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RAPID THERMAL CONDITIONING OF SEWAGE SLUDGE

by

JIANHONG ZHENG

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

1997

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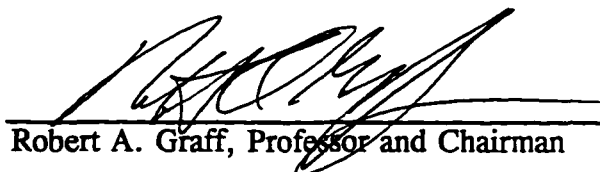
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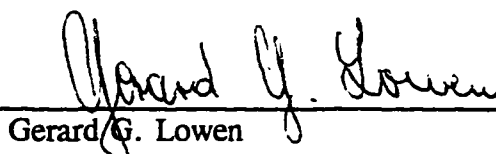


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ABSTRACT**RAPID THERMAL CONDITIONING OF SEWAGE SLUDGE**

by

Jianhong Zheng

Advisor: Professor Robert A. Graff

Rapid thermal conditioning (RTC) is a developing technology recently applied to sewage sludge treatment. Sludge is heated rapidly to a reaction temperature (up to about 220°C) under sufficient pressure to maintain the liquid phase. Reaction is quenched after 10 to 30 seconds when the mixture of sludge and steam pass through a pressure let-down valve. This process reduces the amount of sludge requiring land disposal, eliminates the need for polymer coagulant, improves dewaterability, increases methane production, and further reduces the concentration of pathogens. The odor problem associated with traditional thermal conditioning processes is largely minimized. Ammonia removal is readily integrated with the process.

For this research, a pilot unit was constructed capable of processing 90 liters of sludge per hour. Over 22 runs were made with this unit using sludge from New York City Water Pollution Control Plants (WPCP). Sludges processed in this equipment were tested to determine the effect of RTC operating conditions on sludge dewaterability, biodegradability, and other factors affecting the incorporation of RTC into wastewater treatment plants.

Dewaterability of thermally conditioned sludge was assessed for centrifugeability and filterability. Bench scale centrifugation was used for evaluating centrifugeability, pressure filtration and capillary suction time (CST) for filterability. A mathematical model developed for centrifuge dewatering was used to predict the effect of RTC on full scale centrifuge performance. Particle size distribution and solids density of raw and treated PDS were also analyzed. An observed increase in sludge solids density at least partially explains its improved centrifugeability.

An investigation of thermally conditioned amino acids showed that the L-isomer is highly biodegradable while the D-isomers are generally less so. Glucose is highly biodegradable, but rapidly becomes refractory as thermal conditioning time is lengthened. This shows the fundamental importance of rapid processing.

Rapid thermal conditioning may be incorporated into a wastewater treatment plant where biological treatment is used. For purposes of a concrete example, flow-sheets for the incorporation of the RTC process into the New York City Wards Island WPCP were prepared, and experimental data from the laboratory scale RTC test facility were used to set design parameters. A design incorporating nitrogen removal into the RTC flow sheet was also examined. ASPEN software was used to design the proposed processes and perform economic analyses. Cost estimates for these alternatives show a substantial advantage to implement RTC in comparison to present plant operation. About one third of the current sludge processing cost can be saved by incorporation of RTC into the Wards Island Plant. With nitrogen removal, the economics are even more attractive.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Sludge is the residual slurry of settleable solids from a wastewater treatment plant. Its handling and disposal are of major economic importance. In recent decades, environmental issues have increasingly focussed on sewage sludge, and more stringent regulations have made its allowable disposal increasingly difficult.

Starting in 1930's, New York City sludge was transported by barge to an ocean dump site twelve miles offshore. In 1988, the site was relocated to a point 106 miles off the New Jersey coast. In compliance with the Ocean Dumping Ban, enacted by Congress in 1988, New York City ceased this practice in January 1992 (Lipke, 1990; New York City DEP, 1993). Since then, land disposal has been used requiring transport of dewatered biosolids as far as Texas, Arizona, or Colorado (Maracic, 1993).

