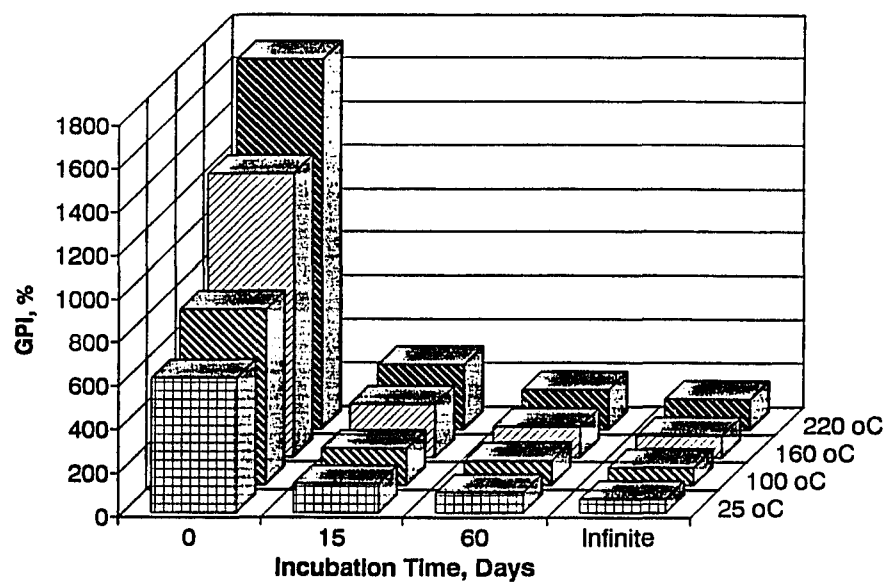


Figure 6-53 compares the ultimate GPI at the three investigated pHs. The results clearly indicate that the lower the pH, the lower the temperature required to reach a predetermined GPI value. For example, at pH6 and room temperature, the GPI of 40% was higher than the pHu GPI at 100°C of 30%; at pH2 and room temperature the GPI was 60%, compared to the pH6 at 160°C of 70%. However, the best condition will depend on the minimum cost associated with pH adjustment and steam production.

Wards Island vs Newtown Creek

Figure 6-54 compares the Wards Island with the Newtown Creek ultimate GPI results. Similar to Wards Island, Newtown Creek PDS gave high GPIs at any tested condition without any evidence of toxicity.

III. Rockaway Beach Results

Rockaway Beach is the only NYC plant that provides mesophilic followed by thermophilic digestion. In addition, the plant has a very long digestion retention time of over 60 days. This final RTC experiment was performed to determine whether thermal conditioning would have the same effect on thermophilic PDS as it had on the mesophilic PDS from Wards Island and Newtown Creek wastewater treatment plants. PDS characteristics were determined on four sampling events for thermophilic PDS, and one sampling event for the mesophilic PDS, the influent to the thermophilic digester. Results

FIGURE 6-53

ULTIMATE GPI AT pH2, pH6 AND pHu

Newtown Creek - August 20, 1991

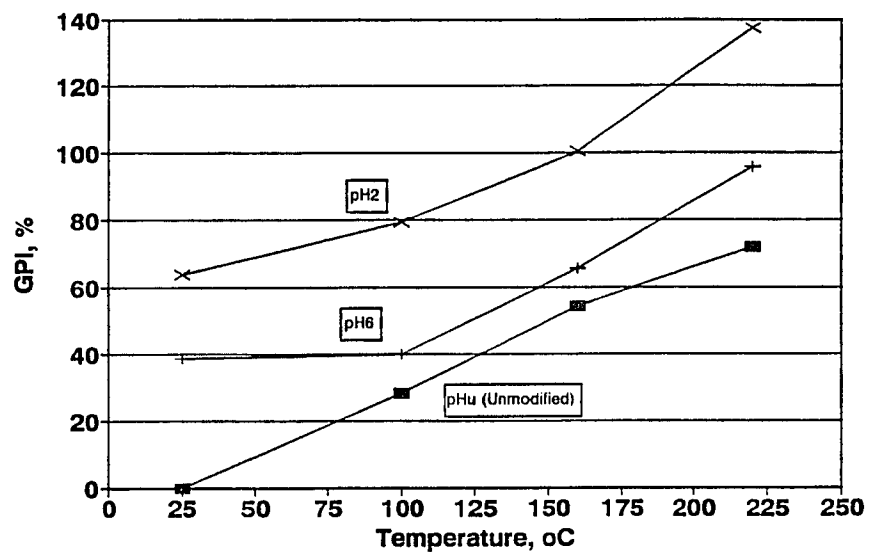
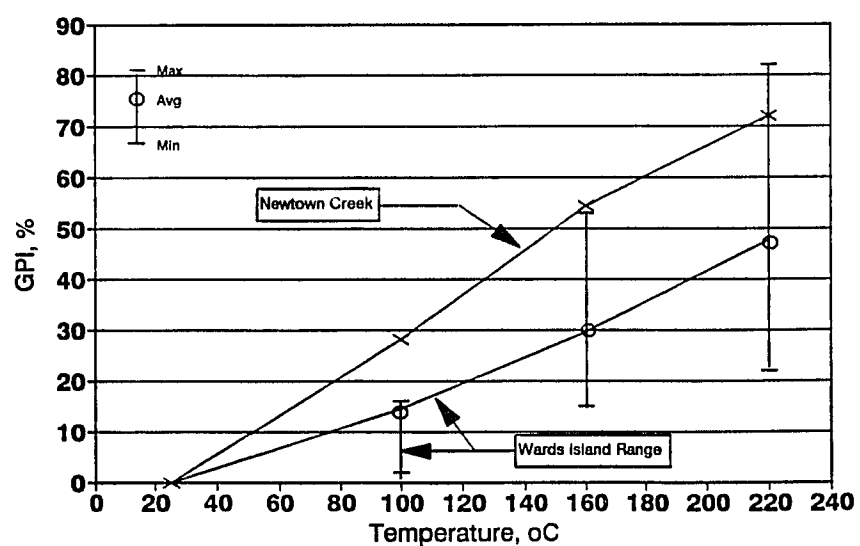


FIGURE 6-54

COMPARISON OF WI AND NC RESULTS

Ultimate GPI, Unmodified pH



are summarized in Table 6-9. The following 10-second RTC conditions were evaluated on April 1, 1992 from the thermophilic PDS collected on March 31:

- Unmodified pH (pHu); 100°C, 160°C, 190°C, and 220°C
- pH2; 25°C, 100°C, 160°C, 190°C, and 220°C

The serum bottles were seeded with the thermophilic PDS collected the day before the RTC experiment. The bottles were half-immersed in a 50°C water bath. Due to the high temperatures, water had to be added often to the bath to replace that lost through evaporation.

Contrary to the Wards Island and Newtown Creek results, the two-term SGP equation did not fit the data very well because the gas production curves for pHu (Figure 6-55) and pH2 (Figure 6-56) had a lag phase at the beginning of the incubation period. For clarity, Figure 6-56 shows up to 60 days incubation, whereas the actual incubation was about 130 days. The unconditioned thermophilic PDS (raw PDS and also the seed) also exhibited a similar lag phase. The reason could be that the seed was stored overnight in the 20°C-25°C laboratory (about half its "natural" environment temperature) and it required some time after incubation to recover, hence exhibiting the lag phase in gas production.

Because of the inability of the SGP equation to fit the data, GPIs were calculated directly from the measured data. Figures 6-57 and 6-58 show the GPI results of pHu and pH2 conditions, respectively. Because of the lag phase, maximum GPIs took place after 10 days of incubation, whereas for Wards Island and Newtown Creek maximums occurred within the first day. The pHu results indicate that the 100°C and 160°C thermal

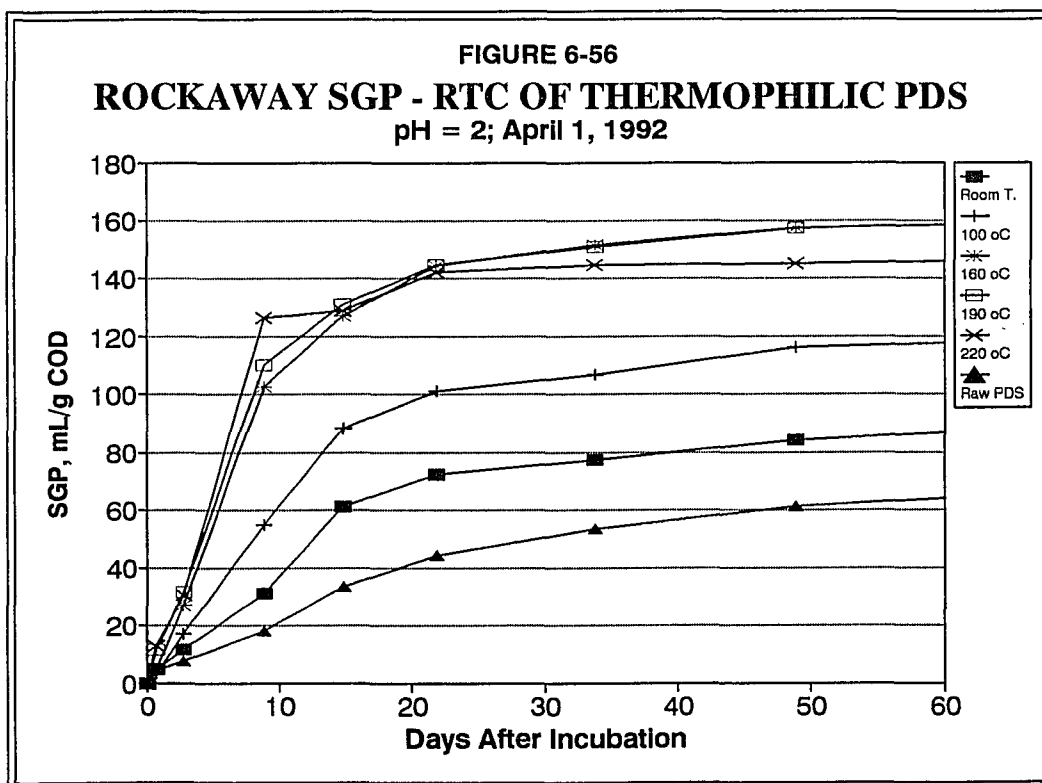
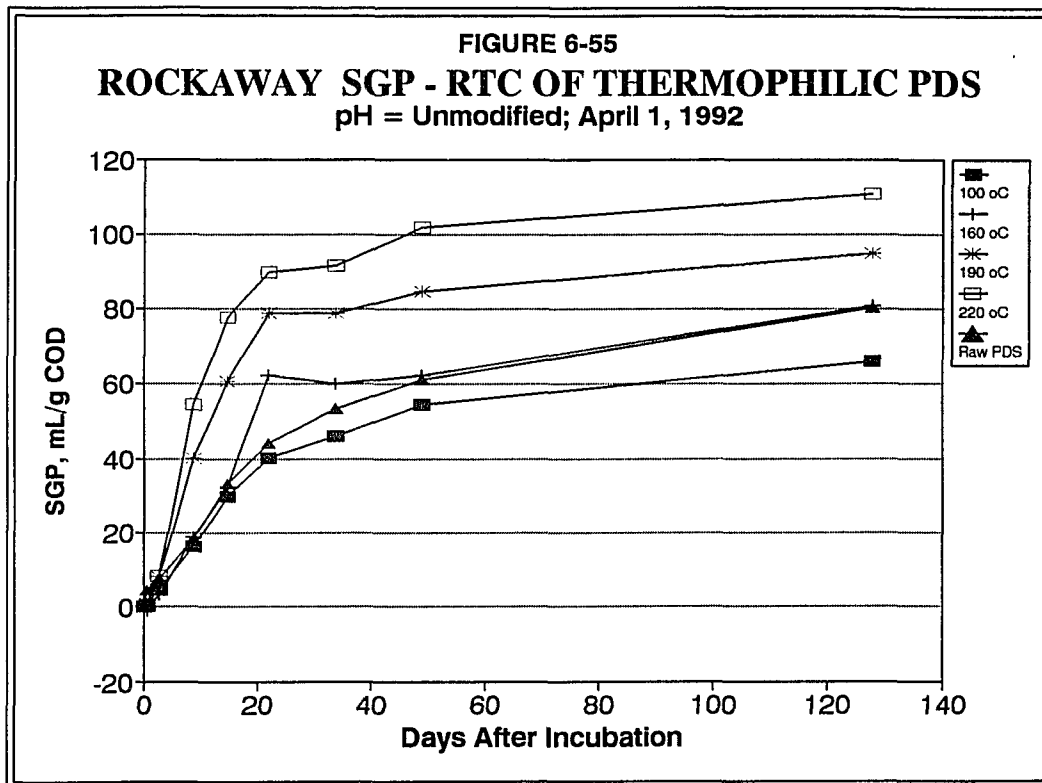
TABLE 6-9

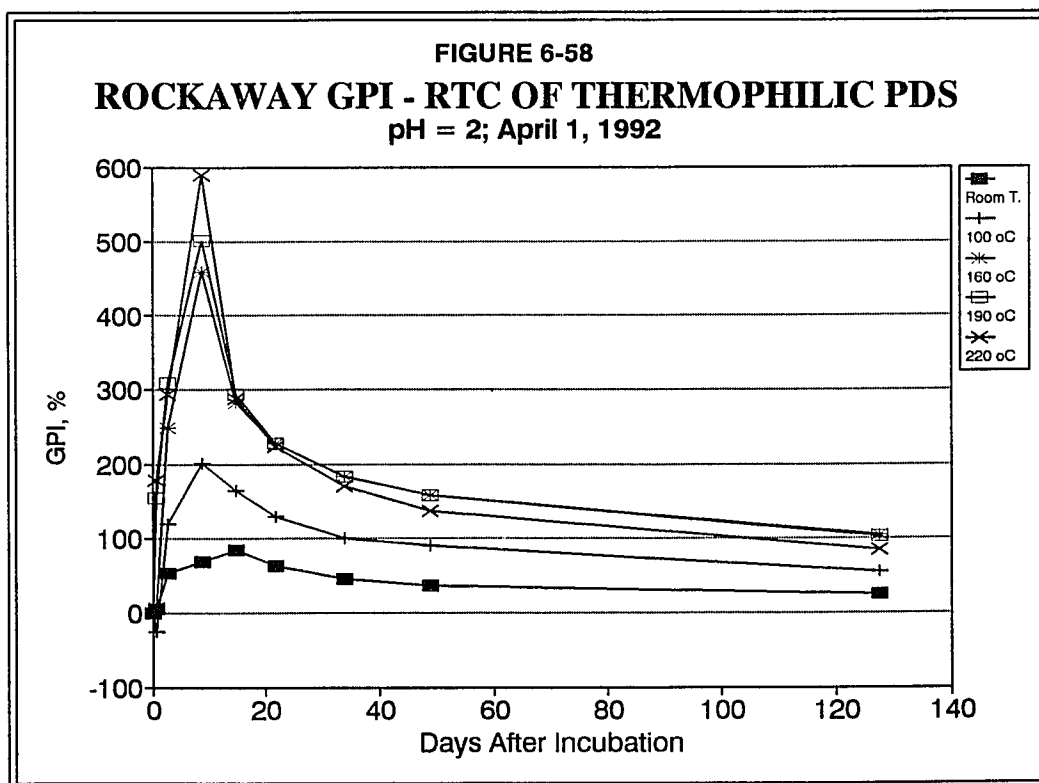
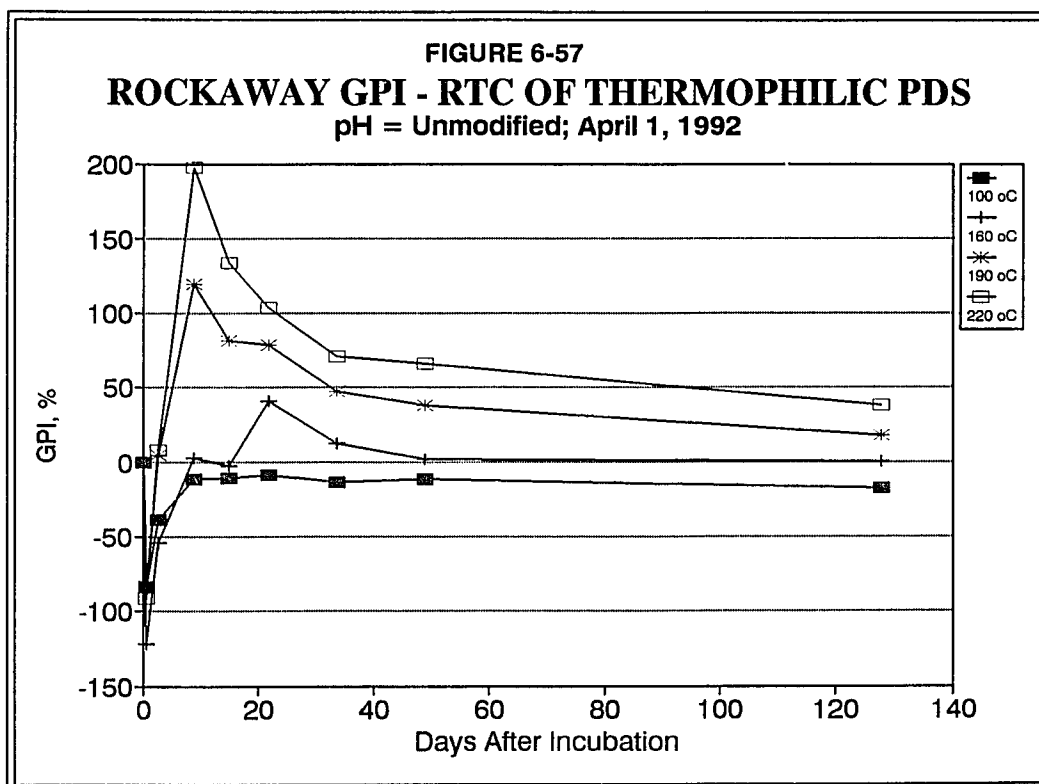
SUMMARY TABLE OF PDS CHARACTERISTICS, ROCKAWAY BEACH

Parameter	3/21/91 Thermophilic	4/15/91		3/31/92 Thermophilic	Thermophilic Average
		Thermophilic	Mesophilic		
TS, %	2.09	2.69	3.16	1.55	2.11
TVS, % of TS	71.0	68.0	69.0	59.9	67.0
DS, %	0.30	0.36	0.37	0.34	0.33
VDS, % of DS	52.0	37.4	36.9	41.1	43.0
TSS, %	1.79	2.33	2.79	1.21	1.78
VSS, % of TSS	74.0	72.8	73.3	65.2	71.5
Total TOC, mg/L	---	2,641	776	---	2,641
Soluble TOC, mg/L	193	157	164	234	195
Total COD, mg/L	15,950	20,175	22,275	20,760	18,962
Soluble COD, mg/L	627	435	525	633	565
TKN-N, mg/L	---	2,691	2,297	---	2,691
NH ₃ -N, mg/L	---	1,226	1,095	---	1,226
TVA, mg/L as Ac.Acid	---	24	32	---	24
pH	7.62	7.48	7.44	7.88	7.66
Alkalinity, mg/L as CaCO ₃	4,130	4,578	4,515	4,600	4,436
Phosphates, mg/L	---	555	960	---	555
Sulfates, mg/L	---	750	---	---	750
Chlorides, mg/L	---	644	618	---	644

Notes:

1. "----" Data not available



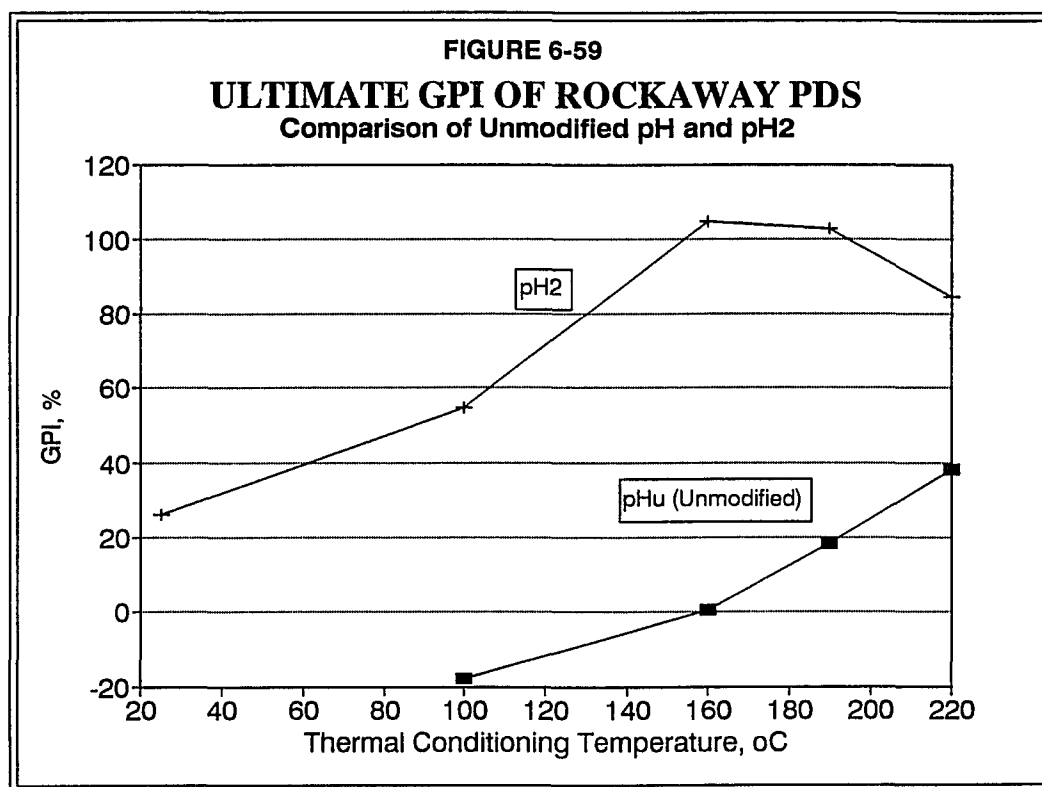


conditioning temperatures had no effect on PDS biodegradability; only the 190°C and 220°C showed improvement, with the 220°C giving the highest improvement. At pH2, all conditions showed improvement to PDS biodegradability, with the 160°C condition giving the highest ultimate GPI. Both the pHu and pH2 ultimate GPI results are illustrated on Figure 6-59, showing that, as with the other plants' results, low pH gave GPI as high as unmodified pH but at lower temperatures. In addition, the low pH exhibited a peak at the temperature range of 160°C to 190°C, where ultimate biodegradability improved over 100%.

RTC improved the ultimate biodegradability and kinetics of biodegradation of thermophilic PDS, exhibiting results similar to the other two plants. However, no improvement was observed when pH-unmodified PDS was thermally-conditioned at 100°C and 160°C. Even though most of the samples exhibited a gas lag phase, the lag phase not only occurred on non-severe conditions (i.e., low temperatures), but the seed also exhibited a lag phase. Therefore, again no toxic compounds were produced by the RTC process and the process can be used to condition thermophilic PDS.

(c) Series 3 - Pressure Cycling

The effect of pressure on the biodegradability of PDS was determined using Wards Island PDS collected on June 12, 1991. PDS was run through the recycle line of the rapid thermal conditioning reactor (RTCT) under room temperature. Because the pressure



control valve of the recycle line was getting plugged (PDS was not sieved), it was not possible to maintain a constant pressure. The pressure fluctuated from 200 psi to 600 psi. A sample was collected after a one-cycle run and was digested. Accumulated gas production (AGP) results are shown on Figure 6-60 for the following samples:

1. 50 mL unconditioned PDS (Raw PDS)
2. 50 mL raw PDS + 0.2 mL HAc
3. 50 mL non-seeded pressure-conditioned PDS
4. 50 mL non-seeded pressure-conditioned PDS + 0.2 mL HAc, and
5. 50 mL raw PDS + 50 mL conditioned PDS

The results indicate that the one-cycle pressure condition had no improvement to PDS biodegradability since Sample #5 gas production was double that of Sample #1. In addition, pressure had no effect on lysing the bacteria since the pressure-conditioned PDS (Sample #3, without seed) gave comparable results to Sample #1; no lag phase was observed and total gas productions were comparable at 145 mL and 155 mL, respectively. Furthermore, the gas production of both samples with 0.2 mL HAc were also comparable, obtaining a gas recovery of over 93%. Gas recoveries are compared on Figure 6-61, where the theoretical HAc gas production of 176 mL compares favorably to the recoveries obtained from the two samples. The gas recoveries indicate that the bacteria viability was not affected by the high pressure conditions.

FIGURE 6-60

PRESSURE EFFECT ON PDS

Pressure Range 200-600 Psi, 1-CYCLE

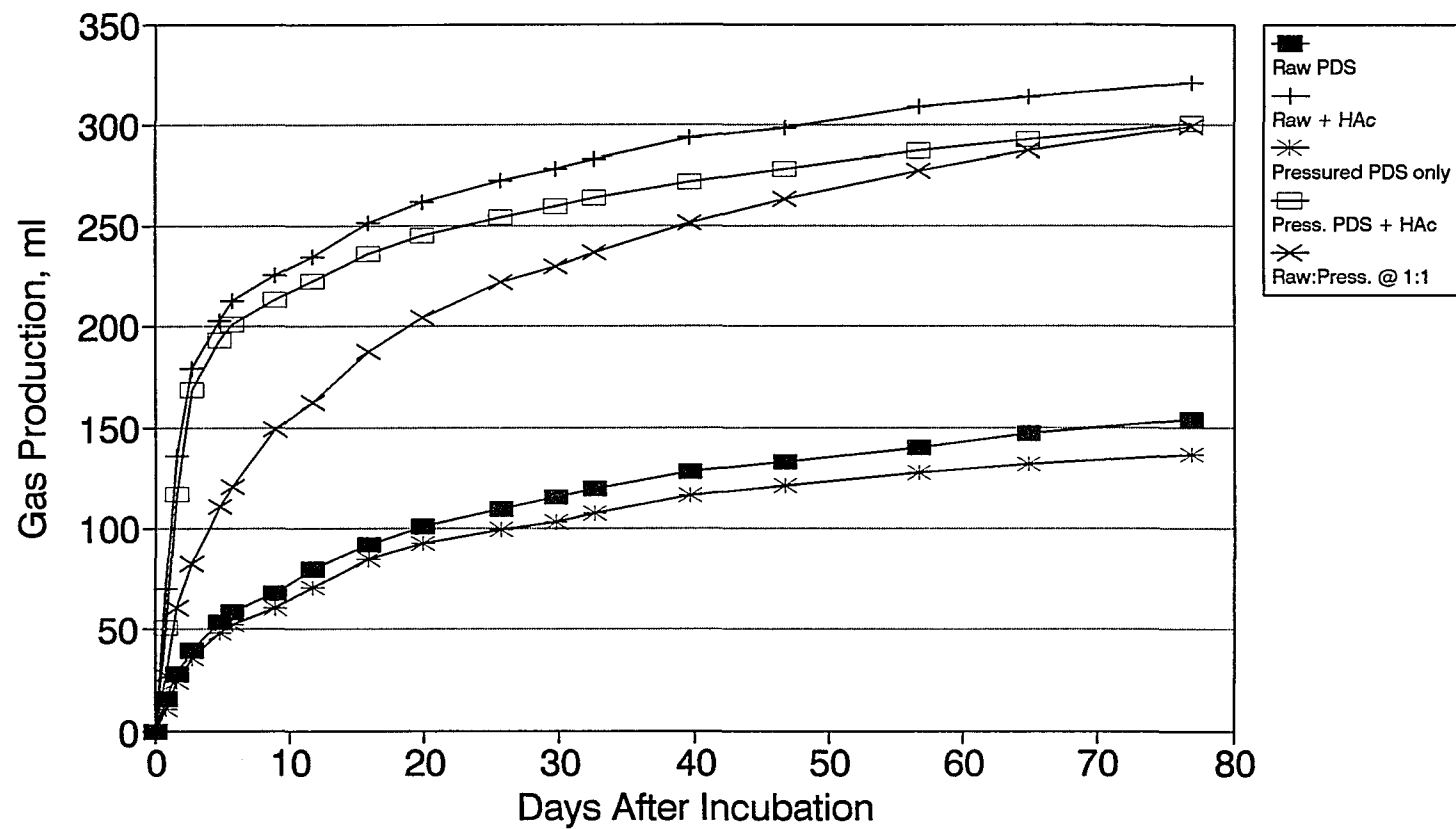
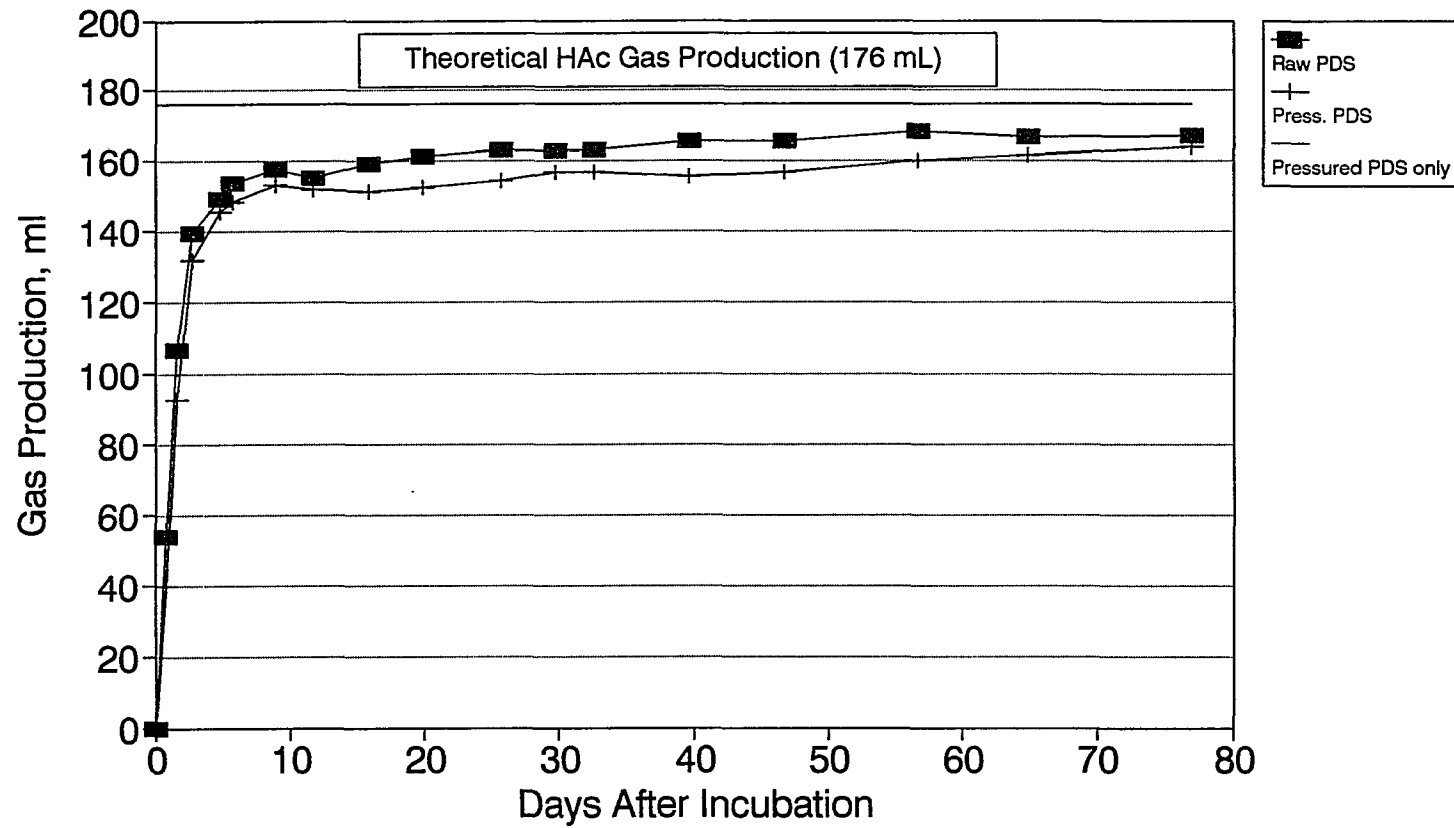


FIGURE 6-61

PRESSURE EFFECT-HAc GAS RECOVERIES

Pressure Range 200-600 Psi, 1-CYCLE



Therefore, pressure cycling alone does not affect the biodegradability and the viability of PDS. Thermal conditioning improvements should be due to the high temperatures and not to the pressure differential caused by the let-down valve of the RTCR.

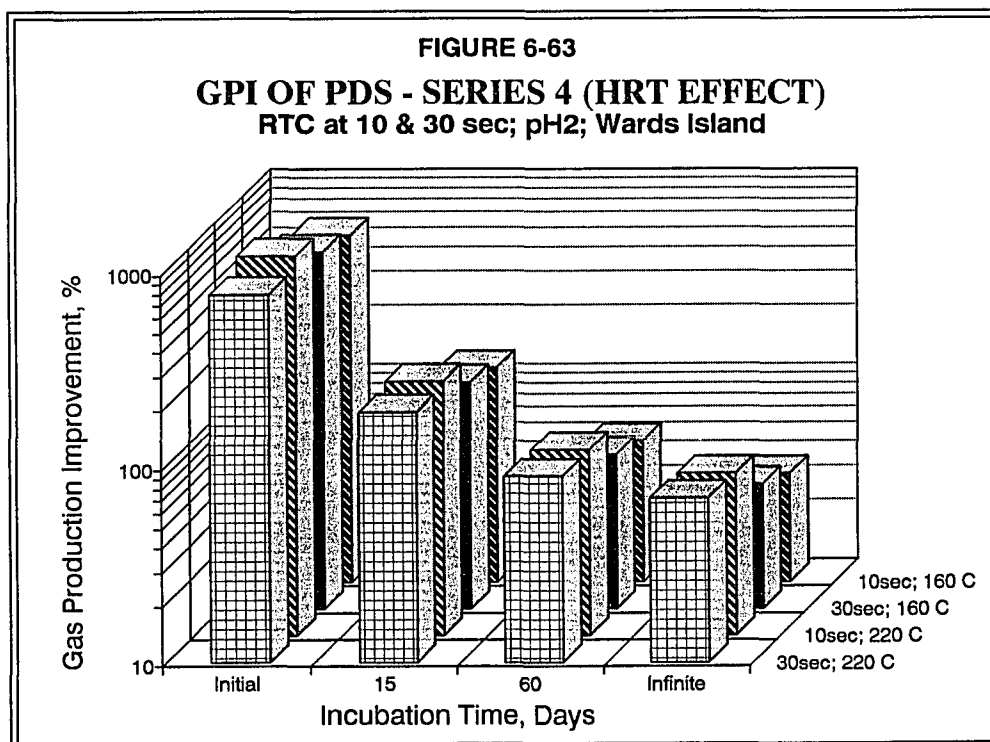
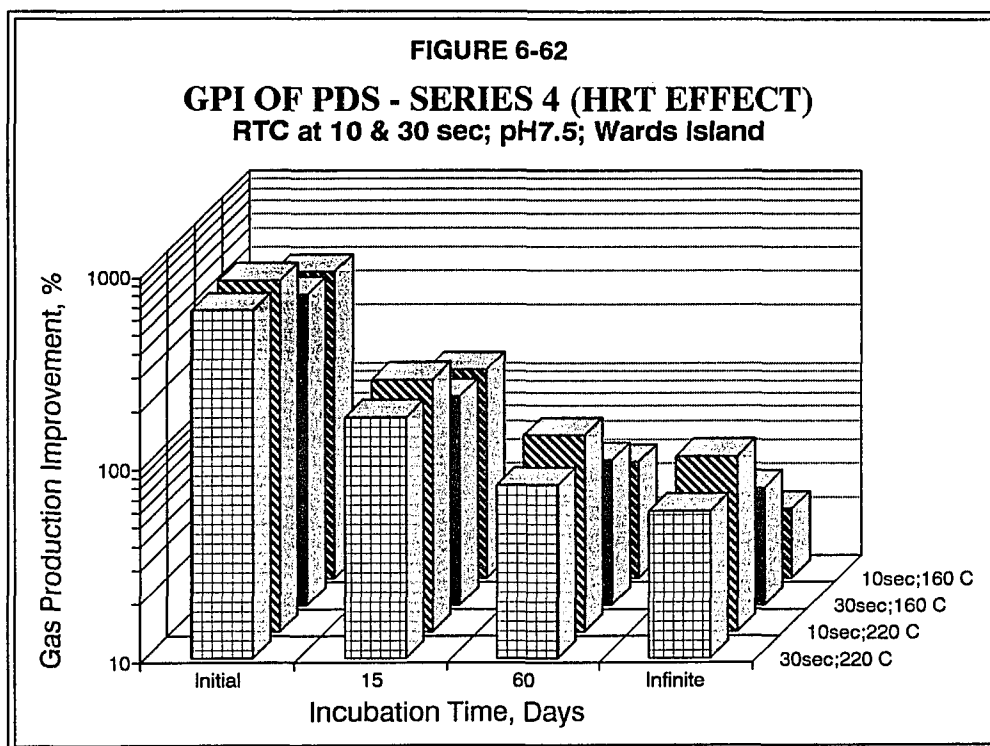
(d) Series 4 - RTC Hydraulic Retention Time

The effect of hydraulic retention time (HRT) was determined on Wards Island sludge collected on September 17, 1991 and January 28, 1993.

September 17, 1991: PDS collection, sieving, thermal conditioning, and biodegradation were all done the same day. Thermal conditioning was performed for an HRT of 10 seconds and 30 seconds at the following conditions:

- Unmodified pH (pHu); 160°C and 220°C
- pH2; 160°C and 220°C

Figures 6-62 and 6-63 present gas production improvements determined at pHu and pH2, respectively. The results indicate a minor increase of ultimate GPI at the 160°C temperature for both pHs. When temperature was raised to 220°C, the additional contact time had no effect on GPI. The GPI results were supported by comparing VS, COD, and TOC solubilization at the respective conditions. Solubilization values are compared on Figure 6-

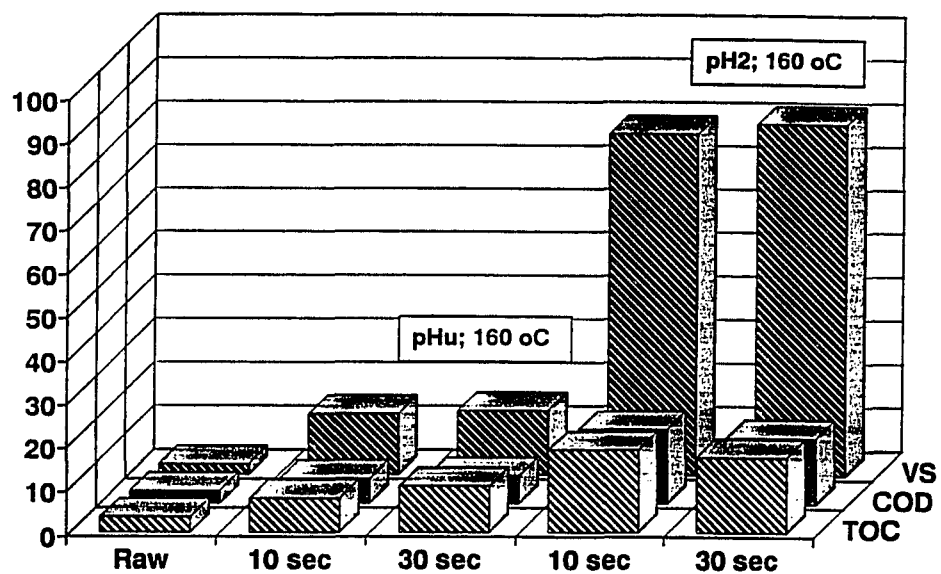


64 and the results are similar to the GPI results. The 30 seconds HRT did not solubilize any parameter more than the 10 seconds HRT.

January 28, 1993: The September testing was performed for a maximum RTC time of 30 seconds because there was only one reactor installed at that time. Afterwards, we installed two additional reactors (all in series) so that the test could run at longer contact times. During this test the contact times were 10, 20, 30, 60, 120 and 180 seconds. The two last times were too long, even with the three-reactor configuration, and could not be obtained by the same flowrate as the short times. For this reason the 10, 20 and 30 seconds times were obtained at a flowrate of 1.31 mL/min, and the 60, 120 and 180 seconds at 0.22 mL/min. Flowrates were easily changed by controlling the speed of the sludge pump. RTC temperature was maintained at 220°C. The experiment was run by the following order:

Step 1.	Adjust flowrate to 0.22 mL/min
Step 2.	Adjust reactor temperature to 220°C
Step 3.	Run one reactor (60 sec)
Step 4.	Run two reactors (120 sec)
Step 5.	Run three reactors (180 sec)
Step 6.	Adjust flowrate to 1.31 mL/min
Step 7.	Run three reactors (30 sec)
Step 8.	Run two reactors (20 sec)
Step 9.	Run one reactor (10 sec)

FIGURE 6-64

**EFFECT OF RTC TIME ON SOLUBILIZATION
OF VS, COD, TOC - WI September 18, 1991**

The serum bottles test was set up similar to previous experiments. However, an additional set of bottles was prepared with thermally conditioned PDS but **without seed** addition.

This test was performed to evaluate:

1. Bacterial survival at the extreme RTC temperature of 220°C and long contact times, and
2. Toxicity and bacterial acclimation.

Gas production improvement (GPI) results are presented on Figures 6-65 and 6-66 for the longer times (60, 120, 180 seconds) and shorter times (10, 20, 30 seconds), respectively. The data was fitted using the two-term equation, with results summarized in Table 6-10. Specific gas production (SGP) curves are presented on Figures 6-67 and 6-68, where data compares very well to the results from the two-term equation. The results indicate improvement to PDS biodegradability with increasing RTC time. Biodegradability increased more at the shorter times and marginally at the longer times; similar results were obtained for the 60-, 120- and 180-second samples. Even at the long retention time of 180 seconds there was no toxicity effect. This was evident since maximum gas production occurred at this condition and no lag-phase was present at the beginning of the incubation period.

The absence of toxicity was also confirmed from the results of the non-seeded samples. Originally it was thought that the high RTC temperature of 220°C (even at a contact time as short as 10 seconds) would kill all the bacteria. However, the results indicate quite the

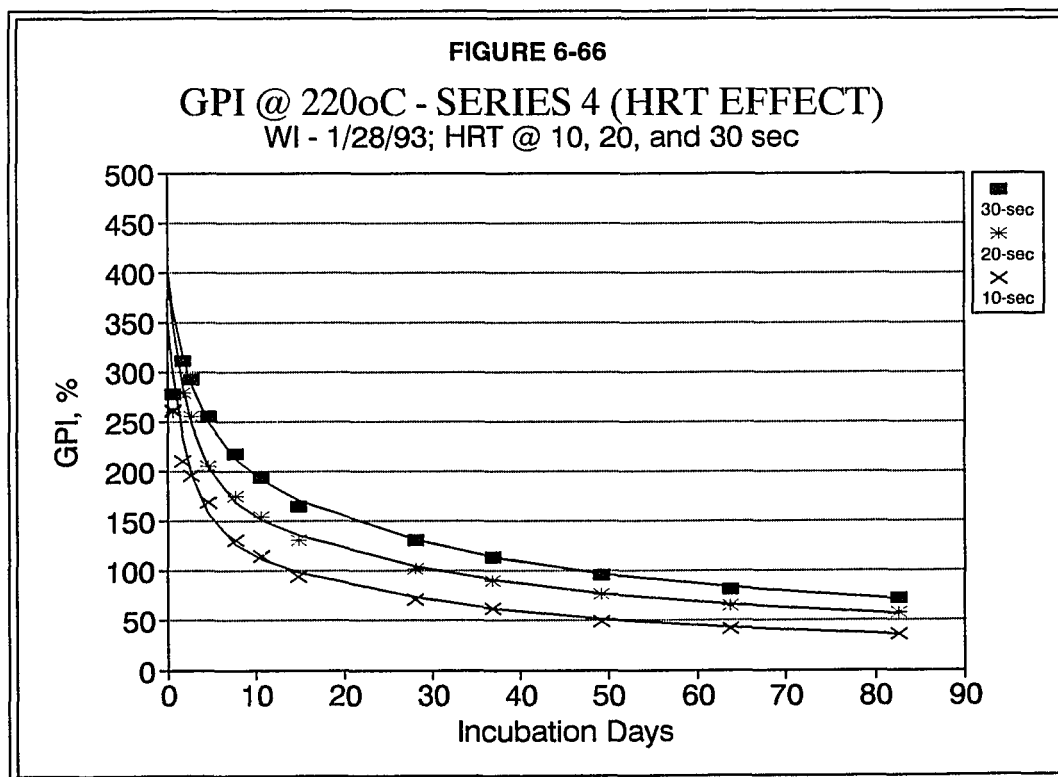
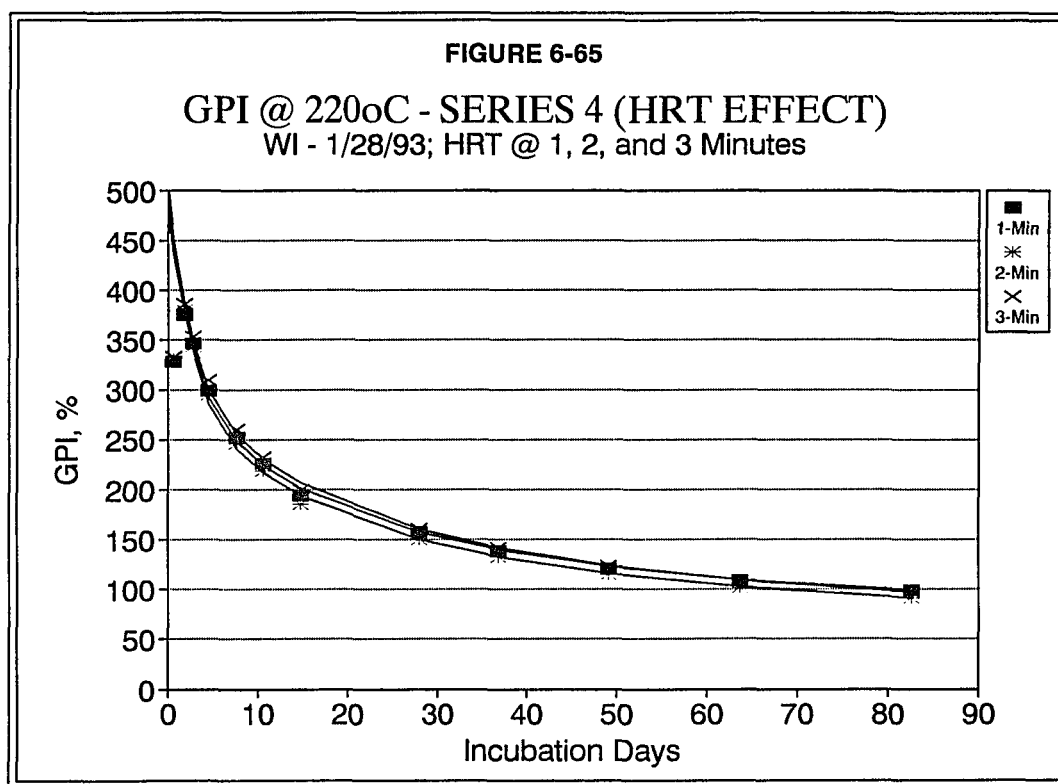


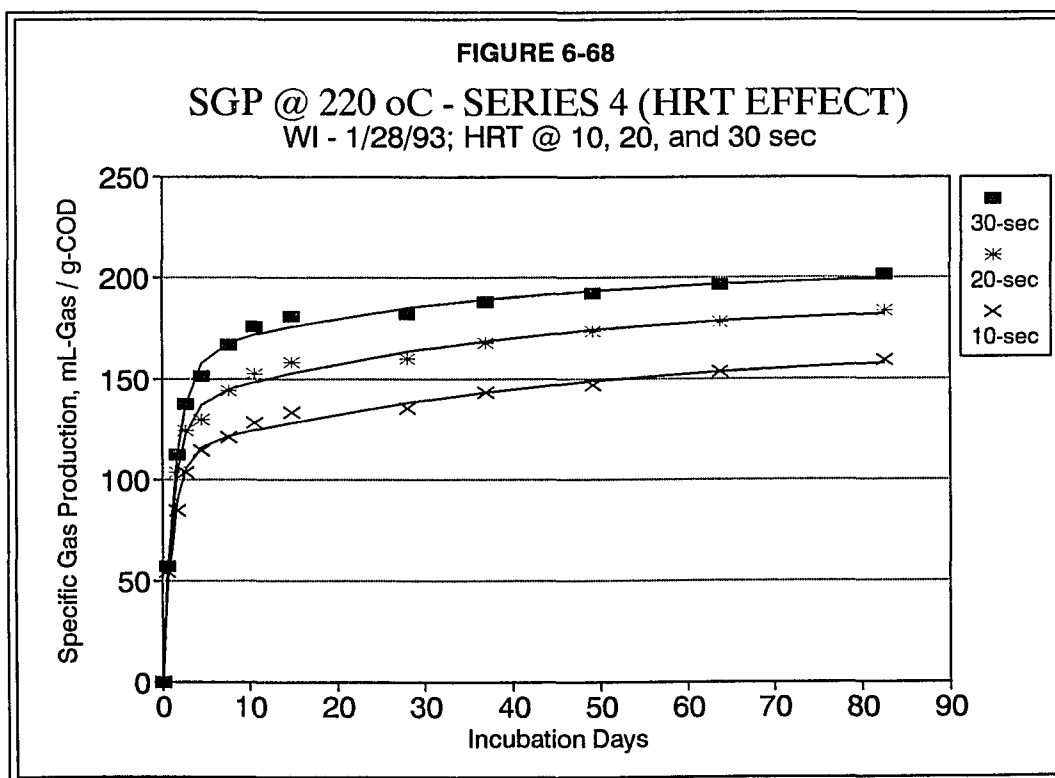
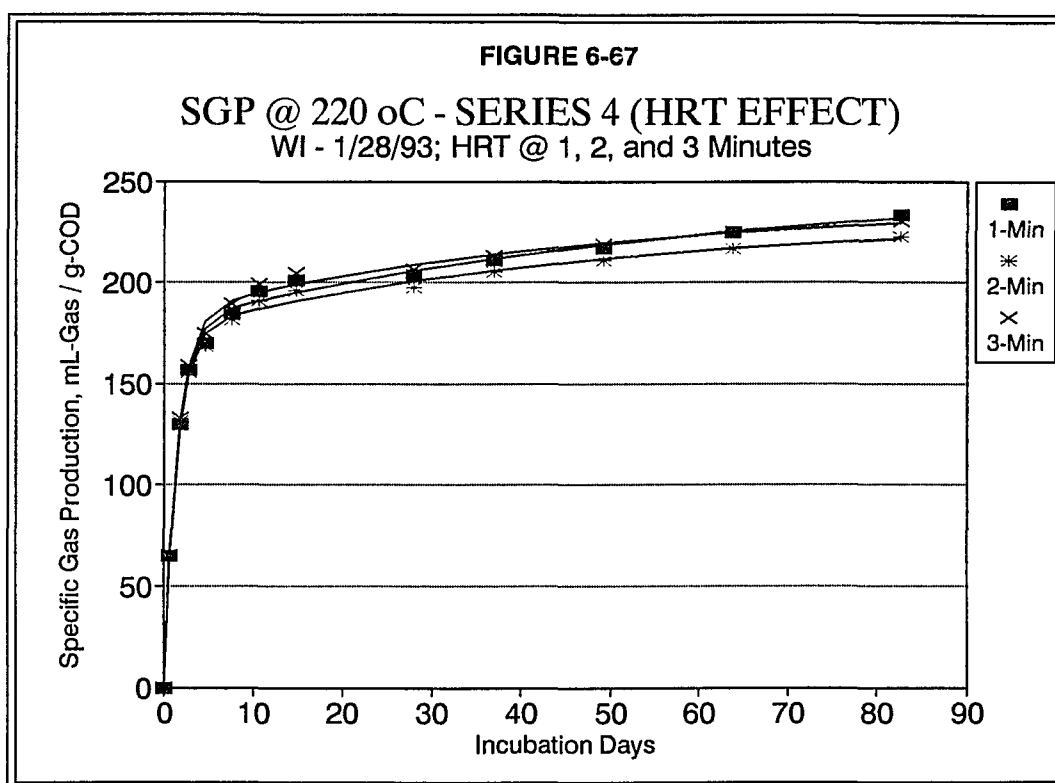
TABLE 6-10

SPECIFIC GAS PRODUCTION (SGP) KINETIC RESULTS, SERIES 4 (HYDRAULIC RETENTION TIME EFFECT)
WARDS ISLAND, JANUARY 28, 1993

RTC Time (sec)	SGP Coefficients				G_1+G_2 (mL/g)	$G_1k_1+G_2k_2$ (mL/g-d)
	G_1 (mL/g)	G_2 (mL/g)	k_1 (1/d)	k_2 (1/d)		
0 (Raw)	43.4	96.6	0.446	0.0170	140	21
10	113.5	51.8	0.825	0.0232	165	95
20	134.5	52.3	0.770	0.0289	187	105
30	160.2	42.8	0.641	0.0309	203	104
60	180.2	70.1	0.671	0.0161	250	122
120	175.6	55.5	0.717	0.0214	231	127
180	183.6	53.7	0.671	0.0227	237	124

Notes:

1. $SGP = G_1(1-\exp(-k_1t)) + G_2(1-\exp(-k_2t))$

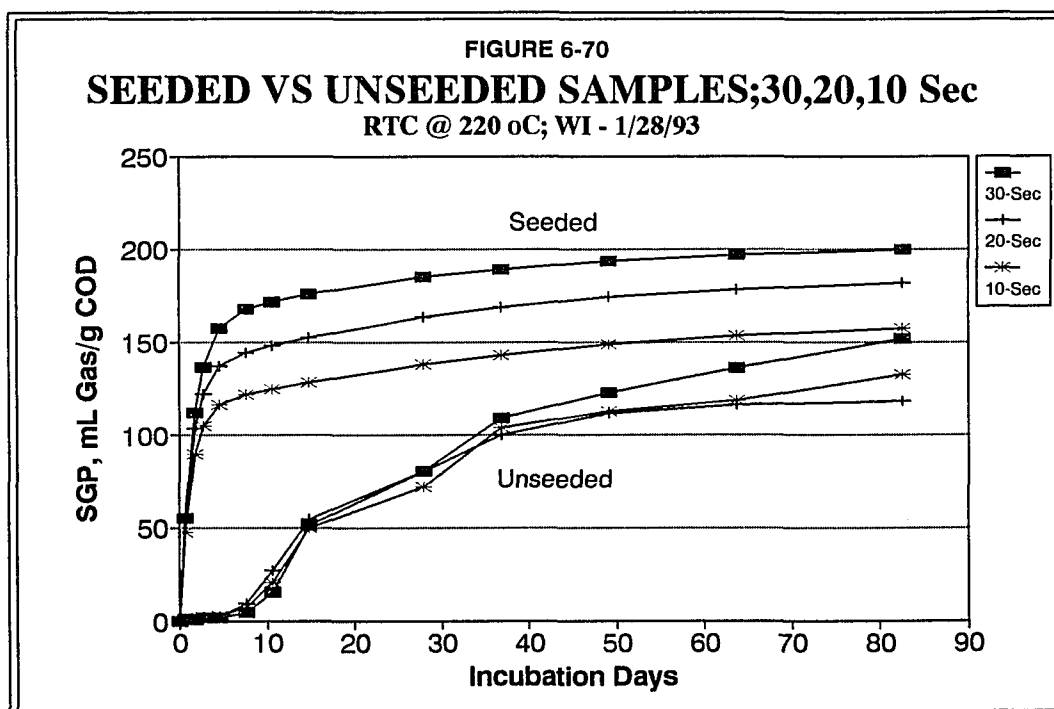
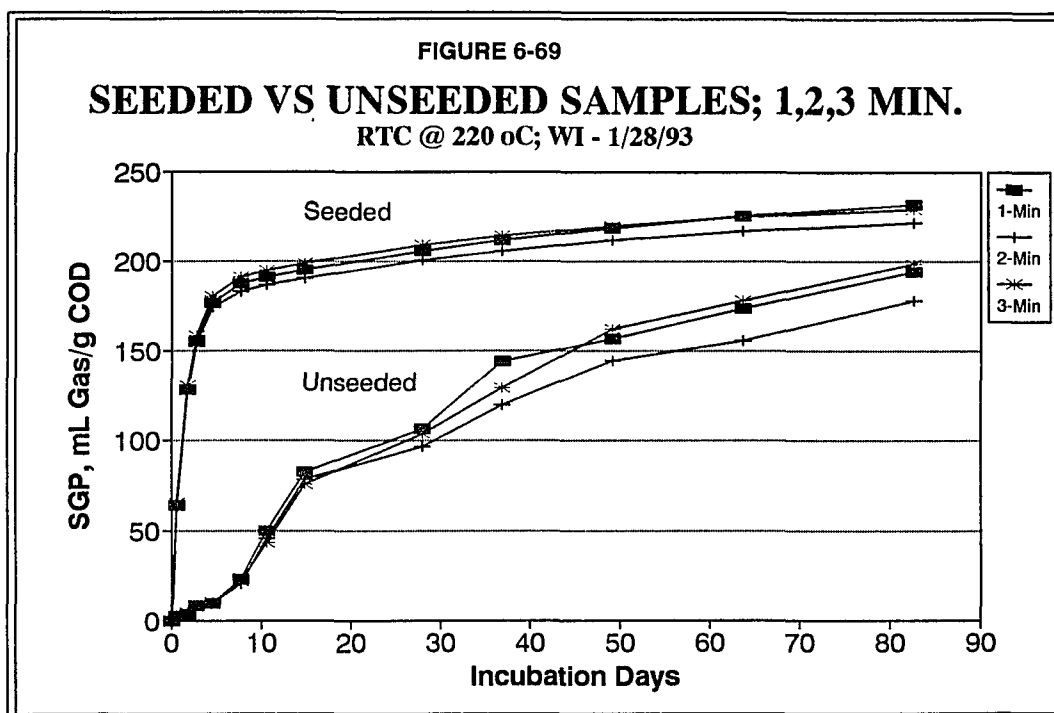


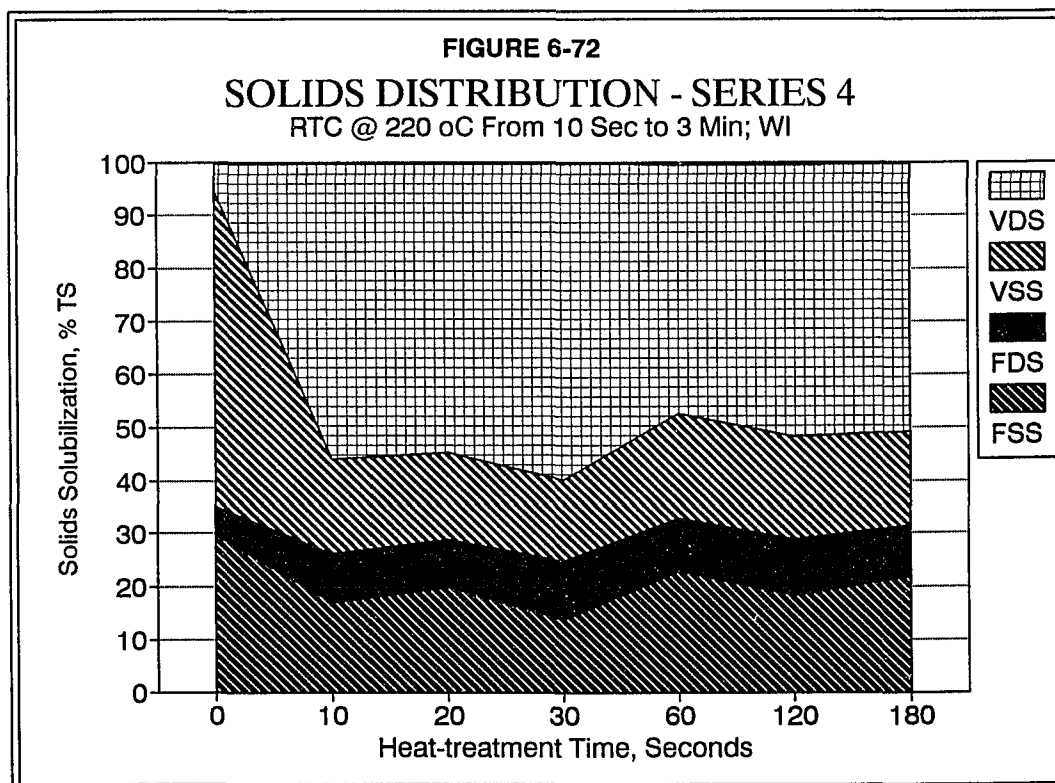
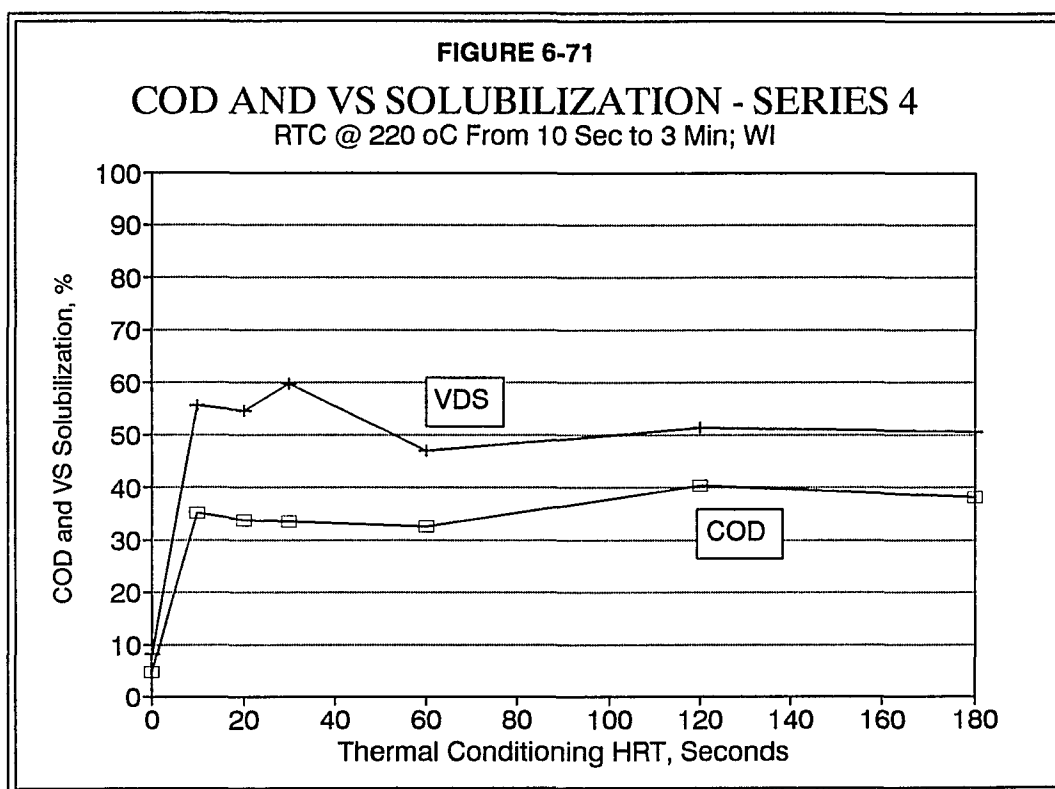
opposite where bacteria survived even at the contact time of 180 seconds. These results are demonstrated on Figures 6-69 and 6-70 which compare the seeded and the non-seeded SGP results. There was a lag-phase in gas production at all conditions, but this was expected since no bacteria were expected to survive. What was not expected, however, was that approximately after 10 days of incubation the gas production rates increased rapidly, approaching that of the seeded samples. These results indicate that still some bacteria survived the severe conditions of the RTC process. After the bacteria revived from the thermal shock and after multiplication, gas production increased, resembling the classical bacterial growth curve.

COD and volatile solids (VS) solubilization are presented on Figure 6-71. Maximum solubilizations were obtained with just 10 seconds of contact time and remained at that level at all contact times. COD solubilization reached 35% to 40% and VS solubilization reached 50% to 60%. Solids distribution is presented on Figure 6-72, where no significant changes were observed beyond the 10 seconds contact time.

In summary, the various RTC contact-time runs indicated:

- Bacteria survived contact times as long as 180 seconds and 220°C
- No toxic compounds were generated at any contact time
- Biodegradability improved with increasing contact times (up-to 60 second)
- Biodegradability did not increase beyond the 60-second contact times
- COD and VS solubilization were not affected by the longer contact times





An important conclusion is that longer HRTs do not generate any inhibitors to anaerobic digestion. Therefore, preheating the PDS prior to RTC (for energy conservation) for a time less than three minutes would not affect biodegradability. Preheating influent PDS with effluent PDS using a heat exchanger, would decrease steam consumption, and thus reduce energy requirements, and make the RTC process less energy intensive.

(e) Series 5 - Thickened PDS

Arrangements were made with Wards Island to collect PDS and thicken it on site. PDS was collected on March 10, 1992, from the heat-exchanger recirculation pump and was stored in a 55-gallon polyethylene drum. Due to the dissolved gases, the sludge was separated into two thick zones, one on the surface and one at the bottom, with a clear zone in between. When the clear phase developed, the liquid was removed by siphoning and new PDS was added. The process was repeated every day for two weeks until no further thickening was observed.

On March 24, the thickened PDS was transferred into carboys and transported to the Environmental Engineering Laboratory for processing. Sieving was done the same day and thermal conditioning was done on March 25. Thermal conditioning was performed at unmodified pH (pH=7.5) and pH2 at temperatures of 100°C, 160°C and 220°C. Biodegradability was assessed by the serum bottle test. Sieved PDS, collected on March 24 from WI digesters, was used as seed. Seed and thickened PDS (before and after RTC)

characteristics are presented in Table 6-11. The 14-days thickening process increased the TS of PDS from about 2% (seed) to 4.8% (UR) and the TCOD from about 29,000 mg/L to 104,000 mg/L. Even though soluble COD (SCOD) was about double the seed's COD, the ratio of SCOD/TCOD decreased from 4.6% to 2.7%.

Solids solubilization results after thermal conditioning are presented on Figure 6-73. For the unmodified pH runs, the DS/TS ratio increased from 5% to 45% and the DVS/DS ratio increased from 47% to 90%. For the pH2 conditioning, DS and DVS were already solubilized by the acid alone to 29% and 59%, respectively. Thermal conditioning further increased the DS/TS ratio to 57% and the DVS/DS ratio to 78%. A broader perspective of the RTC effect on solids is shown on Figure 6-74, which clearly shows the DVS, VSS, FDS, and FSS as a function of TS. Solubilization values of DVS, similar for both the pHu and pH2 conditions, increased with temperature, reaching a maximum of about 30% of TS. Fixed solids solubilization, as a function of temperature, is minimal at both pHs, indicating that thermal conditioning affects only the volatile and not the fixed solids.

Soluble COD (SCOD), and dissolved COD (DCOD) results are presented on Figure 6-75. Dissolved COD was measured through the same glass-fiber filter used for dissolved solids determination. The DCOD measurement was taken to evaluate the amount of COD associated with the DS, which cannot be evaluated by the SCOD. Solubilization results are comparable at the two pH conditions, where COD solubilization increased with the temperature and reached about 13% for the SCOD and 28% for the DCOD. The relationship

TABLE 6-11

THICKENED PDS CHARACTERISTICS AFTER THERMAL CONDITIONING

Sample No.	Treatment Temp.	NH ₃ -N (mg/L)	TS (%)	TVS % of TS	DS (%)	VDS % of DS	VDS (%)	DS/TS (%)	TCOD (mg/L)	DCOD (mg/L)	SCOD (mg/L)	DCOD/TCOD (%)	SCOD/TCOD (%)	STOC (mg/L)
Unmodified pH														
SEED	--	580	2.07	67.8	0.29	48.0	0.14	14.0	29,080	3,140	1,325	10.8	4.6	156
UR	25	730	4.84	66.8	0.230	47.2	0.11	4.8	103,800	5,880	2,840	5.7	2.7	117
U100	100	709	4.84	67.0	0.794	82.9	0.66	16.4	100,327	11,294	4,375	11.3	4.4	266
U170	170	838	4.84	67.2	1.411	88.8	1.25	29.1	105,670	21,233	7,336	20.1	6.9	1,135
U220	220	789	4.84	67.6	2.170	90.0	1.95	44.8	102,812	29,199	13,909	28.4	13.5	--
pH = 2														
2R	25	810	4.84	71.1	1.175	58.9	0.69	24.3	99,000	4,760	2,510	4.8	2.5	616
2-110	110	823	4.84	71.2	1.592	63.5	1.01	32.9	96,188	6,361	3,692	6.6	3.8	637
2-160	160	816	4.84	71.2	1.878	70.6	1.33	38.8	90,301	13,941	5,468	15.4	6.1	1,847
2-220	220	821	4.84	71.2	2.671	78.1	2.09	55.2	89,509	23,474	11,071	26.2	12.4	1,946

NOTES:

1. Results were corrected for steam dilution.
2. DCOD represents COD (dissolved) filtered through the glass-fiber filter used for DS.

FIGURE 6-73
THICKENED PDS - SOLIDS SOLUBILIZATION
 pHu and pH2; WI, March 25, 1992

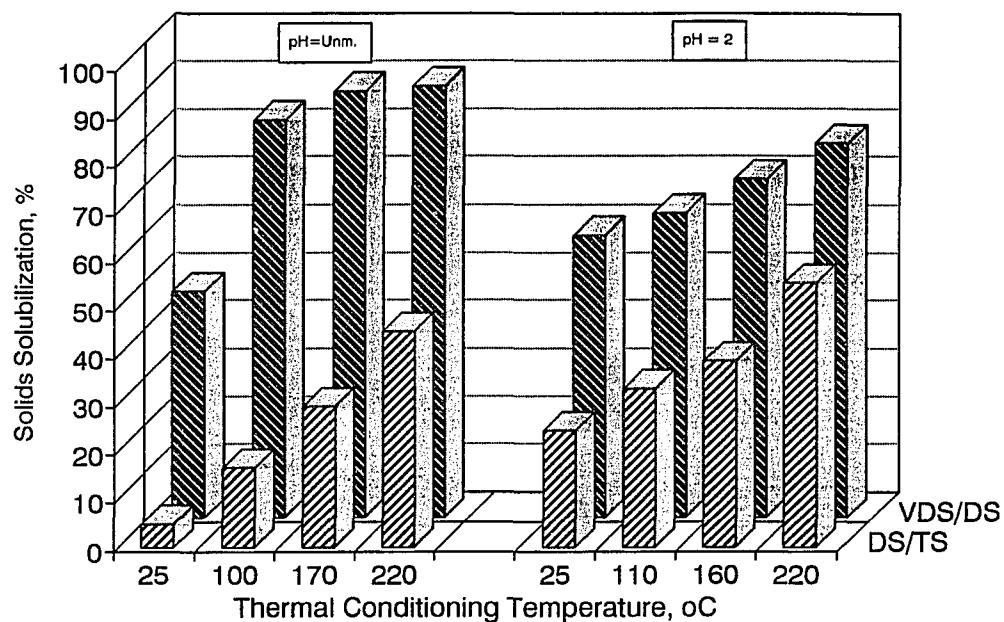


FIGURE 6-74
THICKENED PDS - SOLIDS DISTRIBUTION
 pHu and pH2; WI, March 25, 1992

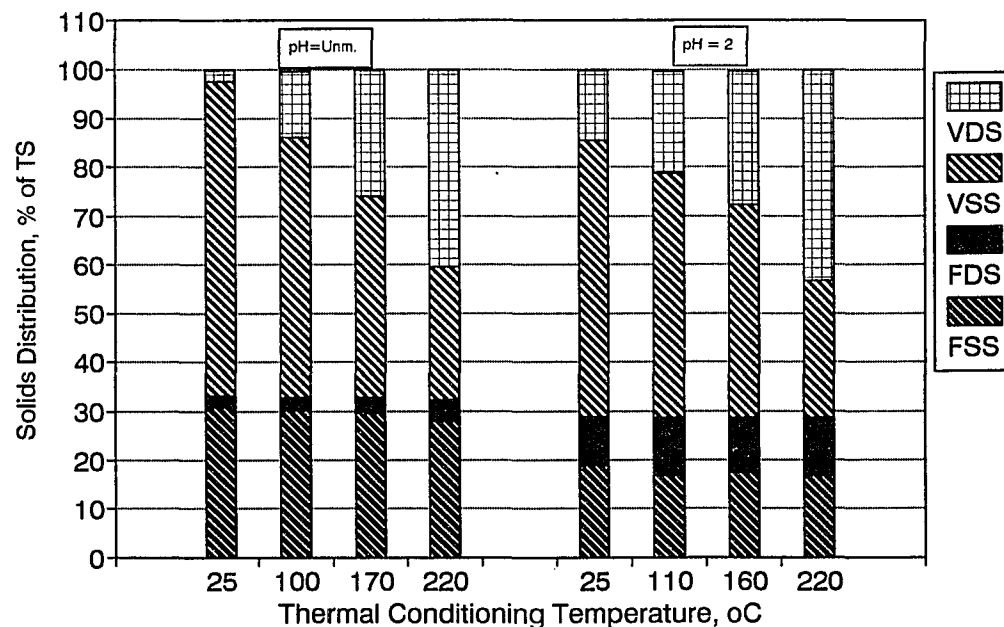
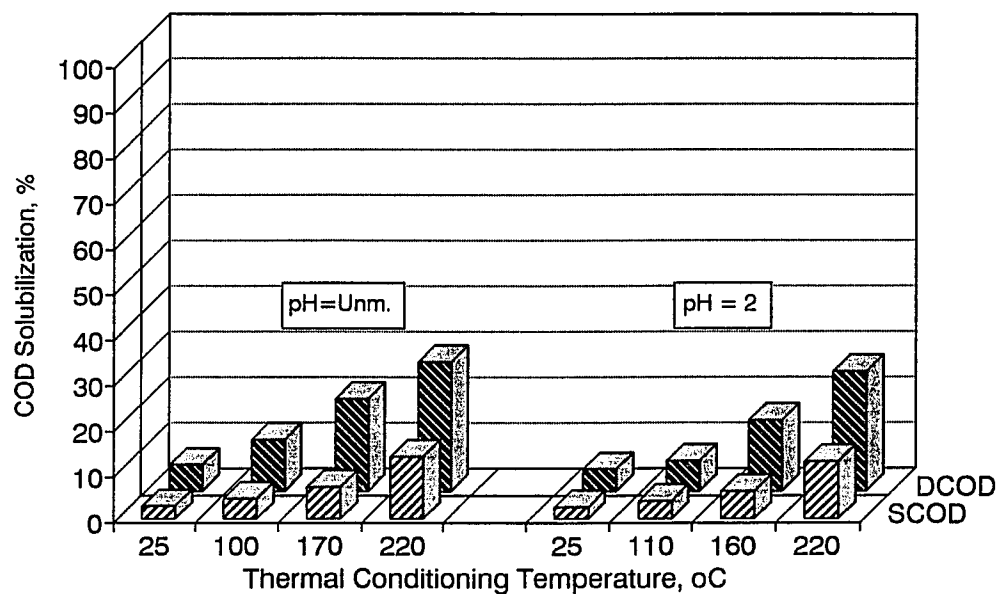


FIGURE 6-75

THICKENED PDS - COD SOLUBILIZATION

pHu and pH2; WI, March 25, 1992



of dissolved and soluble COD with DVS is shown on Figure 6-76. The data indicate that more COD is associated with DVS at the pH-unmodified condition than the pH2 condition.

Anaerobic digestion was terminated after 113 days. Similar to the unthickened PDS, the SGP results fit the two-term equation very well. Kinetic results are summarized in Table 6-12. Using the table's results, the GPIs were calculated, comparing favorable with the measured values. Figure 6-77 and 6-78 illustrate the pHu and pH2 results, respectively. The high initial GPIs clearly demonstrate the kinetics improvement, and the asymptotic values demonstrate the ultimate biodegradability improvement. Ultimate biodegradability was highest at 220°C, where it reached about 20% for pHu and 60% for pH2. The pH2 conditioning, however, outperformed the pHu results at all temperatures, resulting in the same conclusions as the unthickened PDS.

Thickened PDS conditioning obtained similar results with the unthickened PDS, where both kinetics and biodegradability increased with thermal conditioning temperatures. These findings are very important because thickening will drastically decrease the steam consumption, resulting in an energy efficient process. For every doubling of the solids concentration, the steam consumption is cut in half. Even though it was very difficult to gravity-thicken the PDS beyond the 5% TS, mechanical thickening should increase the TS to over 10%, cutting the steam consumption almost five times.

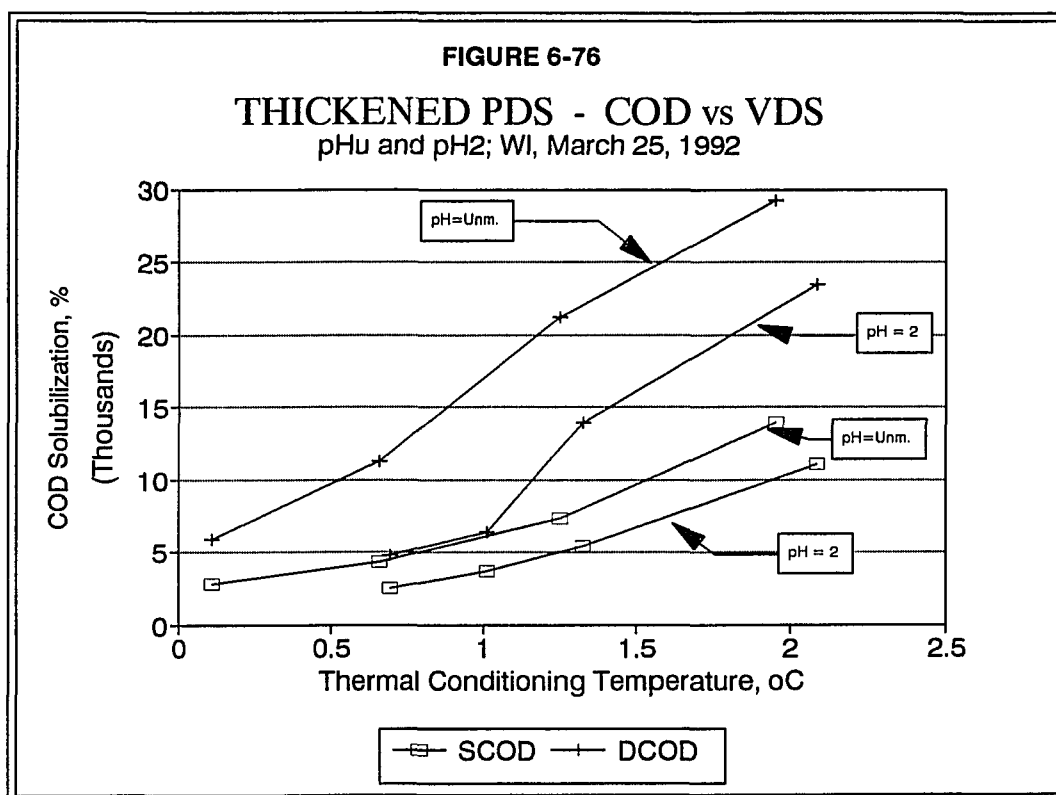


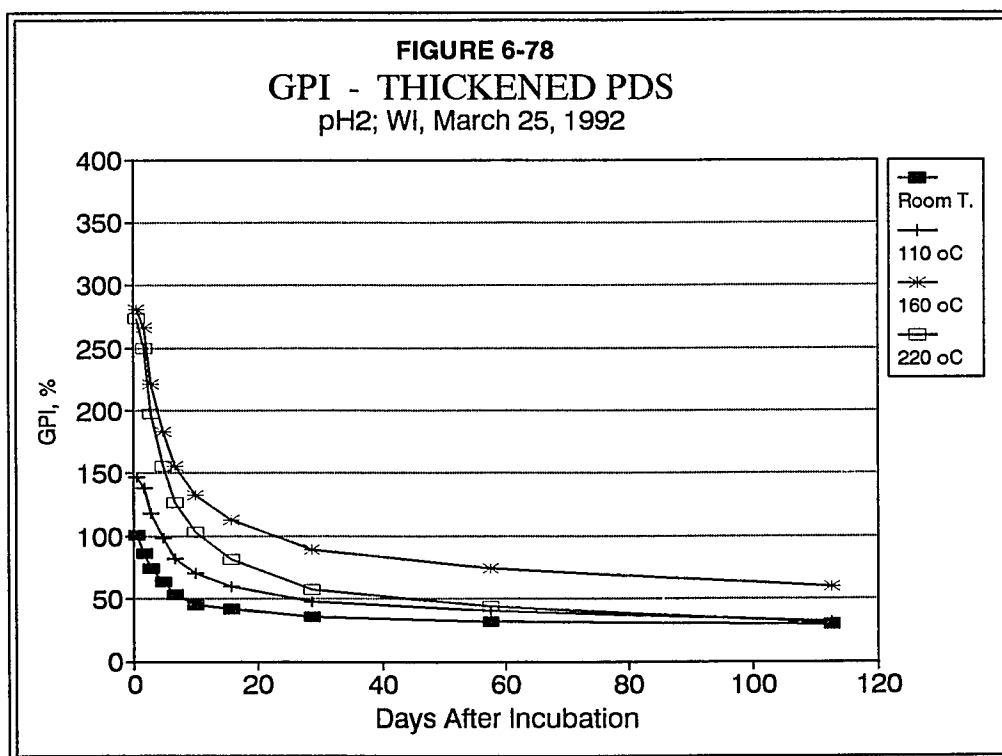
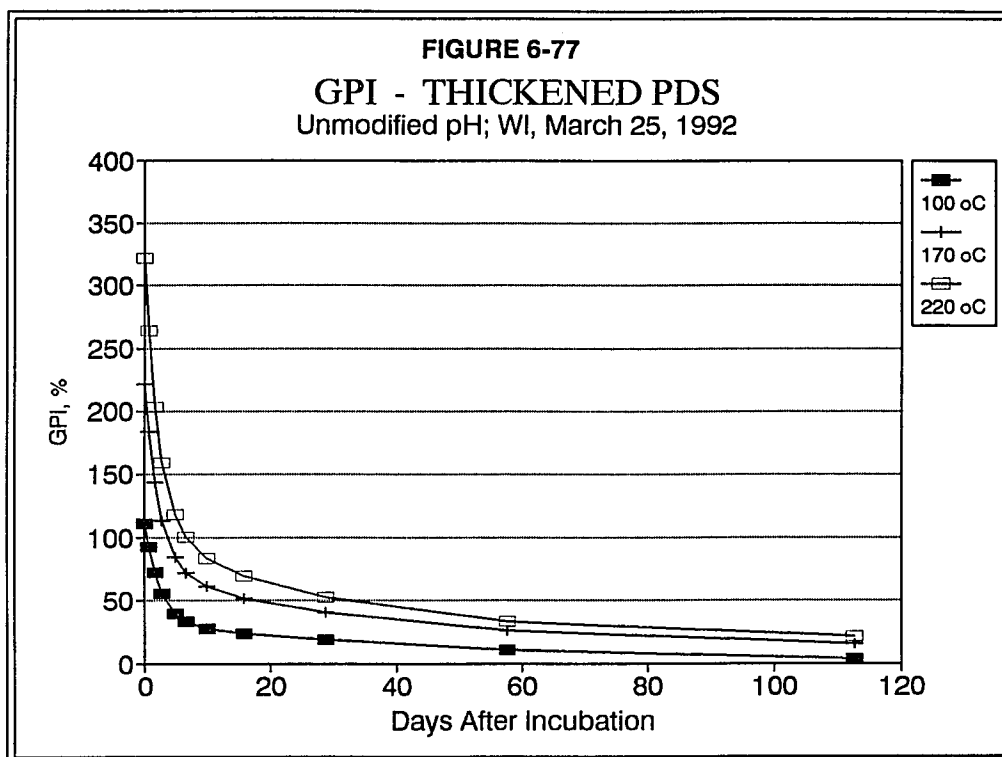
TABLE 6-12

SPECIFIC GAS PRODUCTION (SGP) KINETIC RESULTS, SERIES 5 (THICKENED PDS)

pH Condition	RTC Temperature T (°C)	SGP Coefficients				G ₁ + G ₂ (mL/g)	G ₁ k ₁ + G ₂ k ₂ (mL/g-d)
		G ₁ (mL/g)	G ₂ (mL/g)	k ₁ (1/d)	k ₂ (1/d)		
Seed	25	62.7	88.9	0.471	0.0286	151.6	32.1
Unmodified pH	25	30.1	70.7	0.410	0.0268	100.8	14.2
	100	39.2	62.8	0.706	0.0377	102.0	30.0
	160-170	54.1	59.0	0.800	0.0419	113.1	45.8
	220	66.5	51.6	0.868	0.0441	118.1	60.0
pH = 2	25	46.5	82.0	0.650	0.0291	128.5	32.6
	100-110	58.0	72.2	0.707	0.0326	130.2	43.4
	160	85.3	71.4	0.805	0.0360	156.7	71.2
	220	79.4	48.6	0.888	0.0336	128.0	72.1

Notes:

1. $SGP = G_1(1 - \exp(-k_1t)) + G_2(1 - \exp(-k_2t))$



6.1.1.2 Waste Activated Sludge

PDS is a complex medium of particulate and soluble organic compounds. Particulate organic consists of biomass and non-biomass compounds. Rapid thermal conditioning (RTC) of PDS may affect both types of organics (biomass and non-biomass) but to a different level. To ascertain the impact on the two categories of organics, RTC must be used on a sample that consists mainly of biomass and on a sample that consists mainly of non-biomass organic matter. These two samples are analogous to waste activated sludge (WAS) and primary sludge (PS), respectively. The important result of this test would be to thermally condition one of the sludge types and use the existing digesters to achieve greater digestion and gas production. Several investigators (Haug, 1977; Haug *et al.*, 1978; Stuckey and McCarty, 1984; and Li and Noike, 1992) demonstrated that conventional thermal conditioning improves WAS biodegradability. The effect of RTC was evaluated on WAS and PS. This section presents the WAS results and the following section the PS results.

WAS was collected from Wards Island on July 21, 1992. The sludge was sieved, thermally-conditioned and anaerobically-digested on the same day. RTC was performed at unmodified pH, 10 seconds HRT, and 100°C, 150°C, 185°C and 225°C. RTC was also performed at 220°C and 30 seconds HRT, but the results are suspicious because the RTCR effluent flowrate was less than influent flowrate. The reason for the flowrates discrepancy could be due to short-time plugging of the RTCR.

Cell Disruption

Because WAS consists primarily of biomass, one mechanism by which anaerobic digestion is improved may be that thermal conditioning lyses the cells and releases the cells' cytoplasm. Most of the released cytoplasm can be readily used by the anaerobic bacteria. Furthermore, Dohanyos and Zabranska (1991b) showed that the released cytoplasm, named "lysate", contains vitamins and enzymes that stimulate biodegradability. The lysate, therefore, serves two purposes, as substrate and as biostimulant.

The oxygen uptake rate (OUR) test was used to measure the degree of cells' lysis or viability after the RTC process. Pavlostathis (1985) also used the OUR test to evaluate bacterial viability of WAS. OUR was performed in a 300 mL BOD bottle filled with sample. Dissolved oxygen (DO) concentration was measured with a DO probe over a period of 30 minutes. Before the test started, the sample was aerated to increase its DO concentration so that the test would not be oxygen-limited. OUR was calculated from the slope of the straight line obtained by plotting the remaining DO in the bottle vs. time.

OURs were measured on unconditioned WAS and on WAS thermally-conditioned at 100°C, 150°C, and 225°C for 10 seconds. Figures 6-79 and 6-80 illustrate the OUR graphs of the unconditioned WAS and the 225°C conditioned WAS, respectively.

The parameter that normalizes the OUR is the specific oxygen uptake rate (SOUR), defined as the OUR per gram of VSS. The SOUR units are $\text{mgO}_2/\text{L-min-g VSS}$. Cell

FIGURE 6-79

**OXYGEN UPTAKE RATE OF UNCONDITIONED
WASTE ACTIVATED SLUDGE**

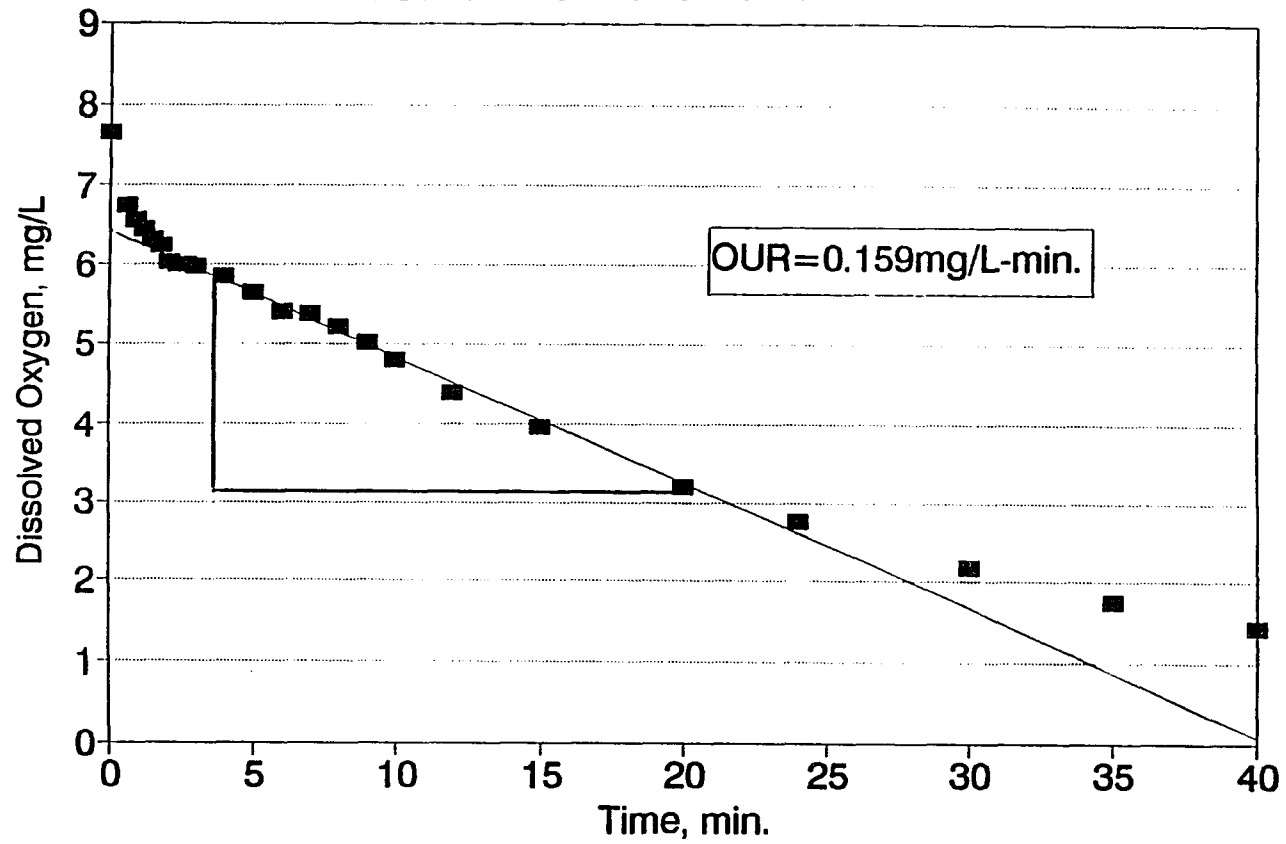
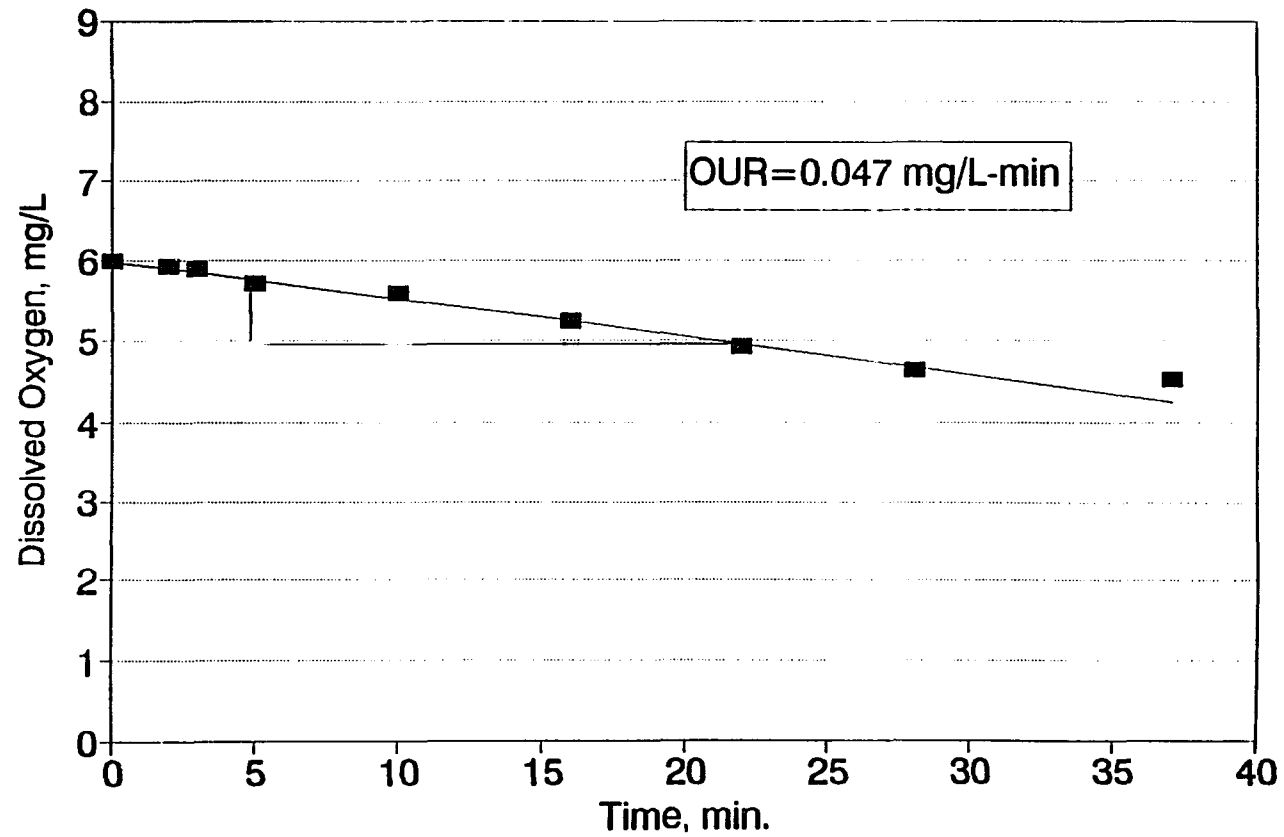


FIGURE 6-80

**OXYGEN UPTAKE RATE OF WASTE ACTIVATED SLUDGE
THERMALLY CONDITIONED AT 225 °C**



disruption is related to the change in SOUR of the thermally conditioned sample over the unconditioned sample.

Table 6-13 summarizes the SOURs and the characteristics of the WAS after thermal conditioning, and Figure 6-81 presents the cell destruction calculated at the various temperatures. Cell destruction reached 80 percent at 100°C and remained at that level over the thermal conditioning temperature range. The 100°C and 150°C sample results may be questioned since the straight-line section of the DO vs. time figures was not well-defined. The 220°C sample has a well-defined straight line confirming cell disruption.

At the thermal conditioning temperature of 225°C only a little over 80% disruption was observed by the OUR tests. This shows that either the thermal conditioning time is too short, even at 225°C, to kill all the bacteria, and/or there is something in the sample that chemically consumes the dissolved oxygen.

Some bacterial survival was confirmed in Section 6.1.1 where PDS that was thermally-conditioned at 220°C for as long as 3 minutes showed gas production when it was incubated in serum bottles without seed addition. No gas production was measured during the first week of incubation. Gas production started approximately one week after incubation indicating that it is not possible for 20% of the bacteria, as estimated by the OUR test, to survive thermal conditioning. Less than 20% of the bacteria survived. Therefore, there must be something in the sample that consumed the dissolved oxygen, resulting in higher SOURs.

TABLE 6-13

WASTE ACTIVATED SLUDGE (WAS) CHARACTERISTICS AFTER THERMAL CONDITIONING

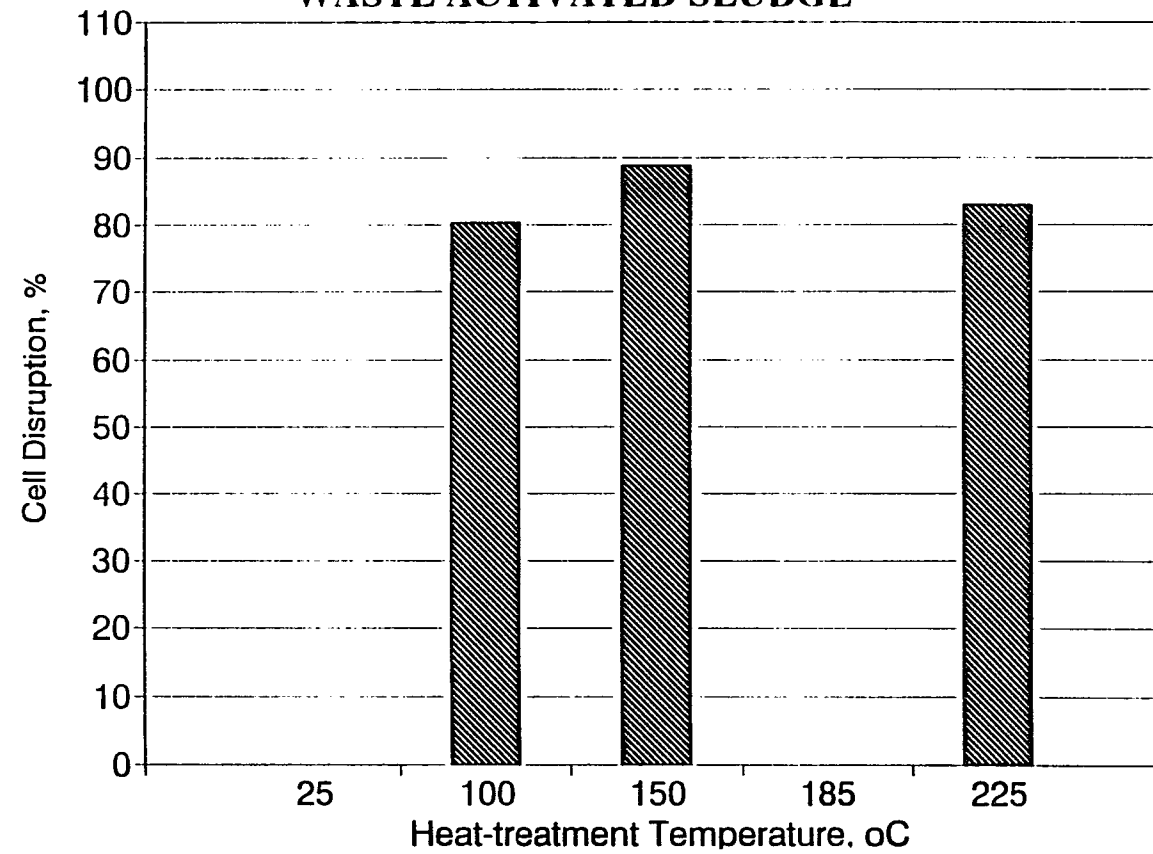
Sample No.	Temp. (°C)	TS (%)	TVS % of TS	DS (%)	VDS % of DS	DS/TS (%)	TCOD (mg/L)	SCOD (mg/L)	SCOD/TCOD (%)	OUR (mg/L-min)	Spec. OUR (mg/L-min/g VSS)	Cell Disruption (%)
SEED ⁽²⁾	--	2.84	64.9	0.231	41.0	8.1	24,200	769	3.2	--	--	--
10 Seconds HRT												
R	25	0.56	68.7	0.121	17.6	21.5	5,055	1,108	21.9	0.795	72.6	--
100	100	0.56	66.7	0.168	36.7	29.9	5,055	1,024	20.3	0.133	14.2	80.5
150	150	0.56	66.6	0.189	45.4	33.7	5,055	1,111	22.0	0.070	8.1	88.9
185	185	0.56	67.5	0.205	49.4	36.5	5,055	1,181	23.4	--	--	--
220	225	0.56	66.9	0.280	60.1	49.9	5,055	1,880	37.2	0.077	12.4	83.0
30 Seconds HRT												
220-3	220	0.56	67.4	0.307	63.2	54.6	5,055	1,709	33.8	--	--	--

NOTES:

1. Results were corrected for steam dilution.
2. Seed represents the PDS used for the serum-bottle biodegradation test.

FIGURE 6-81

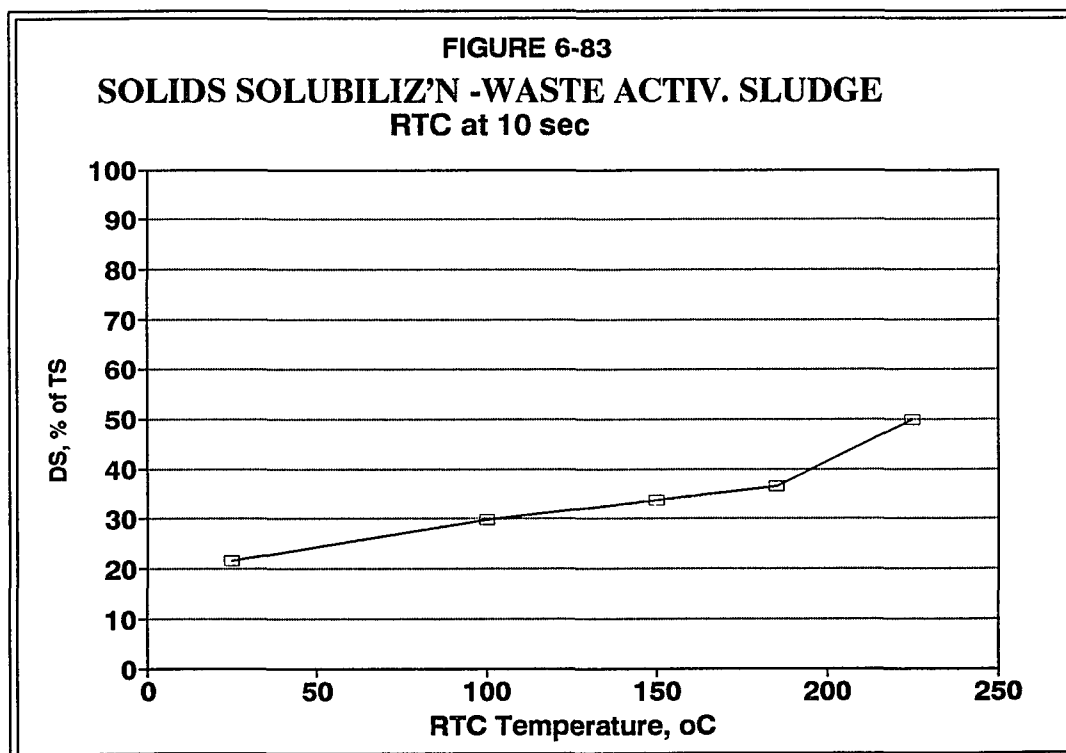
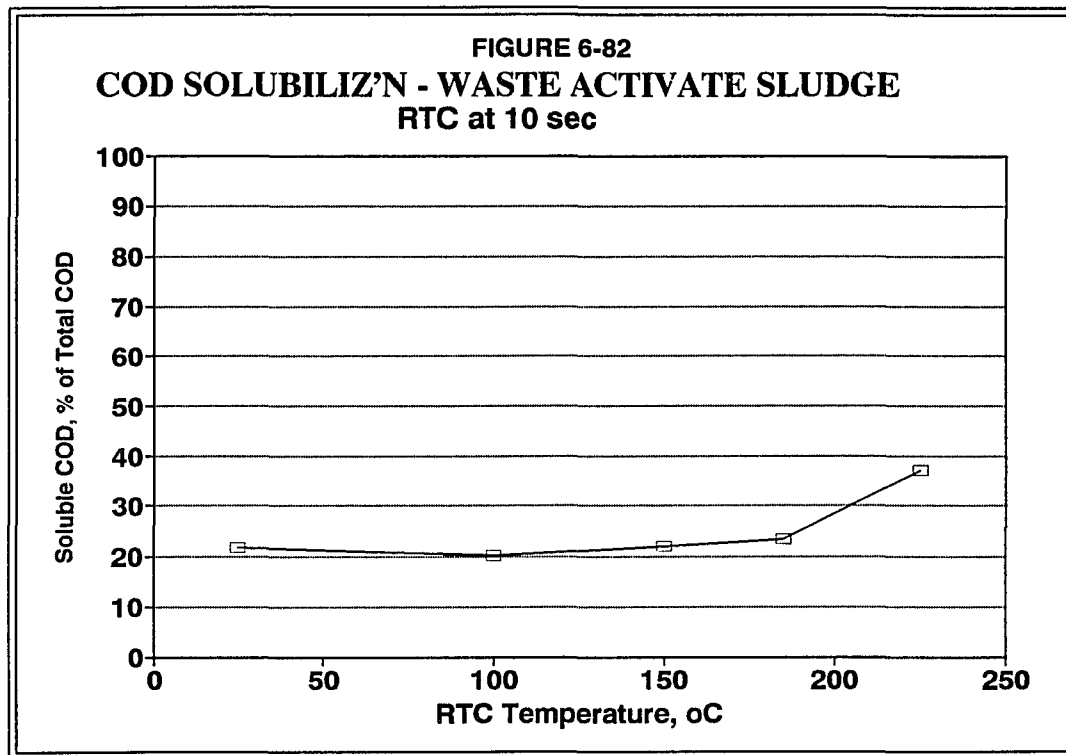
**CELL DISRUPTION OF THERMALLY CONDITIONED
WASTE ACTIVATED SLUDGE**

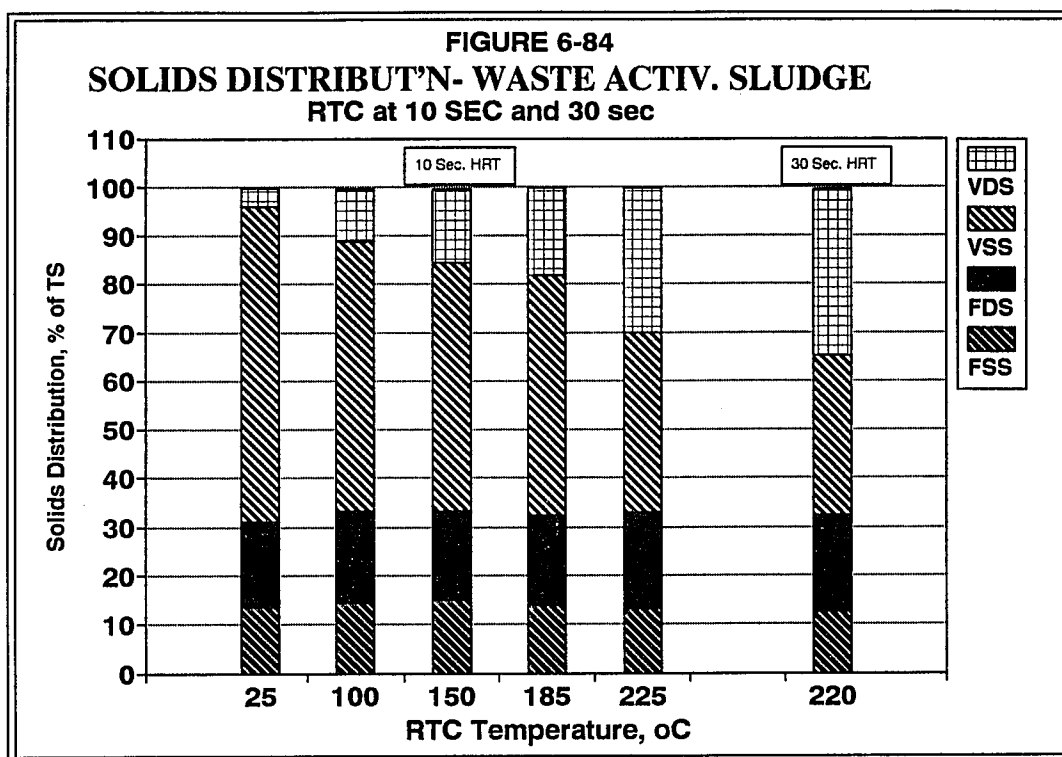


Adler (1990) reported that cytoplasmic membranes of many aerobic and facultative bacteria contain enzymes that catalyze dissolved oxygen to water and, as a result, produce anaerobic conditions. Some of the bacteria species that produce these oxygen catalyzing enzymes are *Escherichia coli*, *Pseudomonas aeruginosa*, *Gluconobacter oxidans*, *Azotobacter vinlandii*, *Mycobacterium phlei*, and *Salmonella typhimurium*. During bacterial cell disruption, as by a high pressure cell, sonic oscillator, or in our case an RTCR, the enzymes are released from the cell's cytoplasm. If the released enzymes are not destroyed during the RTC process then these enzymes will catalyze from the sample's dissolved oxygen the formation of water. Due to the short RTC times and to the fact that even some bacteria survived the RTC process, it is very likely that the catalyzing enzymes released were not destroyed. Therefore, the oxygen consumption measured during the OUR test should be attributed to the combined effect of the released enzymes and the surviving bacteria.

Solids and COD Solubilization

Soluble COD and dissolved solids (DS), shown on Figure 6-82 and Figure 6-83, respectively, increase with thermal conditioning temperatures. At 225°C, soluble COD reached 37% of total COD compared to the initial of 22%, and DS reached 50% of the total solids compared to the initial of 22%. COD solubilization was minimal up to the thermal conditioning temperature of 185°C with an abrupt increase at 225°C, whereas solids solubilization increased more uniformly over the evaluated temperature range. The full solids distribution spectrum is presented on Figure 6-84, showing that solubilization





took place only for the volatile solids but not for the fixed solids. Thermal conditioning at 220°C and 30 seconds HRT gave similar solubilization as the 10 seconds HRT. The VDS and VSS were fitted with a second degree polynomial, shown on Figure 6-85.

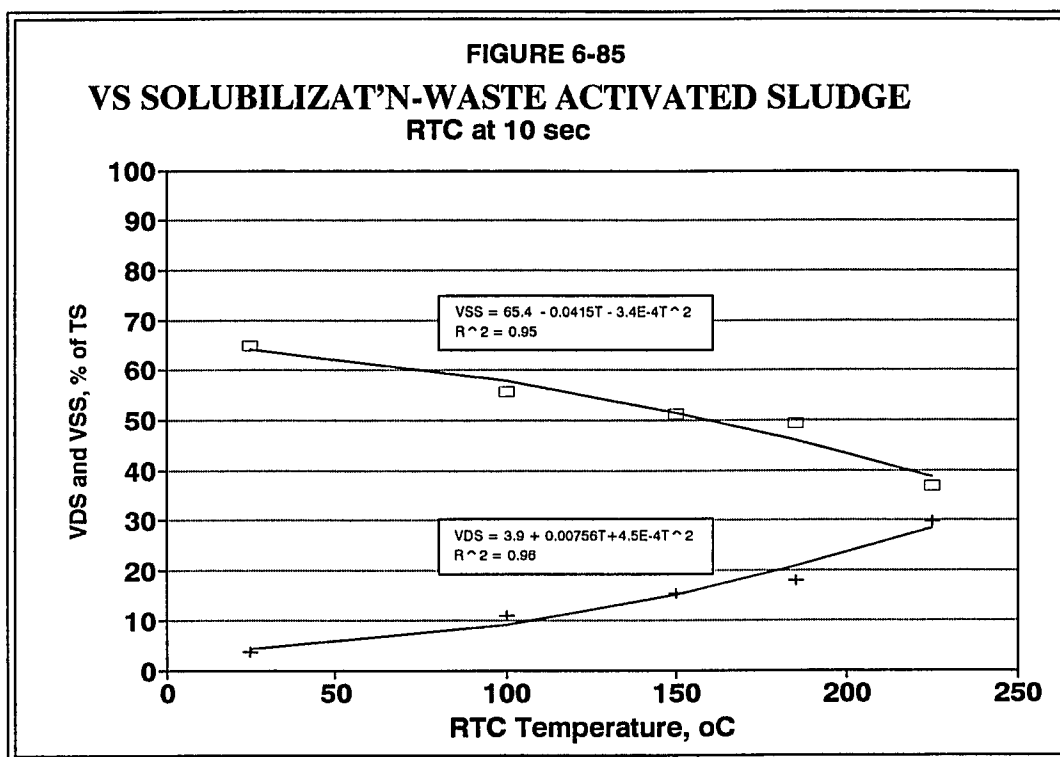
$$VSS/TS (\%) = 65.4 - 0.0415T - 3.4E-4T^2 \quad (6-12)$$

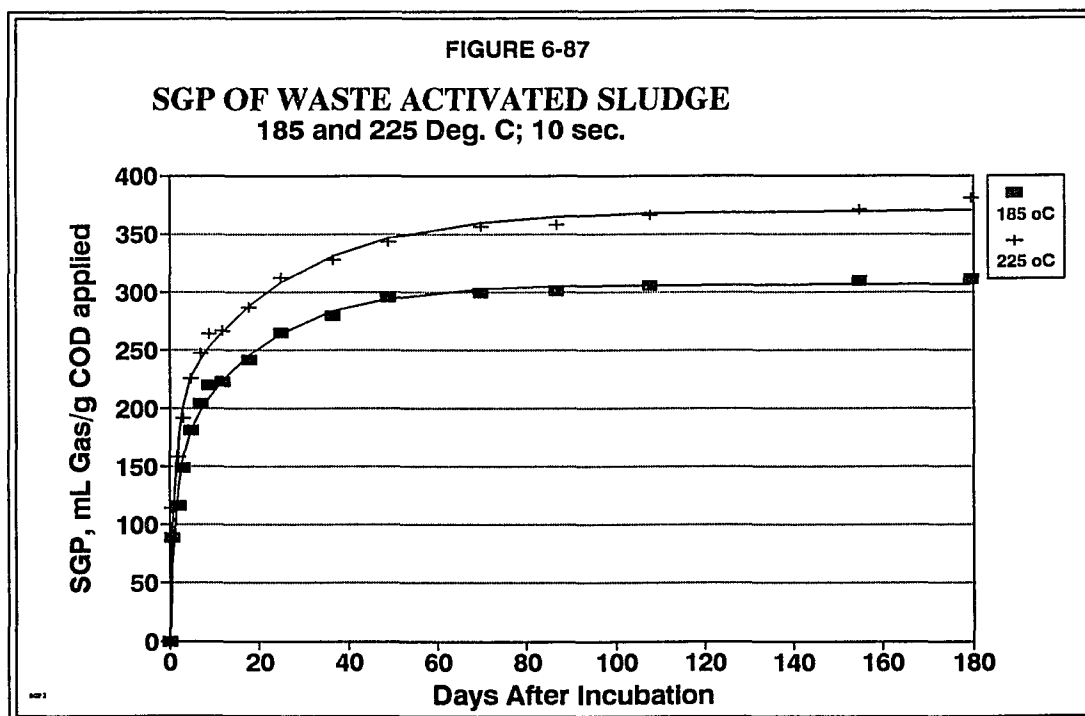
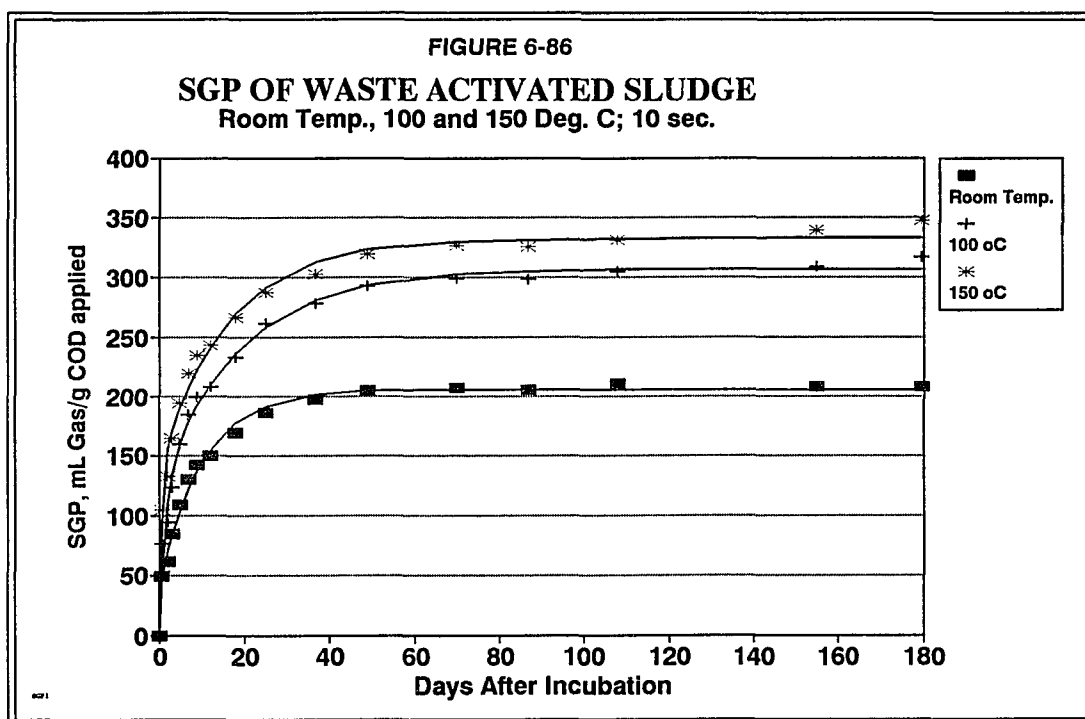
$$VDS/TS (\%) = 3.9 + 0.00756T + 4.5E-4T^2 \quad (6-13)$$

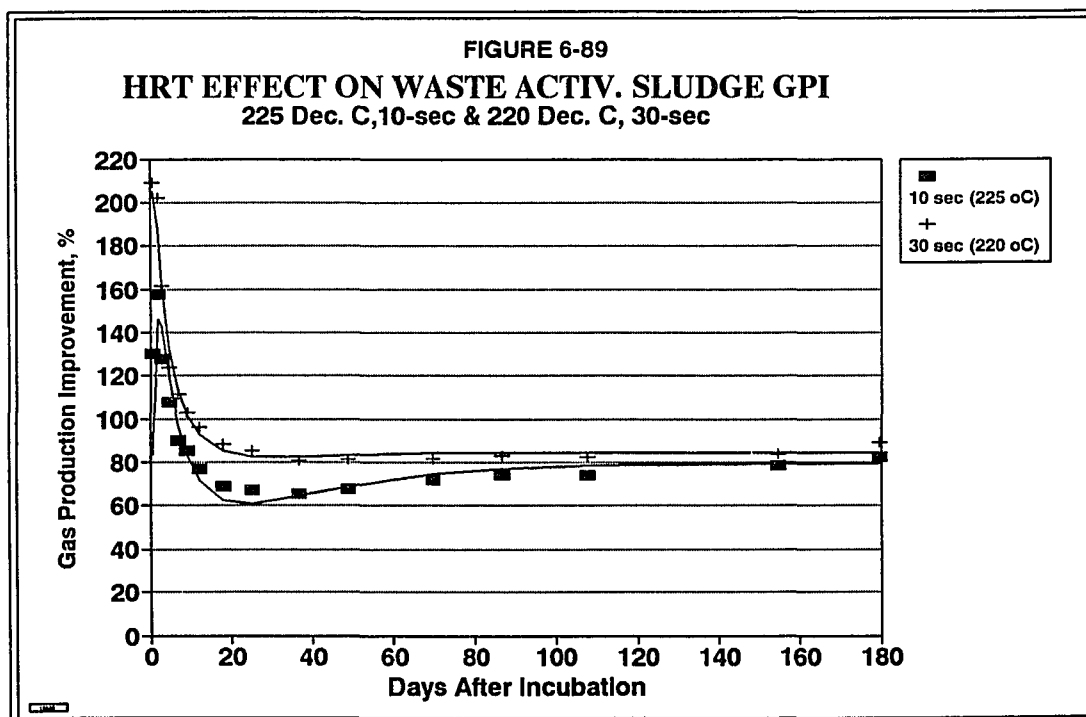
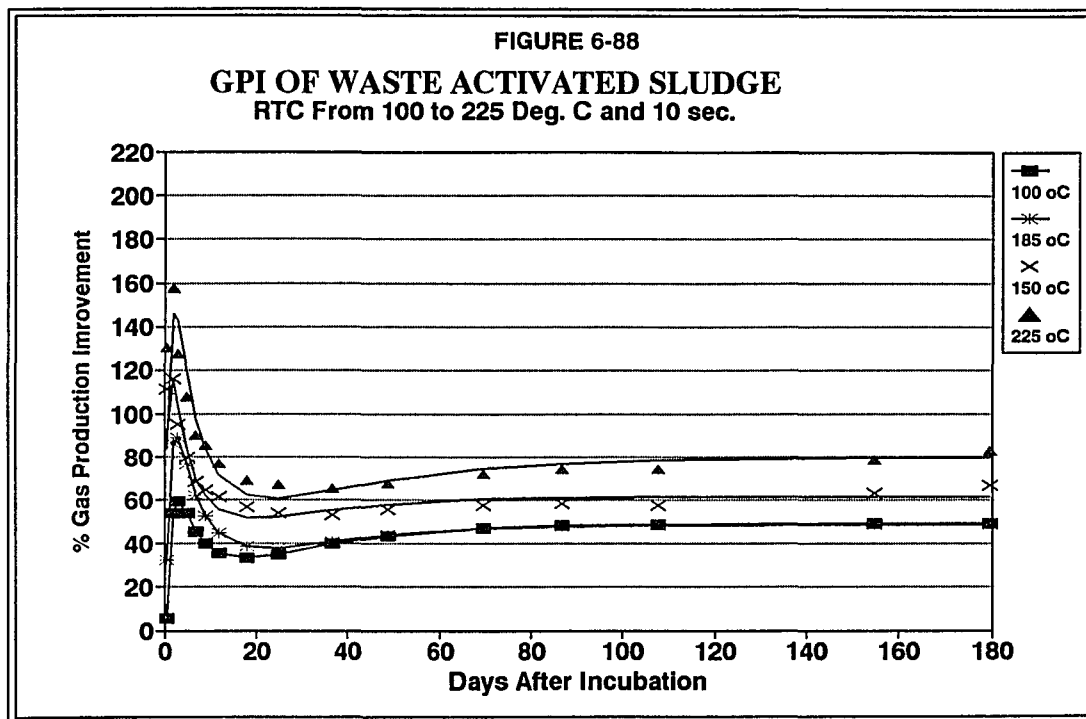
Biodegradation Results

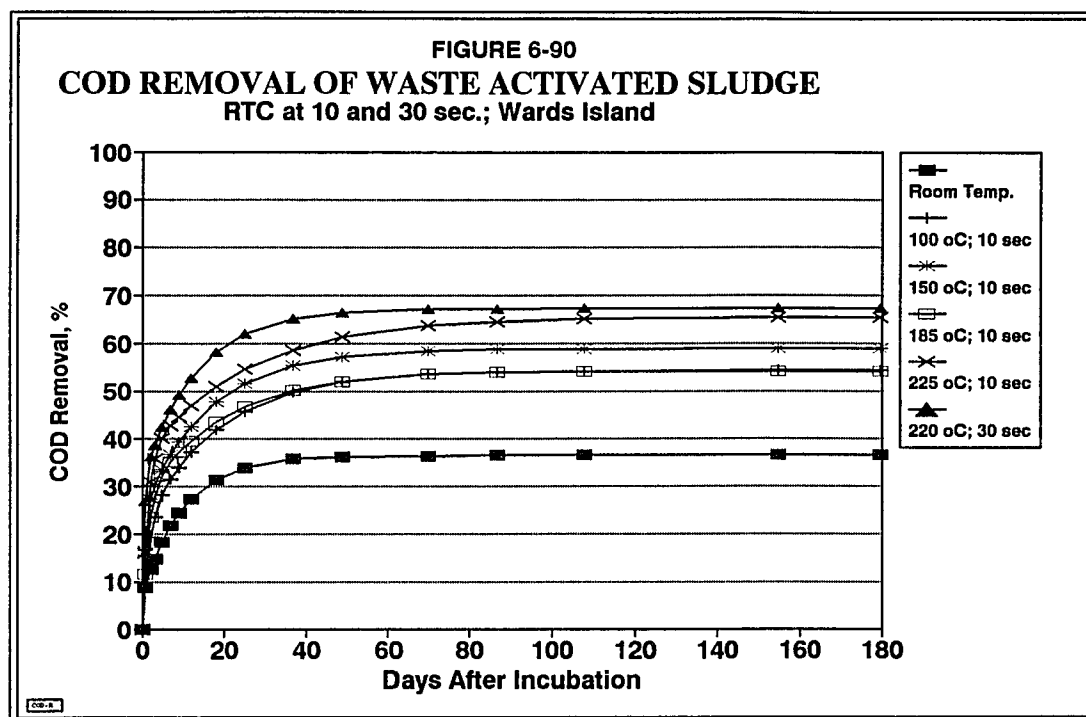
Biodegradation testing of the thermally conditioned WAS was performed by the serum bottles test. SGP results were also fitted to the two-term equation, and they are demonstrated on Figures 6-86 and 6-87. As with the PDS results, the fitness of the equation to the data is excellent, indicating that the two-term equation can be used to evaluate the GPI of the WAS. The GPI results, summarized on Figures 6-88, show a biodegradation improvement of 50% to 80% corresponding to a low temperature of 100°C and a high temperature of 225°C, respectively. Thermal conditioning at 220°C and 30 seconds slightly improved biodegradation, compared to the thermal conditioning at 225°C for 10 seconds (Figure 6-89).

The COD removed from each serum bottle was then calculated and is shown on Figure 6-90. Removals were calculated from the gas production, assuming that 70% of the gas volume consists of methane. Previous gas composition analysis showed 70% to 75% methane in the gas phase. The untreated WAS gave an ultimate COD removal of 37%,









whereas the thermally conditioned WAS produces COD removals from a low 54% (100°C and 185°C) to a high 66% (225°C). The RTC of WAS at 220°C for 30 seconds gave a slightly increased COD removal of 67%.

To summarize, RTC improved the biodegradation of WAS by as much as 80%, at the temperature of 225°C. Lysing the cells and making the cytoplasm readily available to anaerobic digestion may be the major mechanism. Another mechanism might be that the "lysate" stimulates the metabolism of the anaerobic bacteria resulting in high gas production. In addition, Gossett and Belser (1982) reported that some portion of WAS biomass is able to persist and escape the anaerobic digestion process intact as conventionally operated. They hypothesized that during WAS digestion much of the anaerobic substrate is enclosed within viable cells, requiring preliminary conversion of the "cell-bound" substrate to more available forms before it can be utilized by anaerobic digestion. During the RTC process, the cell-bound substrate is released, making the substrate available to anaerobic digestion and resulting in higher gas productions.

The results showed that conditioning **temperature** and not conditioning **time** has the greatest impact on both organic solubilization and ultimate biodegradation improvement.

6.1.1.3 Fermented Primary Sludge

Particulate organic hydrolysis is believed to be the rate limiting step in digesters fed with particulate slurry or solid feeds (Ghosh, 1987). Thermal conditioning was tried by Haug (1977) on primary sludge (PS) to hydrolyze particulate solids into soluble organic matter. The results indicated no increase in the ultimate biodegradability of PS. Therefore, the effect of RTC directly on PS was not evaluated in this study. Instead, the PS was allowed to ferment first and then conditioned in the RTCR.

During fermentation, some hydrolysis takes place and soluble organics are fermented to form volatile acids (Ghosh, 1987; Eastman, 1977). Eastman (1977) used the fermentation stage to solubilize organics, producing a carbon source for the denitrification process. During Ferguson's experiments, volatile acid production dropped the pH to 6. The effective hydraulic retention times of the experiments were between three and five days.

On July 30, 1993, PS was collected from Wards Island from the pumps that send the PS to the thickener. Because the PS was very dilute (the pumps from primary clarifiers to thickener are operated continuously), PS was gravity-thickened in carboys before it was transported to City College. At the Environmental Engineering Laboratory, PS was put in a 55-gallon drum and was mixed with a variable speed mixer for six days without aeration. This test was performed to biochemically acidify the PS and generate volatile acids (VA) by the acidic-phase of digestion. During the six-day fermentation phase, the

pH of PS decreased from 6.7 to 6.0, and the VA concentration increased from 187 to 950 mg/L as HAc.

Solids and COD Solubilization

On August 5, the fermented PS was sieved, thermally-conditioned, and digested. Thermal conditioning was performed on the fermented PS at 100°C, 140°C, 180°C, and 220°C for 10 seconds, and at 180°C and 220°C for 30 seconds. Table 6-14 presents the characteristics of the fermented primary sludge before and after thermal conditioning.

Figures 6-91 and 6-92 show the COD and solids solubilizations, respectively. There was **no increase** in dissolved solids at the various thermal conditioning conditions. Only soluble COD increased linearly from 19% (room temperature) to 40% (225°C) of total COD. Dissolved solids were measured after filtration through the Whatman 934-AH glass fiber filter that retains solids greater than 1.5 μm in size; soluble COD was measured after filtration through a membrane filter with a pore size of 0.45 μm . The result of thermal conditioning on solids and COD solubilization indicate that solubilization takes place on **dissolved** organics and not on suspended organics, hence the increase in COD solubilization and the no-effect in solids solubilization. In other words, the suspended solids remaining after the fermentation phase of PS were not affected by thermal conditioning. Figure 6-93 presents the solids distribution and compares the 10 seconds with the 30 seconds results. There is no significant increase in solubilization taking place at 30 seconds, as compared to the 10-second thermal conditioning.

TABLE 6-14

FERMENTED PRIMARY SLUDGE CHARACTERISTICS AFTER THERMAL CONDITIONING

Sample No.	Temp. (°C)	TVA (mg/L)	TS (%)	TVS (% of TS)	DS (%)	DVS (% of DS)	DS/TS (%)	TCOD (mg/L)	SCOD (mg/L)	SCOD/ TCOD (%)
SEED	--	1,174	2.57	64.6	0.240	43.0	9.3	27,240	1,259	4.6
PRIMARY	--	812	1.70	72.8	0.190	34.4	11.2	19,080	1,364	7.1
10 Seconds HRT										
R	25	953	0.52	54.6	0.240	46.3	46.6	6,240	1,108	17.8
100	100	881	0.52	62.0	0.243	45.2	47.2	6,240	1,529	24.5
140	140	861	0.52	63.2	0.233	47.1	45.2	6,240	1,869	30.0
180	180	911	0.52	61.0	0.243	43.3	47.2	6,240	1,994	32.0
220	220	967	0.52	60.3	0.274	49.0	53.1	6,240	2,556	41.0
30 Seconds HRT										
180-3	180	809	0.52	60.6	0.251	42.7	48.6	6,240	2,015	32.3
220-3	220	946	0.52	58.6	0.265	53.5	51.5	6,240	2,467	39.5

NOTES:

1. Results were corrected for steam dilution.
2. Seed is anaerobic sludge used for serum bottles test.
3. Primary is PS collected on August 5 and used only for anaerobic digestion.
4. All other samples are from the fermented PS collected on July 30.

FIGURE 6-91
COD SOLUBILIZATION - PRIMARY SLUDGE
RTC at 10 sec

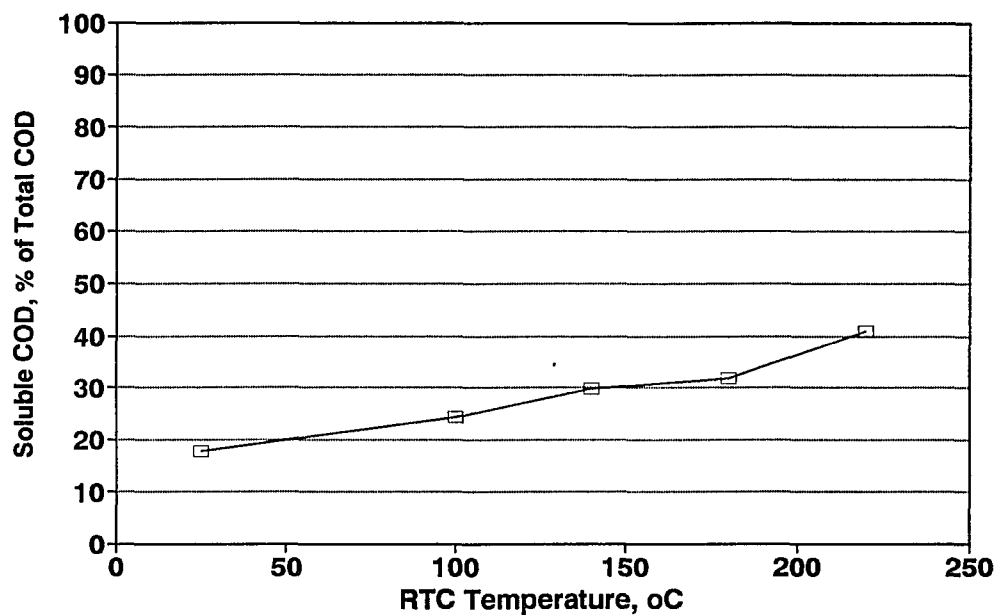
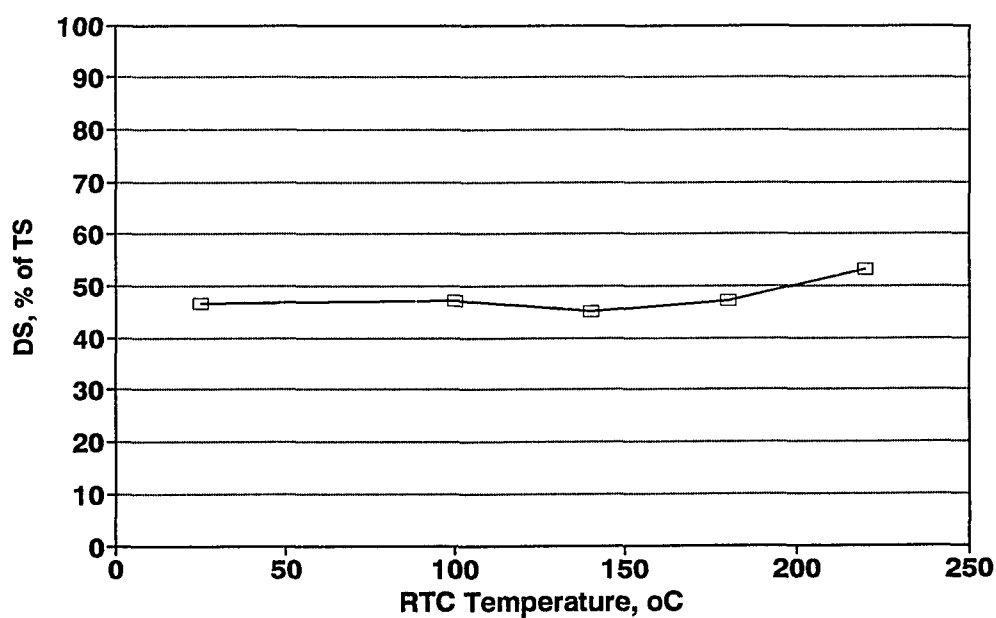
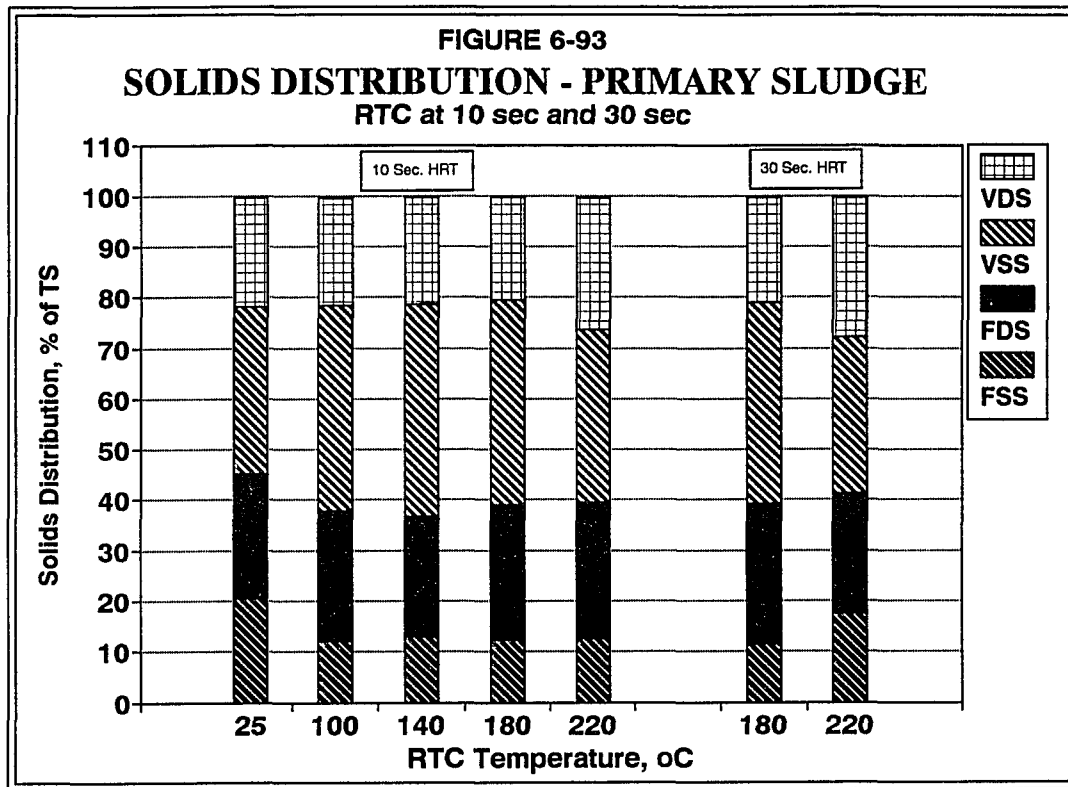


FIGURE 6-92
TS SOLUBILIZATION - PRIMARY SLUDGE
RTC at 10 sec



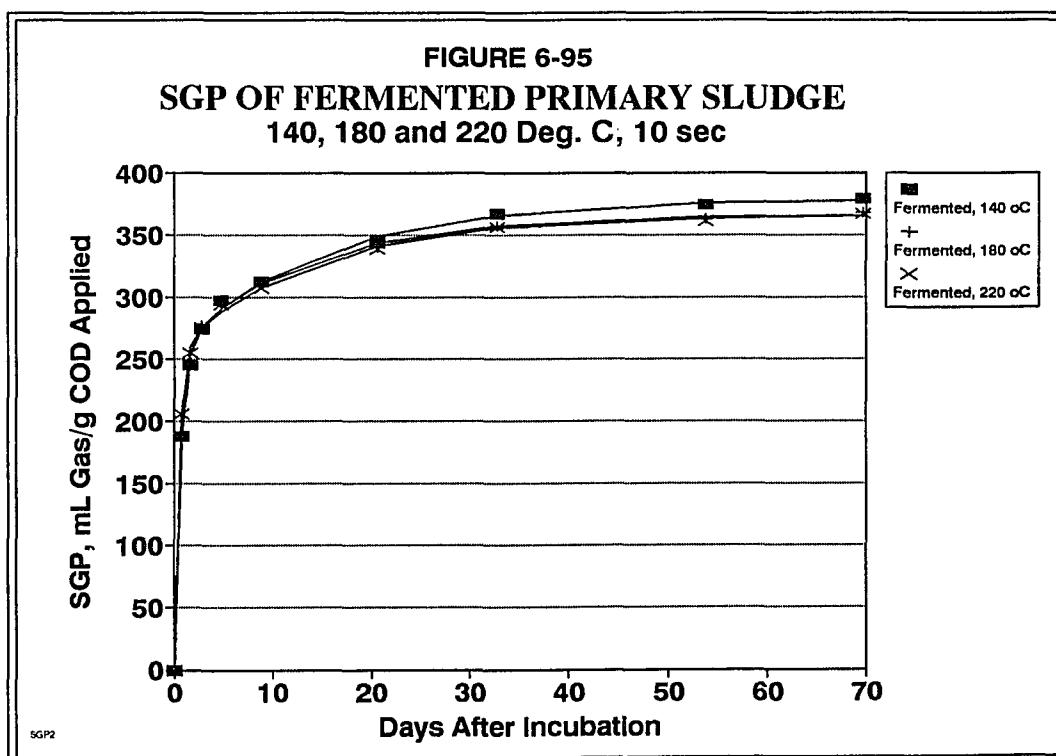
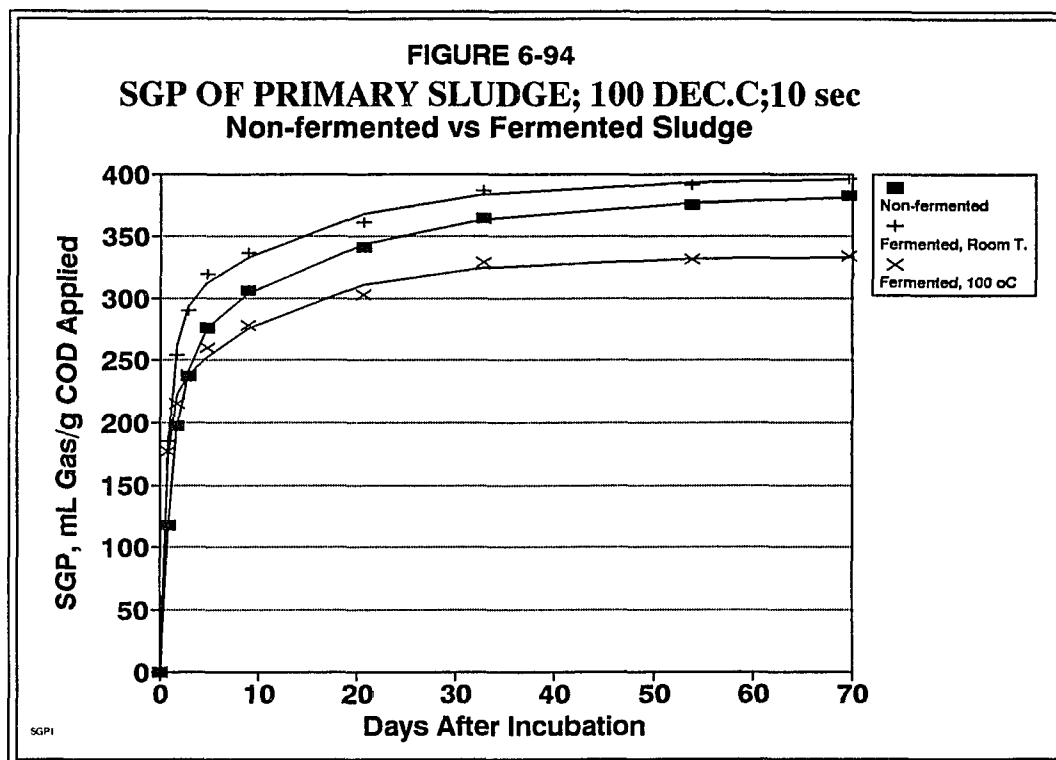


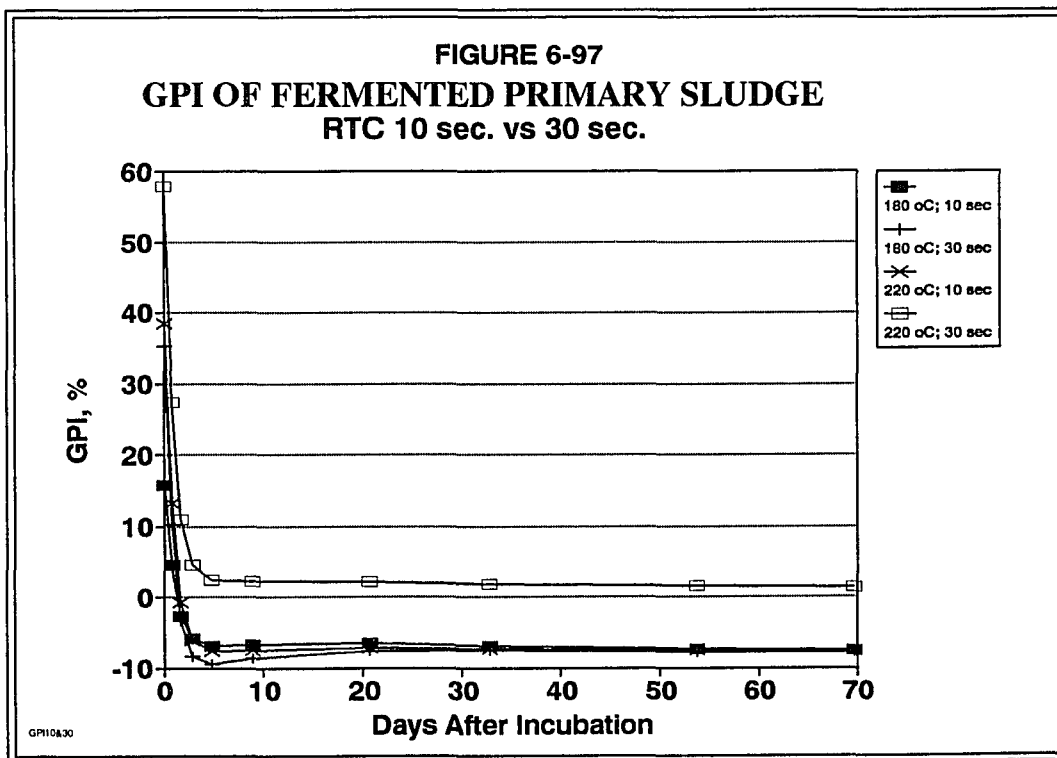
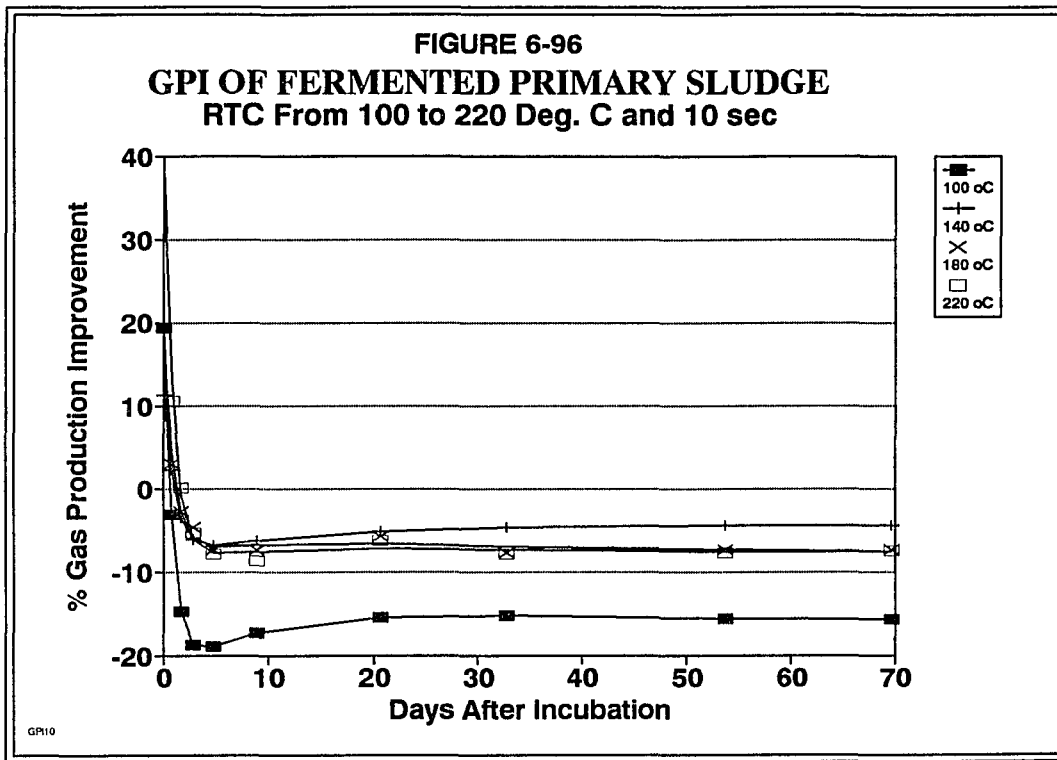
Biodegradation

Fresh anaerobically digested sludge was collected from Wards Island on August 5, 1992, and was used as seed for the conditioned PS. Fresh primary sludge was also used to compare its biodegradability with the fermented PS, and with the fermented thermally conditioned PS. The comparisons would determine whether any effect on PS's biodegradability was due to fermentation alone (prior to the RTC process) or to fermentation combined with thermal conditioning.

SGP results were again fitted with the two-term equation. Figures 6-94 and 6-95 present the SGP results for (1) the non-fermented PS, (2) the fermented but non-thermally conditioned PS, and (3) the fermented and 10-second thermally conditioned PS. The results indicate little change in the biodegradability of the fermented non-thermally conditioned PS over the non-fermented PS (Figure 6-94). In addition, RTC did not improve the fermented PS's biodegradability, indicated by similar SGP results of the long incubation times.

Figures 6-96 and 6-97 present the GPI results for the 10-second RTC and 30-second RTC, respectively. The GPI values were calculated using the SGP of the fermented non-thermally conditioned PS as reference value. All conditions, except the 30-second 220°C conditioned PS, resulted in negative ultimate GPI values, indicating that RTC decreased the PS's biodegradability. There was only improvement during the first day of incubation, where GPI's for the 10-second RTC ranged from 19% (100°C) to 38%

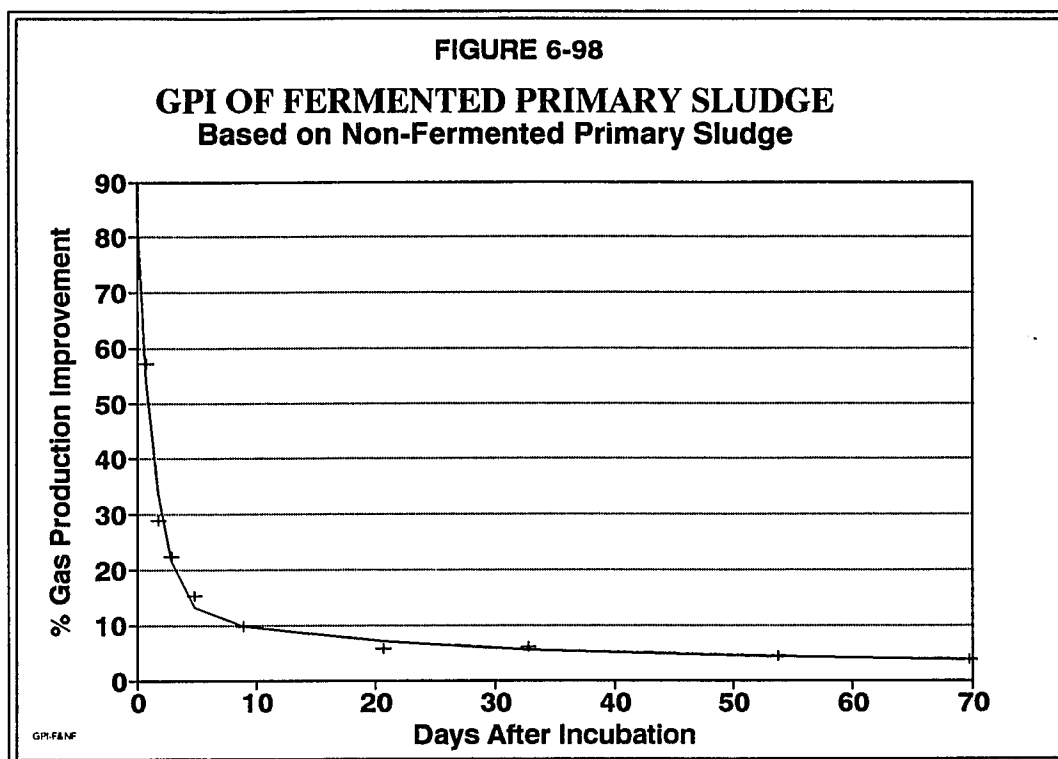


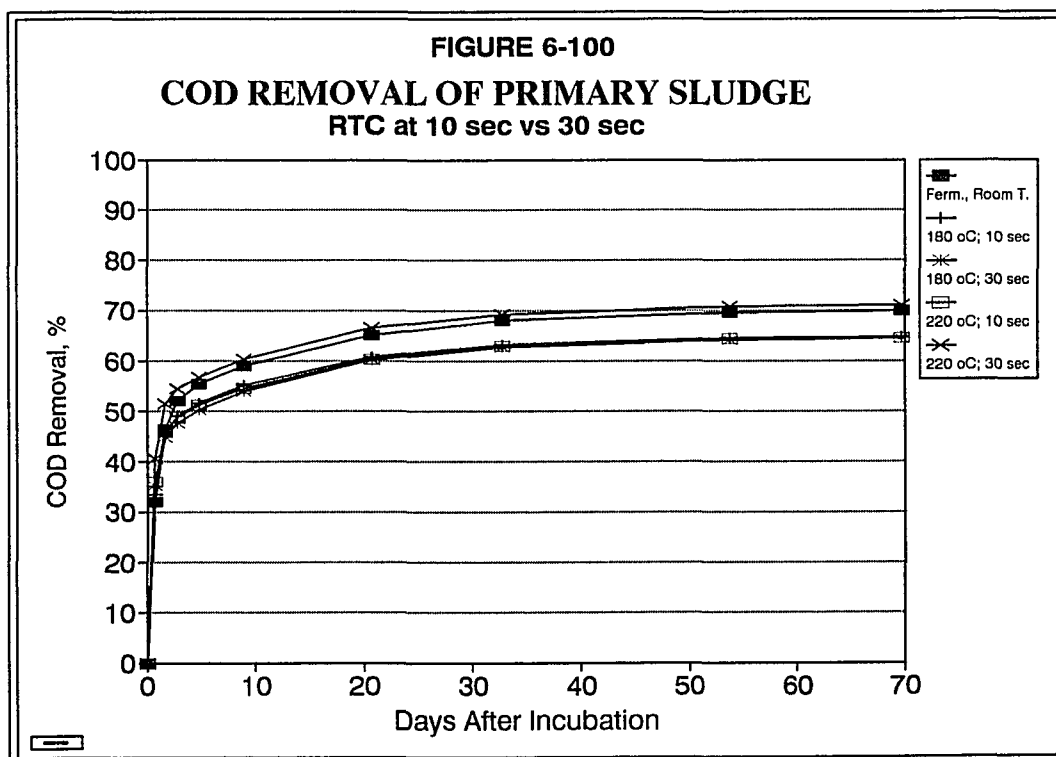
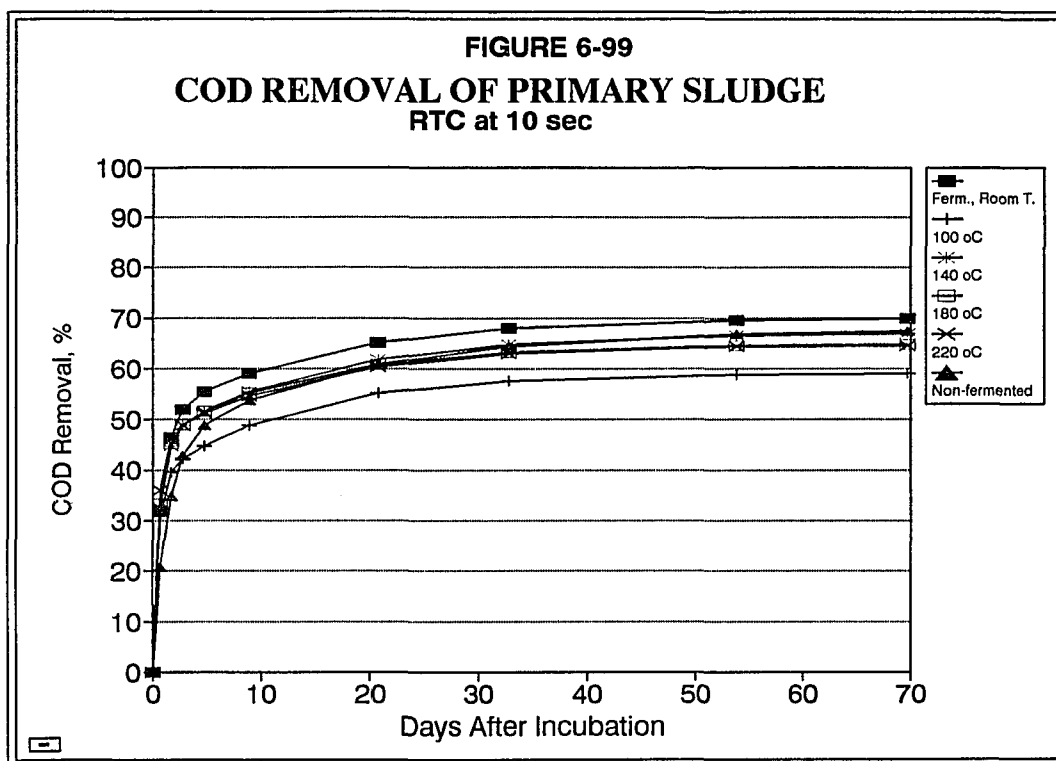


(220°C). For the 30-second RTC, improvement was 35% (180°C) and 58% (220°C). The initial improvement indicates that thermal conditioning hydrolyzed some organics and made them readily available to the bacteria. However, the hydrolyzed organics would eventually be degraded by the bacteria if thermal conditioning did not take place. This is indicated by the very sharp decrease of GPI, which reached 0% within a short incubation time. Afterwards, GPI was negative and remained negative until the end of the experiment (70 days). Only the 30-second, 220°C RTC gave slightly positive but insignificant GPI results. Therefore, RTC of fermented PS had little improvement on the kinetics, but not on the ultimate biodegradation of fermented PS.

The biodegradability of fermented PS is compared to that of the non-fermented PS on Figure 6-98. The SGP results of the non-fermented PS were used as a reference for calculating the GPI values. The results indicate that fermentation by itself improved the biodegradation kinetics of PS (maximum improvement was 80%). Ultimate biodegradation improvement was only 3% to 5% (at 70-day incubation), which should approach 0% at infinite time. The kinetics improvement and the lack of ultimate biodegradation improvement indicate that the fermentation process converted some of the organics into readily biodegradable compounds. However, these organics would be eventually degraded by the bacteria, but at longer digestion times, if fermentation did not take place.

COD removal, based on 70% methane in the gas phase, reached 65% for the untreated as well as the 10-second thermally conditioned PS (Figure 6-99). From Figure 6-100,





only the 30-second and 220°C thermally conditioned PS showed a slightly greater removal of 70%. Therefore, as with the GPI results, thermal conditioning did not improve the biodegradability of the fermented PS and the process was not considered for further studies.

The lack of improvement to the ultimate biodegradability of the fermented PS (with or without thermal conditioning) is in agreement with Haug's results (Haug, 1977) even though Haug thermally conditioned non-fermented PS. Also, Stuckey and McCarty (1984), after thermally conditioning pure individual nitrogenous compounds (amino acids and proteins) and carbohydrates (ribose, deoxyribose and glucose), found that their biodegradability decreased. This also agrees with this study's results, where some RTC conditions resulted in less biodegradation than the non-conditioned fermented PS. The reason could be that the nitrogenous compounds and carbohydrates that PS mainly consists of were converted from biodegradable organics to refractory organics. Some of the refractory effects of thermal conditioning were attributed to the sulfur-containing amino acids. Sulfur was replaced by oxygen, resulting in a non-degradable organic compound (Stuckey and McCarty, 1984).

For the solids data, RTC only affected the dissolved and not the suspended organic compounds. If RTC did not take place, extracellular enzymes would eventually hydrolyze the dissolved organic compounds, resulting in comparable ultimate biodegradations. The extracellular enzymes would probably require some form of an "outside" assistance on solubilizing the suspended organics (whatever was left after fermentation), assistance that

the RTC process did not provide. In addition, the decrease in biodegradability after thermal conditioning indicates that individual organic compounds were either destroyed or altered, resulting in refractory compounds. Based on these results, RTC may not be a feasible process to enhance the PS biodegradability.

6.1.2 Continuous Flow Reactors Results

All the previous results were obtained by anaerobic batch reactors (serum bottles). Full scale anaerobic digestion, however, takes place in continuous flow reactors such as the CFSTR and the anaerobic filter. The next step of the study evaluated these two reactors to confirm the serum bottle results, and whether thermally conditioned PDS could be feasibly treated by continuous flow reactors. Serum bottle results indicated significant improvements for both ultimate biodegradability and digestion kinetics when pH-unmodified (pHu) PDS was thermally conditioned at 220°C for 10 seconds. Even though some low and high pH conditions gave better biodegradation results, the pHu 220°C condition was chosen for the continuous flow studies.

6.1.2.1 Continuous Flow Stirred Tank Reactor (CFSTR)

(a) Baseline Run

The CFSTR was placed in the Environmental Chamber where the initial shakedown runs were completed by July 1992. Feed was stored in a 20-L carboy equipped with a mechanical mixer. A magnetic mixer failed to keep the feed well-mixed and after a few trials it was replaced by the mechanical mixer. The carboy was kept at 4°C inside a refrigerator which was also located in the Environmental Chamber. A drilled hole on the refrigerator's side

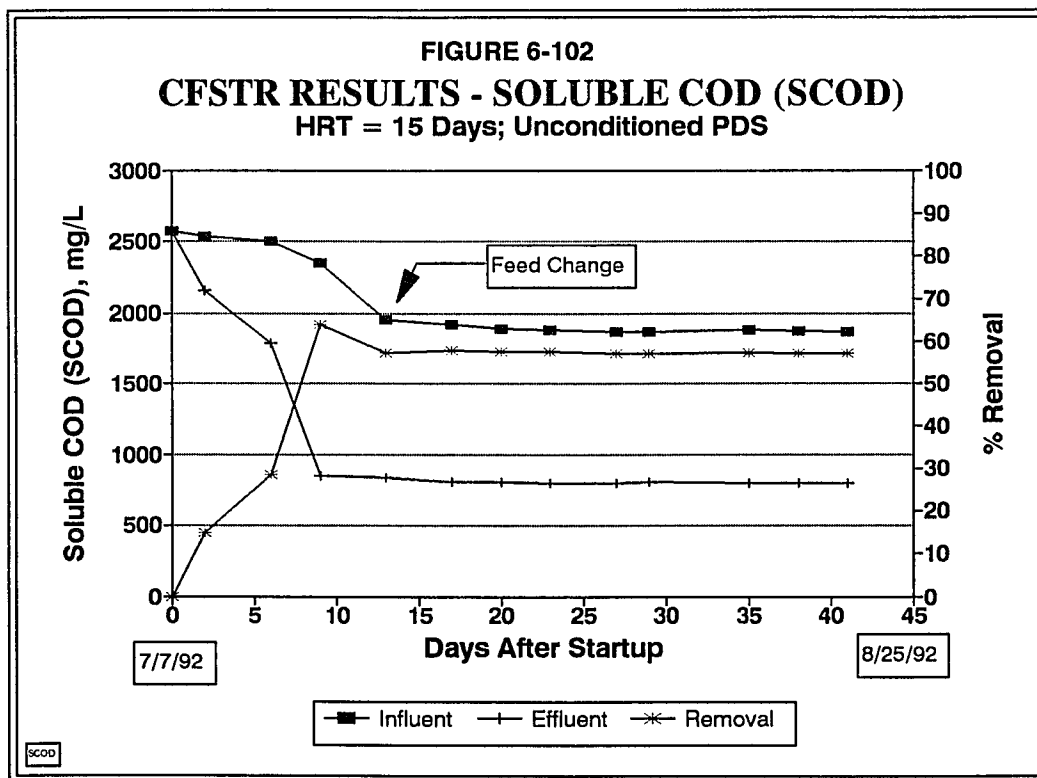
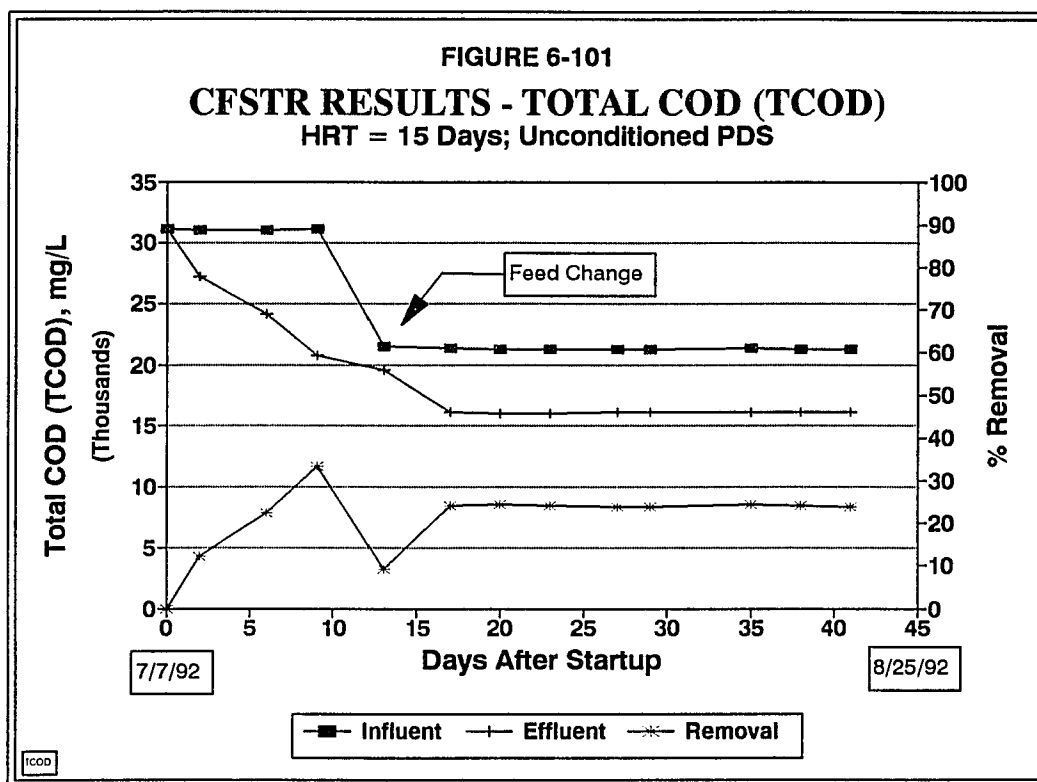
provided access for the feeding tube and electric wires needed to run the mixer. The overall apparatus functioned well throughout all the runs.