This has greatly increased wastewater treatment costs. Four hundred dry tons of sludge must be disposed of daily. New York City DEP operates 14 Water Pollution Control Plants in five boroughs. Digested sludge (in this study referred to as partially digested sludge, or PDS, because of its incomplete digestion) must now be dewatered. This is

done in centrifuge facilities newly implemented for this purpose. Polymer coagulants must be added to achieve dewatering specifications, an additional expense.

More recent rules impose even more stringent controls on biosolids disposal. For example, the USEPA Sewage Sludge Use and Disposal Regulations set national standards for pathogens and a number of heavy metals. To avoid disposal restrictions and improve marketability of the sludge end product, treatment plants may decide to upgrade their pathogen reduction process (Foess and Sleger, 1993). Such conditions create new opportunities for innovative solutions. Any process reducing the amount of cake produced without lowering its quality would significantly reduce overall operating cost. Rapid thermal conditioning (RTC) process studied here, which is characterized by using high temperature and short retention time to condition sludge, shows promise as a technology for advanced sludge treatment.

1.2 OBJECTIVE OF STUDY

This is part of a larger study to evaluate RTC for the treatment of sewage sludge. The primary concerns relate to its effects on dewaterability and bioconvertibility and to its economic viability. Here, the emphasis is on the effect of RTC on sludge dewaterability and on process economics. The effect of RTC on sludge biodegradability was reported in the Ph. D. dissertation of K. Pierides (1993). However, some attention is given to the chemistry of RTC as this aspect is not yet completely resolved.

1.3 SCOPE OF STUDY

Though thermal conditioning of sludge has been researched and practiced for decades in various forms, its literature is deficient in certain aspects: Few research papers deal with rapid thermal conditioning. No paper covers the effect of rapid thermal conditioning on dewaterability. Reasons for the toxicity of thermally conditioned sludge to anaerobic digestion are still not clear. In this study we aim to answer these questions in order to raise our understanding of the RTC process and improve our ability to apply it to wastewater treatment. The scope of the study is as follows:

1. A laboratory scale RTC apparatus was designed and constructed. It can treat sludge continuously, heating it in about 10 seconds to temperatures up to 240°C. This apparatus was used to prepare samples of RTC sludge at various conditions of temperature and residence time for tests of biodegradability and dewaterability.
2. The effect of RTC on sludge dewaterability is assessed using tests of filterability and centrifugeability. The physical basis of this effect is examined. A quantitative description of sludge dewatering in terms of its physical characteristics is developed for the purpose of comparison and prediction.
3. The mechanism of thermal conditioning is explored at a fundamental level using model compounds, which typify sludge composition.
4. Based on this laboratory work, flow sheets, preliminary engineering designs, and

economic assessments are presented for the incorporation of RTC into an existing wastewater treatment plant. Further modification of the RTC process to remove ammonia nitrogen and phosphate is proposed.

A review of the literature is given in Chapter 2. The laboratory scale RTC unit, its parameters and operation procedures are described in Chapter 3. Chapter 4 is devoted to dewaterability. A mathematical model is introduced and the results of filterability tests are reported. Other results related to sludge dewatering characteristics, such as sludge solids particle size distribution, solids densities, and settling velocities are reported in this chapter. Chapter 5 deals with tests of the anaerobic digestibility of and D-amino acids and thermally conditioned L-amino acids; the results are used to explain the toxicity problem encountered in traditional thermal conditioning. In Chapter 6, two alternative flow sheets for incorporation of RTC into the Wards Island Water Pollution Control Plant are provided, along with their engineering design and economics analysis. A modification of the RTC process to remove ammonia and phosphate is also given in this chapter. Conclusions and recommendations are in Chapter 7.