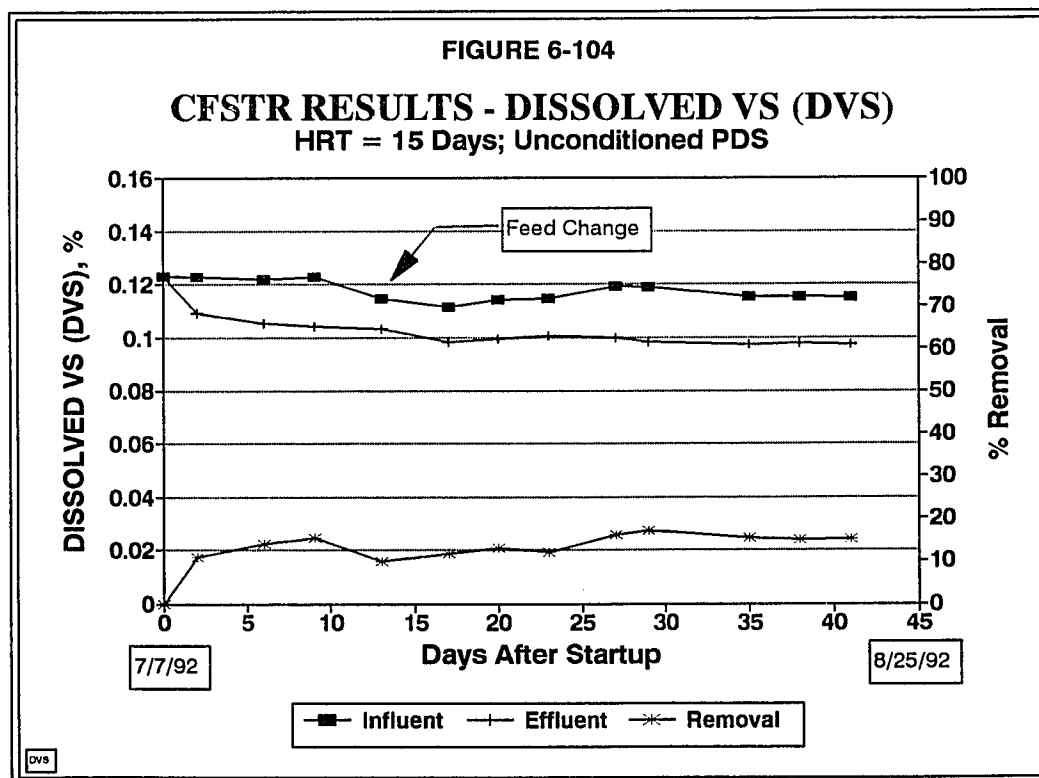
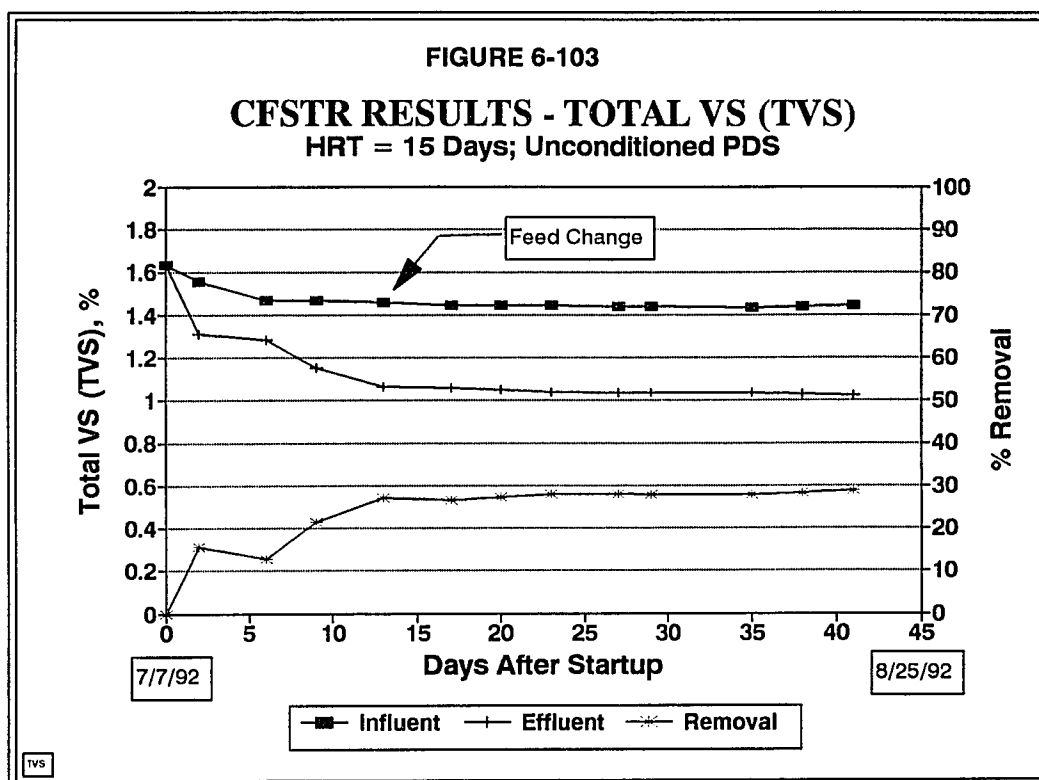
In order to evaluate the reactor's performance on thermally conditioned PDS, the first run was performed using sieved raw PDS (without thermal conditioning) at an HRT of 15 days. These results were the baseline which all subsequent experiments were compared to. The baseline-run started July 7, 1992 and ended August 22, 1992. Feed PDS (20 liters) was collected from Wards Island, sieved and stored in refrigerators at 4°C. The reactor was seeded with 4 liters of the same sieved PDS prior to refrigeration.

Approximately 13 days later, all the feed was used up and the experiment was continued with new feed. The new feed lasted until the end of the experiment when steady state conditions were reached.

Figures 6-101 and 6-102 present the TCOD and SCOD results, respectively. The figures show that the PDS characteristics can vary significantly, as in the case from an influent TCOD of 31,000 mg/L down to 21,000 mg/L. Even though the reactor reached steady state within 30 days (two times its HRT) the experiment was run for 41 days to confirm the steady state conditions. TCOD was removed by 24% and SCOD by 58%. TVS (Figure 6-103) and DVS (Figure 6-104) were removed by 28% and 13%, respectively.

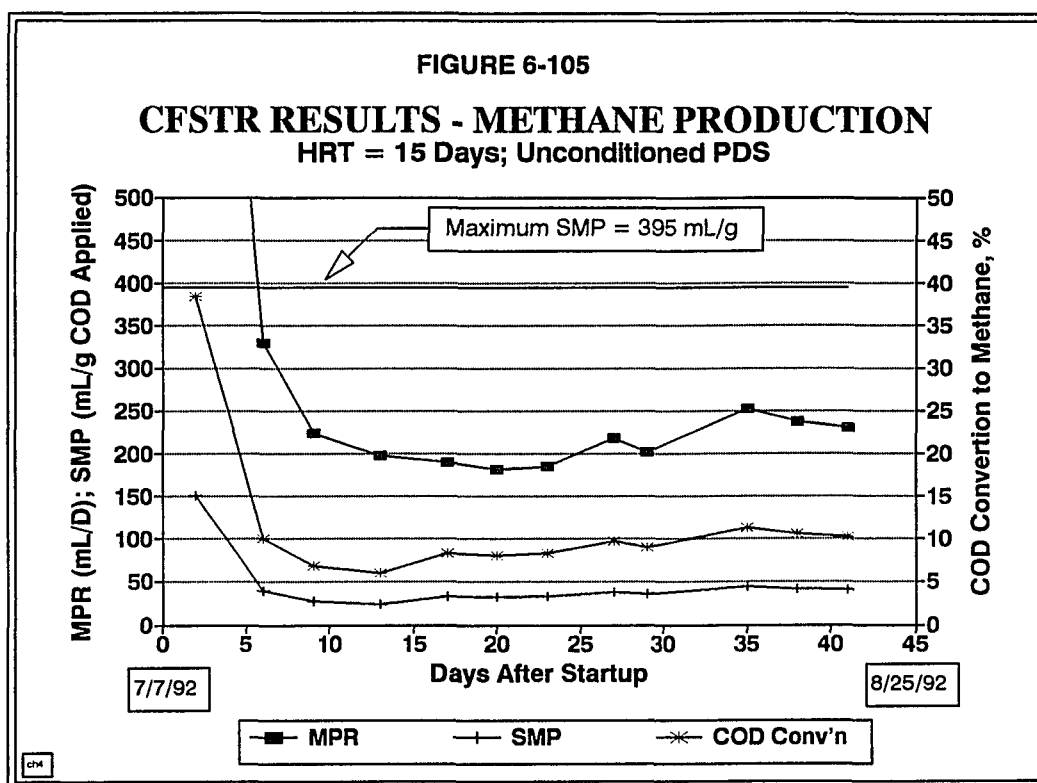
The results confirmed the classification of digested sludge as PDS since an additional 15 days of digestion resulted in further stabilization of COD and VS. The removal of 5,100





mg/L of TCOD, compared to only 1,100 mg/L for SCOD, suggests that particulate hydrolysis was probably taking place within the reactor. This demonstrates the pathway followed in anaerobic digestion which is hydrolysis followed by fermentation and methanogenesis. TVS and DVS removals indicate the same result, where DVS was removed by only 13%, whereas TVS were removed by 28%. TVS were hydrolyzed first into DVS and then removed by methanogenesis.

Methane gas production results are presented on Figure 6-105. The methane production rate (MPR) in mL/day was determined by the gas production rate (measured by the Arthur Respirometer) and the gas methane-content of 67% (measured by gas chromatography). The gas production rate was adjusted to include the gas lost during the venting cycle of the Arthur Respirometer. Each venting cycle, from the beginning of venting to the beginning of the new gas recording, lasts 45 seconds. Also, approximately 15 mg/L of dissolved methane was lost with the effluent, or about 63 mL/day for the 15-day HRT. Even though this volume could be neglected, it was still taken into account. At the lower HRT's, such as the 1.25-day, the methane lost in the effluent is a significant amount of 76 mL/day. The MPR was then divided by the influent (or applied) TCOD to determine the specific methane production (SMP) in mL CH₄/g TCOD. A comparison of the measured SMP to the SMP of 395 mL CH₄/g TCOD (35°C, 1 atm) gives the amount of influent COD that was converted to methane (see Figure 6-105). Only 10% of TCOD was converted to methane gas indicated by the low SMP of 42 mL CH₄/g TCOD. Thermally conditioned PDS's SMP results would be compared to the unconditioned PDS's SMP value of 42 mL/g.



(b) Thermally Conditioned PDS Runs

Once the baseline was determined using unconditioned PDS, the CFSTR was run using PDS thermally conditioned at 220°C and 10 seconds. The CFSTR HRTs were 15, 10, 7.5, 5, 2.5, 1.25, and 0.58 days.

For illustration purposes, the 15-day HRT results are presented from the beginning until the end of the run. Figures 6-106 and 6-107 present the 15-day total and soluble COD results, respectively. Figures 6-108 and 6-109 present the total and dissolved VS results, and Figure 6-110 the methane production results. The reactor was seeded with unconditioned PDS and the effluent concentrations at $t = 0$ represent the unconditioned PDS's characteristics. However, the influent concentrations were of lower concentration throughout the run because thermally conditioned PDS was inherently diluted with steam. This is why during the first 10 days after start-up the TCOD and TVS removals appeared negative.

Steady state conditions were reached within 20-30 days, as indicated by all of the results. TCOD removal was 26%, SCOD 73% (compared to the unconditioned PDS of 58%), TVS 40% and DVS 89%. The DVS of the unconditioned PDS were removed only by 13%. The SMP value reached 123 mL CH₄/g TCOD applied, 190% more than the unconditioned PDS's SMP value of 42 mL CH₄/g TCOD. The 15-day HRT confirmed the serum bottles ultimate biodegradation results, where PDS biodegradability increased with thermal conditioning. Kinetic improvement were evaluated next by running the CFSTR at lower HRTs.

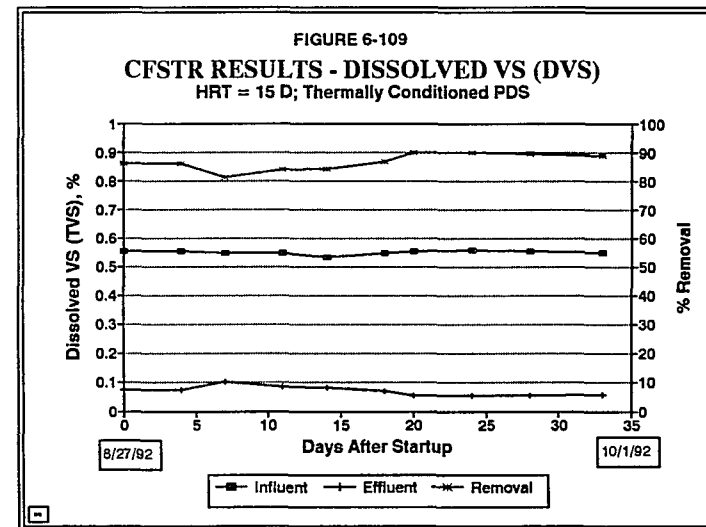
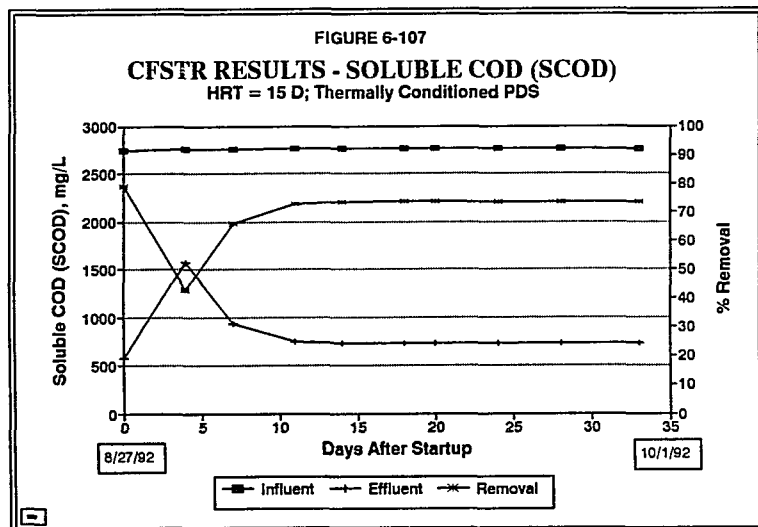
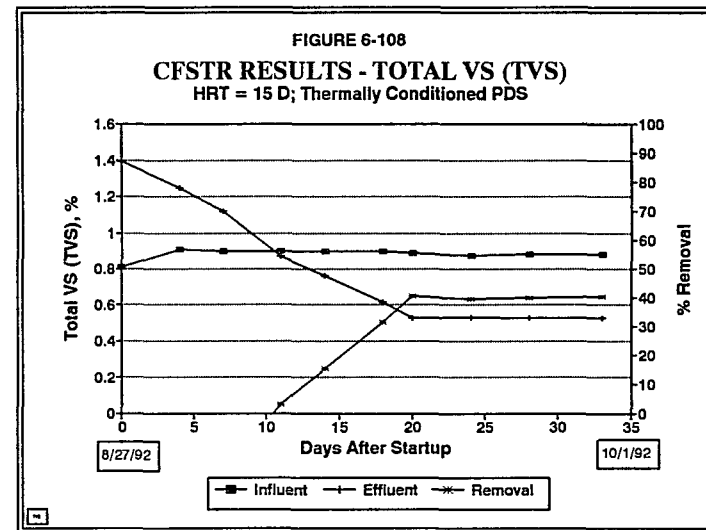
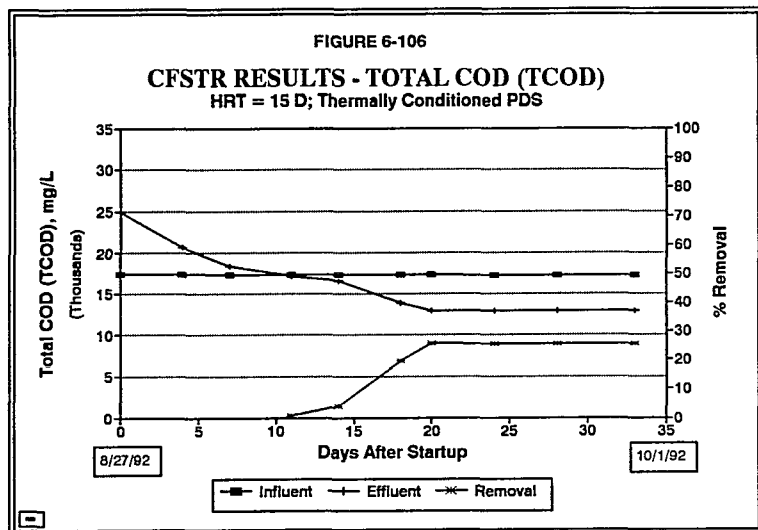
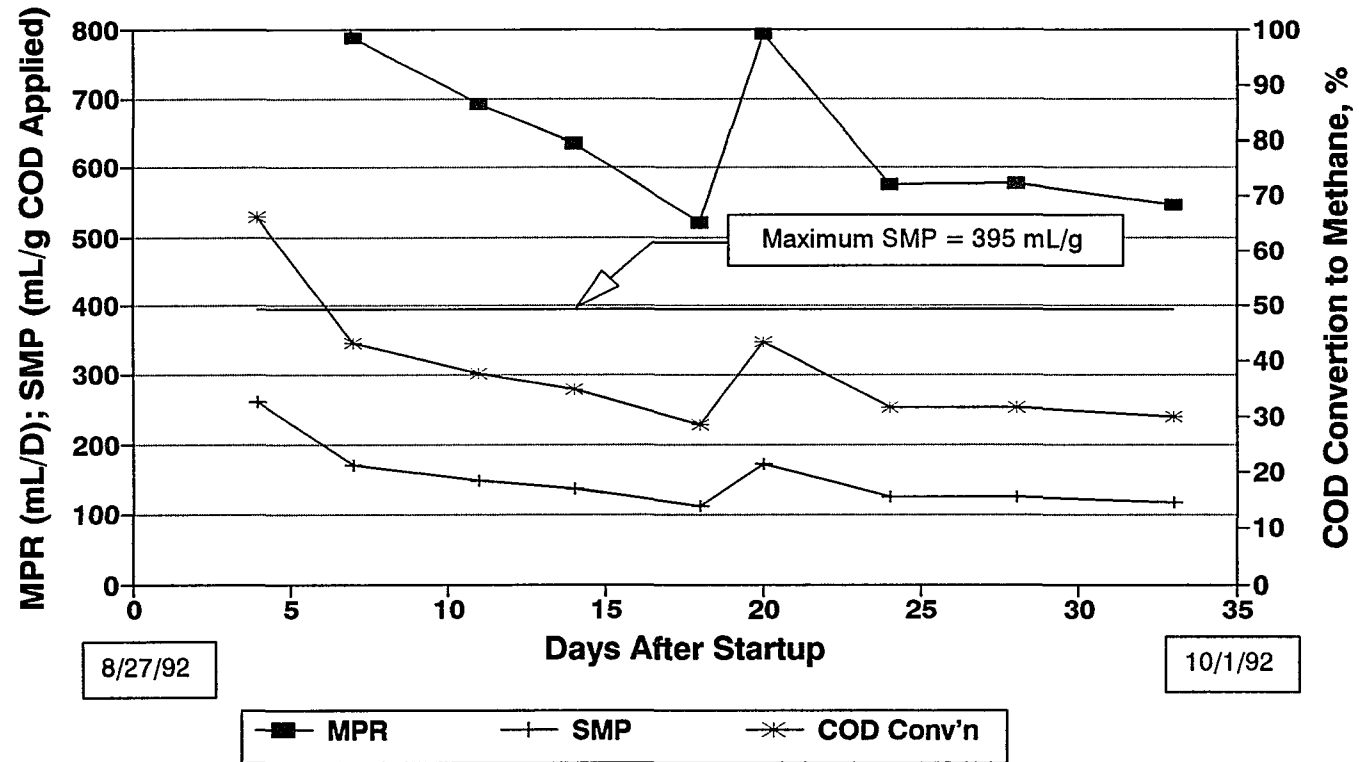


FIGURE 6-110

CFSTR RESULTS - METHANE PRODUCTION

HRT = 15 D; Thermally Conditioned PDS



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Table 6-15 summarizes all the steady state COD and solids results, and Table 6-16 summarizes the methane gas production results. Steady state conditions were confirmed from plots of TCOD and SCOD results, and gas production rates. The 10-day HRT results are shown on Figures 6-111 (TCOD) and 6-112 (SCOD); the 7.5-day on Figures 6-113 (TCOD) and 6-114 (SCOD); the 5-day on Figures 6-115 (TCOD), 6-116 (SCOD), and 6-117 (methane). The remaining 2.5-day, 1.25-day and 0.58-day HRT results are presented on Figures 6-118 (TCOD) and 6-119 (SCOD). Data was not collected from the 13th to the 18th day after startup.

Methane production results for the 5-day HRT are presented because COD data was fluctuating and it was difficult to confirm steady state conditions. The methane production results (Figure 6-117), however, indicated that steady state conditions were reached within 10 days. The 10-day COD and solids results are the ones presented on Tables 6-15 and 6-16 for the 5-day HRT run. Also because during the other runs methane production was not fluctuating as much as COD and solids did, the CFSTR's performance was evaluated using the methane production rate (MPR) and the specific methane production (SMP). The improvement in PDS biodegradability is related to the methane production improvement (MPI). MPI is the increase in the SMP value of the conditioned PDS over the SMP value of the unconditioned PDS. This is similar to the GPI values calculated for the serum bottles test. The only difference is that GPI reflects all the gas, whereas MPI reflects only the methane gas.

TABLE 6-15

CSFTR STEADY STATE COD AND SOLIDS RESULTS FOR UNCONDITIONED AND CONDITIONED SAMPLES

HRT (Days)	Influent					Effluent					Removals, %				
	TCOD (mg/L)	SCOD (mg/L)	TS (%)	TVS (%)	DVS (%)	TCOD (mg/L)	SCOD (mg/L)	TS (%)	TVS (%)	DVS (%)	TCOD	SCOD	TS	TVS	DVS
Unconditioned PDS (Baseline)															
15	21,280	1,890	2.20	1.44	0.114	16,110	803	1.68	1.03	0.099	24	58	24	28	13
Conditioned PDS															
15	17,310	2,760	1.28	0.89	0.550	12,870	733	0.95	0.53	0.058	26	73	26	40	89
10	14,990	3,860	1.16	0.80	0.540	10,110	690	0.80	0.44	0.061	33	82	31	45	89
7.5	18,600	4,690	1.30	0.89	0.490	11,090	910	0.87	0.54	0.079	40	81	33	39	84
5.0	19,860	1,660	1.61	1.08	0.171	15,500	2,000	1.10	0.63	0.085	22	-20	32	42	50
2.5	17,640	6,400	1.69	0.86	0.550	16,040	2,880	1.11	0.62	0.100	9	55	34	28	82
1.25	17,320	6,000	1.13	0.86	0.550	16,000	2,800	1.05	0.66	0.200	8	53	7	23	64
0.58	18,060	7,080	1.30	0.86	0.550	16,680	3,420	1.14	0.73	0.280	8	52	12	15	49

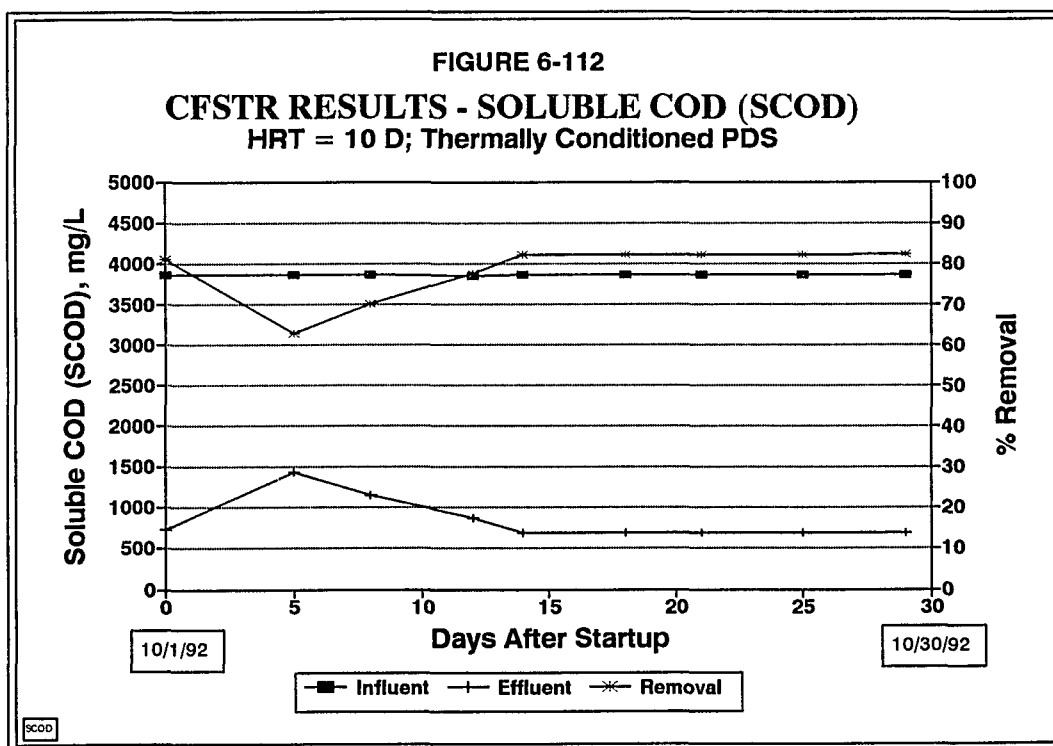
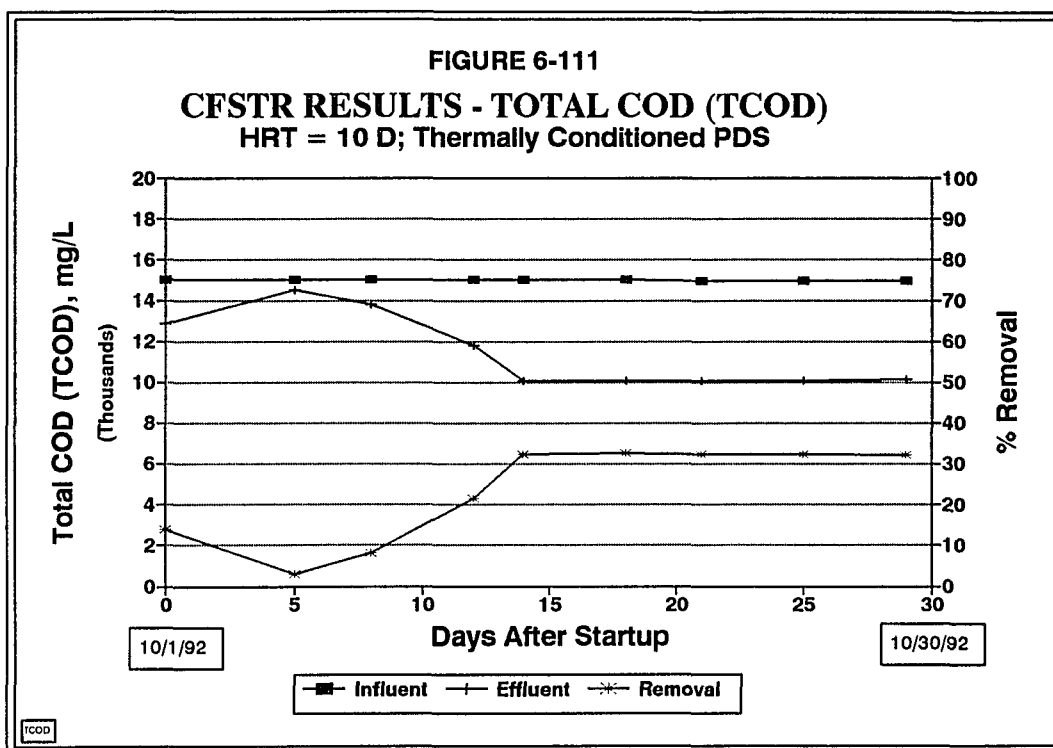
TABLE 6-16

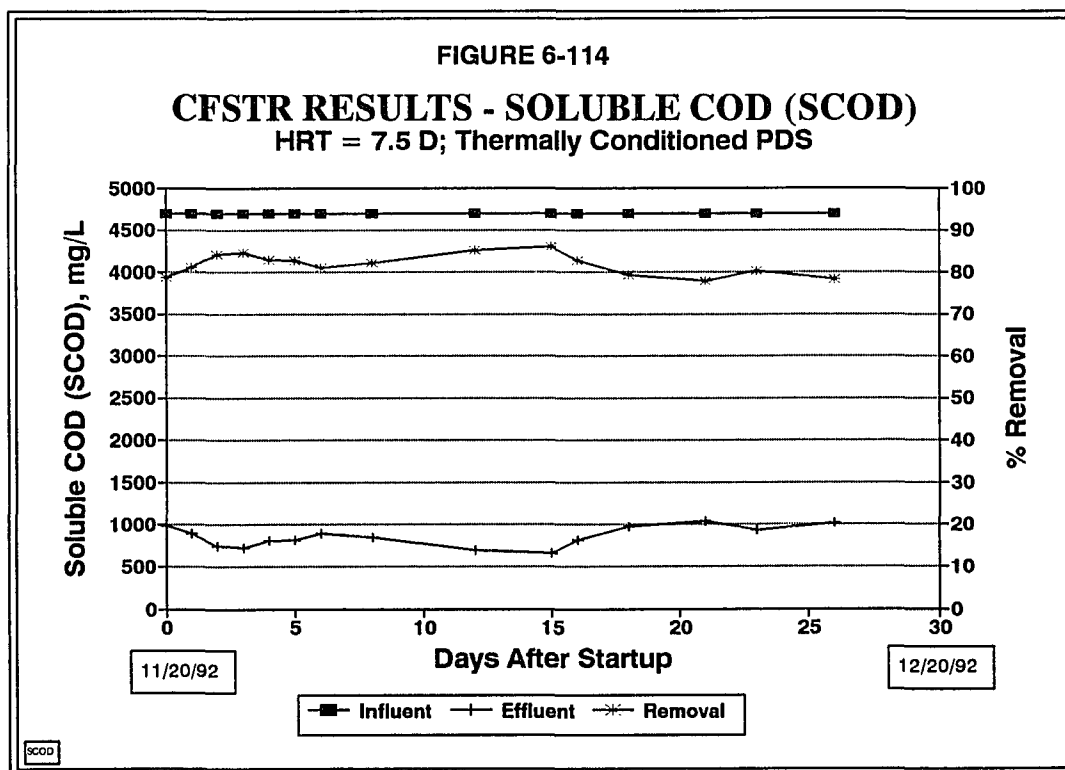
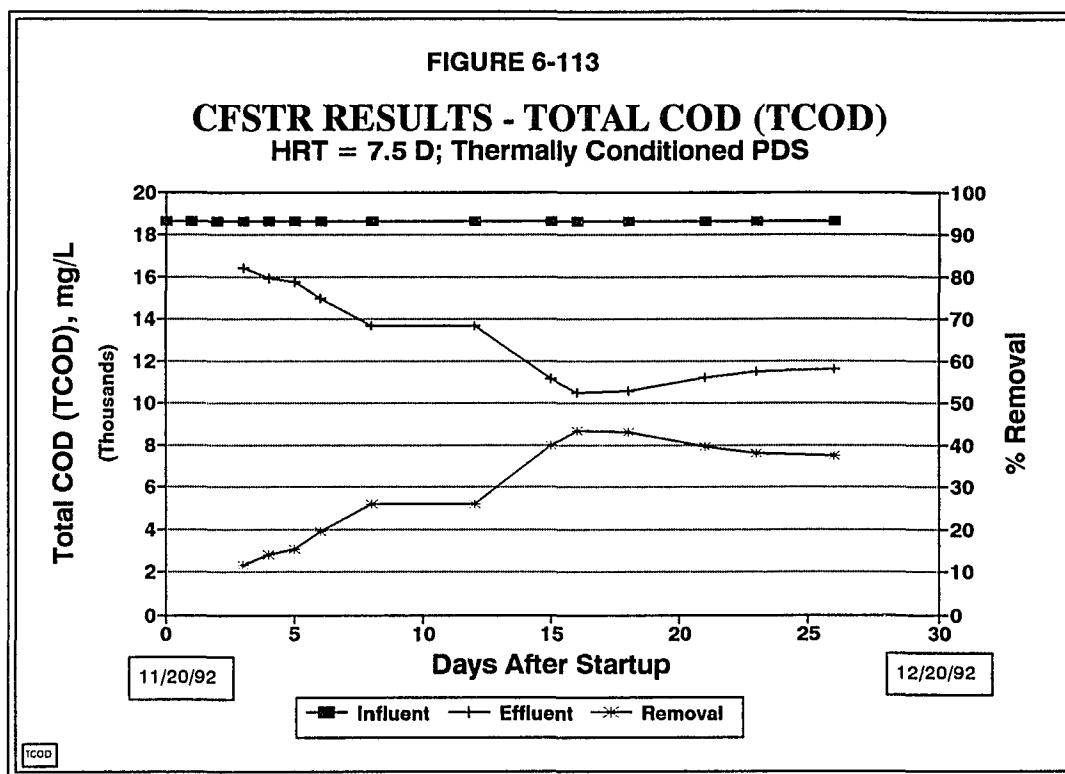
**CFSTR STEADY STATE METHANE GAS PRODUCTION RESULTS FOR
UNCONDITIONED AND CONDITIONED SAMPLES**

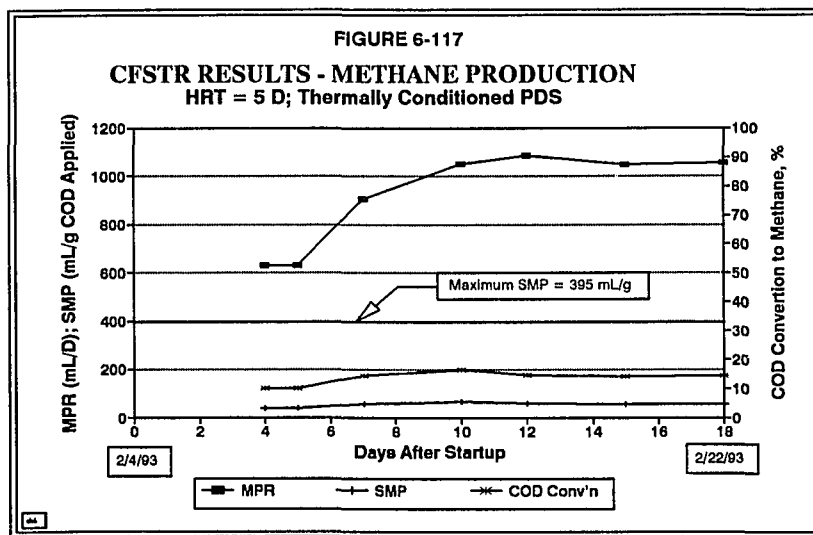
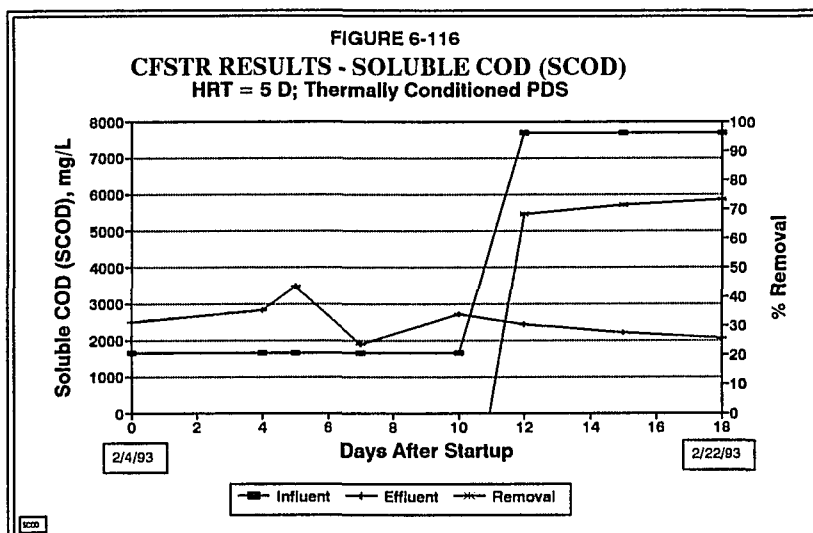
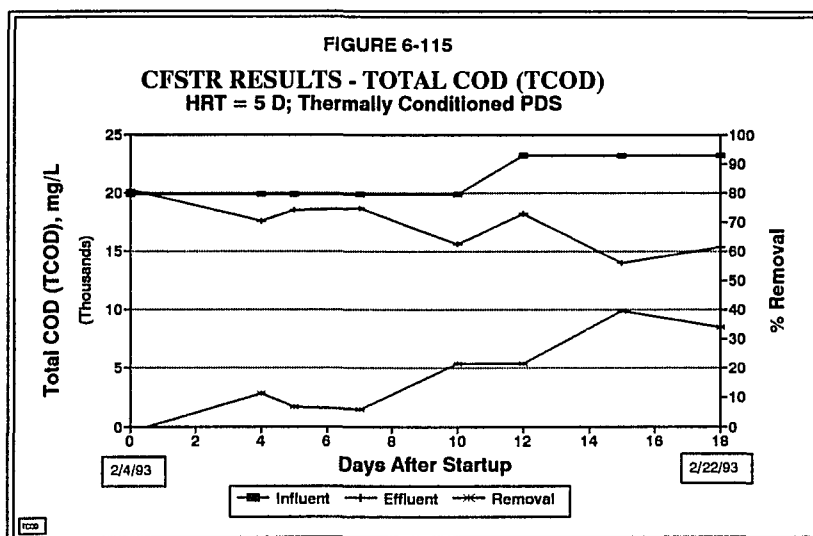
HRT (Days)	MPR (mL/day)	SMP_c (mL/g)	MPI_c (%)	SMP_v (ft³/lb)	MPI_v (%)
Unconditioned PDS (Baseline)					
15	240	42	---	1.00	---
Conditioned PDS					
15	566	123	193	3.83	282
10	621	104	148	3.11	210
7.5	805	81	93	2.72	171
5.0	1,050	66	57	1.95	95
2.5	756	26	-38	0.88	-12
1.25	903	16	-62	0.53	-48
0.58	1,190	8	-81	0.32	-68

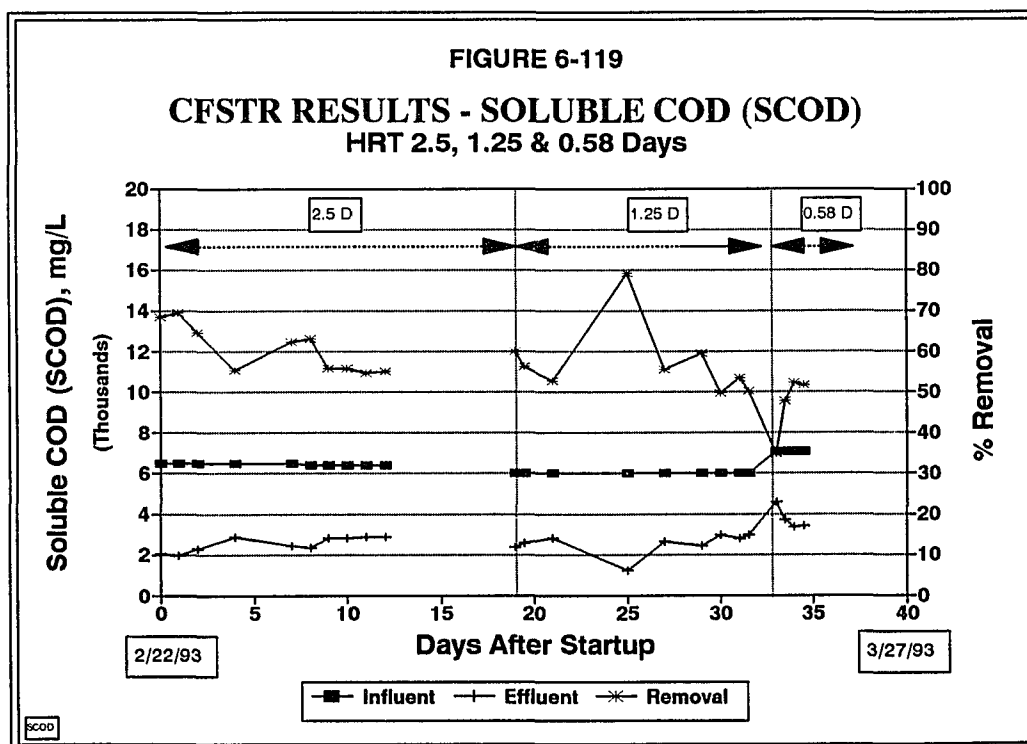
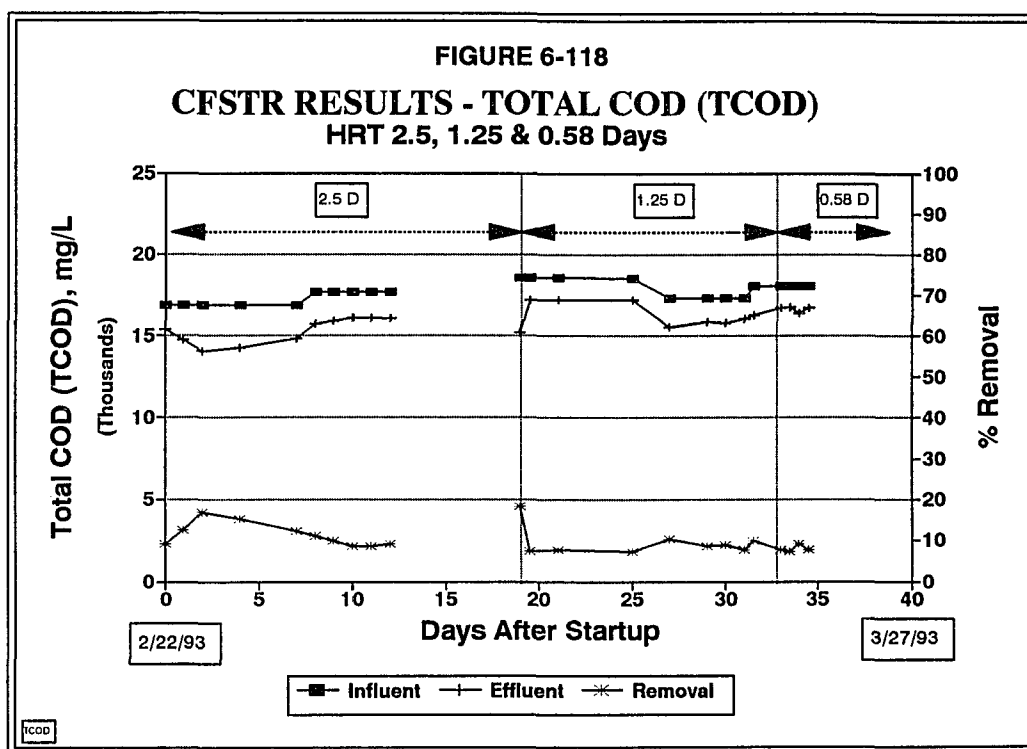
NOTES:

MPR = Methane production rate
 SMP_c = Specific methane production based on influent TCOD
 MPI_c = Methane production improvement based on influent TCOD
 SMP_v = Specific methane production based on influent TVS
 MPI_v = Methane production improvement based on influent TVS





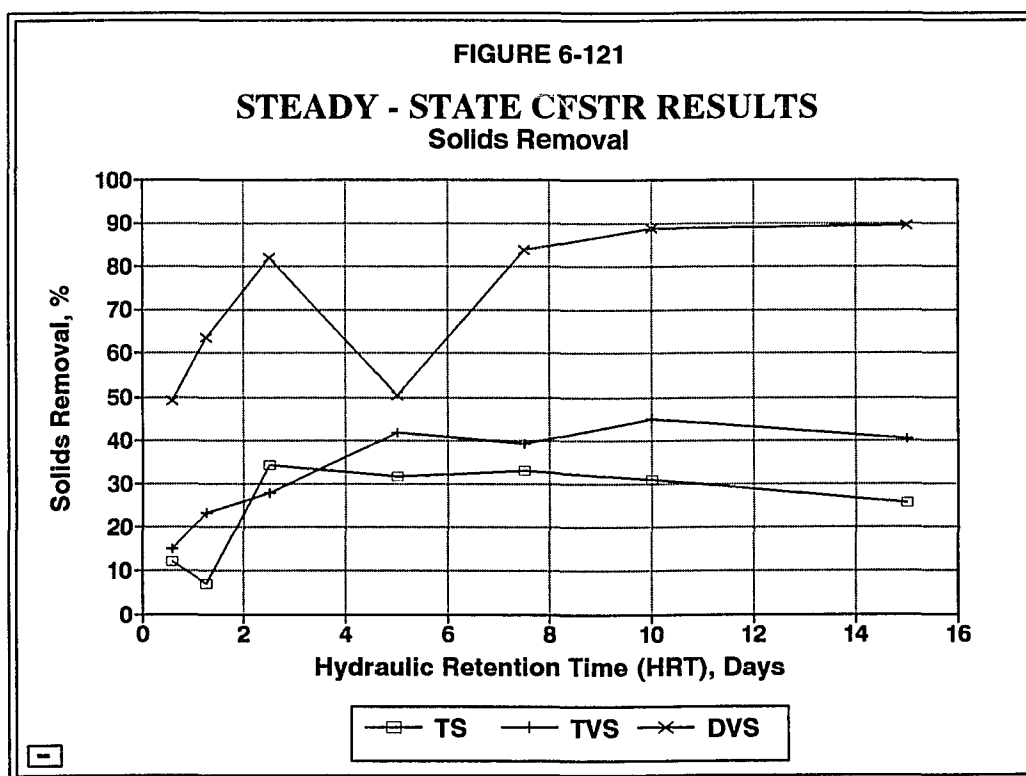
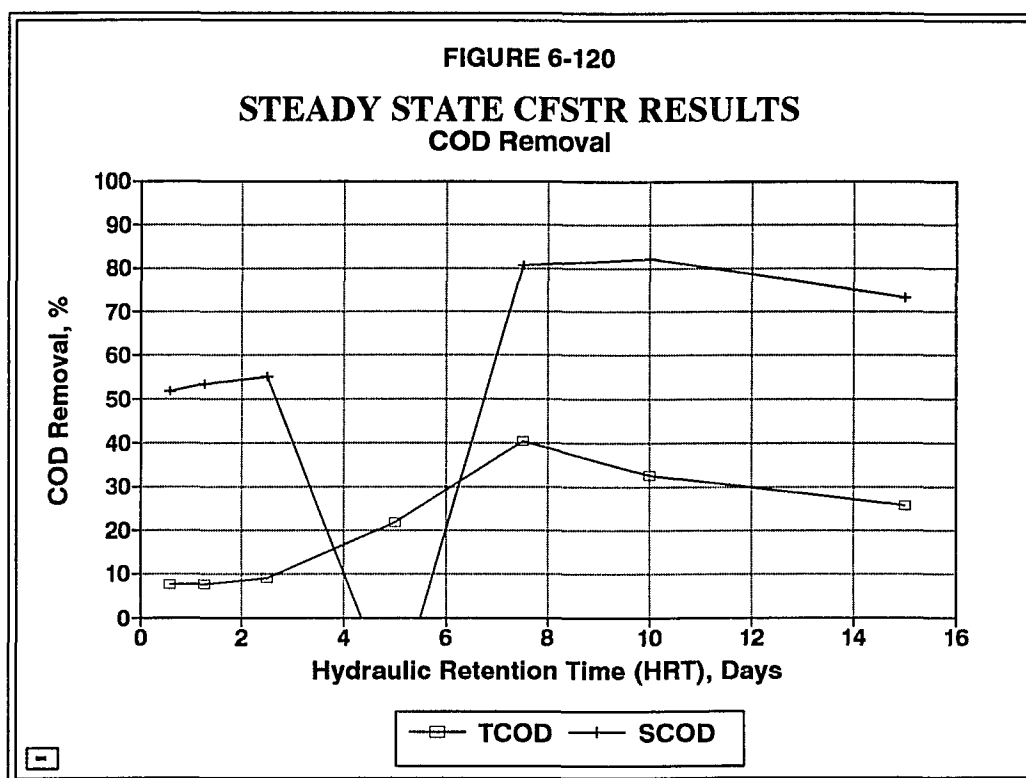


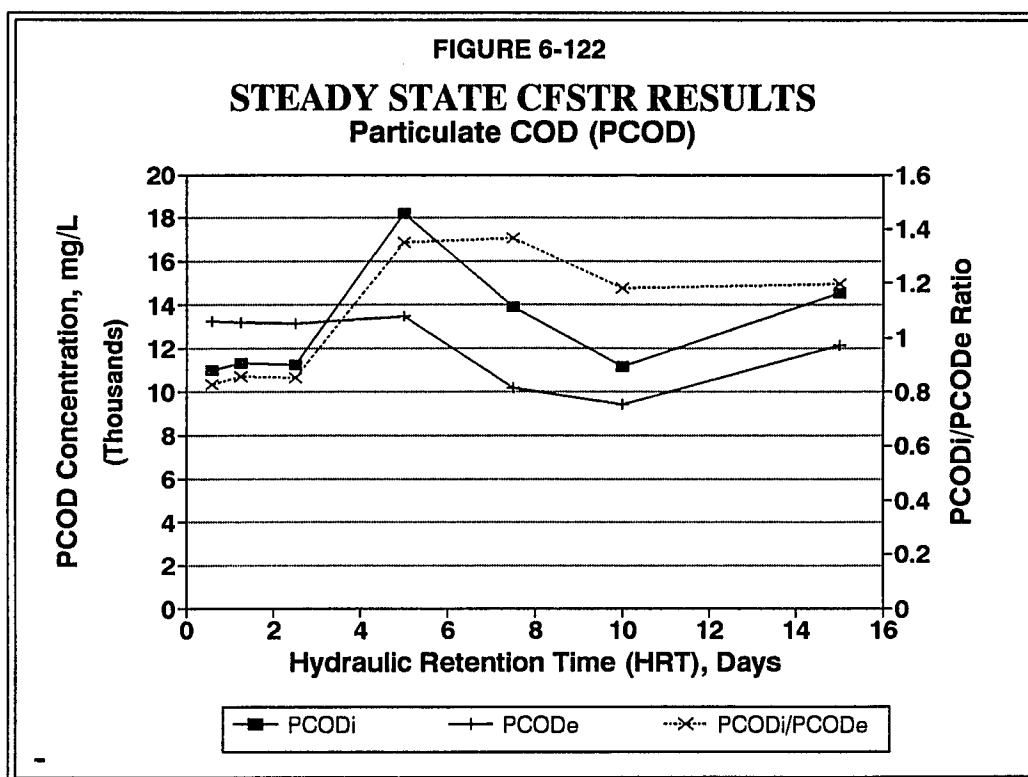


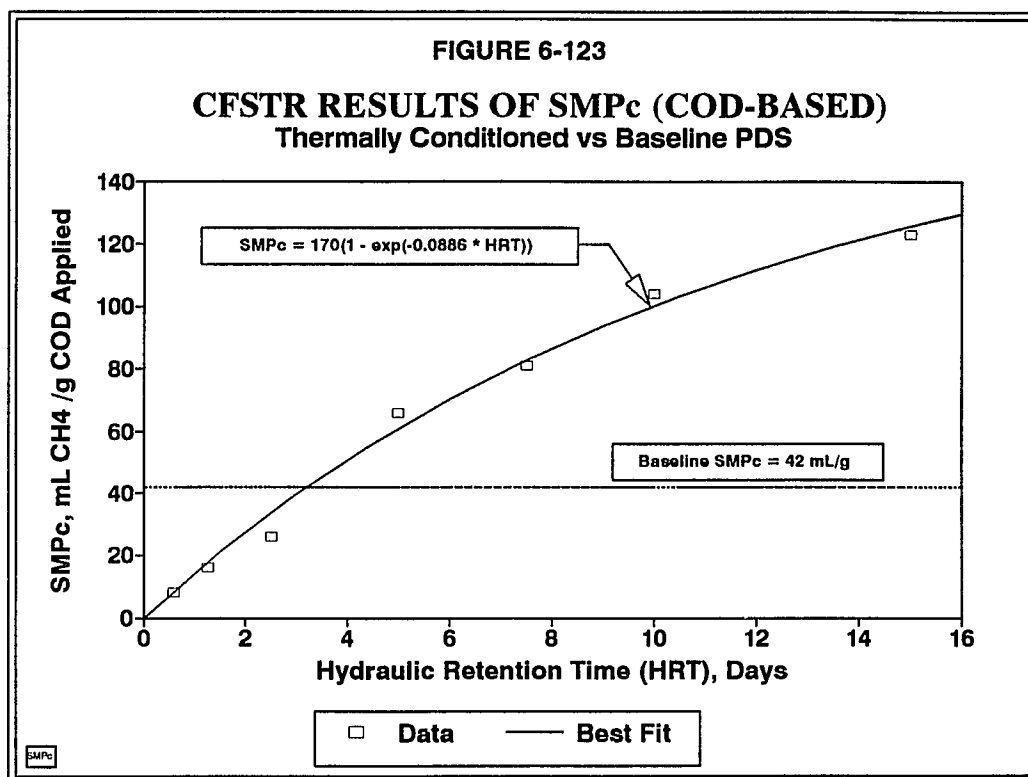
Steady state COD and solids removals are presented on Figures 6-120 and 6-121, respectively. A 7.5-day HRT can provide similar removals as the longer time, and still perform better than the 15-day HRT of the unconditioned PDS. The 5-day HRT showed negative SCOD removals which could be due either to analytical measurement errors, the system not reaching a steady state condition yet, or the particulate hydrolysis rate being much higher than the soluble organics' utilization rate.