CHAPTER TWO

LITERATURE REVIEW

Thermal conditioning of sludge is not a new concept. Significant progress has been made at the fundamental level and in new applications. Improved understanding of the thermal conditioning mechanism has resulted in better control for specific applications. Most work has been focussed on sludge dewaterability and biodegradability. In this chapter the background for sludge dewatering and digestion is introduced, the history of thermal conditioning is reviewed along with other aspects pertinent to the study defined in Section 1.3.

2.1 SLUDGE DEWATERING

2.1.1 Sludge Conditioning and Dewatering

Sludge is typically more than 95 % water (Faisst, 1980). Reasons for dewatering may be among the following: to reduce transportation or disposal costs, for ease of handling, to meet requirements for incineration, composting, or landfill, to eliminate odor and putrescibility.

The available dewatering devices include vacuum filters, centrifuges, belt filter presses, filter presses, drying beds, and lagoons. Device selection depends on the type of sludge

to be dewatered, requirement product characteristics, and space available (Metcalf & Eddy, Inc., 1991; and Cornwell *et al.*, 1987).

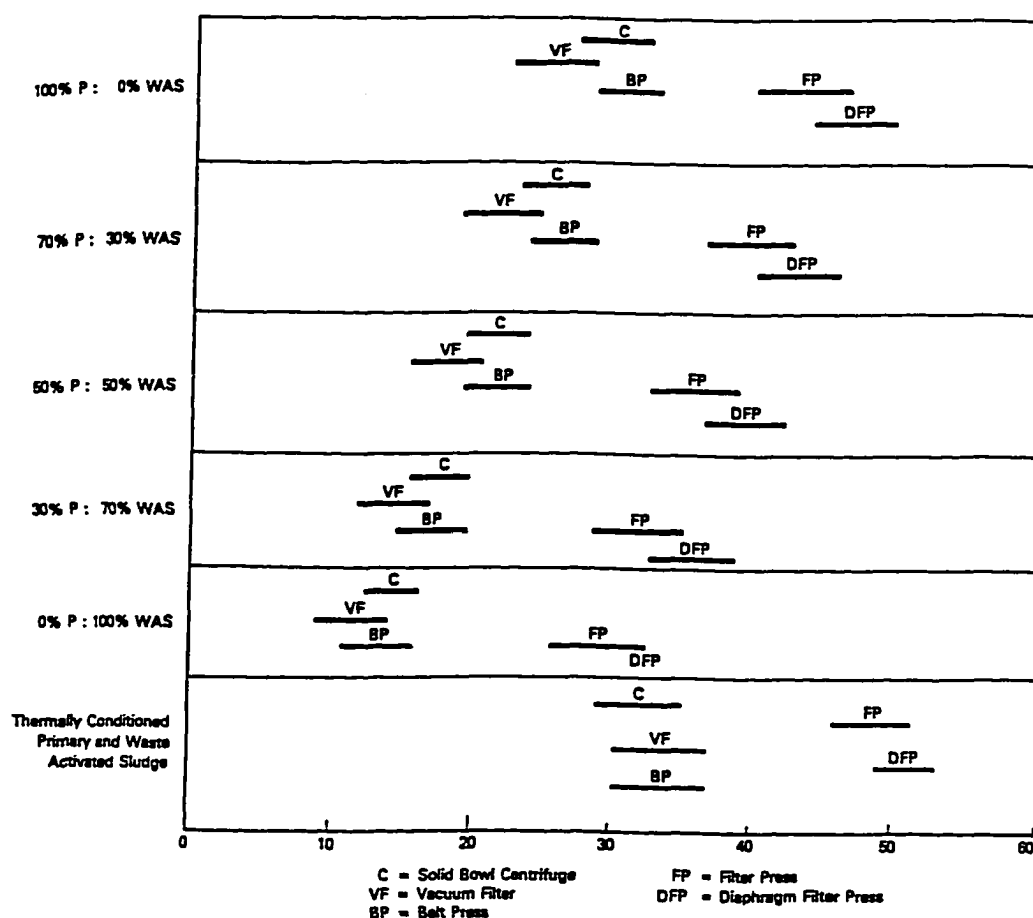
Conditioning of sludge before mechanical dewatering enhances water removal and improves solids capture. The two most commonly used methods are chemical and thermal. Other conditioning methods such as irradiation, freeze-thaw, solvent extraction (Metcalf & Eddy, Inc., 1991), and enzymatic treatment (Thomas *et al.*, 1993), have so far been limited to the laboratory or pilot-scale demonstration.

Particles in municipal sludge carry a negative charge. Mutual repulsion impedes settling and compaction. This is overcome by the addition of a coagulant which neutralizes surface charge, eliminates repulsion, and allows agglomeration. The increased effective particle size raises settling rate. As the assemblage contracts, part of water contained between particles is released. Therefore, dewatered sludge cake with higher solids content is achieved (Huebner, 1989).

Inorganic chemical conditioning, in which lime and ferric chloride are usually used in conjunction, is principally associated with filtration dewatering. In itself, the addition of inorganic chemicals typically increases sludge solids mass by 15 to 30 percent. During the past decade, newly developed organic polymers have increased in popularity. Reasons for selecting polymers over inorganic chemicals include insignificant increases in sludge solids mass, and lower operating costs (USEPA, 1987).

Conditioned sludge can be mechanically dewatered to solids concentrations as high as 30

to 50 percent. All of the various methods of mechanical sludge dewatering are capable of good recovery (>90%) of suspended solids; consequently the major difference is in cake solids concentration. Figure 2-1 shows typical ranges of cake solids for sludges with and without thermal conditioning (Note: In Figure 2-1, for thermally conditioned sludge, the ratio of PS to WAS is not given in the original source). Although thermal conditioning reduces coagulant consumption, either organic (polymer) or inorganic conditioning agents may still be needed, adding 2 to 5 percent to total solids (USEPA/625/1-87/014, 1987).



(After USEPA/625/1-87/014, 1987)

Figure 2-1. Dewatered sludge percent solids.

2.1.2 Methods to Evaluate Sludge Dewaterability

Sludge dewaterability is the extent to which water can be separated from suspended solids by mechanical methods. Filtration and centrifugation are most commonly used. Dewaterability depends on both the properties of sludge and the method of dewatering; unfortunately, the later is often improperly ignored. Traditionally, capillary suction time (CST) and specific resistance to filtration (SRF) have been the dominant methods of assessing dewaterability. Therefore, in much of the literature, dewaterability is restricted to filterability, and measured only by the SRF or CST tests. Centrifugeability, in contrast, has received little attention.

2.1.2.1 Capillary Suction Time Test. In the CST method a small volume of sample, about 10 ml, is placed in a collar bottomed by a standard filter paper (Figure 2-2). Due to capillary pressure, the water in the sample is absorbed into and spreads inside the fibrous matrix of the filter paper. The time required for the liquid to travel a specified radial distance between two probes is designated CST.

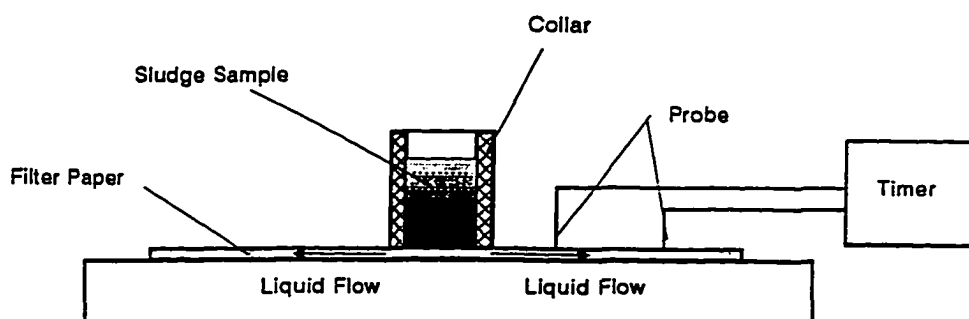


Figure 2-2. Capillary suction time (CST) apparatus.