Both Figures 6-120 and 6-121 unexpectedly show significant SCOD and DVS removals at the 2.5-day, 1.25-day, and even the 0.58-day HRTs. TCOD removal, however, was only about 10%, and TVS removals ranged from 28% (2.5 days) to 15% (0.58 days). Because it didn't seem reasonable for such low HRTs to achieve such high SCOD removals, the particulate COD ($\text{PCOD} = \text{TCOD} - \text{SCOD}$) was calculated for each condition. Figure 6-122 presents the influent PCOD (PCOD_i), effluent PCOD (PCOD_e), and the $\text{PCOD}_e/\text{PCOD}_i$ ratio. For the low HRTs, the effluent PCOD is higher than the influent, indicating that soluble COD is not degraded but is converted into particulate form. The conversion could be most likely due to bacterial uptake and storage within the cell. However, some TCOD and TVS were removed even at the lowest HRT of 0.58 days, indicating that bacterial fermentation was active.

As it was mentioned before, the best parameter that can be used for the CFSTR evaluation is the specific methane production (SMP). The SMP values were calculated based on influent TCOD (SMP_c) and on influent TVS (SMP_v). Figure 6-123 presents the TCOD SMP_c results at each tested condition. The results exhibit a better fit than the COD and







solids data, and show an increase of SMP_c with HRT, as expected. The three lowest HRTs showed also some negative SMP_c values, as expected from the COD and solids data. Only HRTs greater than 5 days resulted in a methane production greater than the baseline of 42 mL CH_4 /g COD applied. The data was fitted with an exponential type of equation. A two-term exponential equation (the same as the one used for the serum bottles) was tried but the two kinetic rates k_1 , and k_2 were close to each other so they could be combined into one term.

$$SMP_c = 170 (1 - e^{-0.0886 t}) \quad (6-14)$$

where,

SMP_c = Specific Methane Production, mL CH_4 /g TCOD applied

t = HRT, days

Methane production improvement (MPI_c) reflects the increase in biodegradability and is shown on Figure 6-124.

Figures 6-125 and 6-126 present the SMP_v and MPI_v , respectively, based on the influent TVS. As with the COD SMP_c , the SMP_v was fitted with an exponential type of equation.

$$SMP_v = 5.1 (1 - e^{-0.0941 t}) \quad (6-15)$$

where,

SMP_v = Specific Methane Production, ft³ CH_4 /lb TVS applied.

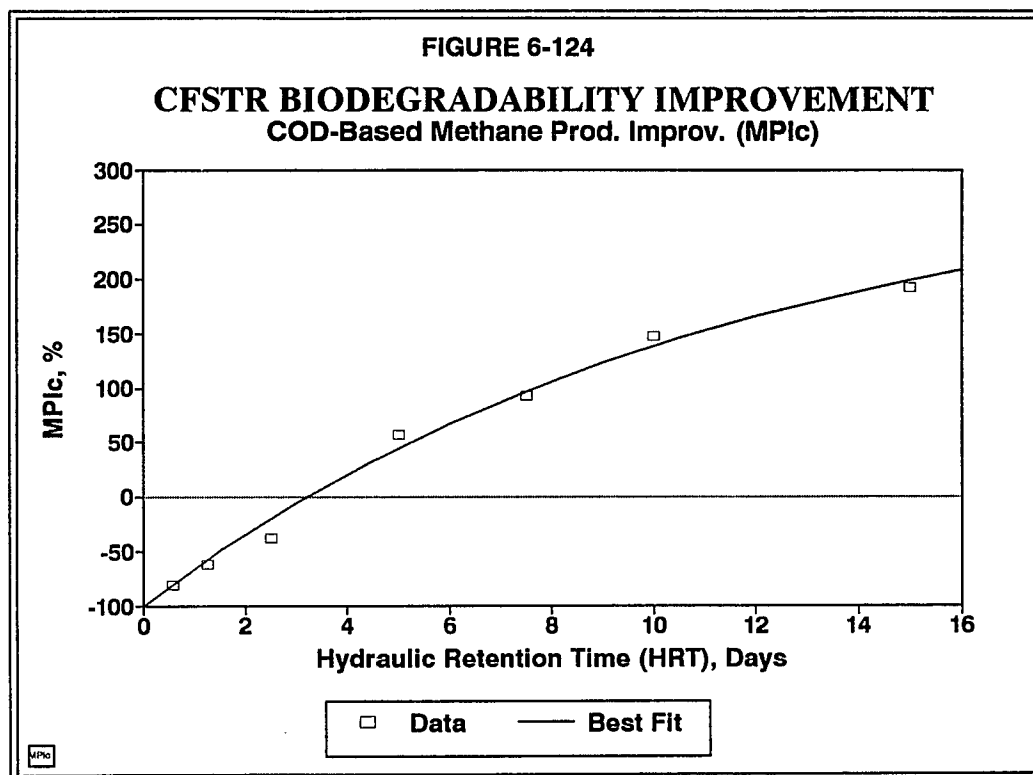


FIGURE 6-125

CFSTR RESULTS OF SMP_v (TVS-BASED) Thermally Conditioned vs Baseline PDS

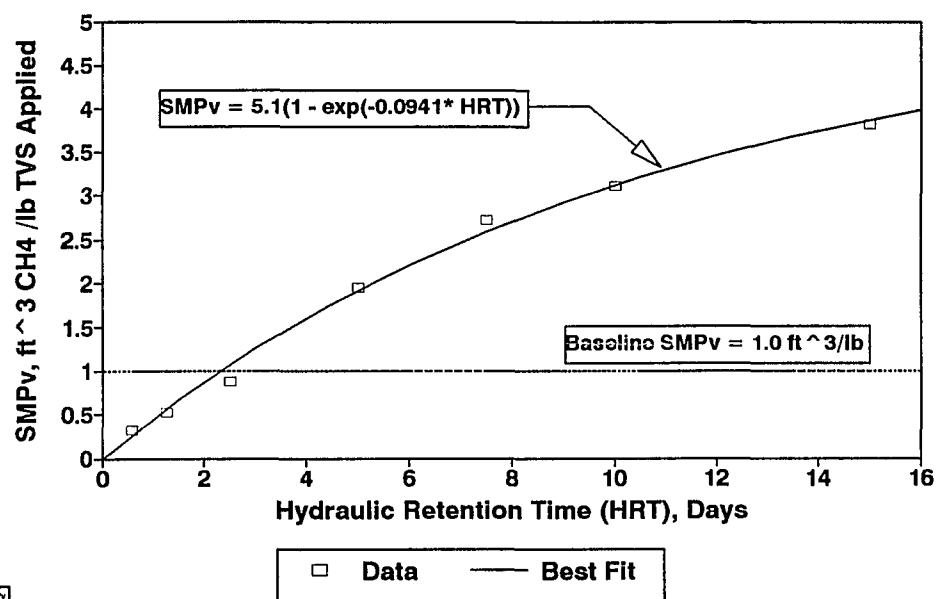
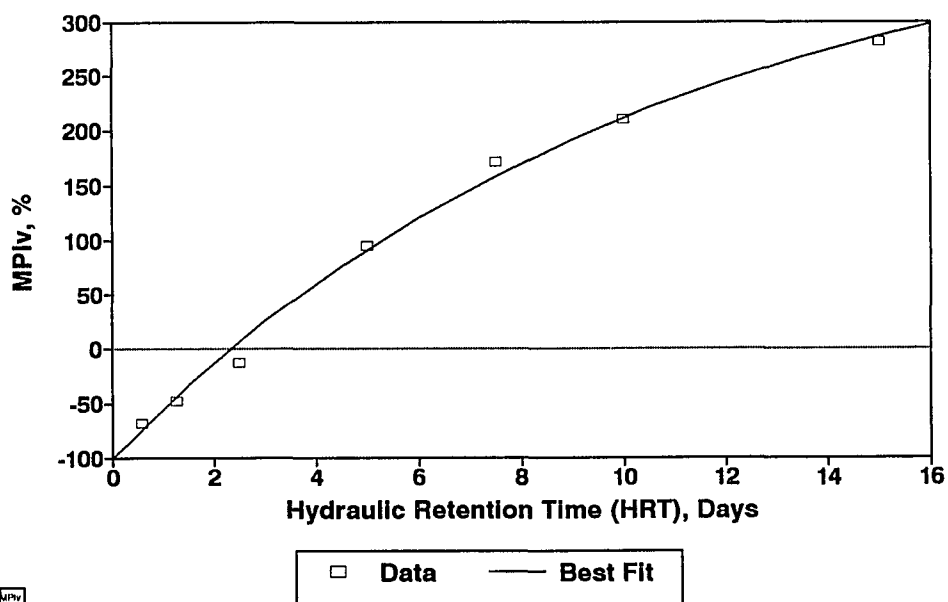


FIGURE 6-126

CFSTR BIODEGRADABILITY IMPROVEMENT TVS-Based Methane Prod. Improv. (MPI_v)



The improvement in methane production (MPI_v), based on the SMP_v of the 15-day baseline PDS, indicates slightly higher results than the improvement based on COD (see Figure 6-124). Both MPI_c and MPI_v results show that if conditioned PDS is anaerobically digested at an HRT as little as 3 days, it can produce the same biodegradation results as unconditioned PDS digested at a 15-day HRT.

To summarize, the results confirmed the serum bottle data, which demonstrated that RTC of PDS at 220°C improves kinetics and ultimate biodegradability. Conditioned PDS can produce similar gas production as the 15-day digestion of unconditioned PDS but at an HRT as low as three days. Gas productions results also confirmed that the RTC process did not produce the digestion-inhibiting compounds indicated in the literature.

6.1.2.2 Anaerobic Filter

The anaerobic filter was installed in the Environmental Chamber and the seeding and shakedown runs were completed by September 1992. The feeding system and feed were the same as those used for the CFSTR. Some of the filter runs were run concurrently with CFSTR runs and using the same feed for both systems.

A baseline run was attempted using unconditioned PDS, but solids accumulated very fast and plugged the packing. The run was terminated well before steady state conditions

were reached. Therefore, the thermally conditioned PDS runs could not be compared with unconditioned PDS. However, the filter runs evaluated the treatability of the conditioned PDS, the primary objective of the study.

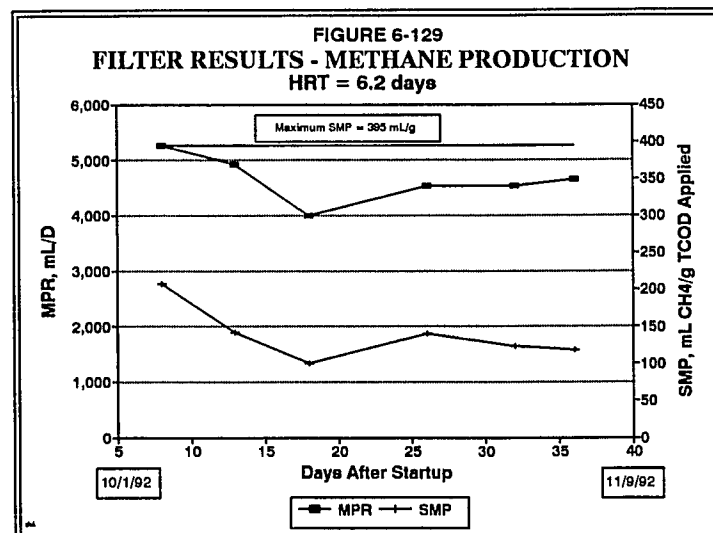
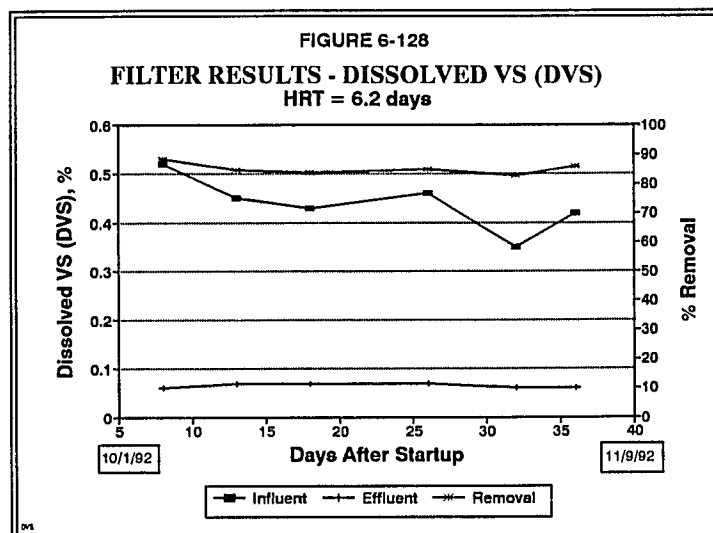
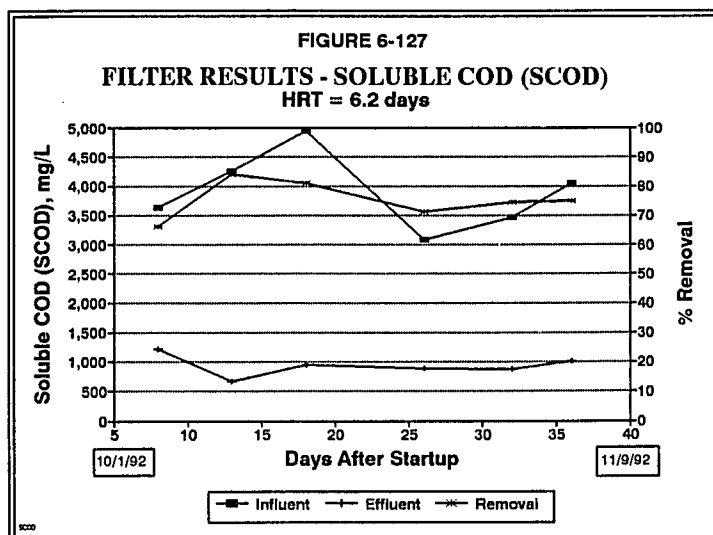
On October 1, 1992, the filter started operating with thermally conditioned PDS. The first filter HRT of 6.2 days was based on a total filter void volume of 14.3 L (including the influent lower zone). This HRT was maintained by a continuous-flow peristaltic pump operating at 1.6 mL/min. After steady state conditions were reached, retention times were changed to 2.7, 1.8, and 1.0 days. Because of the slow upflow velocities, especially during the low HRT runs (2.7, 1.8, and 1.0 days), it was realized that particulate COD and SS were accumulating in the lower section of the filter, especially the influent zone. Bottom TCOD concentrations reached over 100,000 mg/L and TS concentrations reached over 5%. To prevent solids accumulation within the packing section, some of the settled solids were removed daily from the filter's bottom zone.

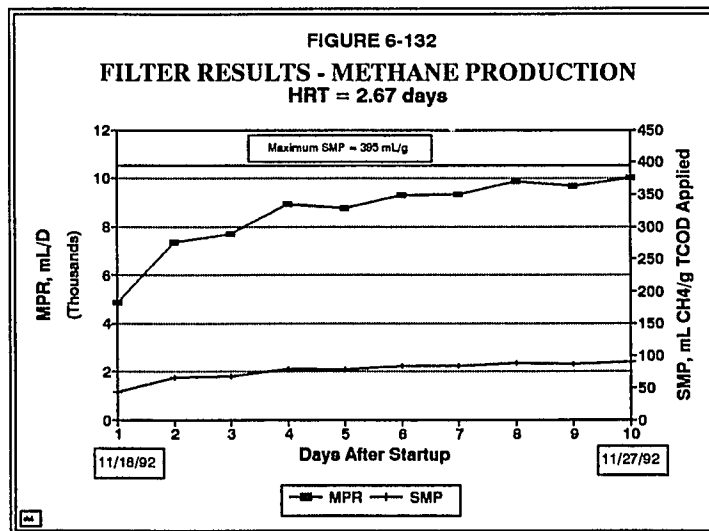
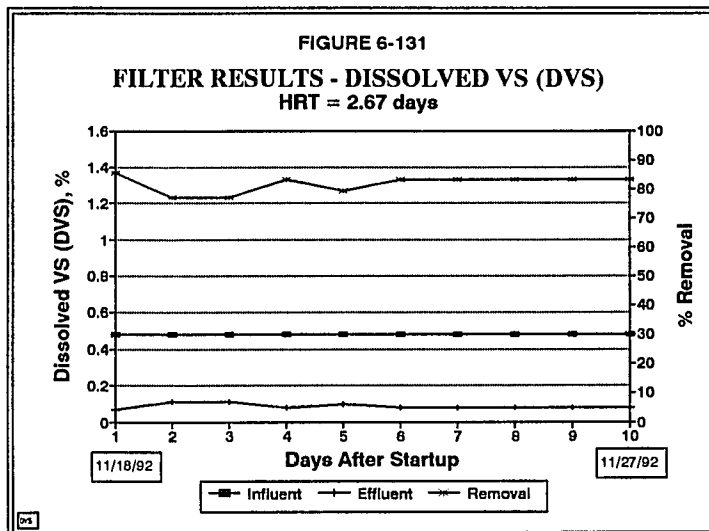
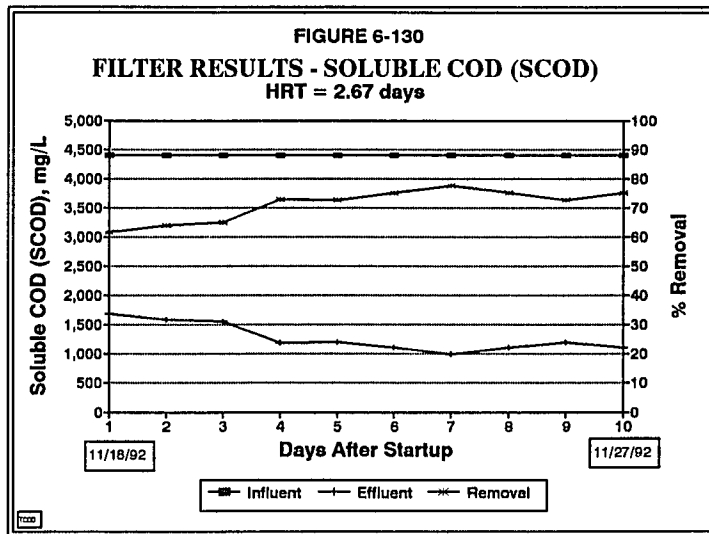
Because of the solids accumulation and withdrawal, the TCOD and TVS removal efficiencies (calculated from influent and effluent concentrations), were not used to evaluate the filter's performance. Instead, SCOD, DVS and methane production rates were used. Methane production rates (MPR) and specific methane production (SMP_c - based on influent TCOD) were also used to evaluate steady state conditions. For illustration purposes, filter results are graphically presented for all conditions.

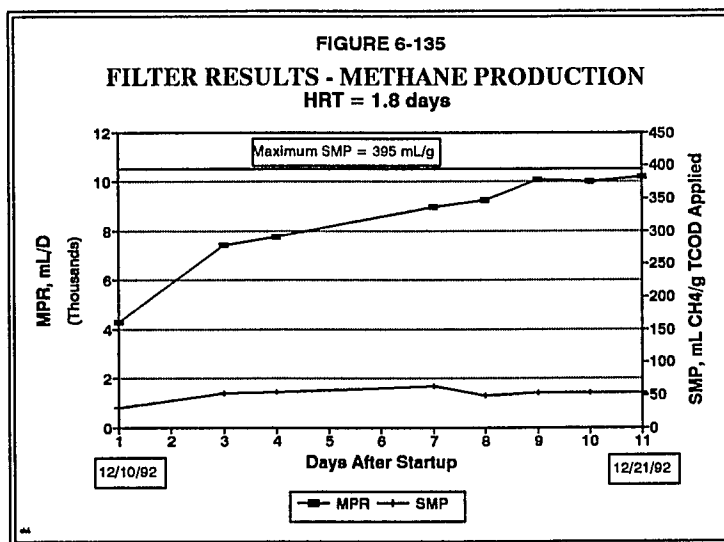
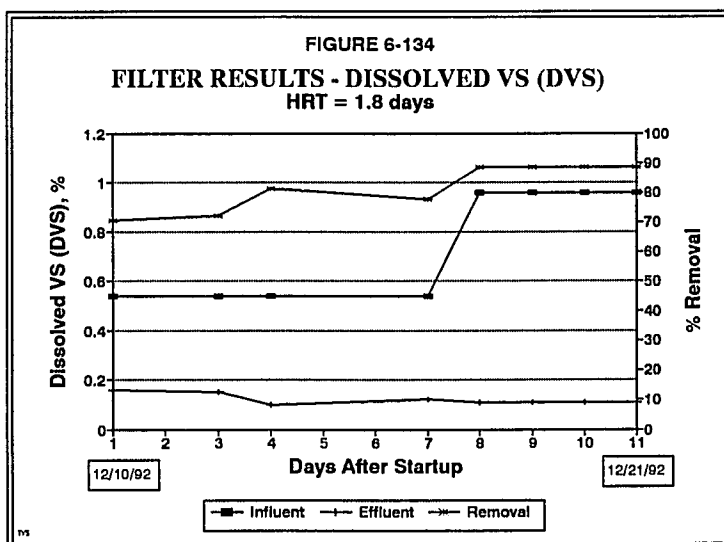
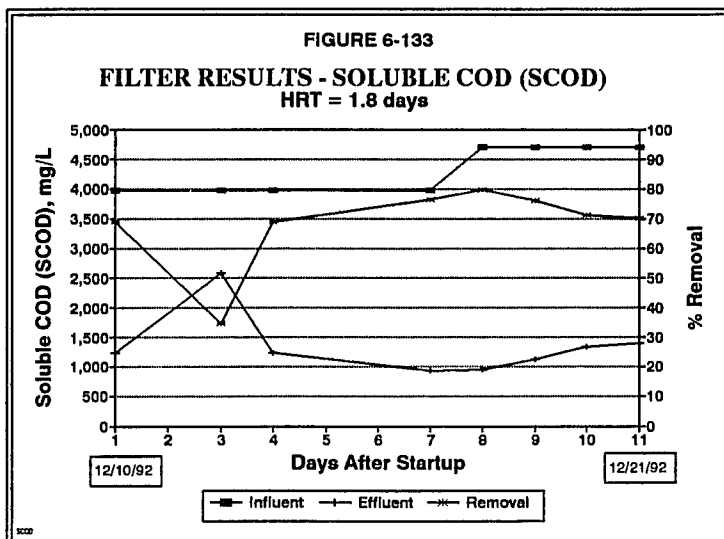
Figures 6-127 to 6-129 present SCOD, DVS, and methane production results for the 6.2-day HRT run. Removal efficiencies were based on influent and effluent characteristics. Removals for SCOD (Figure 6-127) and DVS (Figure 6-128) reached over 70%, indicating that the filter can be efficiently used to treat the thermally conditioned PDS. The filter reached steady state within 25-35 days of operation, demonstrated clearly by the methane production results (Figure 6-129). MPR reached 4,500 mL/day and SMP_C (based on influent TCOD) reached 115 mL/g. The maximum SMP_M of 395 mL/g represent the theoretical methane-COD value at 35°C. If all TCOD was converted to methane gas, the SMP_C should be 395 mL/g. The biological TCOD removal efficiency can be estimated as the SMP_C to SMP_M ratio, resulting in a removal of 30% ($115/395 \times 100$).

Similarly, Figures 6-130 to 6-132 represent the 2.7-day HRT results. SCOD (Figure 6-130) and DVS (Figure 6-131) removal efficiencies reached over 70%, similar to the 6.2-day HRT. Even though MPR was higher at 10,000 mL/day (Figure 6-132), the SMP_C was lower at 90 mL/g (compared to the 6.2-day HRT). The methane-based TCOD removal efficiency was 23%.

The 1.8-day HRT results, shown on Figures 6-133 to 6-135, also gave high SCOD and DVS removal efficiencies of 70%, but the SMP_C was only 53 mL/g. The methane-based TCOD removal efficiency dropped down to 13%. At the HRT of 1.0 day (Figures 6-136 to 6-138), SCOD and DVS removals dropped down to less than 60% and the SMP was only 4 mL/g. Only 1% of TCOD was removed.







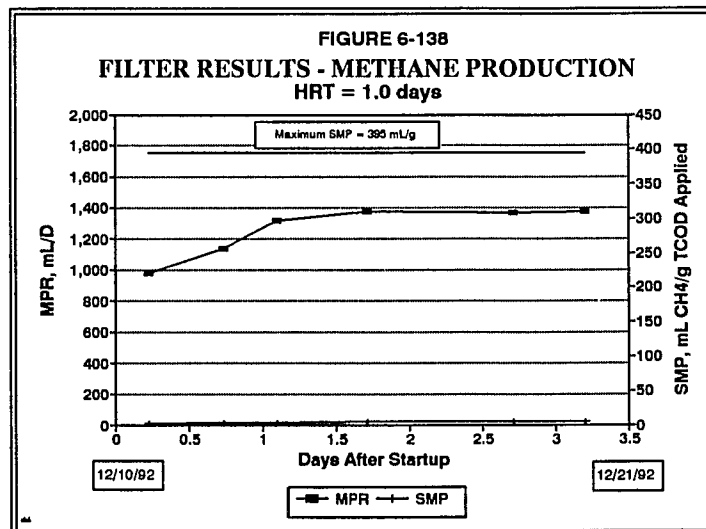
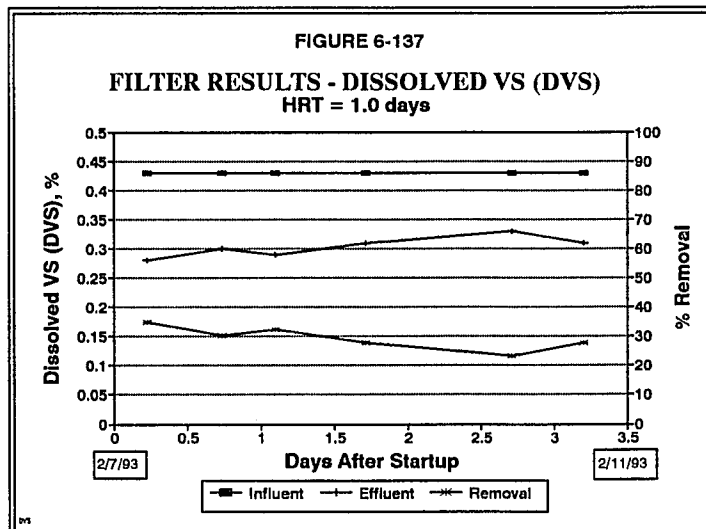
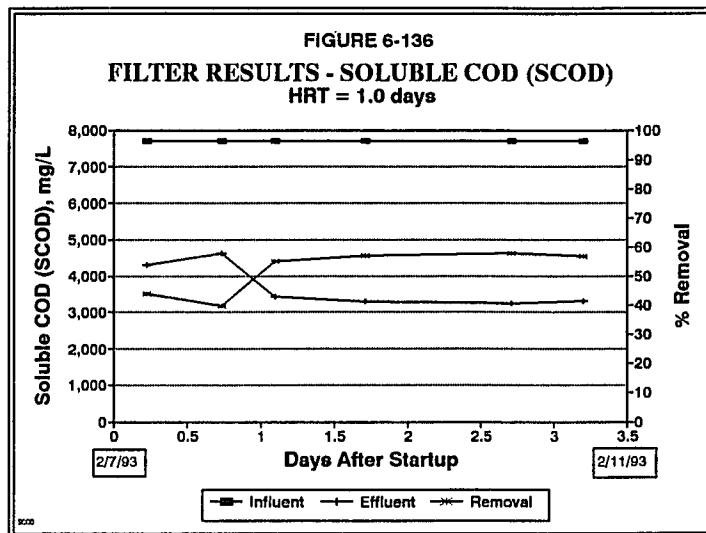


Table 6-17 summarizes the COD and the solids steady-state results. TCOD removals were based on methane gas production results. Figures 6-139 and 6-140 present the TCOD-SCOD and DVS removal efficiencies, respectively. Young and McCarty (1969) used the following equation to describe the removal of soluble BOD from anaerobic filters:

$$E = 100 - \frac{7.5}{t} \quad (6-16)$$

where,

$$\begin{aligned} E &= \text{removal efficiency, \%} \\ t &= \text{hydraulic retention time, days} \end{aligned}$$

Equation 6-16 shows that the removal efficiency would decrease to zero at an HRT of 0.075 days and would reach 100% at long HRTs. Since this study's results were based on COD and DVS, Equation 6-16 was modified to:

$$E = a - \frac{b}{t} \quad (6-17)$$

Equation 6-17 is a linear-type representation of E versus 1/t. The parameters "a" and "b" were determined from the best-fit line of E versus 1/t, where "a" represents the y-intercept, and "b" the line's slope. The best-fit results for TCOD, SCOD, and DVS are presented in the following equations.

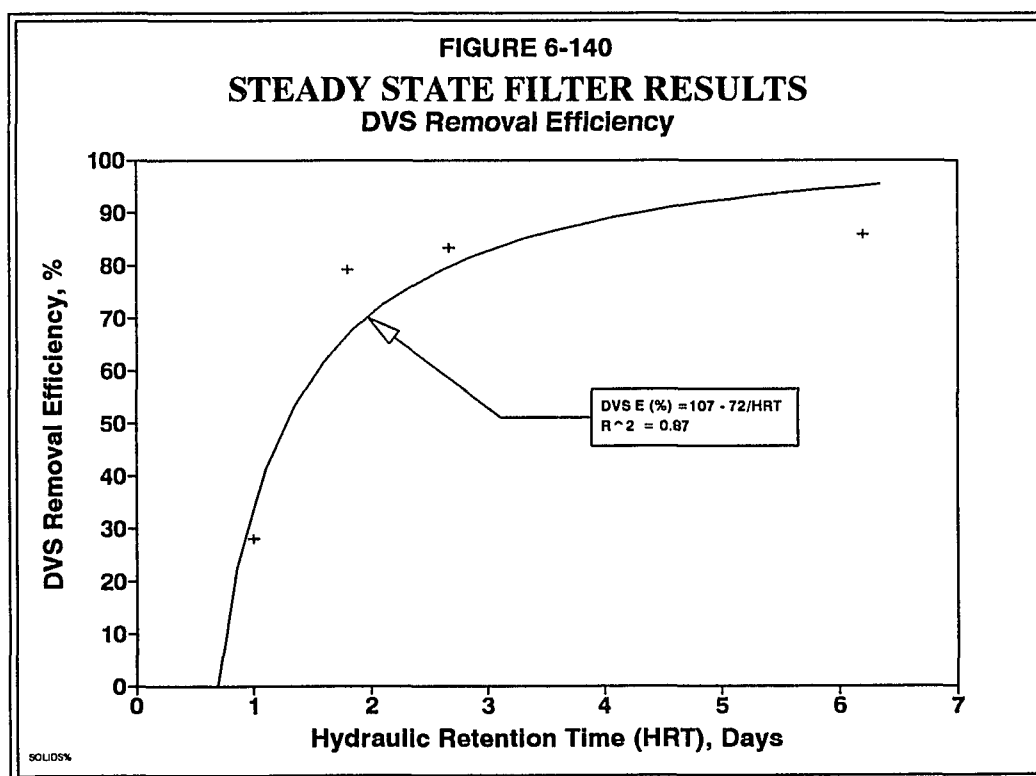
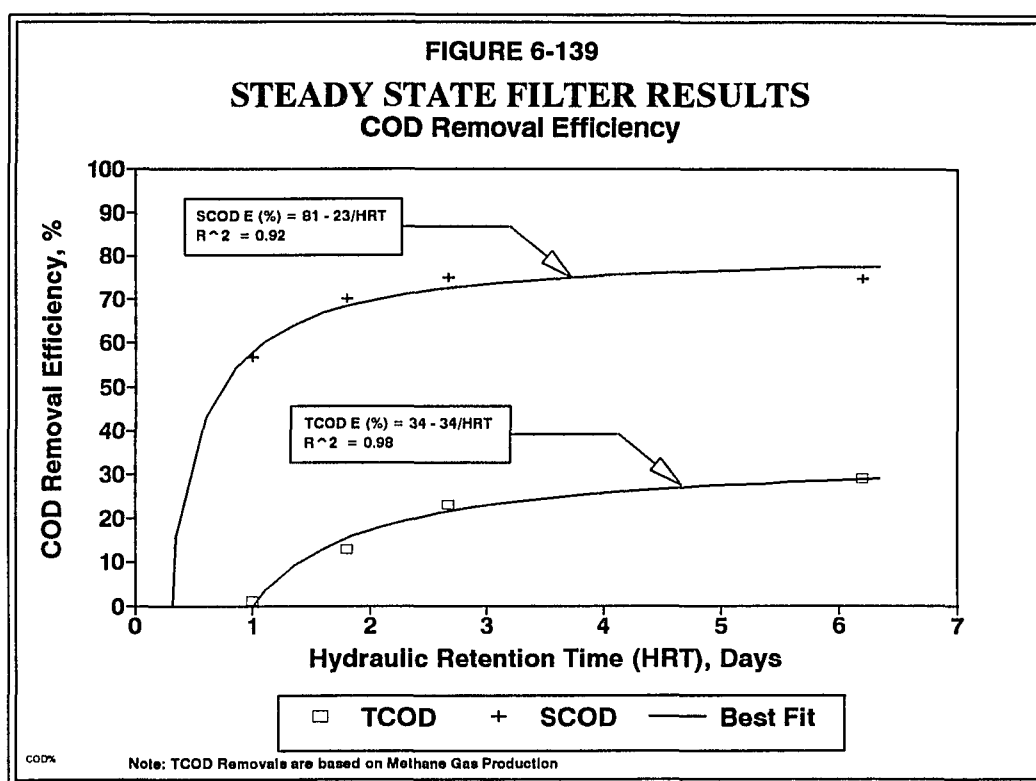
TABLE 6-17

ANAEROBIC FILTER STEADY STATE COD AND SOLIDS RESULTS
FOR CONDITIONED SAMPLES

HRT (Days)	Flow, Q (mL/min)	Influent						Removals, %			
		TCOD (mg/L)	SCOD (mg/L)	TVS (%)	DVS (%)	SCOD (mg/L)	DVS (%)	TCOD	SCOD	TVS	DVS
6.2	1.6	17,000	4,050	0.80	0.420	1,020	0.06	29	75	75	86
2.7	3.7	20,900	4,400	0.88	0.480	1,100	0.080	23	75	74	83
1.8	5.5	24,000	4,700	1.16	0.960	1,400	0.200	13	70	76	79
1.0	9.8	23,200	7,690	1.03	0.430	3,320	0.310	1	57	49	28

Notes:

1. TCOD removals were based on methane production results



$$TCOD\ E, \% = 34 - \frac{34}{t} \quad (6-18)$$

$$R^2 = 0.98$$

$$SCOD\ E, \% = 81 - \frac{23}{t} \quad (6-19)$$

$$R^2 = 0.92$$

$$DVS\ E, \% = 107 - \frac{72}{t} \quad (6-20)$$

$$R^2 = 0.87$$

where R^2 is the statistical correlation coefficient.

The fitness of the model to the data is presented on Figure 6-139 (TCOD-SCOD) and Figure 6-140 (DVS). TCOD, SCOD, and DVS will not be removed at HRTs less than 1 day, 0.28 days, and 0.67 days, respectively. Even though SCOD and DVS were removed at 1-day HRT, the removals may not be due to methanogenesis but, rather, to conversions into particulate organics, as indicated by the TCOD removal efficiencies. Equation 6-20 shows that the maximum DVS removal would be more than 100%. The data was fitted for HRTs between 1.0 day and 6.2 days, and the best-fit equations cannot extrapolate at HRTs outside the evaluated range.

Specific methane production (SMP) results are summarized in Table 6-18. Calculations were based on influent loadings of TCOD (SMP_C), SCOD (SMP_{SC}), TVS, (SMP_V) and DVS (SMP_{DV}). As with SCOD and DVS removal efficiencies, Equation 6-17 was also

TABLE 6-18

ANAEROBIC FILTER STEADY STATE GAS PRODUCTION RESULTS FOR CONDITIONED SAMPLES

HRT (Days)	Flow, Q (mL/min)	MPR (mL/d)	SMP _c (mL/g TCOD)	SMP _{sc} (mL/g SCOD)	SMP _v (ft ³ /lb TVS)	SMP _{DV} (ft ³ /lb DVS)
6.2	1.6	4,500	115	482	3.9	7.5
2.7	3.7	10,000	90	425	3.4	6.3
1.8	5.5	10,100	53	271	1.8	2.1
1.0	9.8	1,400	4	13	0.2	0.4

NOTES:

1. SMP values were calculated based on influent loadings.

used to fit the specific methane production data. Because SMPs are based on influent and not removed loadings, the TCOD and TVS results can also be used to predict methane productions. Fitting Equation 6-17 to the data, the following results were obtained:

COD Basis

$$SMP_C = 135 - \frac{134}{t} \quad (6-21)$$

$$R^2 = 0.99$$

$$SMP_{SC} = 602 - \frac{583}{t} \quad (6-22)$$

$$R^2 = 0.98$$

Volatile Solids Basis

$$SMP_V = 4.77 - \frac{4.69}{t} \quad (6-23)$$

$$R^2 = 0.96$$

$$SMP_{DV} = 8.69 - \frac{8.86}{t} \quad (6-24)$$

$$R^2 = 0.89$$

where,

SMP_C = specific methane production, mL CH_4 /g TCOD applied

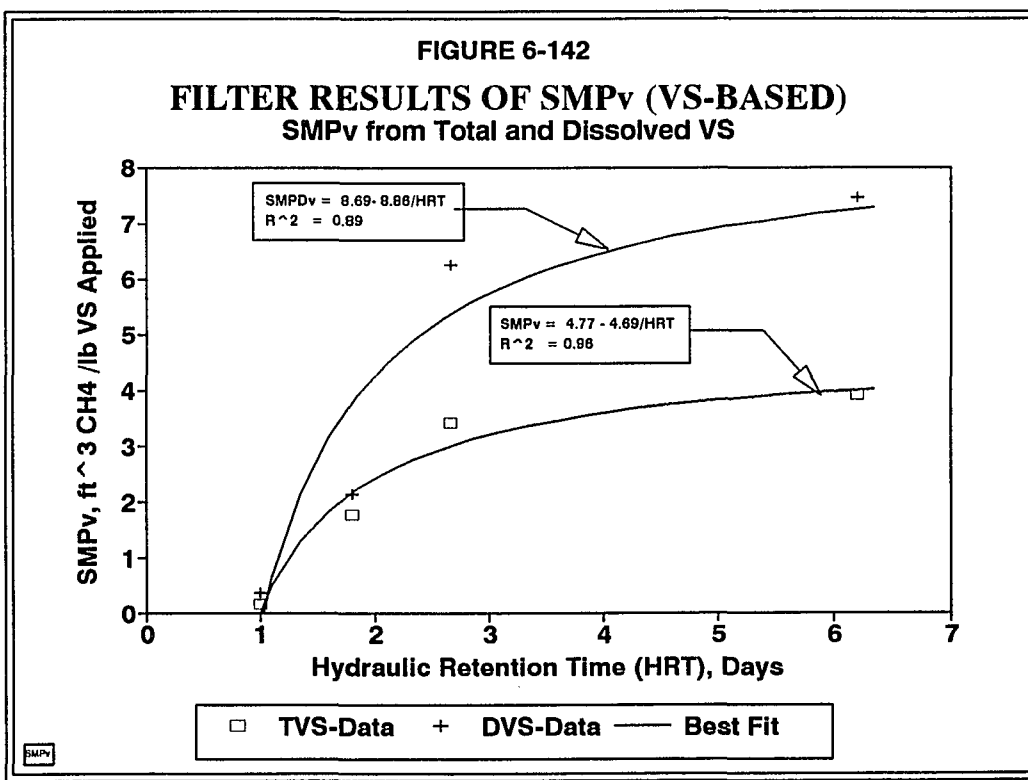
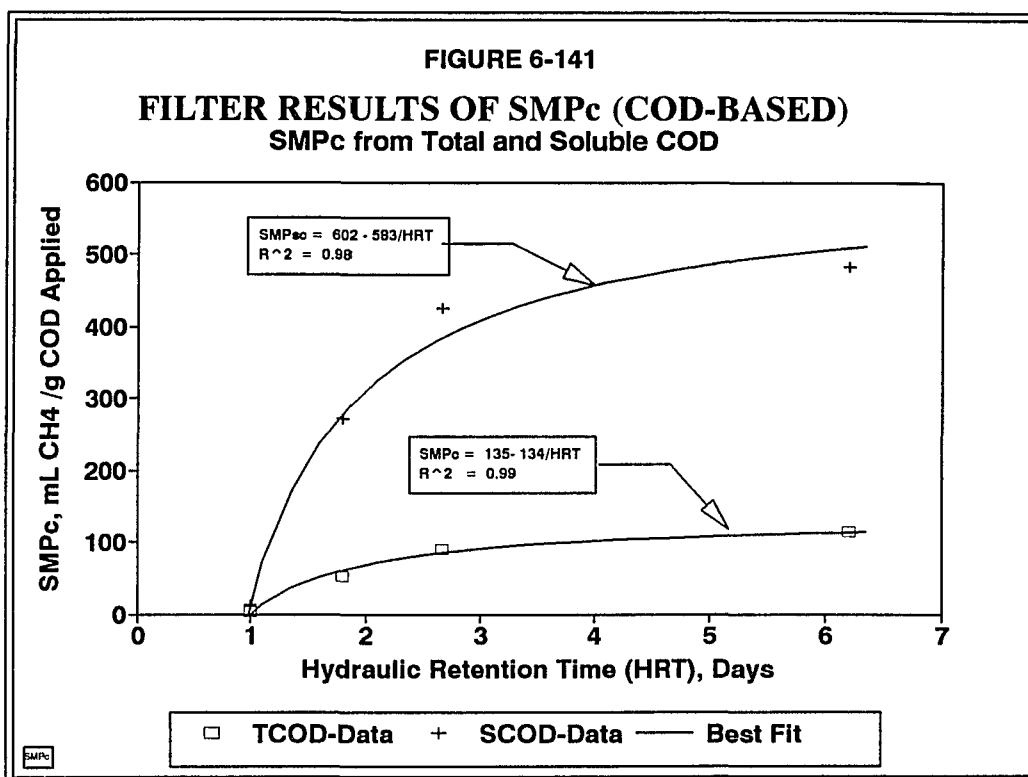
SMP_{SC} = specific methane production, mL CH_4 /g SCOD applied

SMP_V = specific methane production, ft³ CH_4 /lb TVS applied

SMP_{DV} = specific methane production, ft³ CH_4 /lb DVS applied

Figures 6-141 and 6-142 present the fitness of the model to the COD and solids data, respectively. Using Equations 6-18 through 6-24, the filter's COD and VS removal efficiencies and methane production rates can be estimated.

The operation of the pilot anaerobic filter was more difficult than the CFSTR due to solids buildup and partial clogging of the space between the filter packing. However, these problems can be minimized in full-scale operations by either removing the SS before treatment or by recirculating the filter's effluent to increase the flow velocity through the filter. Even with the minor operations problems, the results demonstrated that thermally conditioned PDS can be successfully treated by the anaerobic filter at HRTs of the fraction of the ones needed for completely mixed reactors. Greater than 70% SCOD and DVS removals can be achieved with retention times as low as two days. Again, similar to the CFSTR and serum bottle results, no inhibition effects were apparent in the thermally-conditioned PDS.



6.1.3 BOD Results

Five-day BOD analyses were performed on Wards Island PDS samples that were thermally conditioned at 100°C, 130°C, 160°C, 190°C and 220°C, on November 18, 1992. The BOD test was done (1) to confirm the biodegradability improvement obtained by the serum-bottle test, (2) determine any correlation between BOD and five-day GPI (GPI_5), and (3) correlate BOD with COD solubilization. BOD improvement (BOD_i) was calculated similar to the GPI calculation:

$$BOD_i = \frac{(BOD_T - BOD_r) \times 100}{BOD_r} \quad (6-25)$$

where,

BOD = five-day biochemical oxygen demand, mg/L

BOD_i = BOD improvement, %

BOD_T = BOD of RTC-sample at temperature T, mg/L

BOD_r = BOD of raw PDS (at room temperature), mg/L

Figure 6-143 presents the BOD_i as a function of RTC temperatures. Improvement was 100% at 100°C, increasing linearly to 250% at 190°C, and reaching of 260% at 220°C. The PDS's BOD increased from 1,380 mg/L (without RTC) to 5,000 mg/L at 220°C (Table 6-19). A second-degree polynomial correlated well the BOD_i data with a correlation coefficient of 0.97:

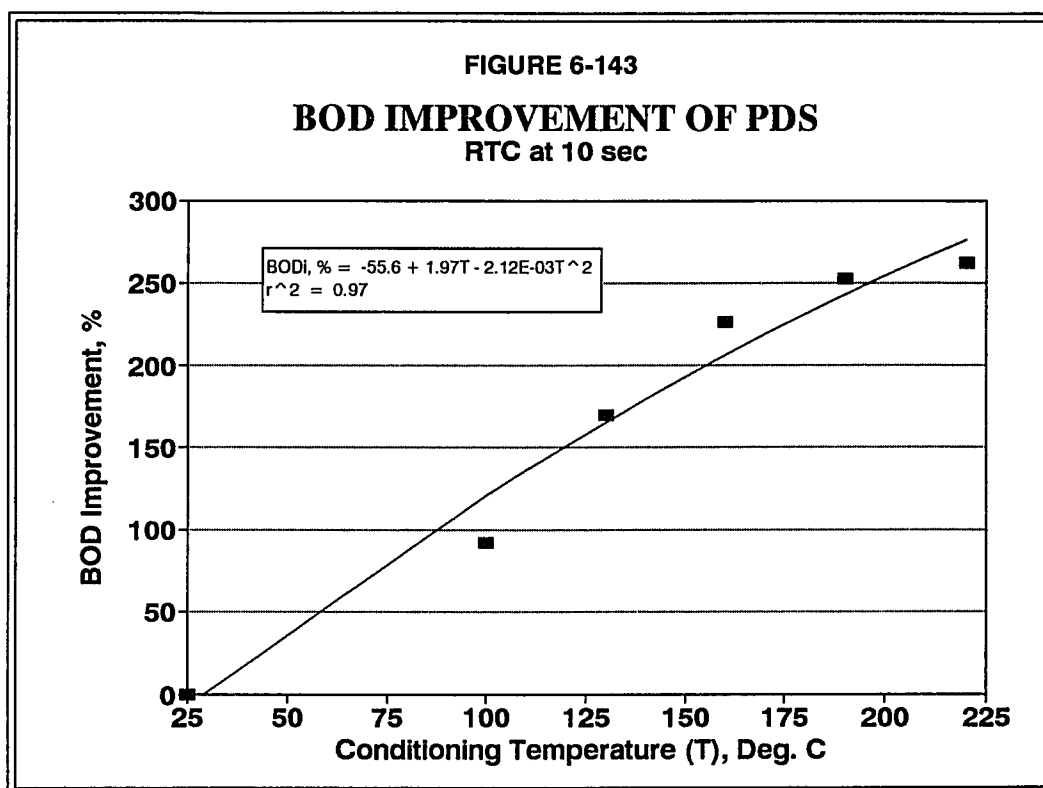


TABLE 6-19

RELATIONSHIP OF BOD WITH SCOD AND GPI

RTC Temperature (°C)	BOD		COD		GPI (%) at Various Incubation Times ⁽²⁾			
	Concentration (mg/L)	Improvement ⁽¹⁾ (%)	Concentration (mg/L)	Improvement ⁽¹⁾ (%)	0-day	1-day	4-day	5-day
25	1,380	0	740	0	0	0	0	0
100	2,660	92	1,830	147	345	181	52	42
130	3,720	169	3,860	421	617	411	188	162
160	4,510	226	3,920	429	620	460	246	216
190	4,870	252	5,550	650	755	532	268	234
220	5,000	262	7,270	883	920	685	373	328

NOTES:

1. BOD and SCOD improvements are based on 25°C sample (unconditioned PDS).
2. GPI calculated from best-fit two-term equation.

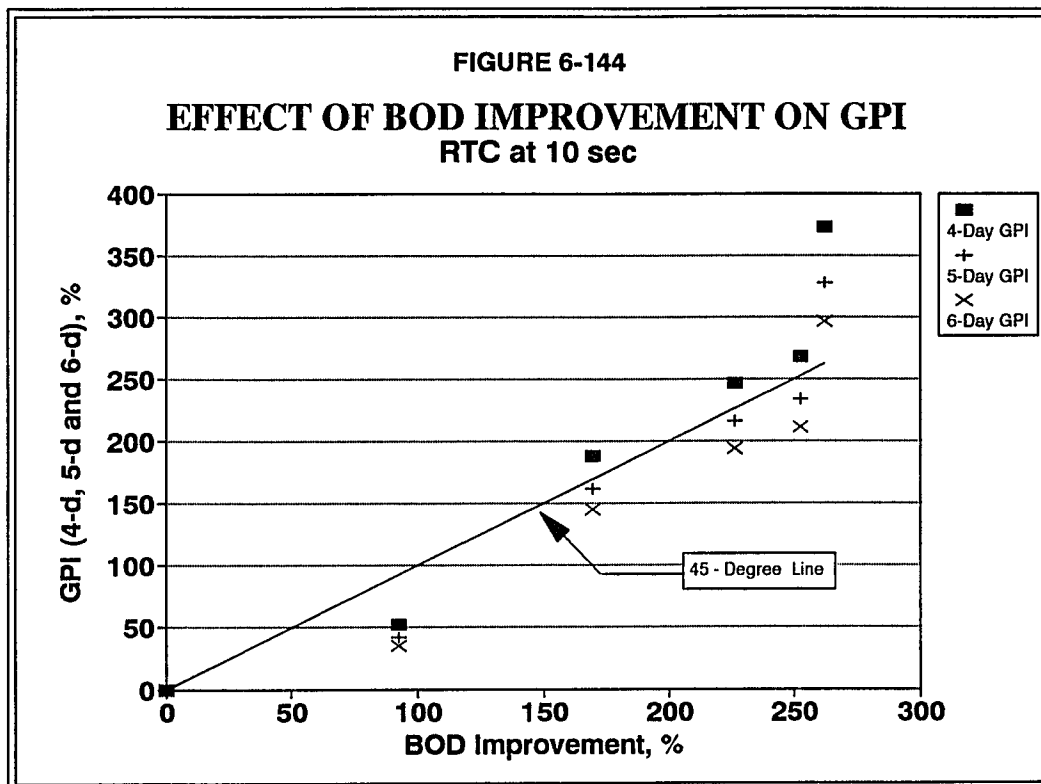
$$BOD_i = -55.6 + 1.97T - 0.00212T^2 \quad (6-26)$$

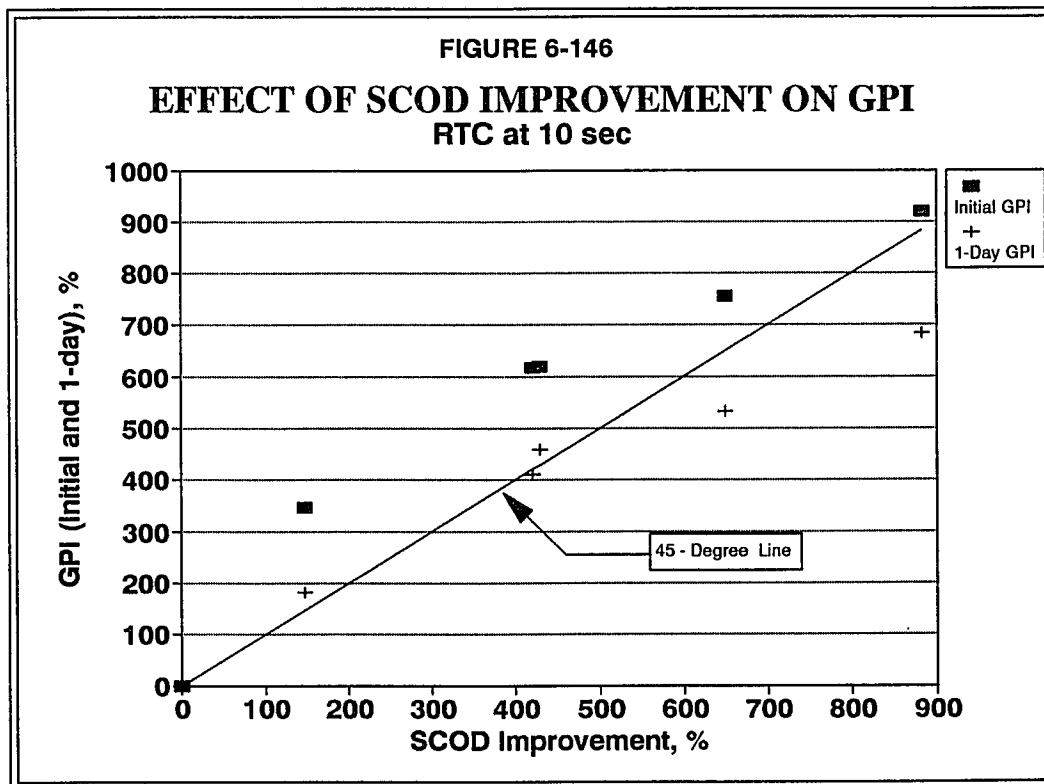
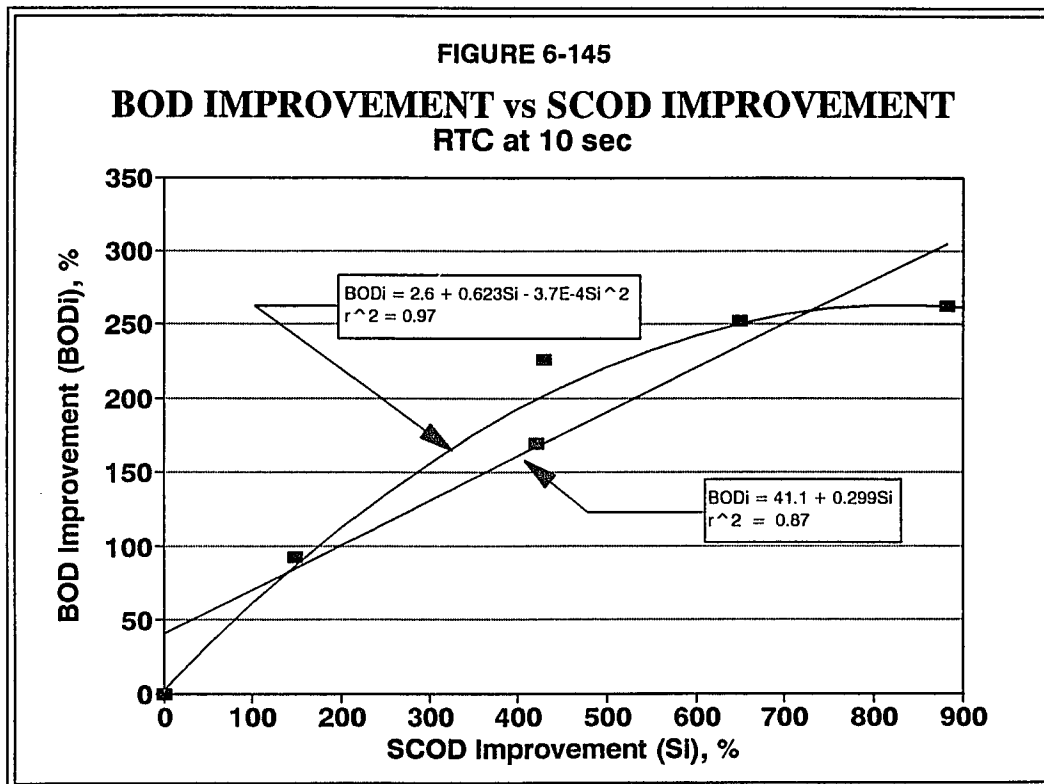
Figure 6-144 compares the BOD_i to the four-, five- and six-day GPI results. The 45° line fits better the GPI_5 , indicating that biodegradability can be measured aerobically or anaerobically. Organic material, released during the RTC process, can be degraded equally at both environmental conditions. It could be possible that either aerobic or anaerobic testing can be used to evaluate future biodegradation studies.

To understand better the biodegradation process, BOD_i was also compared to SCOD improvement (SCOD at RTC temperatures compared to SCOD of raw PDS) on Figure 6-145. The results do not show a one-to-one relationship, since SCOD improvement (S_i) was much higher than the BOD_i at any temperature. A second-degree polynomial fitted the results better than a linear equation, resulting to an r^2 of 0.97:

$$BOD_i = 2.6 + 0.62S_i - 0.00037S_i^2 \quad (6-27)$$

Equation 6-27, because of the limited tested conditions, cannot replace the BOD test but it can only estimate the five-day biodegradability improvement of PDS. The inability of Figure 6-145 to have a one-to-one relationship is evident on Figure 6-146, a presentation of the SCOD improvement with the initial and one-day GPI. The results show that SCOD improvement correlates better with the initial GPI values (within one-day incubation period),





than the five-day BOD value. Figure 6-146 shows that the high GPIs obtained at the beginning of the serum-bottles incubation period are due to the high COD solubilizations. Because of the high COD solubilizations, biodegradation kinetic rates were increased.

To summarize, the BOD analysis of the RTC PDS confirmed the improvement in biodegradability, established a one-to-one relationship between the BOD_i and GPI_5 , and it correlated with the SCOD improvement. SCOD is responsible for the high GPIs at the beginning of incubation periods, and for the kinetics improvement.

6.1.4 DHA Results

DHA was measured during a sampling event of Wards Island PDS on February 18, 1993. PDS was thermally conditioned at unmodified pH and at pH11, with RTC temperatures of 100°C, 160°C and 220°C. HRTs were 10 seconds except one condition, pH11 and 220°C, where the 30-second HRT was also evaluated. Sample numbers and tested conditions are presented in Table 6-20. The pH11 samples were readjusted back to the unmodified pH range of approximately 7.5 after the RTC process. DHAs of the nine samples were determined on three different times:

1. Immediately after RTC
2. Two days after RTC, and
3. Four days after RTC

The two- and four-day samples were incubated at 35°C prior to DHA measurement to evaluate possible bacterial viabilities and recoveries after exposed to RTC. Each test was conducted without substrate addition, endogenous, and with substrate addition. Substrate addition would differentiate which bacterial groups would be most affected by conditioning. Glucose was added for fermentative bacteria, propionic acid for acetogenic bacteria (added only to the Feb. 18 sample), acetic acid for acetate-utilizing bacteria, and formic acid for hydrogen-utilizing methanogenic bacteria.

TABLE 6-20

SAMPLE CONDITIONS FOR DEHYDROGENASE ACTIVITY (DHA) TESTING

Sample No.	RTC Temperature (°C)	RTC HRT (sec)	pH
1	25	Unconditioned	Unmodified
2	100	10	Unmodified
3	160	10	Unmodified
4	220	10	Unmodified
5	25	Unconditioned	11
6	100	10	11
7	220	10	11
8	220	30	11
9	160	10	11

(a) Immediately After RTC

Originally, the DHAs were measured for an incubation time of one-hour, the time used by Chung (1988). The Feb. 18 sample's DHAs were measured at this time. Only untreated PDS (Sample 1) and 100°C PDS (Sample 2) were active (Figure 6-147). Untreated PDS showed the high response on glucose and highest on formic acid. Acetic acid and formic acid DHA results were similar to endogenous values.

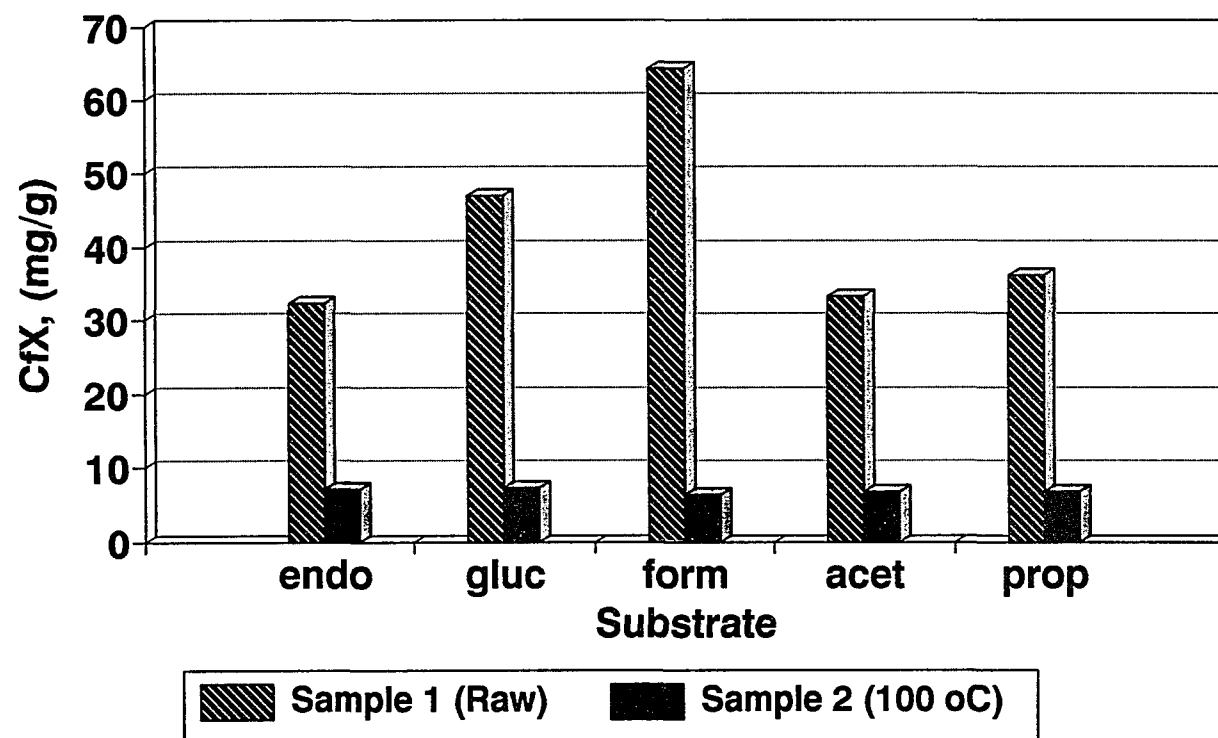
The 100°C RTC sample showed little but equal responses for all substrate conditions. Although DHAs were much less than the unconditioned PDSs, the fact that some activity was measured indicates that a 10-second RTC at 100°C does not inactivate all bacteria. Some bacteria survived at 100°C. However, they need time to regenerate (more than the one-hour test incubation period), resulting in similar activities under any substrate loading. Some bacteria probably survived at all tested conditions, but they showed no activities at such a short incubation period. One-hour incubation time is not sufficient to measure activities of severely damaged bacteria populations, and was increased for the two- and 4-day samples.

(b) Two-day Incubation After RTC

The RTC samples were incubated for two days before performing DHA analysis. DHAs of the two-day sample were measured at incubation times of 2, 4, 72 and 96 hours using as substrates glucose and acetic acid. Endogenous DHA results are presented on Figure 6-148,

FIGURE 6-147

DEHYDROGENASE ACTIVITY OF PDS
Immediately After RTC;1-hour Incubation



CFX-18

FIGURE 6-148
ENDOGENOUS DHA
Two Days after RTC

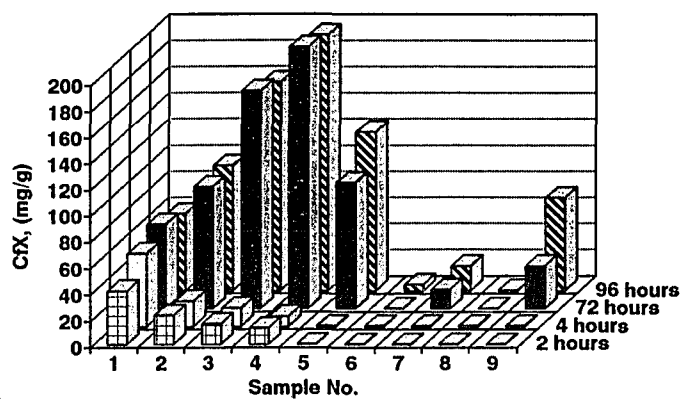


FIGURE 6-149
GLUCOSE DHA
Two Days after RTC

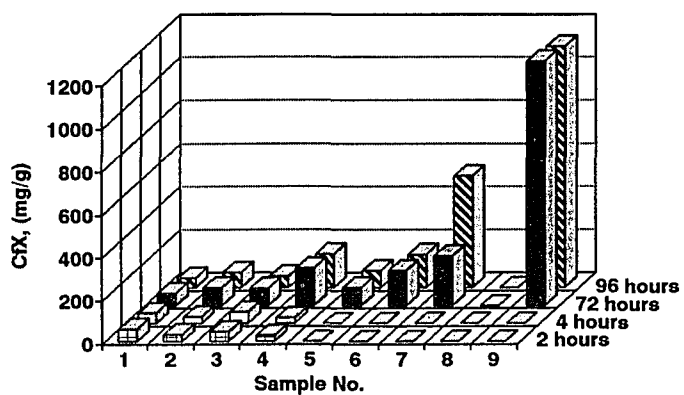
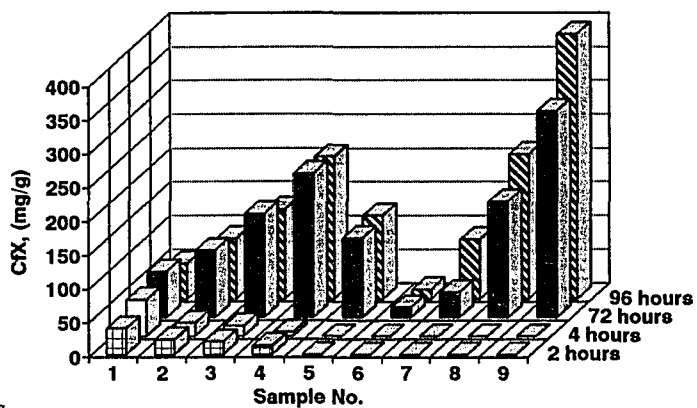


FIGURE 6-150
ACETIC ACID DHA
Two Days after RTC

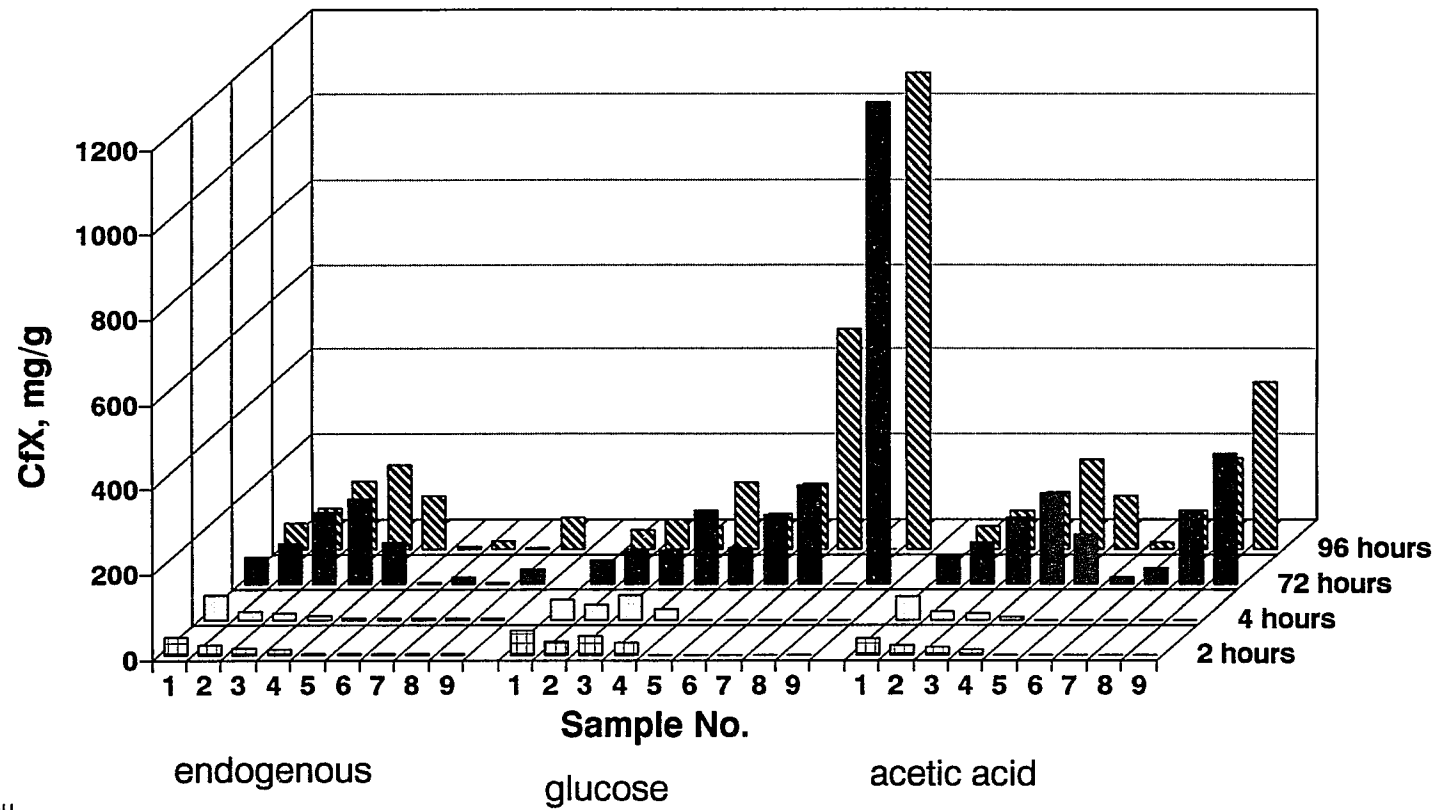


glucose on Figure 6-149, and acetic acid on Figure 6-150. All results are compared on Figure 6-151. The unconditioned PDS responded fast without any significant DHA changes over the longer incubation times. Bacteria were feeding on stored substrate and on solid organic matter remaining in the washed PDS. Samples were washed with tap water prior to testing.

DHA response of conditioned PDS depended on temperatures, pH value, and contact times. Initial shock, cell damage, and low bacterial numbers caused the lag phase at the low incubation times. Endogenous DHA values of the pH-unmodified PDS showed significant improvements over the unconditioned PDS, with maximum at 220°C. Generally, the higher the temperature, the less the DHA at low incubation times, but the higher the activity at the end of the test. Similar results were obtained with glucose and acetic acid addition, with DHA values higher than the unconditioned PDS at the end of the test, and maximum at 220°C.

Adjusting the pH of PDS to 11 showed complete inactivation at the beginning of the incubation periods for all substrates. At endogenous conditions, only Samples 5 and 9 showed high activities at the 96-hour incubation times. Samples 6 and 7 showed low response, and Sample 8 (the 30-sec sample) showed no response. Glucose addition caused highest activities at pH11 than at unmodified pH. Sample 9 had the maximum DHA value among all the tested conditions. Again, Sample 8 showed no glucose activity, indicating that fermentative bacteria were greatly affected by the 30-second contact time.

FIGURE 6-151
DHA FOR ALL SUBSTRATES
Two Days after RTC



ALL

Acetic acid was utilized at all pH11 conditions. Sample 6 showed the minimum DHA value, much less than Sample's 1 value. Samples 5, 7, 8 and 9 DHA values were greater than Sample 1, but only Sample 9 surpassed the DHA of Sample 4. Acetic acid was utilized by Sample 8, the sample that had no activities during endogenous- and glucose-addition conditions.

The results showed comparable results at the 72- and 96-hour incubation times, indicating that DHA reached maximum values before the 72-hour time. Consequently, the four-day-after-RTC sample could be incubated at shorter times.

(c) Four-day Incubation After RTC

DHA values were measured at 1.25, 19 and 43 hours of incubation. Tested conditions were at endogenous (Figure 6-152), glucose (Figure 6-153), acetic acid (Figure 6-154), and formic acid (Figure 6-155). All results are compared on Figure 6-156. The activity pattern is similar to the two-day sample, except Sample 8 that showed activities with all substrates. Again, Sample 9 (pH11, 160°C) showed the maximum activities with all substrate conditions.

(d) Conclusion

DHA measurement confirmed that high RTC temperatures, high pH values and long RTC contact times do not inactivate all bacterial activities. Some groups were affected more than

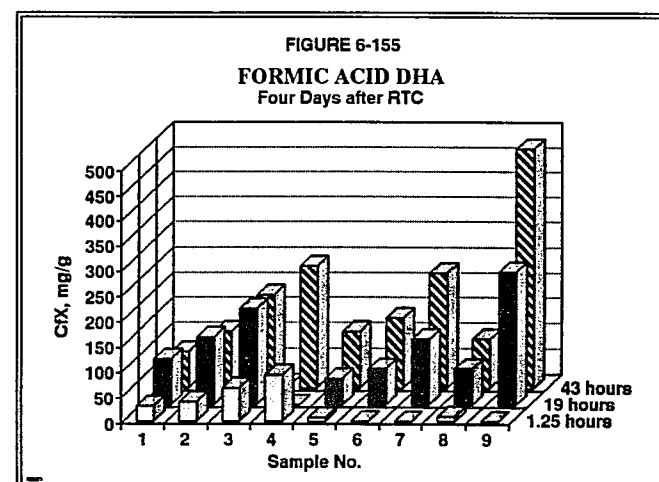
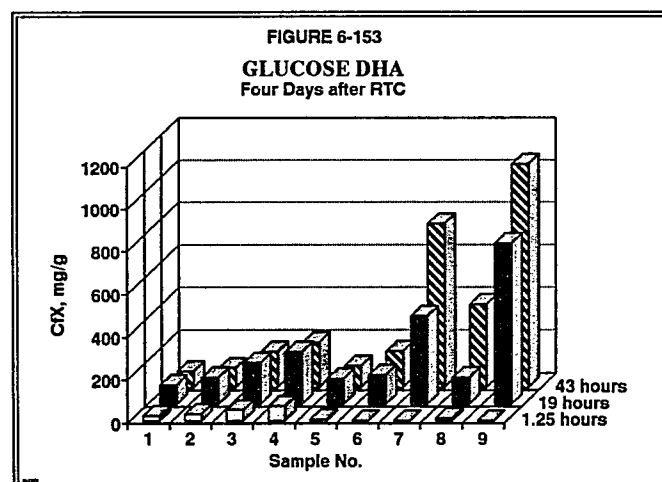
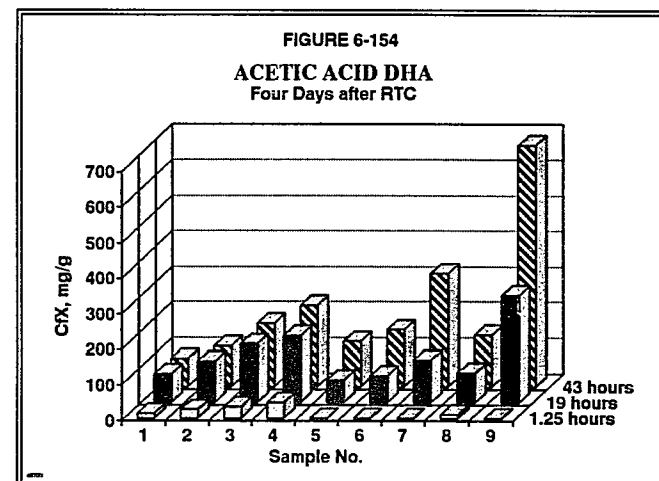
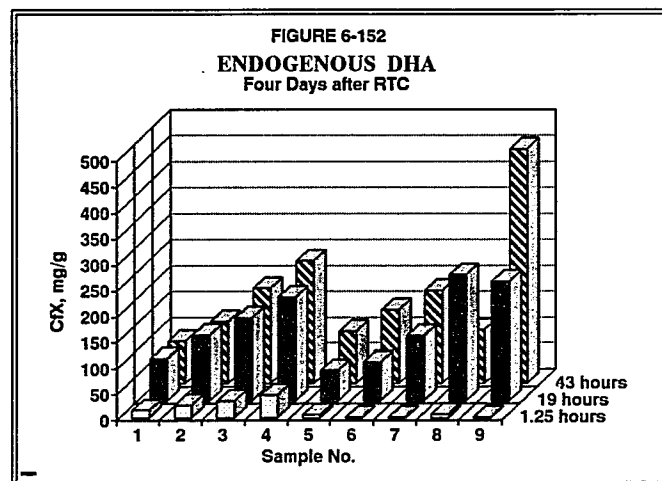
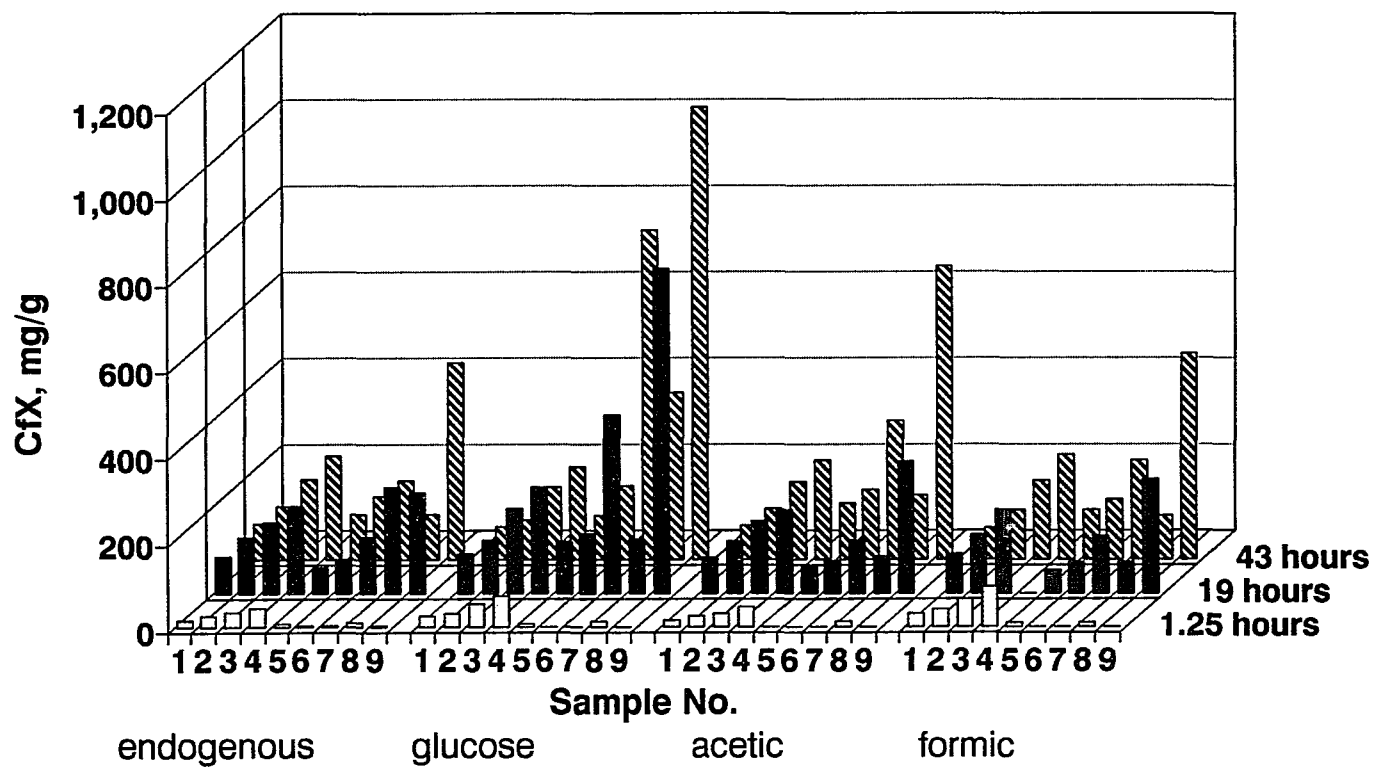


FIGURE 6-156
DHA FOR ALL SUBSTRATES
Four Days after RTC



ALL

other groups, but at the end all bacteria could revive. The activity measurements also confirmed bacterial stimulation, resulting to biodegradability improvement.

Chung (1988) used the DHA test at one-hour incubation period, which may be long enough for active bacteria. For "injured" bacterial populations or for situations where a lag phase is expected, incubation times should be prolonged, as evident by this study's results. Lag phases can be measured by performing the DHA test at different intervals.

The combined results of OUR and DHA analyses support the original observations made with the serum bottles that RTC does not inactivate the sludge. Apparently, the large amount of solids present in sludges protect some bacteria and prevent total inactivation.

6.2 Heavy Metal Solubilization

Table 6-21 summarizes the conditions used to evaluate metals solubilization and metals removal from PDS. PDS was analyzed for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, and Zn. Metal analysis was performed by the New York City DEP laboratory located at Wards Island. The initial tests (June 16, 1992, and July 29, 1992) were performed to evaluate the sole effect of various pHs and pH-contact times on metal solubilizations. Thermal conditioning was not performed during these two experiments. Most of the tests were performed on Wards Island PDS, and one test was performed on Newtown Creek PDS. Wards Island PDS was thermally conditioned at a 10-second retention time, and Newtown Creek PDS was thermally conditioned at a 10-second and a 30-second retention time.

6.2.1 Wards Island Results

June 16, 1992: Metals analyses were performed on samples that were adjusted to pH4, pH2, and pH1, and at contact times of 0 hours, 0.5 hours, 1 hour and 18 hours. Analyses were performed for total, centrifuged, and filtered metals. Centrifugation was conducted by a laboratory centrifuge at 3,000 rpm for 10 minutes, and the centrate (supernatant after centrifugation) was collected for metals analyses. The cake produced by centrifugation was not tested for metals. Cake analyses were performed during subsequent experiments.

TABLE 6-21

EVALUATED CONDITIONS FOR HEAVY METAL SOLUBILIZATION

Test Date	pH	pH Contact Time ⁽¹⁾	RTC Temperature and HRT
WARDS ISLAND			
June 16, 1992	pH4	0.5, 1, and 18 hrs	None
	pH2	0, 0.5, 1, and 18 hrs	None
	pH1	0, 0.5, 1, and 18 hrs	None
July 29, 1992	pH1.3-2	0, 1, 4, 9, and 17 hrs	None
	pH1	0, 1, 4, 9, and 17 hrs	None
Oct. 16, 1992	pHu(7.5) ⁽²⁾	--	220°C, 10 sec
	pH1.5	0, 14, and 17 hrs	220°C, 10 sec
Feb. 18, 1993	pHu(7.5)	--	220°C, 10 sec
	pH11	Minimal time ⁽³⁾	220°C, 10 sec
NEWTOWN CREEK			
Feb. 11, 1993	pHu(7.5)	--	220°C, 10 & 30 sec
	pH1.5	Minimal time	165°C, 10 & 30 sec

NOTES:

1. Time sample remained in contact with the evaluated pH
2. pHu is unmodified pH at about 7.5
3. Minimal time: as soon as the sample pH was adjusted to the required value inside the sludge storage tank, the pH-adjusted sample was run through the RTCR.

Sample filtration was performed by filtering the centrate through a 0.45 μm membrane filter. Only a few samples were filtered in order to have an estimate of the metals in solution. However, the centrate data is of more practical use because it predicts the quality of the centrate from the sludge dewatering facilities at the NYC treatment plants.

Table 6-22 lists the various sample conditions and heavy metal concentrations analyzed by the DEP laboratory. Metal solubilization, defined as the metal concentration in the centrate or filtrate, divided by the average total metal concentration, is shown in Table 6-23. Figures 6-157, 6-158, and 6-159 graphically present the metal solubilizations at pH1, pH2, and pH4, respectively.

Results indicated that at the "minimum contact times" (0-hours) at pH1 and pH2 solubilized some of the metals, had no effect in metals such as Cu and Hg, and had little effect on Cd and Pb. The 0.5-hour and 1-hour contact times gave similar results at pH1 and pH2. A sharp increase in Cu and Pb solubilization was observed after the 18-hour contact time, where at pH1 the solubilization was 80% for Cu and 77% for Pb; at pH2 the solubilization was 44% for Cu and 12% for Pb. Metals solubilization at pH4 was insignificant at all contact times.

Comparing centrate with filtrate results (Table 6-22) for the 18-hours contact time at pH1 and pH2, demonstrated that there is very little difference between the two, indicating that the metals remaining in the centrate are likely to be in solution. For clarity, the centrate and filtrate results are also compared on Figures 6-160 (pH1) and 6-161 (pH2).

TABLE 6-22

METAL ANALYSIS AT pHu, pH1, pH2 AND pH4, AND CONTACT TIMES FROM 0 TO 18 HOURS
WARDS ISLAND; JUNE 16, 1992

Sample No.	Metal Concentration, mg/L							Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Hg	
U1T	32	1.7	3.8	36.	0.29	8.0	0.04	pH = Unmodified; Total Metal
U1C	0.17	0.007	0.023	0.27	0.0031	<BDL ⁽¹⁾	0.0008	pH = Unmodified; Centrate Metal
42C	0.9	0.12	0.16	0.83	0.011	0.18	0.0014	pH4; 30 Min.; Centrate Metal
43C	0.8	0.13	0.13	0.68	0.01	0.063	0.0012	pH4; 60 Min.; Centrate Metal
44C	1.4	0.2	0.15	1.5	0.0067	0.23	0.0025	pH4; 18 Hrs; Centrate Metal
21T	30	1.65	3.8	35.	0.42	8.5	0.063	pH2; 0 Min.; Total Metal
21C	6.9	0.26	1.3	0.41	0.021	0.097	0.00006	pH2; 0 Min.; Centrate Metal
22C	11	0.35	1.4	1.1	0.028	0.23	0.0019	pH2; 30 Min.; Centrate Metal
23C	10	0.34	1.3	0.49	0.023	<BDL	0.00082	pH2; 60 Min.; Centrate Metal
24T	32	1.6	3.9	35.	0.29	6.8	0.068	pH2; 18 Hrs; Total Metal
24C	21	0.5	0.54	16.	0.098	1.0	0.0022	pH2; 18 Hrs; Centrate Metal
24S	20	0.53	0.5	15.	0.1	0.77	0.0073	pH2; 18 Hrs; Filtered Metal (0.45 μ m)
11T	38	1.9	4.6	37.	0.42	9.2	0.08	pH1; 0 Min.; Total Metal
11C	18	0.37	1.6	0.54	0.057	0.95	0.00007	pH1; 0 Min.; Centrate Metal
12C	19	0.41	1.6	0.65	0.065	1.7	0.0011	pH1; 30 Min.; Centrate Metal
13C	20	0.41	1.7	0.68	0.076	2.1	0.00095	pH1; 60 Min.; Centrate Metal
14C	22	0.56	1.63	29.	0.11	6.1	0.0097	pH1; 18 Hrs.; Centrate Metal
14S	21	0.53	1.65	26.	0.12	5.7	0.0021	pH1; 18 Hrs; Filtered Metal (0.45 μ m)
Average Total ⁽²⁾	33	1.7125	4.025	35.75	0.355	8.125	0.06275	

NOTES:

- BDL = Below detection limit
- Average of Total Metal Concentrations (Samples U1T, 21T, 24T, and 11T)

TABLE 6-23

METALS SOLUBILIZATION AT pHu, pH1, pH2 AND pH4, AND CONTACT TIMES FROM 0 TO 18 HOURS
WARDS ISLAND; JUNE 16, 1992

Sample No.	Metals Solubilization, % of Average Total ⁽¹⁾							Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Hg	
U1T	--- ⁽²⁾	---	---	---	---	---	---	pH = Unmodified; Total Metal
U1C	0.5	0.4	0.6	0.8	0.9	0.0	1.3	pH = Unmodified; Centrate Metal
42C	2.7	7.0	4.0	2.3	3.1	2.2	2.2	pH4; 30 Min.; Centrate
43C	2.4	7.6	3.2	1.9	2.8	0.8	1.9	pH4; 60 Min.; Centrate
44C	4.2	11.7	3.7	4.2	1.9	2.8	4.0	pH4; 18 Hrs; Centrate
21T	---	---	---	---	---	---	---	pH2; 0 Min.; Total
21C	20.9	15.2	32.3	1.1	5.9	1.2	0.1	pH2; 0 Min.; Centrate
22C	33.3	20.4	34.8	3.1	7.9	2.8	3.0	pH2; 30 Min.; Centrate
23C	30.3	19.9	32.3	1.4	6.5	0.0	1.3	pH2; 60 Min.; Centrate
24T	---	---	---	---	---	---	---	pH2; 18 Hrs; Total
24C	63.6	29.2	13.4	44.8	27.6	12.3	3.5	pH2; 18 Hrs; Centrate
24S	60.6	30.9	12.4	42.0	28.2	9.5	11.6	pH2; 18 Hrs; Filtered (0.45 µm)
11T	---	---	---	---	---	---	---	pH1; 0 Min.; Total
11C	54.5	21.6	39.8	1.5	16.1	11.7	0.1	pH1; 0 Min.; Centrate
12C	57.6	23.9	39.8	1.8	18.3	20.9	1.8	pH1; 30 Min.; Centrate
13C	60.6	23.9	42.2	1.9	21.4	25.8	1.5	pH1; 60 Min.; Centrate
14C	66.7	32.7	40.5	81.1	31.0	75.1	15.5	pH1; 18 Hrs.; Centrate
14S	63.6	30.9	41.0	72.7	33.8	70.2	3.3	pH1; 18 Hrs; Filtered (0.45 µm)

NOTES:

1. Average of Total Metal Concentrations (from Table 6-22)
2. "---" Sample used as baseline for metal solubilization calculations

FIGURE 6-157
METAL SOLUBILIZATION AT pH1
 Wards Island; June 16, 1992

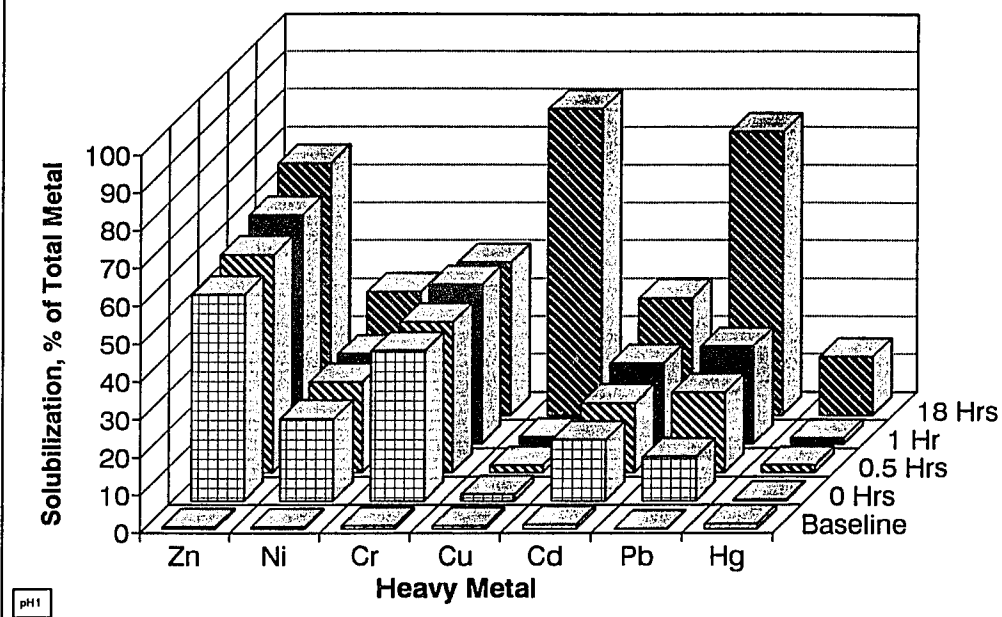
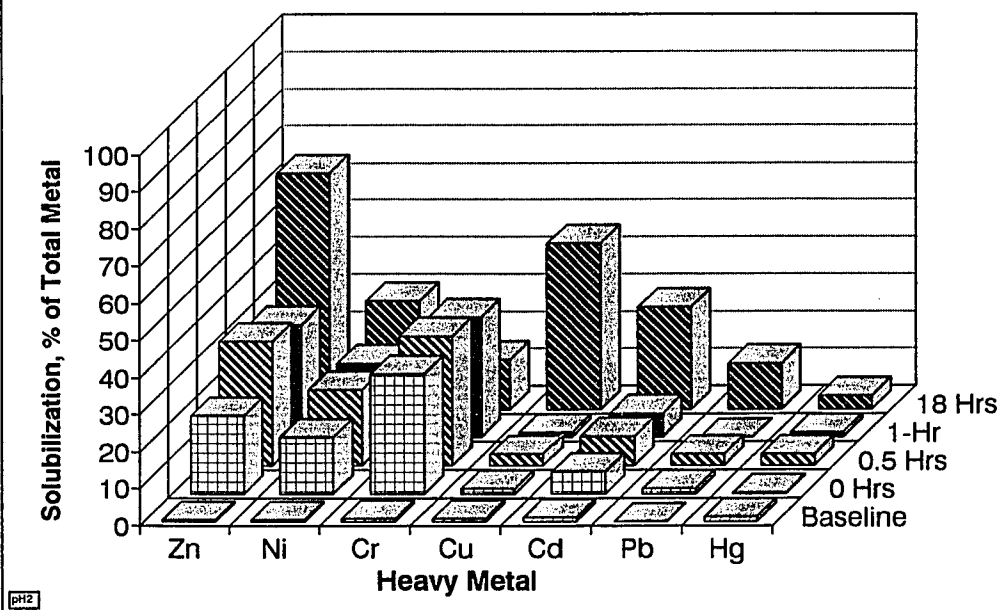
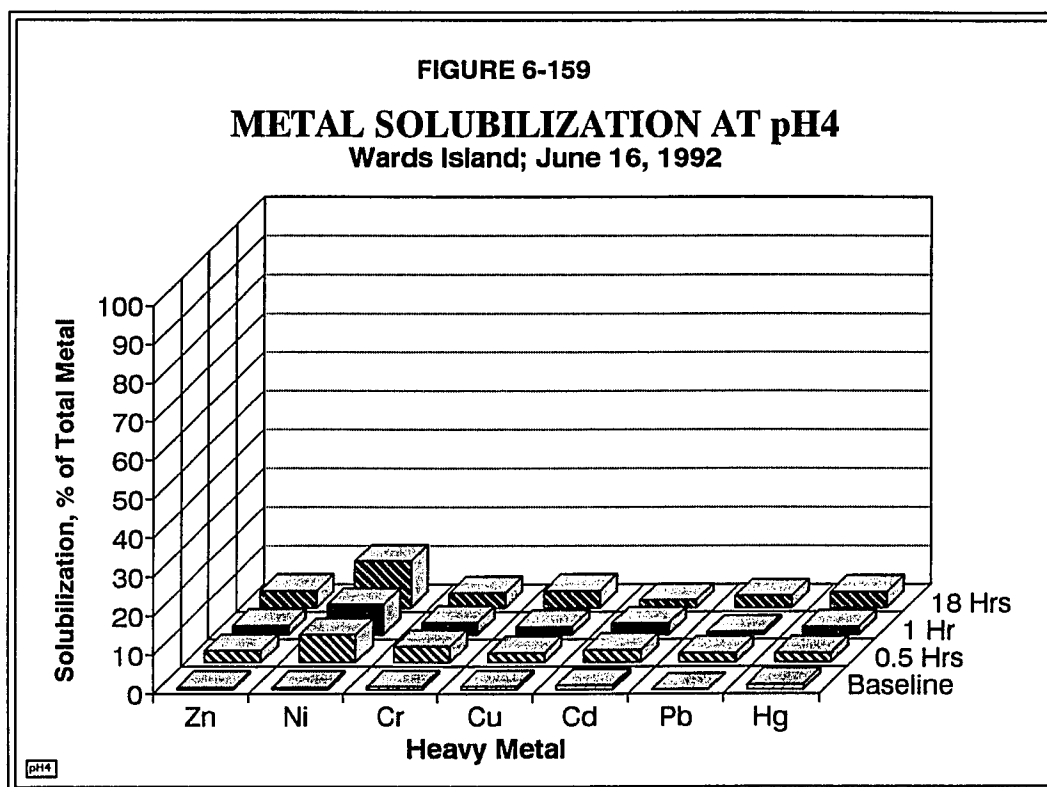
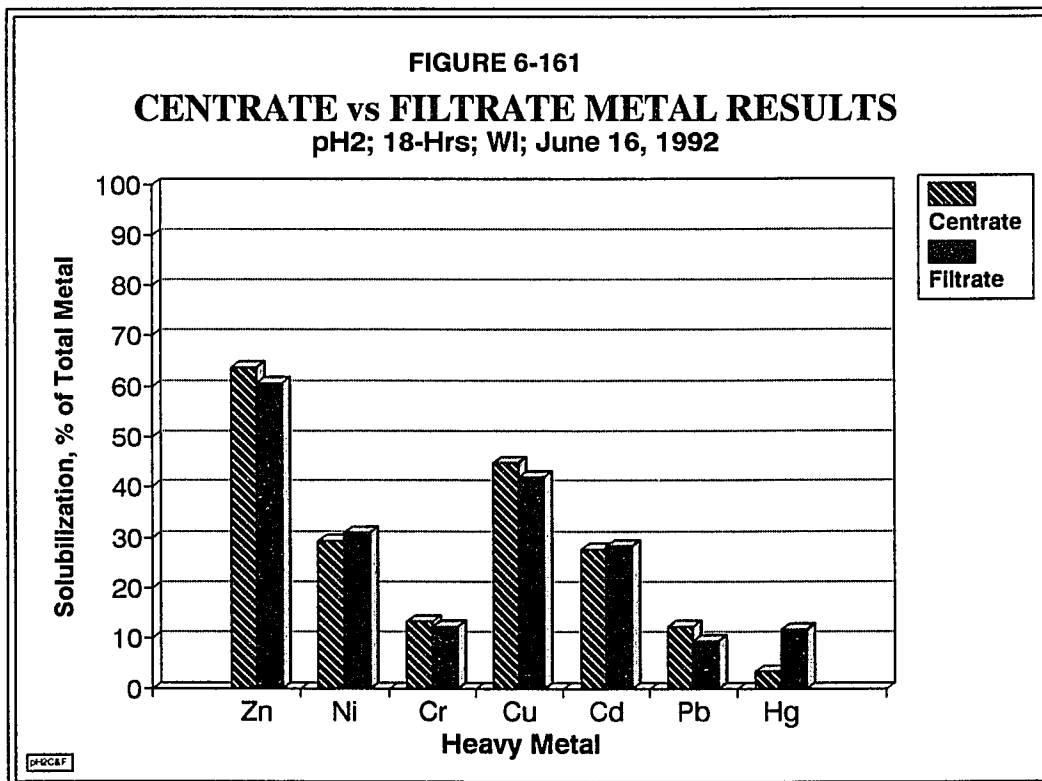
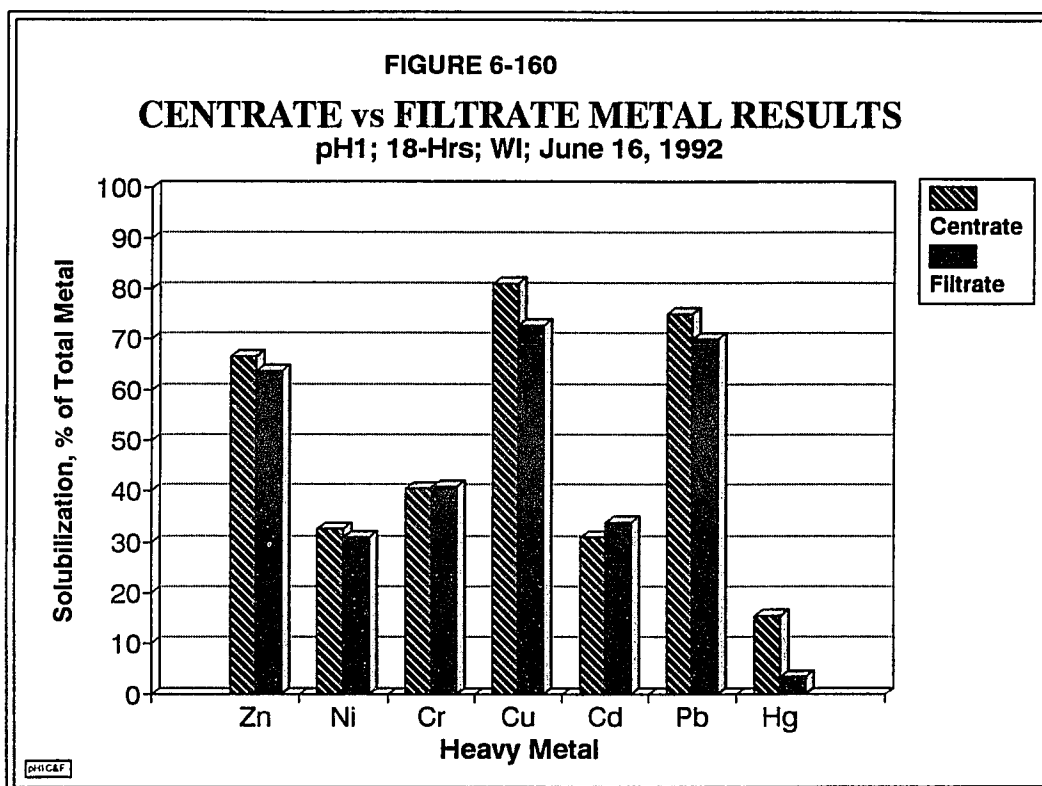


FIGURE 6-158
METAL SOLUBILIZATION AT pH2
 Wards Island; June 16, 1992







An important observation, not considered in previous published studies, was that solubilization of metals occurs concurrently with solids solubilization. TS and VS solubilizations are presented on Figures 6-162 and 6-163, respectively. Both figures demonstrate that contact time had no significant effect on solids solubilization. The dissolved solids reached 30% TS at pH1, compared to 11% for untreated PDS, while dissolved VS reached 20%. The land application regulations (both NYS and EPA 503) specify the metals concentration in mg per kg of dry solids. Therefore, if solids solubilization during acid pretreatment is much greater than metals solubilization then the remaining sludge cake may contain as high a concentration of metals as before any treatment.

To evaluate this assumption, a mass balance was performed on both the metals and solids concentration in order to calculate the metals concentration in the cake produced after centrifugation (Table 6-24). Figures 6-164, 6-165 and 6-166 graphically illustrate the cake metal concentrations at pH1, pH2, and pH4, respectively. In some cases, the metals concentration in the cake increased. This result is clearly observed for Cu at pH1 and 1-hour contact time where the non-acidified PDS contained 1,459 mg Cu/kg dry solids, and the cake contained 1,794 mg Cu/kg dry solids. This was the result of high solids solubilization where the mass of cake decreased at a rate greater than the rate that the metals were removed from the cake. The Cu solubilization was just 2%, which was much less than the solids solubilization of 30%.

However, the Cu concentration in the cake at pH1 and 18-hours contact time was calculated to be 610 mg Cu/kg dry solids, meeting both the NYS Land Application and EPA 503

FIGURE 6-162
TOTAL SOLIDS SOLUBILIZATION
Wards Island; June 16, 1992

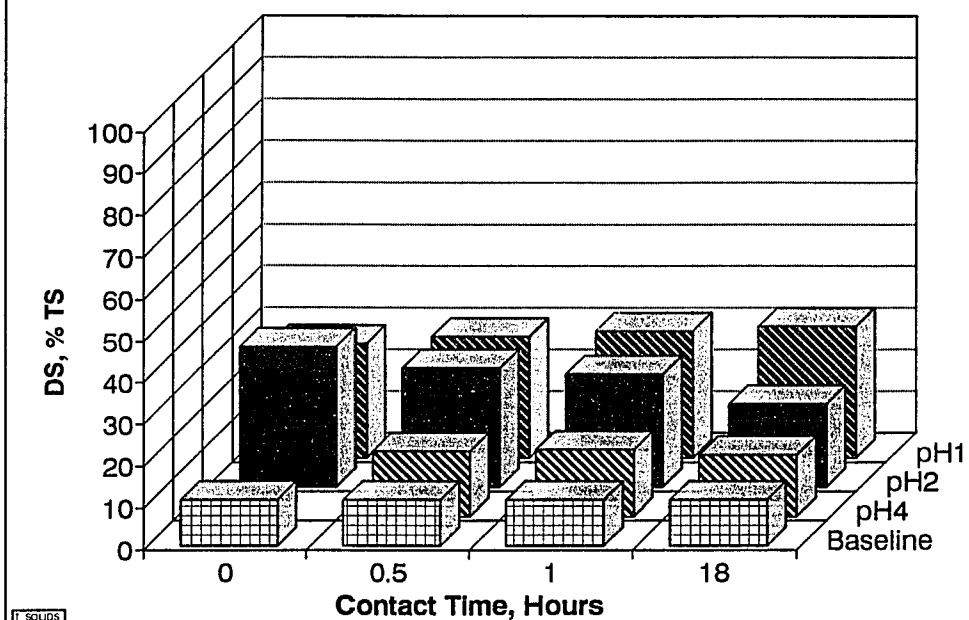


FIGURE 6-163
VOLATILE SOLIDS SOLUBILIZATION
Wards Island - June 16, 1992

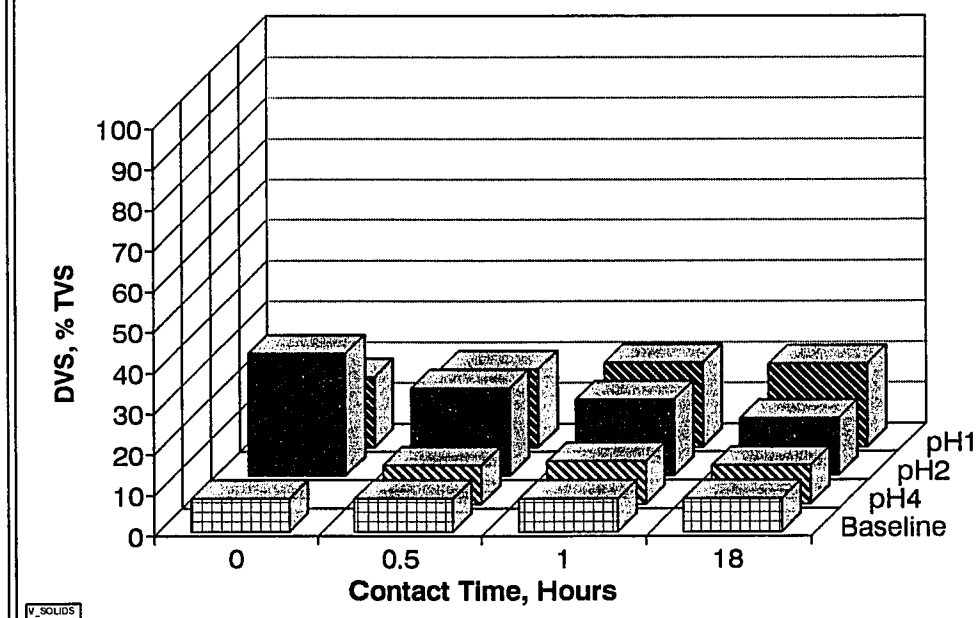


TABLE 6-24

METAL CONCENTRATIONS DISPOSED WITH SLUDGE (AFTER CENTRIFUGATION) AT pHu, pH1, pH2
AND pH4, AND CONTACT TIMES FROM 0 TO 18 HOURS, WARDS ISLAND; JUNE 16, 1992

From Sample No.	Cake Metal Concentrations, mg/kg Dry Solids ⁽¹⁾							Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Hg	
UIT ⁽²⁾	1,347	70	164	1,459	14	332	2.6	pH = Unmodified; Total Metal
UIC ⁽³⁾	1,463	76	178	1,582	16	362	2.8	pH = Unmodified; Centrate Metal
42C	1,419	71	171	1,542	15	351	2.7	pH4; 30 Min.; Centrate
43C	1,432	71	174	1,557	15	357	2.7	pH4; 60 Min.; Centrate
44C	1,420	69	174	1,539	16	354	2.7	pH4; 18 Hrs; Centrate
21T	1,089	57	133	1,180	12	268	2.1	pH2; 0 Min.; Total
21C	1,457	80	159	1,868	18	424	3.3	pH2; 0 Min.; Centrate
22C	1,194	70	144	1,681	16	383	3.0	pH2; 30 Min.; Centrate
23C	1,224	70	146	1,723	16	396	3.0	pH2; 60 Min.; Centrate
24T	1,065	55	130	1,153	11	262	2.0	pH2; 18 Hrs; Total
24C	717	60	167	1,041	13	340	2.8	pH2; 18 Hrs; Centrate
24S	--- ⁽⁴⁾	---	---	---	---	---	---	pH2; 18 Hrs; Filtered (0.45 µm)
11T	1,119	58	136	1,212	12	275	2.1	pH1; 0 Min.; Total
11C	924	70	136	1,754	15	366	3.1	pH1; 0 Min.; Centrate
12C	905	70	138	1,761	15	339	3.1	pH1; 30 Min.; Centrate
13C	870	71	136	1,794	15	329	3.2	pH1; 60 Min.; Centrate
14C	774	66	141	610	14	160	2.9	pH1; 18 Hrs.; Centrate
<u>NYS Land Application Metal Limit</u>								
	2,500	200	1,000	1,000	25	1,000	10	
<u>EPA 503 Regulations Metal Limit</u>								
	2,800	420	1,200	1,500	39	300	17	

NOTES:

1. Cake concentrations were calculated from mass balance
2. "T" or Total Samples are without Centrifugation
3. "C" or Centrate Samples are for the Cake after Centrifugation
4. "---" Solids Data not Available

FIGURE 164
CAKE METAL CONCENTRATION AT pH1
 Wards Island; June 16, 1992

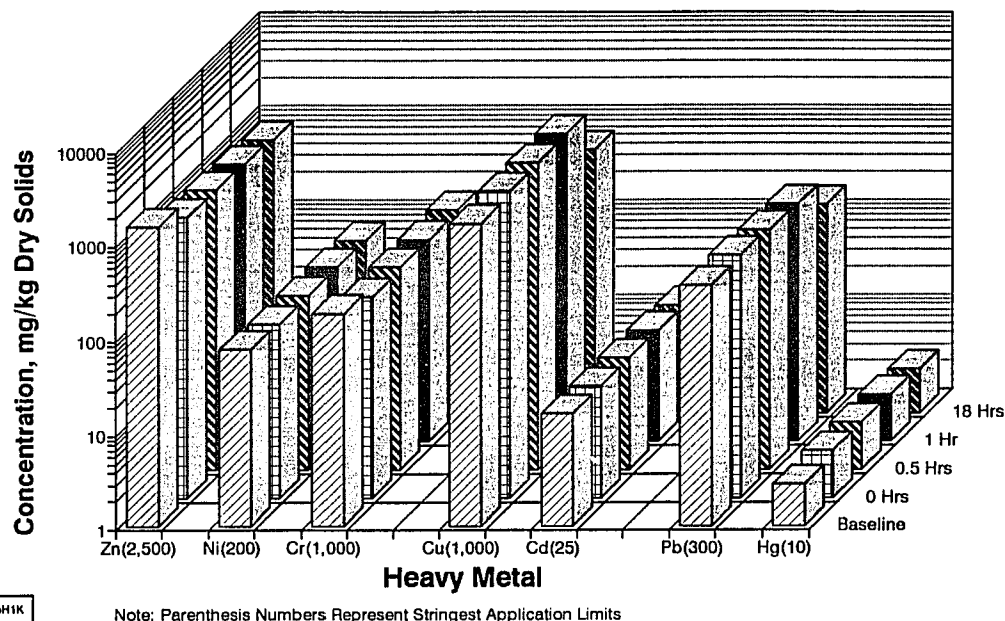


FIGURE 6-165
CAKE METAL CONCENTRATION AT pH2
 Wards Island; June 16, 1992

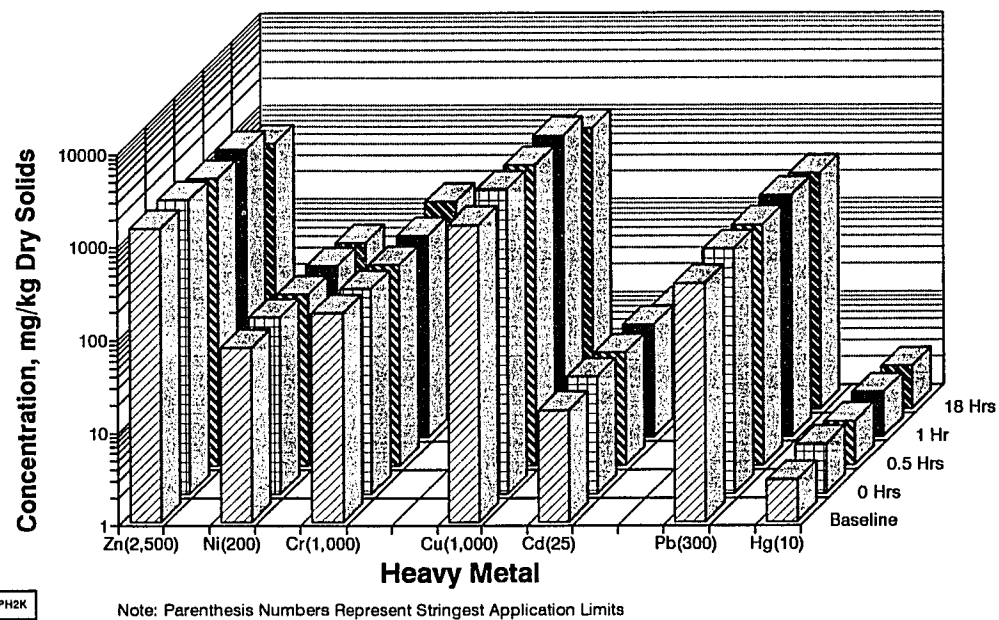
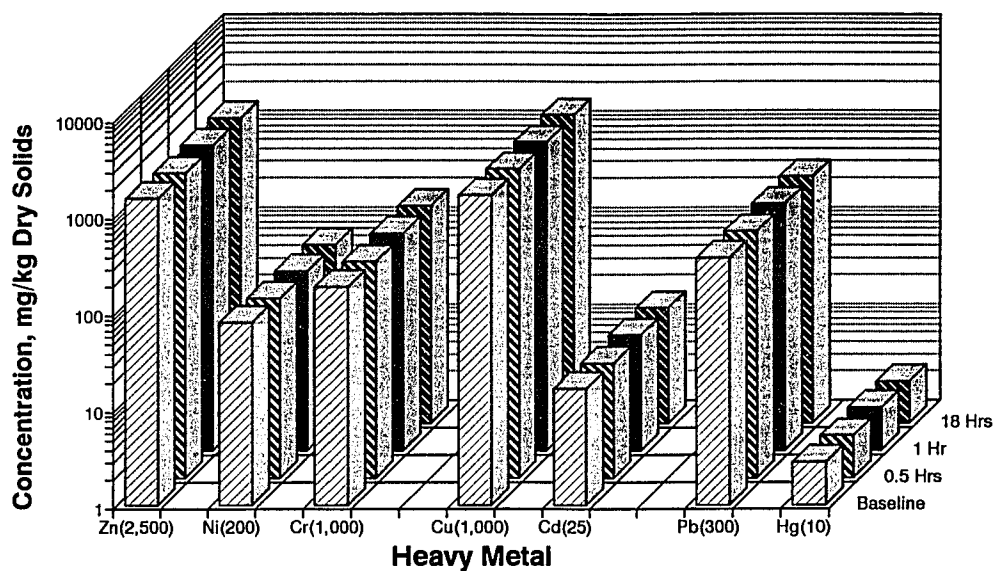


FIGURE 6-166

CAKE METAL CONCENTRATION AT pH4 Wards Island; June 16, 1992



PH&K

Note: Parenthesis Numbers Represent Stringest Application Limits

standards. The reason for this low Cu concentration in the cake is that the 81% Cu solubilization was much more than the 30% solids solubilization. The Cd cake concentration, however, did not change since only 31% Cd was solubilized at pH1 and 18-hours contact time, compared to the 30% solids solubilization.