According to the theory of this method, capillary pressure is dominant over the hydrostatic head of sludge in the sample reservoir. Therefore, the effect of the height of sludge sample in the collar is negligible. CST test is a purely empirical test, and results depend on solids concentration (Vesilind, 1988; Dohanyos *et al.*, 1988) and test paper properties (Tiller *et al.*, 1990; Unno *et al.*, 1983). It is not meaningful to compare CST values from one plant to another, and CST cannot be considered a fundamental sludge dewaterability measurement (Vesilind, 1988). However, because it is a rapid and simple measurement, the CST test is widely used as a primary indicator of sludge dewaterability (Karr and Keinath, 1978). It is commonly used to establish polymer dose requirements for full-scale dewatering devices (Novak and Bandak, 1989; Cornwell *et al.*, 1987).

2.1.2.2 Specific Resistance to Filtration Test. The SRF test is based on an application of Darcy's law to liquid flow through a porous medium under a pressure differential, SRF being the permeability of the sludge. Theoretically, SRF is independent of solids concentration, volume of sludge, and area of filtering surface (Chritensen and Dick, 1985a; Karr 1976). The application of the SRF test to sludge was developed by Coackley (1956), and it has since been widely accepted as a standard technique for the characterization of sludge filterability.

Figure 2-3 shows the apparatus for pressure filtration. A sludge sample is added to and sealed in the filter chamber. As soon as pressurized gas is introduced into the chamber, a timer is started. The relation between filtrate volume and time are recorded. Then a curve of t/V versus V is plotted, and the slope of the curve and other operating

parameters are used to obtain specific resistance to filtration, r_s , defined by Equation 2-1

$$r_s = \frac{2pA^2}{(C\mu)} b. \quad (2-1)$$

Where,

b = slope of curve t/V verses V , s/cm^6

t = time of filtration, sec

V = volume of filtrate, cm^3

p = pressure across the filtration cake, dyn/cm^2

A = filter area, cm^2

μ = viscosity of filtrate, poise

C = mass of solids deposited per unit volume of filtrate, g/cm^3

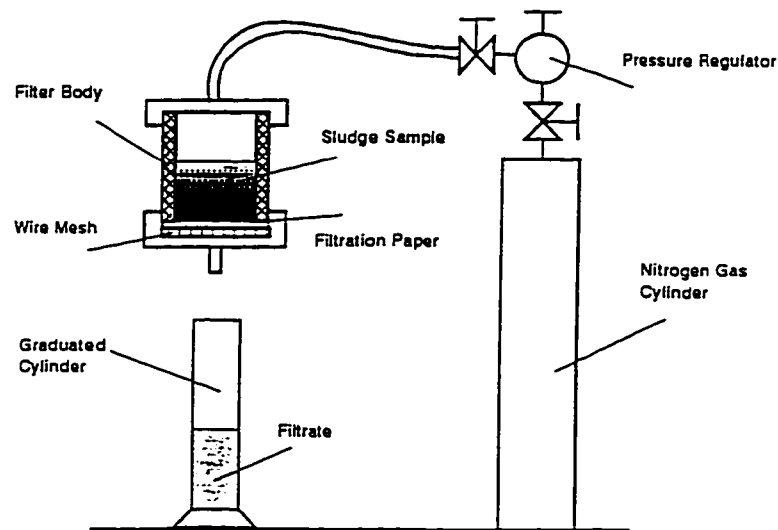


Figure 2-3. Pressure filtration test apparatus.