The untreated Wards Island PDS does not meet the NYS standards due to high Cu concentrations, and it does not meet the EPA standards due to high Pb concentrations. If PDS is acidified to pH1 and at an 18-hours contact time, then the plant will meet the Cu and Pb standards.

To summarize, significant solubilization was obtained at 18-hours contact time at pH1 for all the metals. Metals such as Zn, Ni and Cr solubilized at the minimal contact time at both pH1 and pH2. Acidification at pH4 had no effect on metals solubilization. However, high metal solubilizations do not guarantee lower cake metal concentrations due to solids solubilization.

Because there is a large gap of contact times between 1-hour and 18-hours, and in order to evaluate whether there is any significant solubilization taking place within this range, a new set of experiments was performed on July 29.

July 29, 1992: Wards Island PDS was adjusted to pH1 at contact times of 0, 1, 4, 9, and 17 hours, and to pH2 at contact times of 0, 1, and 4 hours. Table 6-25 presents the results. The cake metals concentration was analyzed for two of the centrifuged samples, the one at

TABLE 6-25

METALS ANALYSIS AT pHu, pH1 AND pH2 AND CONTACT TIMES FROM 0 TO 17 HOURS
WARDS ISLAND; JULY 29, 1992

Sample No.	Metals Concentration, µg/L. ⁽¹⁾									Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg	
1	29,000	1,800	3,000	42,000	400	8,000	190	3.4	38	pH=Unmodified; Total pH=Unmodified; Centrate pH=Unmodified; Filtered (0.45 µm) pH=Unmodified; Cake
2	400	44	50	760	3.3	160	8.4	0.12	1.1	
3	20	85	21	63	0.67	310	6	1.7	0.34	
4	106	5	12	151	2	26	0.72	0.31	0.173	
5	8,000	340	1,300	590	11	340	3.6	0.46	1.6	pH2; 0 Hrs; Centrate pH2; 1 Hr; Centrate pH2; 4 Hrs; Centrate pH2; 9 Hrs; Centrate pH2; 17 Hrs; Total pH2; 17 Hrs; Centrate pH2; 17 Hrs; Filtered (0.45 µm)
6	11,000	390	1,400	680	21	120	5.2	0.5	1.8	
7	16,000	490	1,300	730	44	2,500	3.8	1.1	0.96	
8	20,000	520	1,200	1,400	95	3,900	4.4	3.2	1.2	
9	28,000	1,500	3,000	42,000	320	6,800	190	95	32	
10	26,000	650	1,900	41,000	120	6,500	13.2	0.18	9.4	
11	23,000	940	1,700	36,000	120	6,200	4.4	1.2	1.2	
12	18,000	400	1,800	1,100	56	1,000	6.7	0.8	1.2	pH1; 0 Hrs; Centrate pH1; 1 Hr; Centrate pH1; 4 Hrs; Centrate pH1; 9 Hrs; Centrate pH1; 17 Hrs; Total pH1; 17 Hrs; Centrate pH1; 17 Hrs; Filtered (0.45 µm) pH1; 17 Hrs; Readjust Centrate's pH to 7.5 & Centr. pH1; 17 Hrs; Cake from Sample #17
13	22,000	500	1,900	1,400	74	2,400	7.8	0.67	1.8	
14	21,000	410	1,600	900	81	3,800	6.2	0.08	1	
15	23,000	550	1,800	19,000	110	6,600	8.4	0.14	3	
16	26,000	1,200	2,500	41,000	340	7,600	140	0.24	47	
17	24,000	580	1,900	37,000	110	6,900	10.2	0.13	6.6	
18	25,000	1,000	1,800	36,000	120	6,800	4.6	1.2	0.69	
19	260	260	16	1,800	1	44	1.7	22	0.44	
20	38	7.8	10	61	2.6	21	1.4	0.273	0.3	
Average Total ⁽²⁾	27,667	1,500	2,833	41,667	353	7,467	173	33	39	

NOTES:

1. Metals in Cake are in mg/kg wet solids.
2. Average of total metal concentrations.

unmodified pH, and the other at pH1 and 17-hours contact time. In addition, one set of experiments was performed to evaluate the removal of the dissolved metals from the centrate of the pH1 and 17-hours contact time sample. The centrate's pH was readjusted from pH1 to pH7.5 (original pH of non-treated PDS) by adding 12.6N NaOH. The sample was centrifuged again to separate the precipitated metals and the centrate was analyzed for metals. The final pH of 7.5 was chosen because the centrate would require further biological treatment after the metals are precipitated.

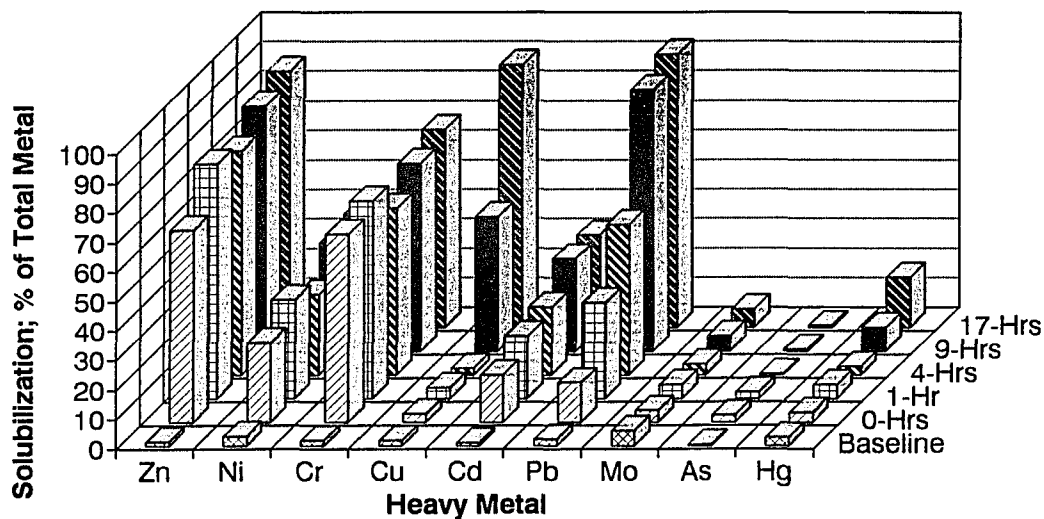
Metal solubilization results are presented on Figures 6-167 and 6-168 for pH1 and pH2, respectively. Similar to the June 16 experiment, some metals (Zn and Cr) were solubilized at minimal contact times and their solubilizations increased over the contact-time range for both pH1 and pH2. One of the concerned metals, Cd, reached a maximum solubilization of 34% at pH1 and 17-hours contact time, which was a small improvement over the solubilization at the 9-hour contact time. The second metal of concern, Cu, solubilized very little (2.2%) up to the 4-hours contact time and pH1; the Cu solubilization jumped to 46% at the 9-hours contact time at pH1 and to 89% at the 17-hours contact time at pH1. The third metal of concern, Pb, showed very little solubilization at pH2 for 0-hours and 1-hour contact times; at 4-hours the solubilization increased to 36% and at 9-hours to 52%. At pH1, Pb showed some solubilization at 0-hours (13%) and increased to 88% at 9-hours; from the 9-hours to the 17-hours the Pb solubilization increased slightly to 92%.

Filtrate metal results (samples were filtered through a 0.45 μ m membrane filter) are compared to centrate results (supernatant after filtration) on Figure 6-169 (pH1 at 17-hour

FIGURE 6-167

METAL SOLUBILIZATION AT pH1

Wards Island; July 29, 1992

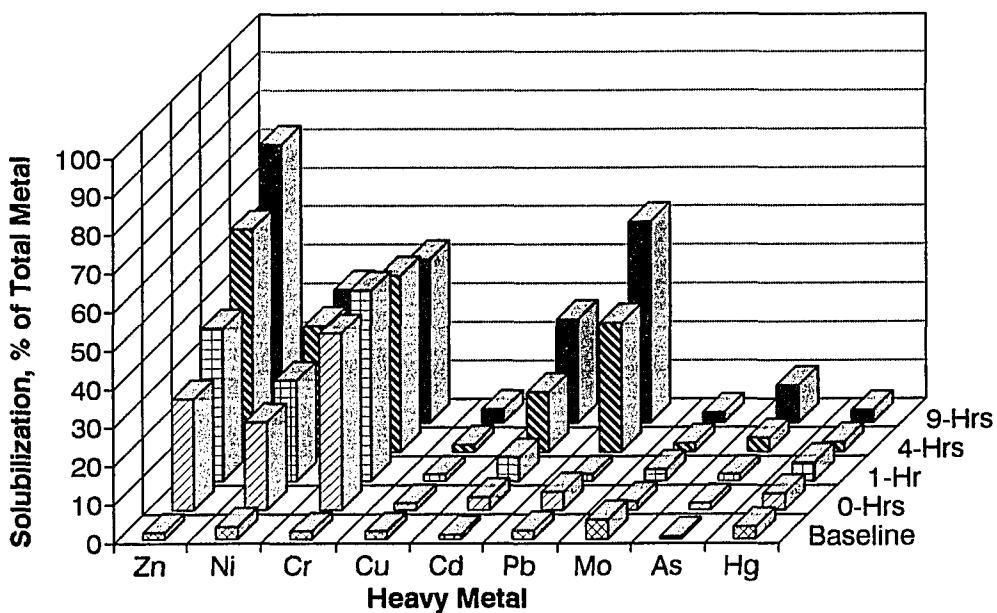


PH1

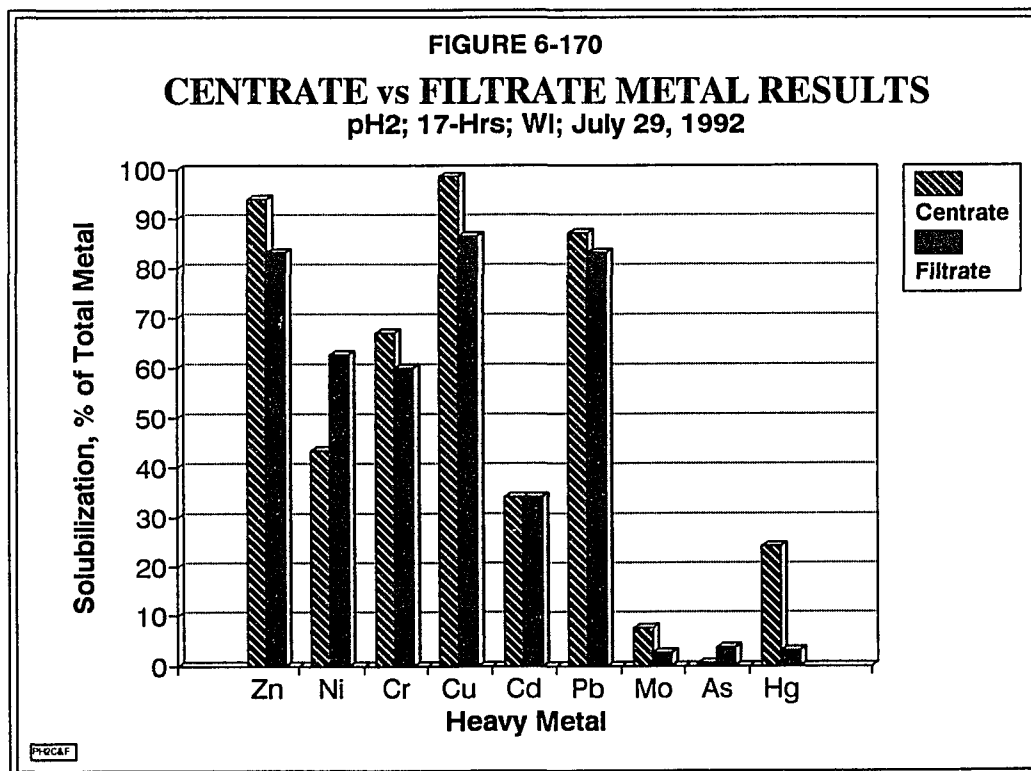
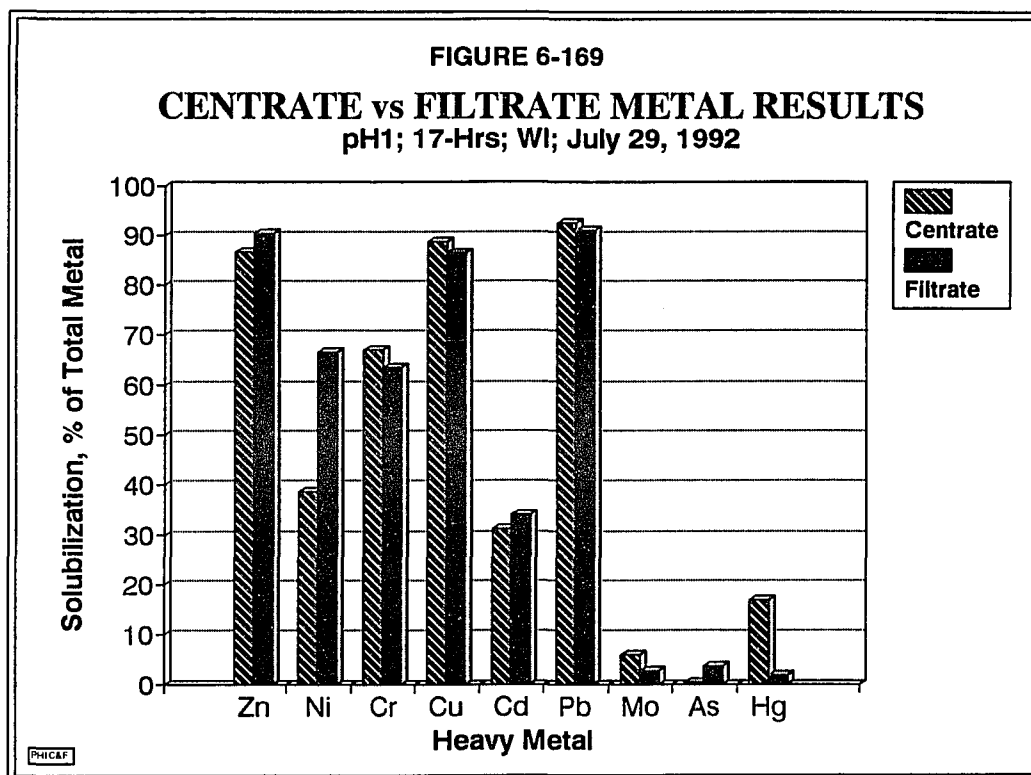
FIGURE 6-168

METAL SOLUBILIZATION AT pH2

Wards Island; July 29, 1992



PH2



contact time) and Figure 6-170 (pH2 at 17-hour contact time). Similar to the June 16, 1992 results, there is no significant difference between the two samples, indicating that centrate metals are in their soluble form. Based on these results and to save time, all subsequent experiments on metal solubilization were done only on centrate samples.

Metals concentrations on the basis of dry solids are compared to the standards in Table 6-26. The results were calculated from Table 6-25 and from solids analyses results. Cake results of PDS acidified to pH1 for 17 hours contact time showed that still Cd was very close to the NYS standard concentration of 25 mg Cd/kg dry solids; the Cd concentration **increased** from 22 mg/kg (non-acidified PDS's cake) to 24 mg/kg. This resulted from higher solids solubilizations than Cd solubilization, 36% solids were solubilized compared to 34% Cd solubilization. Figures 6-171 and 6-172 present the total solids and volatile solids solubilizations, respectively. Most of the solids (TS and VS) solubilized within the first contact hour. Prolonged contact times did not affect solids solubilization.

At pH1 and 17-hour contact time, both Cu and Pb were solubilized at a greater extent than the solids solubilized. Cu solubilized by 89% and Pb solubilized by 92%, compared to the total solids solubilization of 36%. The Cu and Pb cake concentrations were 555 mg/kg and 191 mg/kg dry solids, respectively, which was well below the stringent standards of 1,000 mg Cu/kg and 300 mg Pb/kg dry solids.

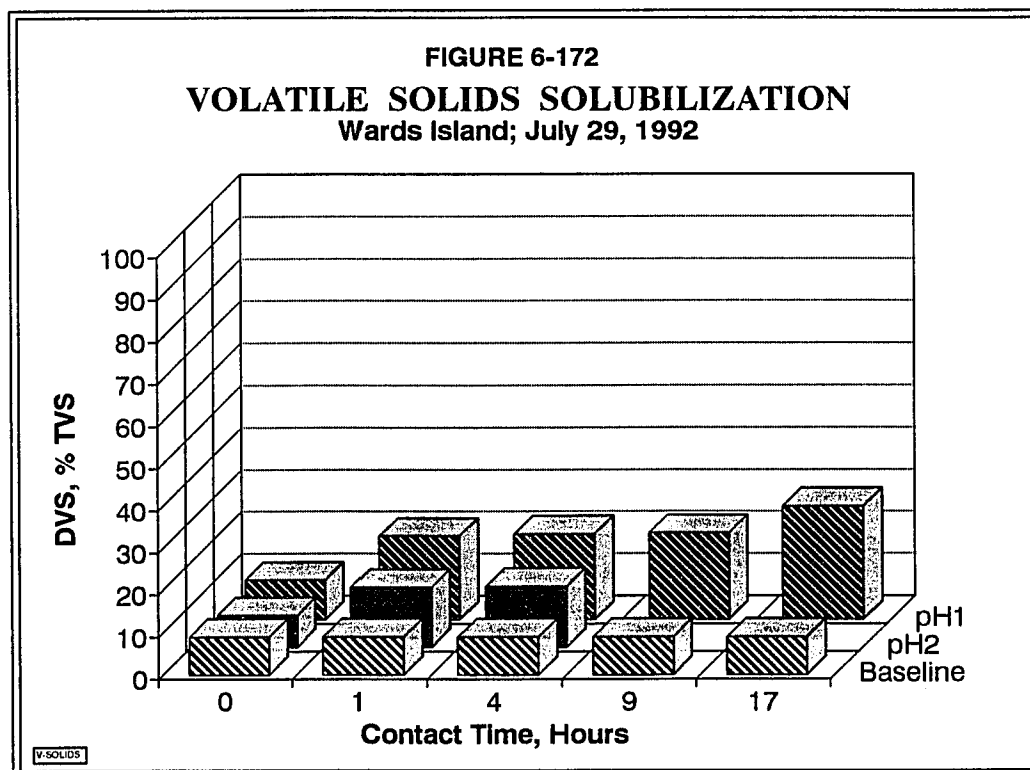
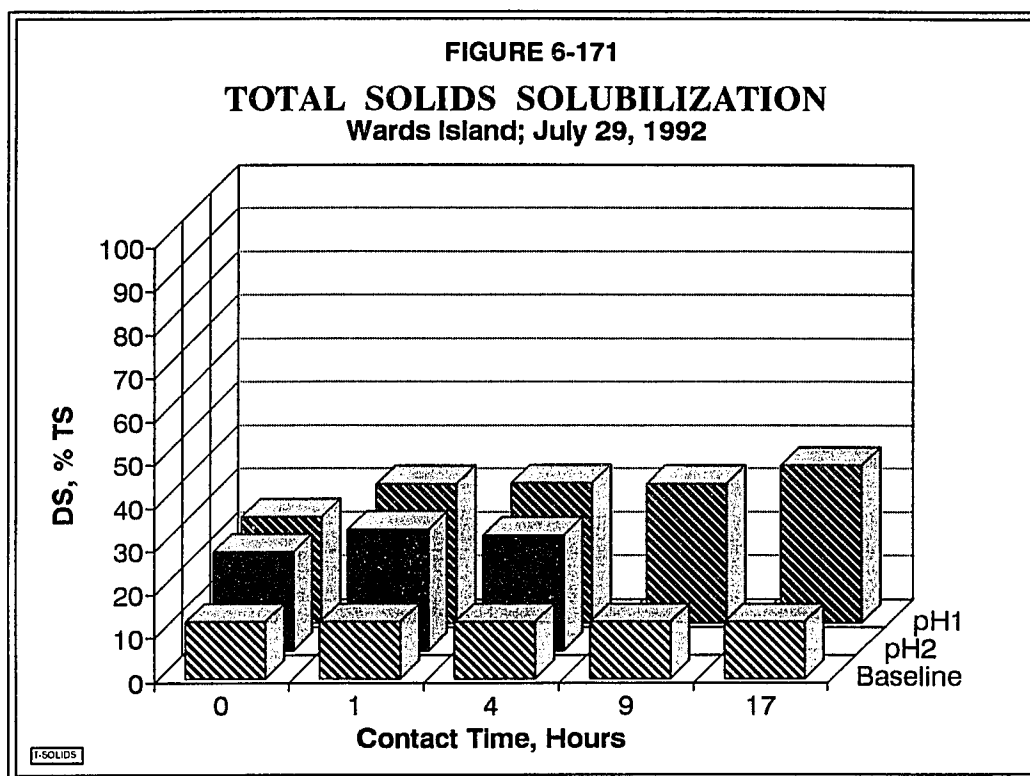
TABLE 6-26

**METALS CONCENTRATION (mg/kg DRY SOLIDS) AT pHu, pH1 AND pH2, AND CONTACT TIMES
FROM 0 TO 17 HOURS, WARDS ISLAND; JULY 29, 1992**

From Sample No	Metals Concentration, mg/kg Dry Solids									Sample Description	
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg		
1	1,224	66	125	1,844	16	330	7.67	1.45	1.73	pH=Unmodified; Total pH=Unmodified; Centrate pH=Unmodified; Filtered (0.45 µm) pH=Unmodified; Cake	
2	138	15	17	262	1	55	2.90	0.04	0.38		
3	--	--	--	--	--	--	--	--	--		
4	991	50	112	1,411	22	243	6.73	2.90	1.62		
5	825	35	134	61	1	35	0.37	0.05	0.16	pH2; 0 Hrs; Centrate pH2; 1 Hr; Centrate pH2; 4 Hrs; Centrate pH2; 9 Hrs; Centrate pH2; 17 Hrs; Total pH2; 17 Hrs; Centrate pH2; 17 Hrs; Filtered (0.45 µm)	
6	1,009	36	128	62	2	11	0.48	0.05	0.17		
7	1,509	46	123	69	5	236	0.36	0.10	0.09		
8	1,754	46	105	123	8	342	0.39	0.28	0.11		
9	1,017	55	104	1,532	13	275	6.37	1.21	1.43		
10	2,031	51	148	3,203	9	508	1.03	0.01	0.73		
11	--	--	--	--	--	--	--	--	--		
12	1,782	40	178	109	6	99	0.66	0.08	0.12	pH1; 0 Hrs; Centrate pH1; 1 Hr; Centrate pH1; 4 Hrs; Centrate pH1; 9 Hrs; Centrate pH1; 17 Hrs; Total pH1; 17 Hrs; Centrate pH1; 17 Hrs; Filtered (0.45 µm) pH1; 17 Hrs; Readjust Centrate's pH to 7.5 & Centr. 17 Hrs; Cake from Sample #17	
13	1,864	42	161	119	6	203	0.66	0.06	0.15		
14	1,765	34	134	76	7	319	0.52	0.01	0.08		
15	1,949	47	153	1,610	9	559	0.71	0.01	0.25		
16	1,017	55	104	1,532	13	275	6.37	1.21	1.43		
17	1,875	45	148	2,891	9	539	0.80	0.01	0.52		
18	--	--	--	--	--	--	--	--	--		
19	19	19	1	131	0	3	0.12	1.61	0.03		
20	346	71	91	555	24	191	12.74	2.48	2.73		
NYS Land Application Regulations Metal Limit											
2,500 200 1,000 1,000 25 1,000 N/A N/A 10											
EPA 503 Regulations Metal Limit											
2,800 420 1,200 1,500 39 300 18 41 17											

NOTES:

1. "---" Solids Data not Available
2. N/A: Not Available



The results from adjusting the centrate's pH and pH1 to pH7.5, recentrifuging and re-analyzing the new centrate for metals, revealed excellent metals removal; the Cu removal was 95%, the Cd removal was 99%, and the Pb removal was also 99%.

To summarize, the experiments conducted on June 16 and July 29 showed that the Wards Island PDS would be able to meet the metal application standards by acidification at pH1 and a contact time of 17-hours. The Cd concentration, however, would be very close to the required standards due to higher solids solubilization than Cd's solubilization.

Both the June and July experiments were conducted at room temperature. The effect on thermal conditioning along with acidification was evaluated in the October 16 experiment.

October 16, 1992: The June and July results showed that pH between 1 and 2 gave the greatest metal solubilizations. Therefore, the effect of thermal conditioning was evaluated at pH1.5, and at unmodified pH; RTC temperature was 220°C and residence time was 10 seconds. The pH1.5 PDS was also kept at 14-hours and 17-hours contact times, but without thermal conditioning. Table 6-27 presents the evaluated conditions and the metal results. The table shows two additional experiments that were performed to evaluate the removal of the dissolved metals from the centrate of the pH1.5 samples. The centrate's pH was readjusted from 1.5 to 7.3 (original pH of non-treated PDS) by adding 12.6N NaOH. The samples were centrifuged again to separate the precipitated metals; the centrate was analyzed again for metals. The readjusted samples were Nos. 10, 11 and 13 (for pH1.5, 17-hours) and Nos. 25, 26, 27, and 12 (for the pH1.5, 220°C).

TABLE 6-27

METALS ANALYSIS AT pHu AND pH1.5, pH CONTACT TIMES 0, 14 AND 17 HOURS,
AND 220°C RTC TEMPERATURE, WARDS ISLAND; OCTOBER 16, 1992

Sample No.	Metals Concentration, µg/L									Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg	
1	20,000	930	2,250	29,000	300	5,500	210	76	27	pH=Unmodified; Total pH=Unmodified; Centrate pH=Unmodified; Cake
2	250	17	26	330	0.7	36	6.1	2.8	0.51	
3	145	7	18	209	0.52	40	0.89	0.49	0.12	
4	13,000	440	1,300	1,100	93	390	10	1.2	0.94	pH1.5; 0 Hrs; Centrate pH1.5; 14 Hrs; Centrate pH1.5; 17 Hrs; Total pH1.5; 17 Hrs; Centrate pH1.5; 17 Hrs; Filtered (0.45 µm) pH1.5; 17 Hrs; Cake of #7
5	19,000	610	1,400	5,800	160	4,700	9.7	2.2	1.2	
6	35,000	1,600	4,100	53,000	400	9,800	180	120	26	
7	19,000	610	1,400	15,000	140	4,700	13	2.1	2	
8	18,000	570	1,200	12,000	140	4,600	3.7	12	0.18	
9	57	3	11	177	0.37	20	1.3	0.44	0.09	
10	30,000	2,900	2,700	18,000	320	7,500	33	52	3	pH7.3; 17 Hrs; Total pH7.3; 17 Hrs; Centrate pH7.2; 17 Hrs; Cake of #11
11	140	260	6	150	3.1	12	1.1	14	0.07	
13	350	7	28	222	1.8	93	0.23	0.18	0.064	
14	31,000	2,200	3,500	45,000	270	8,200	170	92	26	pH=Unmof; Room Temp; Total pH=Unmof; Room Temp; Centrate pH=Unmof; 220; Total pH=Unmof; 220; Centrate pH=Unmof; 220; Filtered (0.45 µm) pH=Unmof; 220; Cake of #17
15	350	22	31	480	1.1	54	8.2	3.5	0.42	
16	15,000	720	1,700	22,000	400	2,900	110	48	22	
17	5,200	190	530	12,000	12	1,100	68	16	0.06	
18	1,000	72	98	2,300	3.1	260	1	22	0.14	
19	355	22	48	457	3	98	1.5	0.59	0.18	
20	13,000	470	1,300	750	99	1,900	10	7.2	0.75	pH1.5; Room Temp.; Centrate pH1.5; 220; Total pH1.5; 220; Centrate pH1.5; 220; Filtered (0.45 µm) pH1.5; 220; Cake of #22
21	15,000	840	2,200	19,000	240	4,300	90	31	18	
22	13,000	510	1,100	7,000	88	2,900	1.2	3.8	4.2	
23	12,000	460	880	230	80	2,600	3.5	1.5	0.5	
24	50	16	48	764	0.21	24	3.8	1.1	0.37	
25	18,000	950	1,600	7,500	260	4,600	68	21	7.50	pH7.3; 220; Total pH7.3; 220; Centrate pH7.3; 220; Cake of #26 pH7.3; 220; Filtered (0.45 µm)
26	99	290	19	19	2.1	6	1.2	2.5	0.17	
27	278	4.4	26	143	0.96	66	0.59	0.37	0.04	
12	77	280	17	35	0.08	6.7	1.00	2.30	0.08	

NOTES:

1. Metals in Cake are in mg/kg wet solids.

Metal solubilizations are presented on Figure 6-173. Similar to the previous tests, the longer the acid contact time the greater the solubilizations. However, the increase from the 14-hour contact time to the 17-hour contact time resulted in marginal solubilization improvement. The metal solubilizations obtained at 220°C and without pH adjustment gave comparable and even better results (Cu, Mo, and As) than the low pH and 17-hour contact time. Thermal conditioning and a low pH further improved the solubilizations.

However, just the metal solubilization results were not sufficient to compare the various conditions. The metal concentrations that remained in the sludge cake after centrifugation are summarized in Table 6-28 and compared on Figure 6-174 (Zn, Cu, Cr, and Pb) and Figure 6-175 (Ni, Cd, Mo, As, and Hg). Again, the Cu cake concentrations did not meet the land application standards, even at pH1.5 and 17-hour contact time. The June and July results showed acceptable Cu and Pb concentrations, but the raw PDS cake concentrations for June were 1,580 mg Cu/kg and 360 mg Pb/kg, and for July were 1,410 mg Cu/kg and 240 mg Pb/kg, compared to the October results of 2,500 mg Cu/kg and 480 mg Pb/kg. These results indicate that metal cake concentrations after pretreatment depend on the initial (untreated) metal concentrations. Rapid thermal conditioning at unmodified pH marginally decreased the Cu concentration, whereas it greatly increased the metal's cake concentration at pH1.5. Other metal cake concentrations decreased greatly at low pH and increased at unmodified pH.

The results from adjusting the centrate's pH from pH1.5 to pH7.3, recentrifuging and re-analyzing the new centrate for metals, revealed excellent metals removal. This was indicated

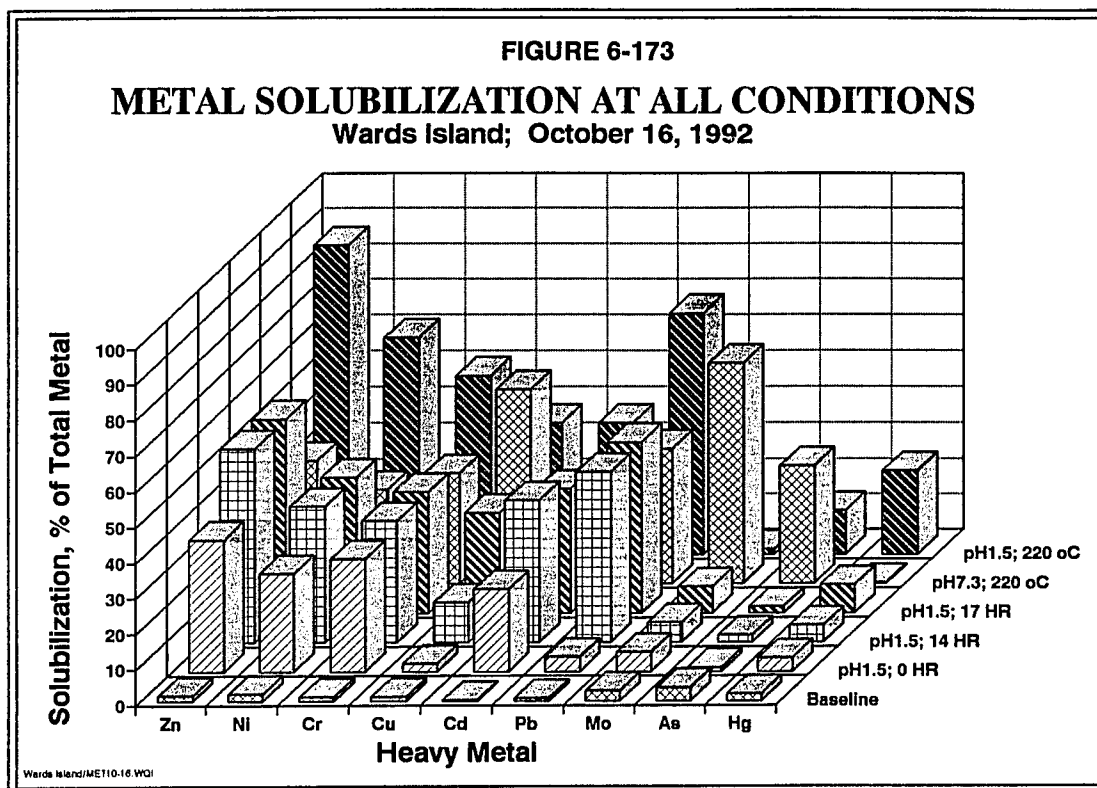


TABLE 6-28

**METALS CONCENTRATION (mg/kg DRY SOLIDS) AT pHu AND pH1.5, pH CONTACT TIMES 0, 14 AND 17 HOURS
AND 220°C RTC TEMPERATURE, WARDS ISLAND; OCTOBER 16, 1992**

Sample No.	Metals Concentration, mg/kg Dry Solids									Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg	
1	1,000	47	113	1,450	15	275	10.5	3.8	1.4	pH=Unmodified; Total
2	89	6	9	118	0.2	13	2.2	1.0	0.2	pH=Unmodified; Centrate
3	1,734	78	215	2,500	6	478	10.6	5.9	1.4	pH=Unmodified; Cake
4	1,066	36	107	90	8	32	0.8	0.1	0.1	pH1.5; 0 Hrs; Centrate
5	1,357	44	100	414	11	336	0.7	0.2	0.1	pH1.5; 14 Hrs; Centrate
6	1,306	60	153	1,978	15	366	6.7	4.5	1.0	pH1.5; 17 Hrs; Total
7	1,570	50	116	1,240	12	388	1.1	0.2	0.2	pH1.5; 17 Hrs; Centrate
8	---	---	---	---	---	---	---	---	---	pH1.5; 17 Hrs; Filtered (0.45 µm)
9	573	26	111	1,779	4	201	13.1	4.4	0.9	pH1.5; 17 Hrs; Cake of #7
10	1,948	188	175	1,169	21	487	2.1	3.4	0.2	pH7.3; 17 Hrs; Total
11	12	22	0.5	13	0.3	1.0	0.1	1.2	0.01	pH7.3; 17 Hrs; Centrate
13	5,983	111	479	3,795	31	1,590	3.9	3.1	1.1	pH7.2; 17 Hrs; Cake of #11
14	1,598	113	180	2,320	14	423	8.8	4.7	1.3	pH=Unmof; Room Temp; Total
15	121	8	11	166	0.38	19	2.8	1.2	0.1	pH=Unmof; Room Temp; Centrate
16	1,316	63	149	1,930	35	254	9.6	4.2	1.9	pH=Unmof; 220; Total
17	732	27	75	1,690	1.7	155	9.6	2.3	0.0	pH=Unmof; 220; Centrate
18	---	---	---	---	---	---	---	---	---	pH=Unmof; 220; Filtered (0.45 µm)
19	1,760	109	238	2,266	15	486	7.4	2.9	0.9	pH=Unmof; 220; Cake of #17
20	1,313	47	131	76	10	192	1.0	0.7	0.1	pH1.5; Room Temp.; Centrate
21	955	54	140	1,210	15	274	5.7	2.0	1.1	pH1.5; 220; Total
22	1,193	47	101	642	8	266	0.1	0.3	0.4	pH1.5; 220; Centrate
23	---	---	---	---	---	---	---	---	---	pH1.5; 220; Filtered (0.45 µm)
24	228	73	218	3,477	1.0	109	17.3	5.0	1.7	pH1.5; 220; Cake of #22
25	1,475	78	131	615	21	377	5.6	1.7	0.6	pH7.3; 220; Total
26	11	33	2.2	2.2	0.24	0.7	0.1	0.3	0.02	pH7.3; 220; Centrate
27	3,977	63	372	2,046	14	944	8.4	5.3	0.6	pH7.3; 220; Cake of #26
12	---	---	---	---	---	---	---	---	---	pH7.3; 220; Filtered (0.45 µm)
NYS Land Application Metal Limit										
	2,500	200	1,000	1,000	25	1,000	N/A	N/A	10	
EPA 503 Regulations Metal Limit										
	2,800	420	1,200	1,500	39	300	18	41	17	

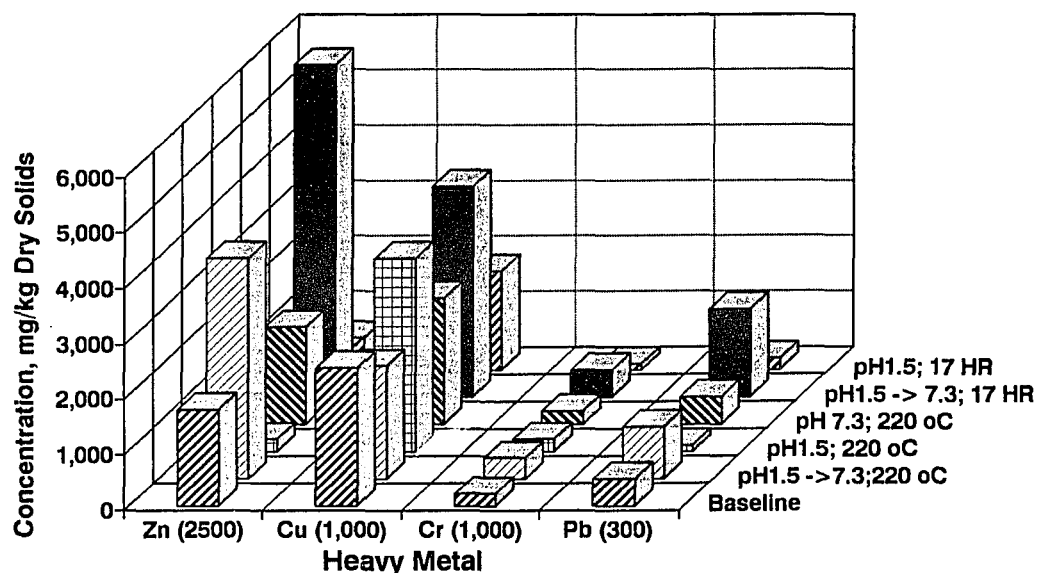
NOTE:

1. Solids Data not Available
2. N/A: Not Available

FIGURE 6-174

CAKE METAL CONCENTRATION-ALL CONDITIONS

Zn, Cu, Cr, Pb; WI; Oct. 26, 1992

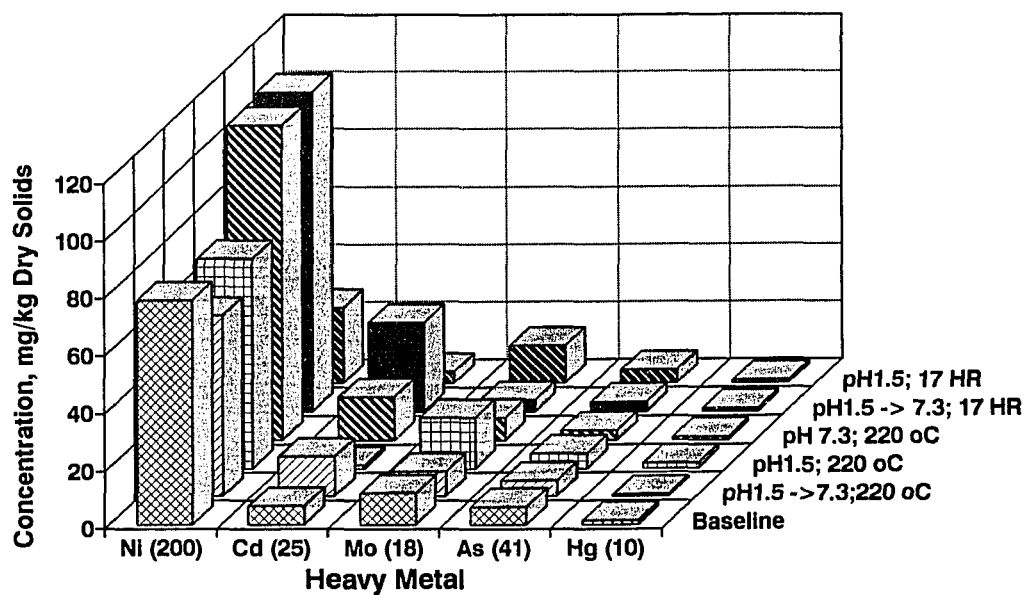


Wards Island/MET10-16.WQ

FIGURE 6-175

CAKE METAL CONCENTRATION-ALL CONDITIONS

Ni, Cd, Mo, As, Hg; WI; October 16, 1992



Wards Island/MET10-16.WQ

by the large increase of metal concentration on the cake and the decrease of metal concentration in the centrate (see Table 6-27).

The October results indicated that neither the low pH nor the pH with or without RTC conditions can decrease metal cake concentrations to acceptable values. The reason, as explained earlier, is because both acidic and thermal conditions solubilize metals and suspended solids. Since the low pH with and without thermal conditioning failed because of high solids solubilization, the next experiment tested metal solubilization at alkaline conditions. This was done to evaluate metals amphoteric properties, where some metals can be solubilized at both ends of the pH scale.

February 18, 1993: When rapid thermal conditioning was performed at high pH, it was found that solids solubilization increased (see Section 6.1). Therefore, metals associated with the solids should also be solubilized. In addition, metals are known to have amphoteric properties, i.e., high solubilities at low and high pH. For these reasons, even though metal removals from sludge at high pH was not found in the literature review, we evaluated metal removals at pH11 with thermal conditioning at 220°C. Table 6-29 presents the tested conditions and the metal concentration results.

Metal solubilization results, presented on Figure 6-176, show high solubilizations at unmodified pH and 220°C, low solubilizations at pH11 and without thermal conditioning, and the highest solubilizations at pH11 and 220°C for all metals. However, the metal cake

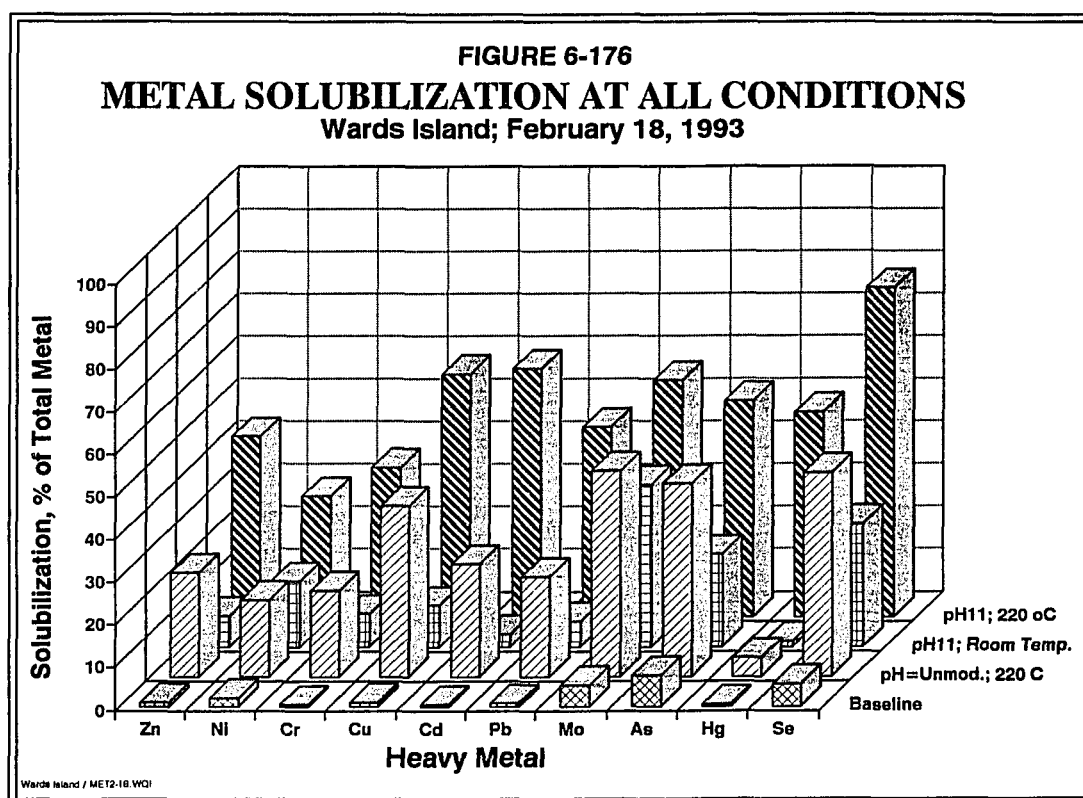
TABLE 6-29

METALS ANALYSIS AT pHu AND pH11, AND 220°C RTC TEMPERATURE
WARDS ISLAND; FEBRUARY 18, 1993

Sample No.	Metal Concentration, mg/L											Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg	Se	Mg	
1-T	20	1	2.4	21	0.19	4.8	0.14	0.091	0.038	0.07	228	pH=Unmodified; Total
1-C	0.18	0.019	0.0093	0.17	0.0009	0.032	0.0069	0.0065	0.00015	0.0035	26	pH=Unmodified; Centrate
1-K	1,198	57	133	1,142	9.6	274	8.5	4.3	0.32	3.5	9,591	pH=Unmodified; Cake
4-T	14	0.96	2	14	0.072	3.3	0.11	0.062	0.023	0.044	136	pH=Unmodified; 220°C; 10 sec; Total
4-C	3.4	0.17	0.4	5.6	0.019	0.77	0.053	0.028	0.001	0.021	23	pH=Unmodified; 220°C; 10 sec; Centrate
4-K	1,852	119	277	1,332	14	427	14	3.3	1.2	3.3	14,481	pH=Unmodified; 220°C; 10 sec; Cake
5-T	21	1.1	2.5	21	0.15	4.8	0.15	0.097	0.037	0.066	219	pH=11; Room Temp; Total
5-C	1.5	0.17	0.19	2	0.0042	0.28	0.057	0.021	0.00043	0.019	8.1	pH=11; Room Temp; Centrate
5-K	1,264	55	149	1,208	9.6	282	6.4	4	0.32	3.6	10,755	pH=11; Room Temp; Cake
7-T	13	0.88	1.8	13	0.06	2.7	0.13	0.061	0.019	0.048	133	pH=11; 220°C; 10 sec; Total
7-C	5.5	0.25	0.63	7.4	0.035	1.2	0.072	0.031	0.0091	0.037	18	pH=11; 220°C; 10 sec; Centrate
7-K	1,560	146	284	914	13	406	13	2.8	0.79	1.9	19,984	pH=11; 220°C; 10 sec; Cake
<u>NYS Land Application Regulations Metal Limit</u>												
	2,500	200	1,000	1,000	25	1,000	N/A	N/A	10	N/A	N/A	
<u>EPA 503 Regulations Metal Limit</u>												
	2,800	420	1,200	1,500	39	300	18	41	17	36	N/A	

NOTES:

1. Metals in cake and in regulations are in mg/kg dry solids
2. N/A: Not Available



concentrations, shown on Figure 6-177 and Figure 6-178, increased for most of the metals, again because of the high solids solubilization.

6.2.2 Newtown Creek Results

February 11, 1993: Newtown Creek contains the highest metal concentrations among all the other plants because it treats a large proportion of industrial wastewater. Some of the thermal conditions evaluated for Wards Island (RTC at 220°C) were also evaluated for Newtown Creek. An additional test was also performed to evaluate the effect of the 30-second RTC on metal solubilization. RTC of PDS was performed at unmodified pH and 220°C (10 seconds and 30 seconds), and at pH1.5 and 165°C (10 seconds and 30 seconds). Table 6-30 presents the evaluated conditions and the metal concentration results.

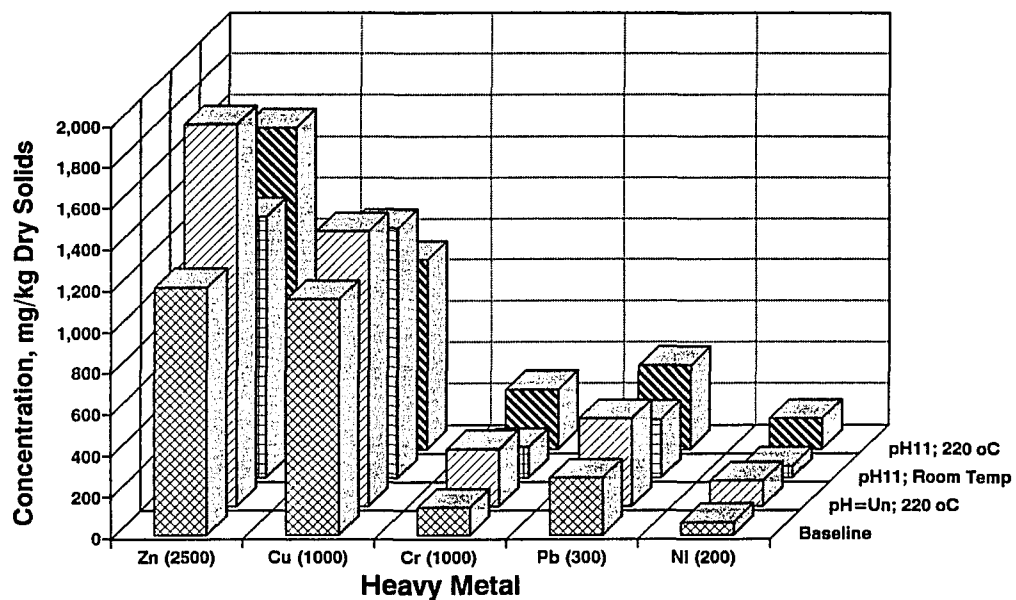
Metal solubilizations for the pH-unmodified and pH1.5 conditions are presented on Figures 6-179 and 6-180, respectively. Similar to Wards Island results, metals are solubilized at 220°C without pH adjustment, but some of them, such as Ni, Cd, and Pb, solubilize more at the lower pH. Cu, Mo, As, and Hg, however, were solubilized less at the lower pH. The longer 30-second RTC conditions showed no improvement on metal solubilizations at both unmodified pH and pH1.5.