The unit of SRF in some literature, such as papers by Brooks *et al.* (1970b) and Conwell *et al.* (1987), is expressed as sec^2/g , which seems incorrect. The problem is that the unit

of pressure used there is the weight of water per unit of area, instead of force per unit area, and a unit of acceleration is missing.

It has been widely recognized that SRF is, in many cases, not constant but varies as filtration progresses. Numerous papers deal with this phenomenon. Sludge cake is compressible, and during filtration a drastic increase in SRF occurs due to a reduction in porosity. The reasons for such reduction of porosity were suggested to be rearrangement of sludge particles, fragmentation of larger particles of low strength, and deformation of elastic particles. Blinding of filter medium due to migration of fine particles is also believed to cause the increase in SRF (Huang, 1979). Notebaert *et al.* (1975) suggested that when SRF is not constant, the neglect of first phase (e.g., first two minutes of filtration as suggested by others) will cause error. Chritensen and Dick (1985b) give a detailed discussion on how to avoid non-parabolic data. Blinding due to the presence of fine particles of 1 to 10 μm in diameter results in a concentration dependent SRF (Novak *et al.*, 1988, Karr and Keinath 1978b). However, it is significant only at very low solids concentration (e.g. 0.5% for aluminum hydroxide slurry, Chritensen and Dick, 1985b). Nevertheless, compared with CST, SRF is influenced by solids concentration (Karr and Keinath 1978b). SRF was also reported to increase as pressure difference over cake increases, especially above 25 kPa (Pires *et al.*, 1989).

Empirical correlations have been developed by several investigators for blinding in filtration. A blinding index, to describe the changes of SRF with solids concentration, was introduced by Karr and Keinath (1978b). Notebaert *et al.* (1975) proposed a power law function for SRF. Since both SRF and CST reflect sludge permeability, correlations

between SRF and CST with solids concentration have been developed by several authors (Vesilind, 1988; Dohanyos *et al.*, 1988), but are rarely used.

2.1.2.3 Centrifugation In centrifuge dewatering, a force 1000 to 6000 times gravity is applied to the sludge (Ramalho, 1983). The dewatering mechanism is solids settling followed by compaction under centrifugal force. Since this is different from filtration, the two processes do not necessarily correlate, and the results from CST and specific resistance may inadequately present sludge dewaterability through centrifugation (Karr and Keinath, 1978).

Tests for estimating centrifuge performance have been developed. However, these are not based on a rigorous mathematical analysis and have no relation to the fundamental properties of sludge (Vesilind, 1988). No procedure for process design based on laboratory data is yet established, but feasibility of centrifugation for a specific sludge may be evaluated employing a laboratory centrifuge (Ramalho, 1983). A literature search turned up predominantly papers dealing with sludge filterability and very few dealing with centrifugeability. Centrifugeability is often ignored in discussions of dewaterability. The reason may be that filtration had been the usual technique for sludge dewatering and was, therefore, the primary object of attention.

In recent decades the solid bowl centrifuge has gained in popularity because of its better performance (Lipke, 1990). Despite its inadequacy, the CST test, which measures the filterability of sludge, is used to assess its centrifugeability in wastewater treatment

plants, since mature methods are not available to evaluate the centrifugeability of sludge on a laboratory scale.

To assess sludge centrifugeability, Vesilind (1977) introduced the concept of settling coefficient, S , defined by

$$S = \frac{V}{\Omega^2 r} \quad (2-2)$$

Where,

v = settling velocity of sludge surface, m/sec

Ω = radial angular velocity of the centrifuge tube, rad/sec

r = radial distance to the sludge surface, m

The settling coefficient is the ratio of settling velocity to its driving force (centrifugal force). It has been shown to depend on sludge solids concentration, and not on centrifugal force. Higher settling coefficients mean better sedimentation properties. Because centrifugal dewatering includes settling and compaction stages, settling coefficient can be only evaluate the former stage, and cannot predict the later.