The metal cake concentrations, presented on Figures 6-181 and 6-182, illustrate the same results as obtained from Wards Island; some metals concentration, such as Se and Mo,

FIGURE 6-177

CAKE METAL CONCENTRATION-ALL CONDITIONS

Zn, Cu, Pb, Cr, Ni; WI; Febr. 18, 1993

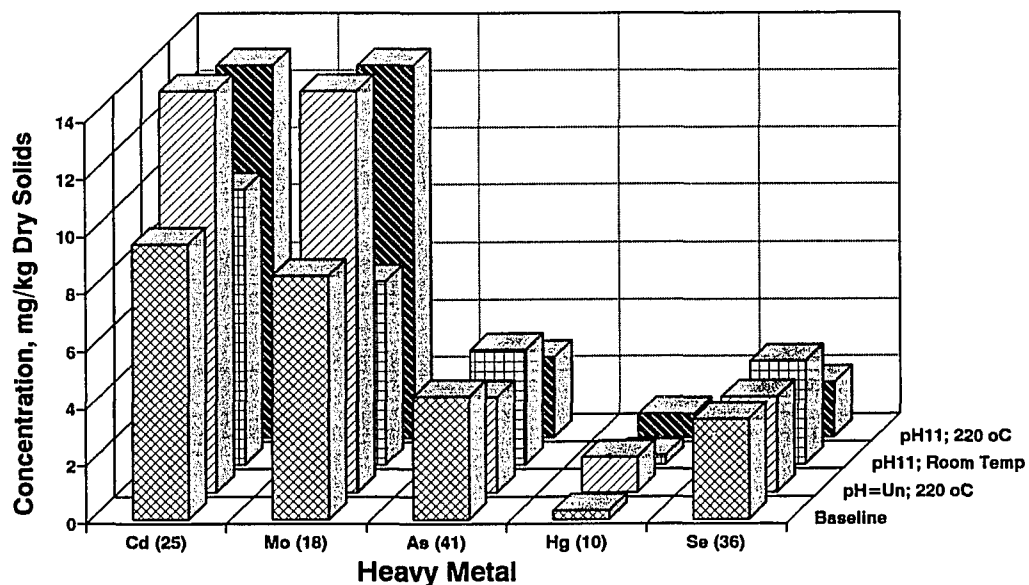


Wards Island/MET2-18 WQI

FIGURE 6-178

CAKE METAL CONCENTRATION-ALL CONDITIONS

Cd, Mo, As, Hg, Se; WI; Febr. 18, 1993



Wards Island/MET2-18 WQI

TABLE 6-30

METALS ANALYSIS AT pH_u AND pH1.5, AND RTC AT 10 AND 30 SEC. AND 165°C AND 220°C
NEWTOWN CREEK; FEBRUARY 11, 1993

Sample No.	Metals Concentration, mg/L											Sample Description
	Zn	Ni	Cr	Cu	Cd	Pb	Mo	As	Hg	Se	Mg	
1	40	3.5	10	40	0.32	7.3	0.51	0.1	0.13	0.1	150	pH=Unmodified; Total pH=Unmodified; Centrate pH=Unmodified; Cake
2	0.64	0.16	0.29	0.89	0.0064	0.055	0.047	0.0063	0.00031	0.027	5.6	
3	1,830	153	472	1,789	17	348	22	2.10	0.52	27	4,510	
4	26	2.6	7.2	27	0.26	4.9	0.38	0.082	0.047	0.068	84	pH=Unmod 220°C; 10 sec; Total pH=Unmod; 220°C; 10 sec; Centrate pH=Unmod; 220°C; 10 sec; Cake pH=Unmod; 220°C; 30 sec; Centrate pH=Unmod; 220°C; 30 sec; Cake
5	8.8	0.66	1.9	13	0.093	1.3	0.22	0.027	0.011	0.021	10	
6	1,716	192	530	1,214	16	413	12	2.7	1.7	2.6	9,396	
7	8.5	0.72	1.9	13	0.086	1.2	0.23	0.0037	0.0011	0.033	11	
8	2,291	216	660	1,627	21	486	9.5	2.5	3.3	2.3	10,349	
9	38	3.4	11	36	0.27	6.1	0.43	0.1	0.083	0.094	134	pH=1.5; Room Temp; Total pH=1.5; Room Temp; Centrate pH=1.5; Room Temp; Cake pH=1.5; 165°C; 10 sec; Total pH=1.5; 165°C; 10 sec; Centrate pH=1.5; 165°C; 10 sec; Cake pH=1.5; 165°C; 30 sec; Centrate pH=1.5; 165°C; 30 sec; Cake
10	19	2.1	4.7	1.6	0.2	4.4	0.018	0.018	0.00034	0.016	73	
11	860	52	270	1,790	6.3	142	19	3.3	0.87	2.7	1,690	
12	30	2.8	8.8	29	0.27	5.2	0.28	0.088	0.063	0.072	108	
13	23	2	3.6	0.54	0.23	4.4	0.017	0.013	0.00016	0.011	64	
14	290	50	372	2,293	3	66	23	4	1.3	2.6	1,541	
15	22	1.9	3.4	0.52	0.21	4.2	0.019	0.0057	0.00025	0.013	63	
16	210	50	402	2,571	2.3	68	24	4.6	1.8	4.2	1,603	
NYS Land Application Regulations Metal Limit												
	2,500	200	1,000	1,000	25	1,000	N/A	N/A	10	N/A	N/A	
EPA 503 Regulations Metal Limit												
	2,800	420	1,200	1,500	39	300	18	41	17	36	N/A	

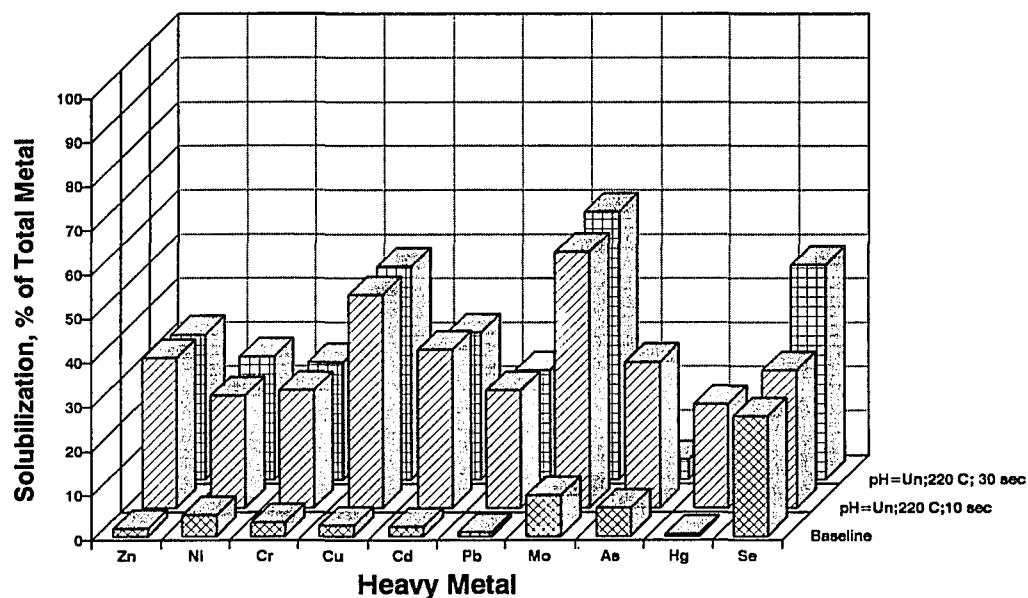
NOTES:

1. Metals in cake and in regulations are in mg/kg dry solids
2. N/A: Not Available

FIGURE 6-179

METAL SOLUBILIZATION - NEWTOWN CREEK

pH=Unmodified; 220 oC; 10&30 sec

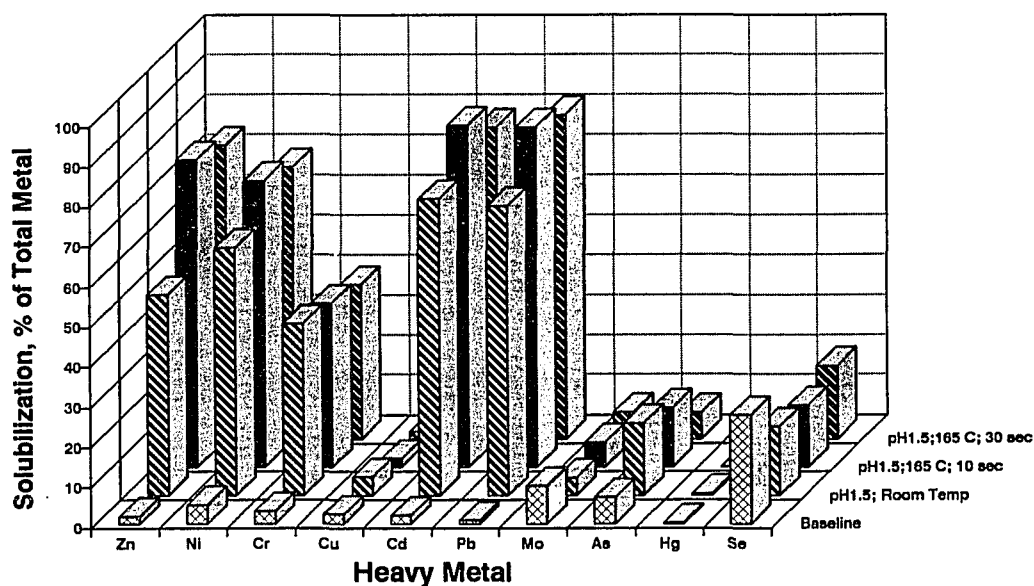


Newtown Creek / MET2-11.WQI

FIGURE 6-180

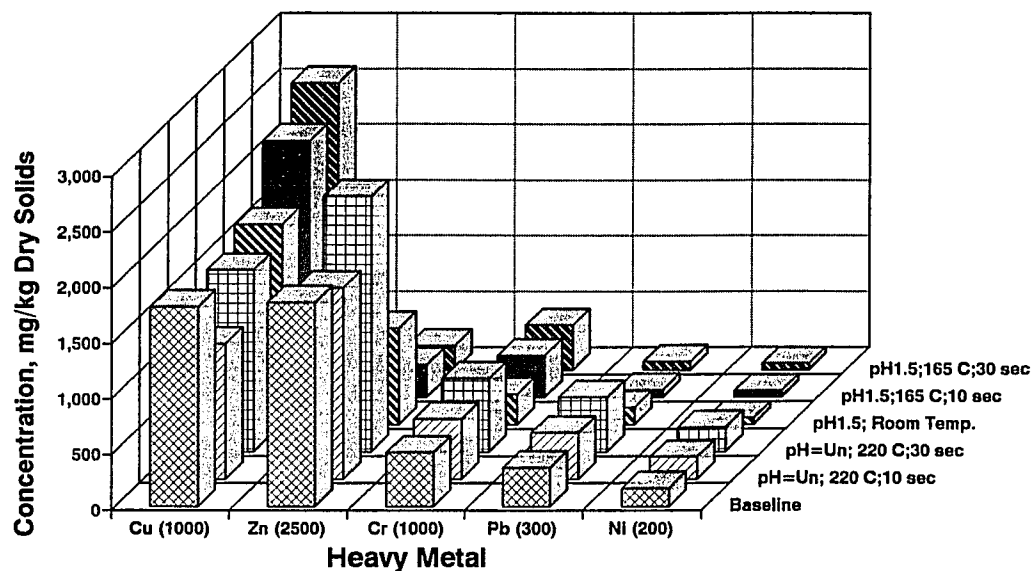
METAL SOLUBILIZATION - NEWTOWN CREEK

pH1.5; Room & 220 oC; 10 & 30 sec



Newtown Creek / MET2-11.WQI

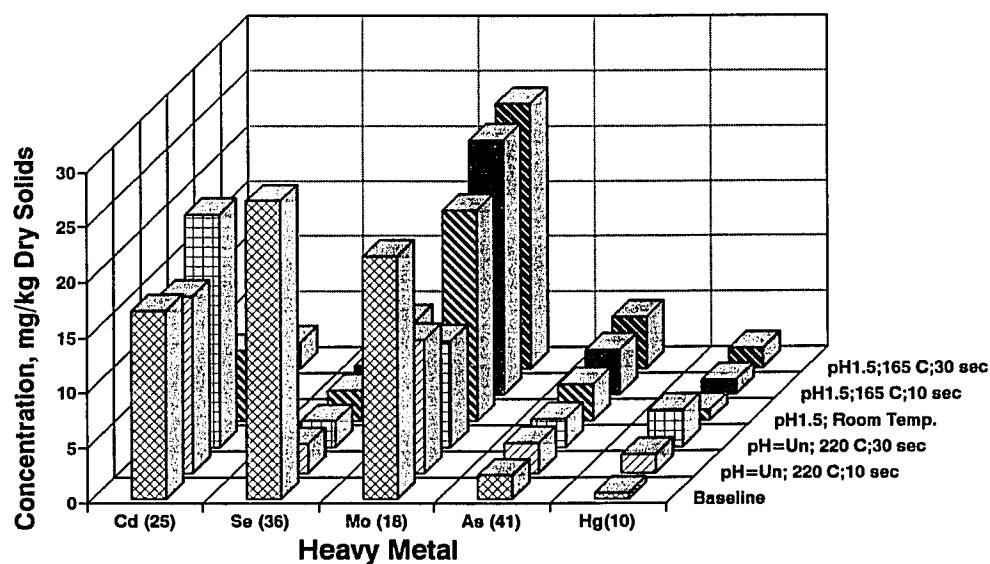
FIGURE 6-181
CAKE METAL CONCENTRATION - NEWTOWN CR.
 All Conditions for Cu, Zn, Cr, Pb, Ni



Note: Parenthesis Numbers Represent Stringest Application Limit

Newtown Creek / MET2-11.WQI

FIGURE 6-182
CAKE METAL CONCENTRATION - NEWTOWN CR.
 All Conditions for Cd, Se, Mo, As, Hg



Note: Parenthesis Numbers Represent Stringest Application Limits

Newtown Creek / MET2-11.WQI

decreased at pHu and 220°C but most of the metals concentration increased. At pH1.5 and 165°C, Zn, Cd, Pb, and Se decreased, but Cu and Mo increased. Similar to solubilization results, the longer RTC time of 30 seconds gave similar results as the 10 seconds time.

6.2.3 Summary

To summarize, the Newtown Creek results were comparable to the Wards Island results, where low pH with and without thermal conditioning did not decrease the metal cake concentration significantly to improve compliance with promulgated regulations. Some of the metals were removed at one pretreatment condition and some were removed at other conditions. A single pretreatment condition was not equally effective for all metals. Therefore, the pretreatment required for metal removal depends on the type of metal present in sludge and which metal controls the overall process. Longer RTC times gave similar results to shorter RTC times.

Even though some of the results were not very promising, an important observation was made. Solubilization by itself does not ensure that metals will be removed from sludge. This is contrary to literature results, which implied that once metals are solubilized they are removed and, therefore, a cleaner cake is produced. Metal concentrations in sludge cake will be reduced only when their solubilization rates exceed the solubilization rates of the solids. A side benefit is that the solubilization of solids will greatly decrease the sludge cake volume decreasing sludge disposal cost.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Summary

The primary objective of the research effort was to evaluate the effect of Rapid Thermal Conditioning (RTC) on sludge biodegradability and metal solubilization. RTC is an innovative process that enhances the anaerobic digestion of municipal sludge producing additional methane gas, and reducing the mass and volume of sludge for disposal. When RTC is combined with pH adjustment, it solubilizes some heavy metals from the sludge. The remaining solids may be more amenable to use as a safe soil conditioner after metals are removed, .

The study was conducted at The City College of New York over a two year period. Thermal conditioning of sludge was done in a continuous flow rapid thermal conditioning reactor (RTCR) by mixing the sludge with steam at different ratios. Operating temperatures were varied between 25°C and 220°C, and hydraulic retention times were varied between 10 and 180 seconds.

Most of the experiments were done on anaerobically digested sludge, referred to in this study as partially digested sludge (PDS). RTC was also applied to primary sludge (PS) and to waste activated sludge (WAS) to explore additional applications of the technology. The sludge used in most of the experimental runs was collected from the digesters of the

Wards Island WPCP which treats primarily domestic wastewater. Selected operating conditions were retested on sludge from the Newtown Creek and Rockaway Beach plants. Newtown Creek treats a significant portion of industrial wastewater while Rockaway is the only NYC plant that provides mesophilic/thermophilic anaerobic digestion.

Sludge was subjected to several thermal conditioning alternatives that included RTC with and without pH adjustment, long RTC retention times, thickened PDS, and pressure cycling. Biodegradation of sludge was evaluated in batch reactors, and the optimum condition was confirmed in CFSTR and anaerobic filter continuous flow reactors. The improvement in biodegradation was determined by establishing a baseline using the gas production from unconditioned sludge. Gas production from the conditioned sludge was compared to the baseline to calculate the percent improvement.

Gas production from the batch reactors was evaluated using a two-term exponential equation (Eq. 6-1), from which the Gas Production Improvement (GPI) was calculated (Eq. 6-2). The CFSTR biodegradation was expressed as Biochemical Methane Production, based on applied COD (Eq. 6-14) and applied TVS (Eq. 6-15). COD and TVS removal rates were calculated for the anaerobic filter.

Metals solubilization tests were done on PDS from the Wards Island and Newtown Creek plants. PDS was subjected to low and high pH conditions with and without thermal conditioning. Metal solubilization and metal concentrations in the cake from unconditioned PDS were used as the baselines to compare the results from the conditioned PDS tests.

An evaluation of the costs to implement RTC in new or existing WPCPs was not included in this study design. A full evaluation of these costs was done by my fellow doctoral student Jianhong Zheng, Chemical Engineering Department, CCNY.

7.2 Conclusions

7.2.1 Biodegradability of Municipal Sludge

This study evaluated the biodegradability of partially digested sludge, waste activated sludge, and primary sludge.

7.2.1.1 Partially Digested Sludge (PDS)

(a) Batch Reactors

Series 1 - Unmodified pH

1. The RTC process improved the biodegradation kinetics and ultimate biodegradability of Wards Island PDS resulting in additional methane production. Maximum improvements were achieved at an RTC temperature of 220°C, which improved ultimate biodegradation by 50% (Figure 6-11).
2. The apparent improvement in biodegradation is related to the solubilization of particulate COD. At unmodified pH, 220°C, and 10 sec, the COD solubilization

(% of total COD) increased from 3.4% (25°C) to 13% (220°C) and the volatile solids (VS) solubilization (% of total VS) increased from 8.1% (25°C) to 60% (220°C), as shown on Figures 6-12 and 6-13, respectively. There was no change in fixed suspended solids and fixed dissolved solids.

3. Because of the high solids solubilization, RTC has the additional benefit of reducing the volume of solids in the sludge that ultimately must be disposed of. Particulate solids decreased by more than 35% (Figure 6-14), resulting in the same sludge volume decrease.
4. Newtown Creek and Rockaway Beach PDS showed similar improvements in ultimate biodegradabilities as the Wards Island samples.

Series 2 - Modified pH

1. Improved sludge biodegradability can also be realized by pH adjustment to either highly acidic or alkaline conditions. When pH adjustment is combined with RTC, the same improvement in biodegradability can be realized at a lower temperature (Figure 6-47). For example, the improvement in gas production from Wards Island PDS at 100°C and a pH of 4 was the same as the pH-unmodified PDS at 220°C (Figure 6-18). When the pH was reduced to two without the RTC, the increased methane production was comparable to pH-unmodified with thermal conditioning at 160°C (Figure 6-22). Adjusting the pH to 12 had the same effect. However, the cost of chemicals and chemical handling could make RTC alone (without pH adjustment) the most feasible way to enhance sludge biodegradability.

2. Adjusting the pH of Newtown PDS resulted in a greater improvement than it did with the Wards Island PDS, where ultimate biodegradabilities at pH6 and pH2 (220°C) improved by 90% and 140%, respectively. When pH adjustment was combined with RTC, equivalent improved biodegradability was realized at a lower temperature compared to RTC without pH adjustment. Rockaway Beach results at 220°C and pH2 were comparable to the Newtown Creek results.

Series 3 - Pressure Effect

1. Subjecting the Wards Island PDS to high pressures (200-600 psi) at room temperature (25°C) did not improve biodegradability (Figure 6-60). Sludge viability remained the same, indicating that bacteria were not lysed during the process. Improved biodegradability results from high temperatures, not a pressure differential.

Series 4 - RTC Hydraulic Retention Time

1. Improved ultimate biodegradation increased with increasing RTC times up to 60 sec. The improvement was 40%, 70%, and 100% at 10 sec, 30 sec, and 60 sec, respectively (Figures 6-67 and 6-68). Operating the RTC at HRT longer than one minute did not improve biodegradation further.
2. Longer RTC times did not generate inhibitors to anaerobic digestion. Preheating the PDS before RTC (for energy conservation) for less than three minutes would not affect biodegradability. Preheating the influent PDS with effluent PDS, by a

heat exchanger, would decrease steam consumption making the RTC process more energy efficient.

Series 5 - Thickened PDS

1. Thickened PDS conditioning gave results similar to the unthickened PDS, where both kinetics and biodegradability increased with thermal conditioning temperatures. Ultimate biodegradabilities improved by 20% at 220°C with unmodified pH (Figure 6-77) and by 60% at 220°C with pH2 (Figure 6-78).
2. Thickening the PDS will drastically decrease steam consumption, resulting in an energy efficient process. Every doubling of the solids concentration will reduce steam consumption by half. Although it was very difficult to gravity-thicken the PDS beyond the 5% TS, mechanical thickening should increase the TS to over 10%, cutting steam consumption by a factor of five.

(b) Continuous Flow Reactors

1. The RTC biodegradation results (220°C, 10 sec) were confirmed in continuous-flow anaerobic reactors. The RTC sludge can be readily anaerobically digested in a completely mixed suspended growth reactor and in an anaerobic filter appropriately designed to handle the remaining sludge solids. Biodegradability improved by more than 200% at a 15-d HRT using the CFSTR. The same biodegradability as the unconditioned PDS at a 15-d HRT was obtained at a 3-d HRT. Using an anaerobic filter, 60% of COD was removed at a 2-d HRT.

7.2.1.2 Waste Activated Sludge (WAS)

1. The improvement in WAS biodegradability was more pronounced than for PDS. Gas production was improved 80% when WAS was thermally conditioned at 225°C (the 220°C temperature was passed before the RTCR reached steady state), without pH adjustment (pH7.3), and for 10 sec (Figure 6-89). The improvement in biodegradability was the same at the 30 sec HRT.
2. At 220°C, solids and COD solubilization reached 50% and 40%, respectively, which may be due to high RTC temperatures lysing the bacteria.

7.2.1.3 Fermented Primary Sludge (PS)

1. RTC decreased the biodegradability of primary sludge at temperature range of 100°C to 220°C with 10 sec retention time. Biodegradabilities decreased by 15% at 100°C, and by 7% at 220°C (Figure 6-96). Biodegradability remained the same with 30 sec RTC time at 220°C.

7.2.2 Metal Removals

1. RTC of Wards Island PDS (220°C, 10 sec) with and without pH adjustment solubilized the heavy metals and volatile solids in the sludge. At pH-unmodified

(pH7.3) RTC conditions (Figure 6-173), metals solubilization was highest for Cu (50%), Mo (60%), and Pb(35%). The solubilizations of Hg, Cr, Cd, and As were low. Decreasing the pH to 1.5 with RTC, most metals solubilized by more than 40%, with the highest solubilizations obtained for Zn (85%), Pb (65%), and Ni (60%). Cu and Mo were solubilized approximately 35% and 5%, respectively.

2. Alkaline pH (pH11) and without RTC had little effect on metals solubilization (Figure 6-176), with the highest values for Mo (35%), Se (25%), and As (15%). RTC (220°C) with pH11 greatly solubilized metals that were not solubilized at pH1.5. Solubilizations were 75% for Se, 55% for the metals Cu, Cd, and Mo, with the rest of the metals falling in the range of 28% to 50%.

3. The concentration of metals remaining in sludge cake after dewatering depends on solids solubilization. In cases where metals solubilization exceeds solids solubilization and sludge dewatering is practical, heavy metal concentrations in the sludge cake will be lower. When metals are solubilized less than the solids, concentration of metals in the cake will increase. For example, Zn concentration decreased from 1,600 mg/kg dry solids (25°C) to 1,330 mg/kg dry solids at pH7.3 and 220°C, compared to Cr that increased from 180 mg/kg dry solids (25°C) to 240 mg/kg dry solids. The choice of the pretreatment condition on metal solubilization depends on the type of metals present in sludge as well as the sludge type.

7.2.3 Overall Conclusions

1. RTC of PDS and WAS solubilizes volatile suspended solids and improves overall biodegradation. The solubilized solids can undergo further anaerobic digestion to produce additional methane. The remaining solids can be dewatered and the cake will have less volume, greater stability, and relatively no odor potential.
2. The conditioned sludge was not inhibitory to further anaerobic digestion, and RTC did not generate offensive odors which are often inherent in other thermal conditioning processes.

7.3 Recommendations

7.3.1 Research

1. The improvement in solids solubilization and biodegradation increases with increasing RTC temperature. Biodegradation and solubilization should be evaluated at temperatures higher than 220°C, the limit of the research's RTC temperature .
2. The RTC process may destroy pathogens, resulting in pathogen-free sludge, and enhancing sludge disposal options. If pathogens are destroyed, regulations requiring mesophilic digestion at over 95°F (35°C) and HRT greater than 15 days

may not apply. Treatment plants that have difficulty meeting these regulations or plants that must increase their digester capacity due to higher flowrates could use the RTC process. Pathogen destruction should be evaluated either in pilot studies or in full-scale application studies.

3. In nutrient-deficient industrial wastewater treatment plants, nutrient recycling should be evaluated since the RTC of waste activated sludge lyses bacteria and releases nutrients. These nutrients could be recycled back to the plant which would decrease or eliminate the need to add nitrogen and phosphorus.

7.3.2 Wastewater Treatment Plant Applications

1. Recycle thermally conditioned PDS back to the digesters. This could generate enough heat without requiring external digester heating. Additional benefits would be improved digestion, an increase in the production of methane, and a decrease in sludge volume. This could be cost-effective and existing systems can be easily retrofitted.
2. RTC increased the biodegradability of waste activated sludge and could be used to condition WAS before digestion. This will increase the destruction of volatile solids because of the improvement biodegradation and because most of the aerobic microorganisms are believed to escape the anaerobic digestion process intact. The

heat capacity remaining after conditioning WAS should be sufficient to heat the digester.

3. RTC solubilized COD from both WAS and PDS that can be used as an organic carbon source for denitrification.

8. APPENDIX

A. AMMONIA ANALYSIS

Ammonia concentration was measured by modifying the Ammonia-Selective Electrode method 4500-NH₃F of the Standard Methods (18th Edition). The measurement by Standard Methods indicate that the electrode must be immersed in the solution whereas our modified method measures ammonia in the gas phase of the sample.

Ammonia concentration was determined by the Orion Ammonia Electrode Model 95-12. The membrane of the electrode is gas-permeable and hydrophobic so that water does not wet the membrane and does not penetrate through the membrane's holes. Dissolve ammonia (NH_{3(aq)} and NH₄⁺) is converted to NH_{3(aq)} by raising the pH to above 11 with a strong base such as NaOH. NH₃ then diffuses through the membrane.

High concentrations of dissolved ions affect the measurements, but color and turbidity do not. Surfactants also affect measurements because they wet the membrane and water penetrates the membrane. This causes problems with samples that contain surfactants such as sewage or sludge. Amines also cause positive interference. For these reasons the electrode manufacturer suggests to measure ammonia in the gas phase.

The ammonia electrode is placed in a closed system saturated with water vapor and

ammonia in the gas phase diffuses through the electrode's membrane. Ammonia concentrations greater than 14 ppm can be measured under these conditions. When the pH of the sample is increased to greater than 11, the gas phase of the closed system will be saturated with water vapor and has a partial pressure of ammonia in equilibrium with the solution. The partial pressure of ammonia in the gas phase is related to the ammonia concentration in the solution by Henry's Law:

$$K_h = \frac{[NH_{3(aq)}]}{P-NH_3} = 56 \text{ moles/L-atm @ } 25^\circ\text{C}$$

where K_h is Henry's constant and $P-NH_3$ is partial pressure of NH_3 in gas phase.

It was found that the best way to measure ammonia in the gas phase was to place the sample in a 160 mL serum bottle and the electrode through the bottle's neck; a nice fit of the electrode to the bottle is achieved by wrapping some teflon tape around the electrode. The sample was kept mixed by a teflon-coated magnetic stirrer. The electrode was placed approximately one inch above the sample so that splashing of the sample does not wet the electrode's membrane. The sample volume used was 50 mL or 25 mL, depending on sample availability.

Ammonia concentration was measured by the Orion Expandable Ion Analyzer EA 920 pH/ISE/mV; the analyser was set to measure concentration directly. Calibration of the analyser was performed by using two ammonia standards that should cover the expected range of the sample concentration.

B. VOLATILE FATTY ACIDS ANALYSIS

Volatile Fatty Acids (VFA) were determined by Gas Chromatography. The Perkin-Elmer Gas Chromatograph Sigma 2000 is used for the analysis. The chromatograph is equipped with two identical 6ft x 4mm ID glass columns filled with 10% SP-1000/1% H₃PO₄ on 100/120 Chromosorb WAW. Although 1/4" OD metal columns can be used for the analyses, glass columns are preferred because peaks separate better and results are faster. Carrier gas is Helium and is supplied at 86mL/min. The oven temperature is set to 150°C and detection is done by a thermal conductivity detector.

To detect VFA in aqueous media, samples are acidified to a pH 2 or below and extracted with ethyl ether, and the extracts are injected into the chromatographic column¹. Before acidification, the salt forms of the acids (R-COONa) are soluble in water but not in ether. After acidification, the acids are in the free acid form (R-COOH) and are soluble in both water and ether. The complete procedure follows:

1. Acidify 6 mL sample to pH 2 or below by 0.1 mL of 50% aqueous H₂SO₄.
2. Pipette 2 mL of acidified sample into centrifuge tube.
3. Add 1 mL ethyl ether, seal tube, and mix contents.
4. Centrifuge briefly to break the ether-sample emulsion.

¹Method from Supelco GC Bulletin 856

5. Transfer ether layer to a test tube by a pipette.
6. Add an amount of anhydrous MgSO_4 or Na_2SO_4 equal to 1/2 the volume of ether in the tube. Wait for 10 minutes to remove all water traces from ether.
7. Inject 14 μL of extract in column.

The chromatograph was connected to the PE Nelson Model 1020 computer-based integrator for data acquisition and analysis. The integrator was set to use the area under the peaks as a way of determining sample concentration. Calibration was performed by running a standard sample containing Formic, Acetic, Propionic, Isobutyric, Butyric, Isovaleric, Valeric, Isocaproic, Caproic, and Heptanoic acids. Calibration was performed before sample analysis. Standards were prepared by the same procedure as the samples. Figure B-1 shows the method "ACIDS.MTH" used by the integrator to calculate the sample's VFA concentrations. Figure B-2 shows the printout from the integrator for the standard solution. The figure shows the retention times and the peaks of each acid.

METHOD ACIDS.MTH VOLATILE ACIDS

CREATED : 14:03:22 Mon Aug 12 1991
 AUTHOR : Kyriacos Pierides
 LAST MODIFIED : 19:30:57 Mon Nov 23 1992

Instrument : Perkin-Elmer Sigma 2000 GC
 Column(s) : Two identical Supelco (10%SP -1000/1% H3PO4
 on 100/120 chromosorm WAW, 6ft x 4mm ID
 glass column)
 Carrier Gas : Helium (High Purity) at 86 mL/min
 Detector(s) : Hot Wire Detector
 Operating Conditions : Isothermal Conditions at 155 oC

Calculation Type : External Standard Peak Data : Area
 Calibration Sequence Number : 16

DATA COLLECTION

Start Time : 0.000 min
 End Time : 20.000 min
 Narrowest Peak : 1.4 - 3.2 sec
 Peak Width : Automatic
 :

PEAK INTEGRATION

Lockout Time : 0.000
 Baseline Treatment : V to V
 Area Sensitivity : 32
 Base Sensitivity : 2
 Skim Sensitivity : 0.00 %

QUANTITATION

RF of Unknowns : 0.00000e+0
 Peak Area Reject : 0.00000e+0
 Calibration Type : Single-Point
 Conc Units : mg/L

PEAK IDENTIFICATION

Identification Type : Absolute
 Unretained Peak Time : 0.000 min
 Component % Tolerance : 0.50

REPORTING

Report Device : Laser #1
 Report Format : 0
 Special Report : None

Plot Device : Laser #1
 Application :
 Interface Ready : Immediate

COMPONENT IDENTIFICATION

RT	Component Name	Calib Amt	Resp Fact	Tol	Ref	Grp
1.900	Acetic	5.25000e+2	8.46987e-2	0.200		
2.500	Formic	6.10000e+2	1.00750e-1	0.200		
2.900	Propionic	4.97000e+2	1.99900e-2	0.200		
4.300	Butyric	4.79000e+2	1.36600e-2	0.200		

PLOTTER

Plot Mode : Continous
 Chart Speed : 7 mm/min
 Baselines : Yes

RT / Components : Comps
 Timed Events : No
 Second Plot : None

Figure B-1: Acids Method Used by the Integrator

File : 8-4_02.D01- standard
 Run : 02 huakang
 Path : C:\CHROM\ACIDS\PRIMARY Type : Sample
 Collection : 15:37:28 Aug 04 1992 Method : ACIDS [15:09:13 Aug 04 1992]
 Integration: 15:37:28 Aug 04 1992 Method : ACIDS [15:09:13 Aug 04 1992]
 Report : 15:57:30 Aug 04 1992 Method : ACIDS [15:09:13 Aug 04 1992]
 Sample Amt : 1.00000e+0 Dilution: 1.00000e+0

EXTERNAL STANDARD (AREA)

RT	Area	BC	ExpRT	RF	mg/L	Name
0.190	10966	V		0.00000e+0	0.0000	Unknown
0.295	24390836	V		0.00000e+0	0.0000	Unknown
0.553	256964			0.00000e+0	0.0000	Unknown
1.955	11551	V	1.900	4.41974e-2	510.5240	Acetic
2.350	4501	V	2.300	1.13237e-1	509.6784	Formic
2.798	28534	V	2.700	2.43013e-2	693.4147	Propionic
3.243	48371		3.100	1.63172e-2	789.2867	Isobutyric
4.098	49922		4.000	1.58319e-2	790.3597	Butyric
5.012	65384		4.900	1.41568e-2	925.6358	Isovaleric
6.521	66793		6.600	1.41769e-2	946.9189	Valeric
8.758	72614	V	8.900	1.44981e-2	1052.7632	Isocaproic
10.318	74853		10.500	1.39465e-2	1043.9349	Caproic
16.298	82940		16.600	1.53297e-2	1271.4475	Heptanoic

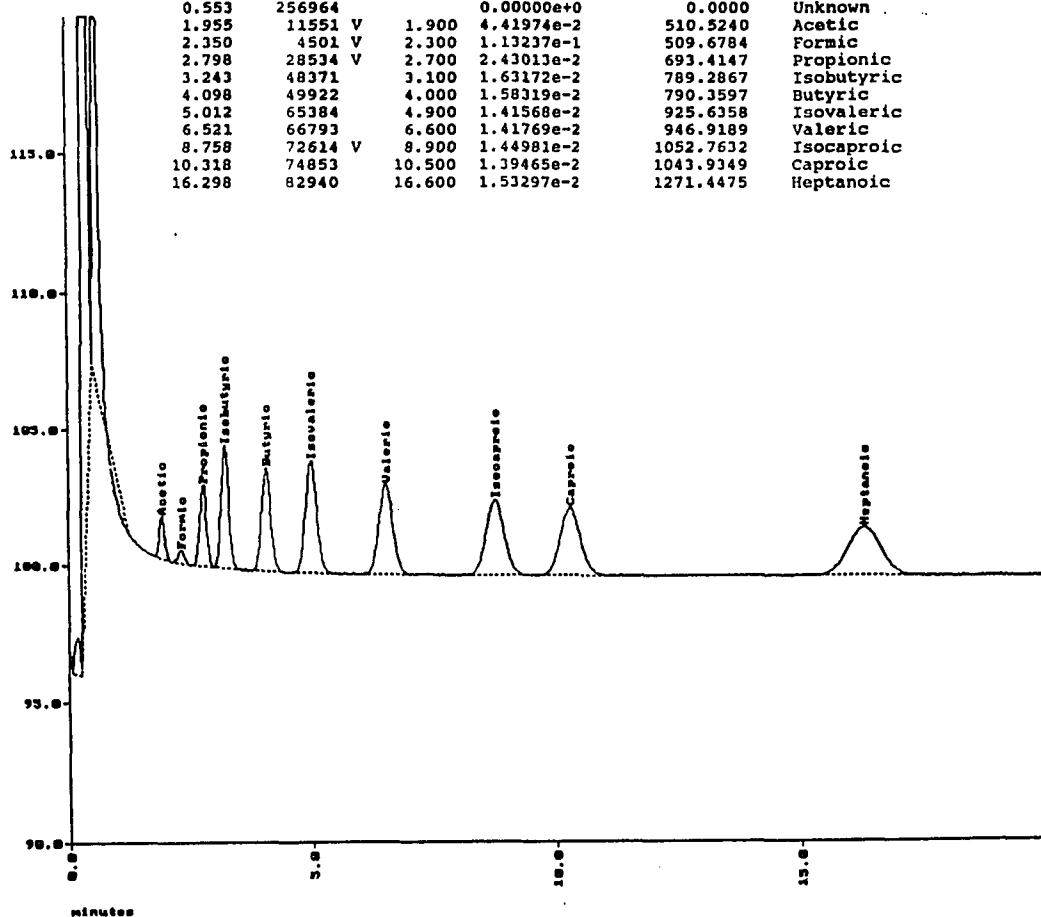


Figure B-2: Volatile Acids Calibration Output for GC

C. GAS COMPOSITION ANALYSIS

Gas composition for CH₄ and CO₂ was determined by the Perkin-Elmer GC and results were integrated by the PE Nelson integrator, described in Appendix B for Volatile Acids. The only difference was that the chromatograph is equipped with two identical 12ft x 1/4" OD Supelco stainless steel columns. The columns were filled with 50/80 Porapak Q. Carrier gas was also Helium and is supplied at 70mL/min. The oven temperature was programmed to remain at 38°C for 2 minutes and then advance to 100°C at a rate of 20°C/min. Detection was also done by a thermal conductivity detector.

There is no preparatory procedure for the gas sample. A gas volume of 500μL was collected by a gas-tight syringe and injected into the column. Calibration was performed similar to the Volatile Acids procedure where a standard containing H₂, O₂, N₂, CH₄, CO and CO₂ was injected into the column. Calibration was performed using the area under the peak-curve and results were normalized to give the component concentration as % of total gas.

Figure C-1 shows the method "GAS2.MTH" utilized by the integrator for the gas composition calculations. Figure C-2 shows a typical gas-standard printout from the integrator. The figure shows the gases O₂, N₂ and CO as on peak because the utilized column does not separate them. For our analysis, though these gases were not required because this gases are present at very low concentrations. Our concern was the CH₄ and CO₂

concentration. Other columns can separate the three aforementioned gas, but they must be operated at much higher temperatures and for longer times. H_2 gas can be detected but only if its concentration in the gas phase exceeds 0.5 to 1%; below this level detection is difficult because H_2 gas has similar properties to He, the carrier gas. This detectable level of H_2 gas is very high for a well-operated anaerobic digestion system and will not be monitored during the study. Low levels of H_2 gas can be detected if the carrier gas is replaced from H_2 to N_2 .

METHOD GAS2.MTH Anaerobic Dig. Gas Analysis

CREATED : 12:09:55 Mon Aug 12 1991
 AUTHOR : Kyriacos Pierides
 LAST MODIFIED : 19:24:41 Mon Nov 23 1992

Instrument : Perkin-Elmer Sigma 2000 GC
 Column(s) : Two identical Supelco Columns (50/80 Porapak Q,
 12ft x 1/4" stainless steel)
 Carrier Gas : Helium (70 ml/min)
 Detector(s) : Hot Wire Detector (HWD)
 Operating Conditions : Column held at 380C for 2 minutes;
 then temperature is raised to 1000C at a rate of 200C/min.

Calculation Type : Normalization
 Calibration Sequence Number : 2

Peak Data : Area

DATA COLLECTION

Start Time : 0.000 min
 End Time : 6.000 min
 Narrowest Peak : 1.4 - 3.2 sec
 Peak Width : Automatic
 :

PEAK INTEGRATION

Lockout Time : 0.000
 Baseline Treatment : B to B
 Area Sensitivity : 20
 Base Sensitivity : 5
 Skim Sensitivity : 0.00 %

QUANTITATION

RF of Unknowns : 0.00000e+0
 Peak Area Reject : 0.00000e+0
 Calibration Type : Single-Point
 Conc'n Units : % Gas

PEAK IDENTIFICATION

Identification Type : Absolute
 Unretained Peak Time : 0.000 min
 Component % Tolerance : 0.50

REPORTING

Report Device : Diconix #1
 Report Format : 0
 Special Report : None

Plot Device : Diconix #1
 Application :
 Interface Ready : Immediate

COMPONENT IDENTIFICATION

RT	Component Name	Calib Amt	Resp Fact	Tol	Ref	Grp
1.100	Hydrogen	1.03000e+0	1.87607e-3	0.500		
1.400	Nitrogen, O2 & CO	9.69700e+1	3.32289e-5	0.500		
2.500	Methane	1.00000e+0	4.04693e-5	0.500		
4.300	Carbon Dioxide	1.00000e+0	2.93013e-5	0.500		

PLOTTER

Plot Mode : Continous
 Chart Speed : 10 mm/min
 Baselines : Yes

RT / Components : Comps
 Timed Events : No
 Second Plot : None

Figure C-1: Gas Method Used by the Integrator

D. DEHYDROGENASE ACTIVITY MEASUREMENT

Dehydrogenase activity (DHA) determination is based on the use of artificial electron acceptors, such as TTC (triphenyltetrazolium chloride), that is reduced to TF (triphenyl formazan). TF has the form of red crystals that are insoluble in water but soluble in organic solvents. The color intensity is proportional to TF yield and to the system's dehydrogenase activity.

The DHA measurement follows Chung's (1988) procedure, and modified by Zabranska (1993).

Sample Preparation

- Before the test, determine the VSS present in the sample. The recommended concentration is between 1 g/L and 10 g/L. Concentration out of this range would give poor results. Dilution of high concentrations must be done with tap water to prevent osmotic shock to the bacteria. For lower VSS concentrations, larger sample volume should be centrifuged.

Biomass Washing (for First Centrifugation)

- Dilute sample with tap water (if necessary) and centrifuge. Use high speed

centrifuge (8,000 to 10,000 rpm is preferred) to create a compact pellet.

- Discard supernatant to remove soluble external organic substrate

Cultivation Media Preparation

- Resuspend pellet, using a mechanical mixer, into a cultivation medium consisting of buffer solution, substrate, dilution water, and TTC.

TTC concentration = 2 g/L

The buffer media consists of:

Biomass Sample = 1 mL

Substrate = 1 mL

Buffer solution = 1 mL

Water = 2.5 mL

The buffer solution is the same used for the BOD test (Standard Methods, 1992).

Substrates

The following substrates can be used to promote the different anaerobic bacterial groups:

- Acetic acid for acetotrophic bacteria

- Formic acid for hydrogen-utilizing methanogenic bacteria
- Propionic acid for acetogenic bacteria
- Glucose for fermentative bacteria

The substrate concentration is 2 g/l, dissolved in buffer solution.

Incubation

Incubate at the bacterial optimum temperature, 35°C for anaerobic mesophilic bacteria

- At various time intervals, withdraw 5 mL of sample and centrifuge
- Centrifuge 5 mL of incubated sample, get the pellet with the red crystals of TF, and disregard supernatant.

Extraction

- Add 5 mL of an organic solvent, such as ethylalcohol, to the pellet and resuspend with a mechanical stirrer.
- Extract in the dark and a low temperature for a minimum time of 30 minutes
- Recentrifuge to separate pellet from extract and disregard the pellet

TF Concentration Measurement

- Measure absorbance of extract at 490 nm, using pure solvent as blank

- From calibration curve slope, determine the TF concentration in the sample as C_f (mg/L) and as specific concentration of TF per mass unit of biomass (expressed as VSS) as C_fX (mg/g):

$$C_f = \frac{A \times k \times V_e}{V_s}$$

$$C_fX = \frac{C_f}{X}$$

where,

C_f	=	TF concentration, mg/l
C_fX	=	TF concentration per VSS, mg/g
A	=	absorbance
k	=	calibration constant from calibration curve, mg/L
V_e	=	extract volume, mL
V_s	=	biomass sample volume, mL
X	=	VSS of biomass sample, g/L

Before running the test, the calibration constant, k , must be determined using known concentrations of TF and measuring its absorbance. Figure D-1 presents the calibration curve obtained from a HACH DR 3000 spectrophotometer.

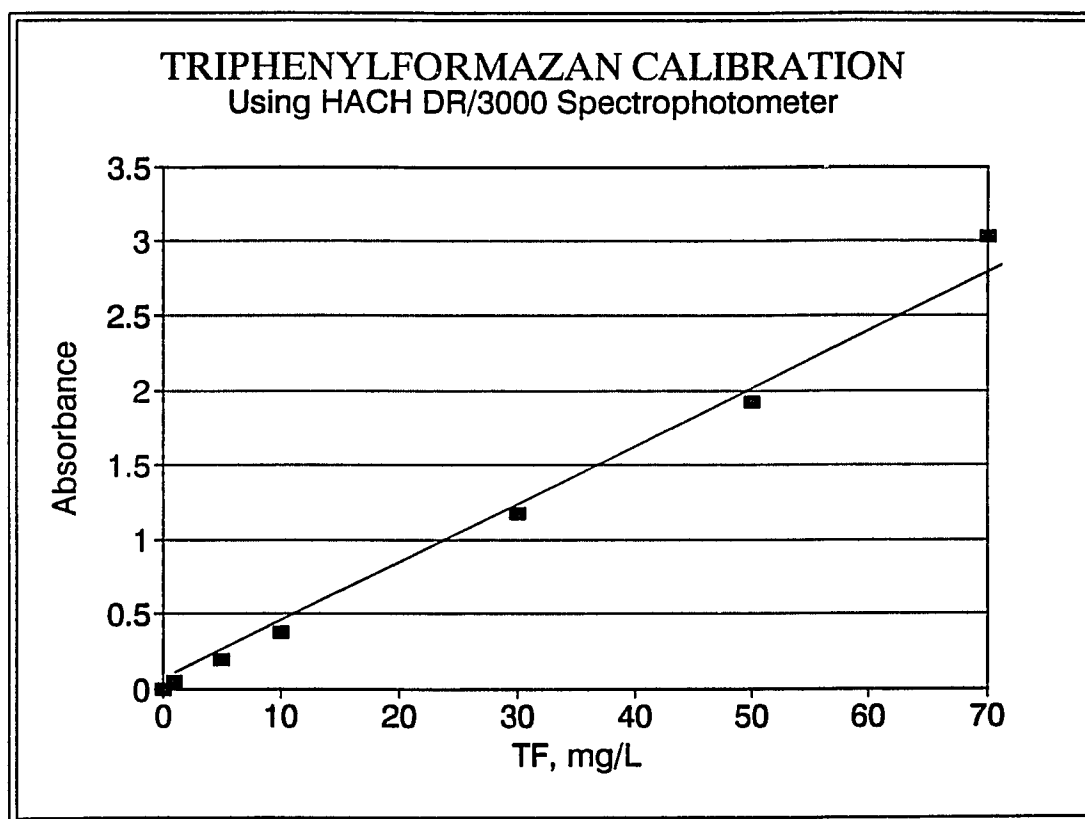
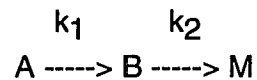


Figure D-1: DHA Standard Curve

E. SIMPLIFIED KINETIC EQUATION OF ANAEROBIC DIGESTION

A simplified kinetic representation has the form:



where,

A = particulate or slowly degraded COD, mg/L

B = soluble or fast degraded COD, mg/L

M = methane gas COD, mg/L

k_1 = first-order conversion rate of A to B, 1/d

k_2 = first-order conversion rate of B to methane, 1/d

$$\frac{d}{dt}A(t) := -k_1 \cdot A \quad ; \text{ at } t = 0, A = A_0 \quad (\text{E-1})$$

$$\frac{d}{dt}B(t) := k_1 \cdot A - k_2 \cdot B \quad ; \text{ at } t = 0, B = B_0 \quad (\text{E-2})$$

$$\frac{d}{dt}M(t) := k_2 \cdot B \quad ; \text{ at } t = 0, M = 0 \quad (\text{E-3})$$

Slowly Degraded COD Solution

By direct integration

$$A(t) := A_0 \cdot e^{-k_1 \cdot t} \quad (\text{E-4})$$

Soluble COD Solution

Substitute E-4 into E-2 and solving the differential equation:

$$B(t) := B_0 \cdot e^{-k_2 \cdot t} + \frac{k_1 \cdot A_0}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (\text{E-5})$$

Methane Production Solution

Substituting E-5 into E-3 and solving the differential equation:

$$M(t) := B_0 \cdot (1 - e^{-k_2 \cdot t}) + A_0 \cdot \left(1 - \frac{k_2}{k_2 - k_1} \cdot e^{-k_1 \cdot t} + \frac{k_1}{k_2 - k_1} \cdot e^{-k_2 \cdot t} \right) \quad (\text{E-6})$$

Figure E-1 graphically presents the Equations E-4, E-5, and E-6. Kinetic rates were typical values measured in this study (Table 6-7). Plots and calculation were made by the software Mathcad 4.0 of Mathsoft, Inc.

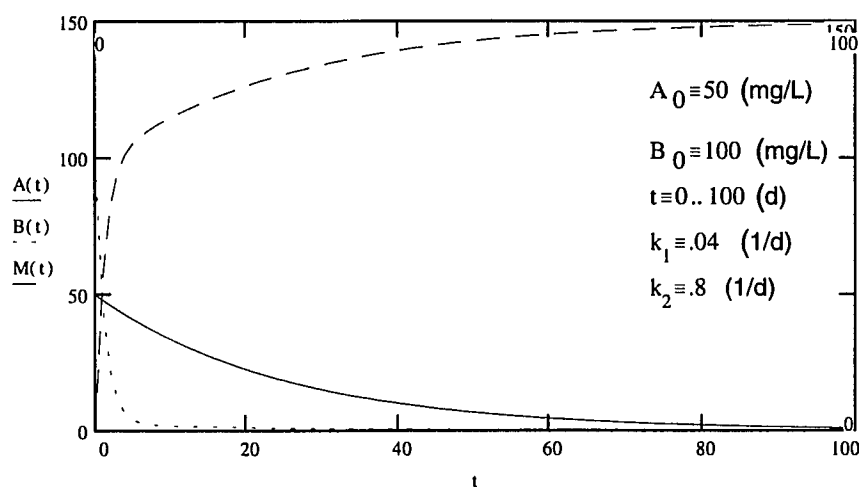


Figure E-1. Methane (as COD) Production

For $k_2 \gg k_1$:

$$\frac{k_2}{k_2 - k_1} = 1, \text{ and } \frac{k_1}{k_2 - k_1} \cdot e^{-k_2 \cdot t} < e^{-k_1 \cdot t}$$

Therefore, Equation E-6 takes the simplified form:

$$M_s(t) := B_0 \cdot (1 - e^{-k_2 \cdot t}) + A_0 \cdot (1 - e^{-k_1 \cdot t}) \quad (\text{E-7})$$

M_s , the simplified methane production equation, is compared to Equation E-6 on Figure E-2, where the results from the two equations are identical.

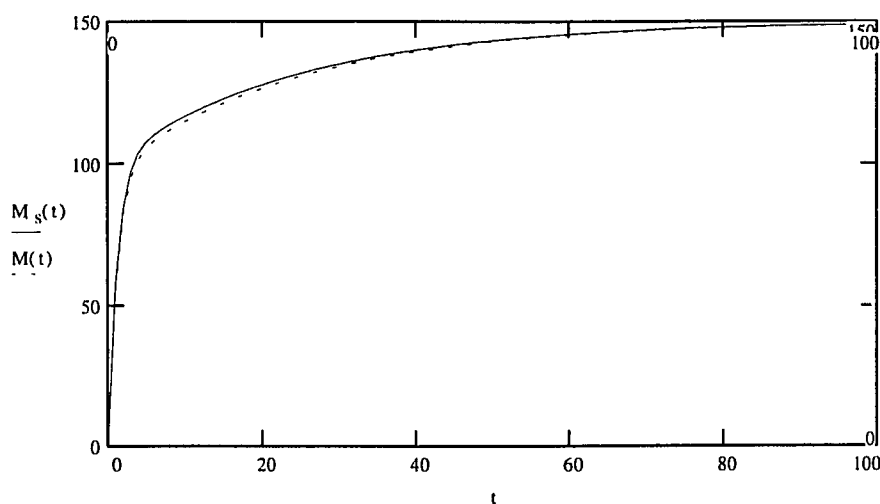


Figure E-2. Comparison of Equations E-6 and E-7

COD is equivalent to methane gas using the stoichiometric relationship of 395 mL of methane per gram of COD at 35°C, one atmosphere. Assuming that digested gas contain a constant percentage of methane gas, Equation E-7 has the same form as the two-term equation,

$$\text{SGP}(t) := G_1 \cdot (1 - e^{-k_1 \cdot t}) + G_2 \cdot (1 - e^{-k_2 \cdot t}) \quad (\text{E-8})$$

where,

- SGP = specific gas production, mL/g
- G_1 = ultimate SGP of fast term, mL/g
- G_2 = ultimate SGP of slow term, mL/g
- k_1 = first-order reaction rate of fast term, 1/d
- k_2 = first-order reaction rate of slow term, 1/d
- t = time from startup, d

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