2.1.3 Factors Influencing Sludge Dewaterability

A number of sludge properties have been noted as major factors in sludge dewaterability. Huang (1979) grouped sludge dewatering properties into two categories: macro properties and micro properties. Dick and Ball (1980, cited by Lotito *et al.*, 1993) separated the factors influencing dewaterability into three categories: (a) fluids properties: bound water

content, viscosity, ionic strength, density; (b) particle properties: size and shape distribution, surface potential and area, density; (c) sludge properties: solids concentration, permeability, yield strength and electrokinetic properties. Categories (a) and (b) represent liquid and solid phase properties individually, and so they are micro properties. Category (c) contains sludge properties as whole which are macro properties. Other factors are sludge chemical composition (Huang 1979), biological properties (Barber and Veenstra, 1986), and structural elements of flocs (Olboter and Vogelpohl, 1993).

The relative importance of each sludge property is not easy to determine, because only a few isolated parameters can be examined in any single study. Nevertheless, particle size is considered to be the single most important factor influencing sludge dewaterability (USEPA, 1987; Karr, 1976). This is obvious, according to the principles of fluid mechanics: For settling, particle size and density affect terminal velocity. For filtration, particle size and particle shape determine the specific surface area of filtering medium, thus affecting resistance to filtration. A larger surface area also traps more adhered water. Sludge filterability mostly can be explained by particle size distribution. Furthermore, changes of sludge filterability due to pH, biological activity, mixing and conditioning also can be explained on the basis of the effects these factors have on the particle size distribution (Karr, 1976).

Classification of particles in terms of size by different investigators is shown in Figure 2-4. The classification of Rudolfs and Balmat (1952) has been used by most workers in sludge particle research (Karr, 1976; Faisst, 1980). Karr (1976) modified Rudolfs and

Balmat's (1952) classification so that settleable (settled for 1 hour) supracolloidal solids are classified as fragile settleable solids, and, consequently, solids with size larger than $100\ \mu\text{m}$ are classified as rigid settleable solids. He found that raw sludge has the highest concentration of rigid settleable solids and the lowest concentration of fragile settleable solids. Conversely, activated sludge has the lowest concentration of rigid settleable solids and highest fragile settleable solids. Digested sludge has the highest concentration of supracolloidal, true colloidal and dissolved solids, while activated sludge has the lowest concentration of these solids. Karr(1976) then separated sludge particles according to the above classification, and adjusted particle size distribution by the addition or subtraction of a particular size fraction. This extensive study on relations between solids distribution and sludge dewaterability, as measured by and SRF and CST, indicates that supracolloidal solids (1 to $100\ \mu\text{m}$) have the most influence on dewatering characteristics. That is, the higher the proportion of supracolloids, the more poorly the sludge dewatered. This is due to the fact that particles in this size range tend to blind the sludge cake and filter medium during filtration, resulting a higher resistance to flow.

10^{-4}	10^{-3}	10^{-2}	10^{-1}	$1\mu\text{m}$	10	10^2	10^3
^a Colloids		Fine		Medium	Coarse	Larger	
^b Molecules		Colloids			Suspended		
“Dissolved	Colloidal			Supra colloidal		Settleable	

Sources:

- (USEPA, 1987) for common material particles.
- (Stumm, 1977) for waterborne particles.
- (Rudolfs and Balmat, 1952) for sludge particles.

Figure 2-4. Particle size spectrum.

Other investigators are in agreement with this conclusion (Huang, 1979; Barber and Veenstra, 1986; Lotito *et al.*, 1993). However, Huang (1979) suggested that it is the weight fraction of supracolloidal solids, not its concentration as suggested by Karr (1976), that predominately controls filtration. He also found that most important size fraction controlling sludge filtering varies with the type of sludge. That is, the weight fraction of true colloidal solids is most important for activated sludge, while the weight fraction of supra-colloidal solids is most important for digested sludge. Coackley and Wilson (1971) reported that SRF of digested sludge is dominated by the material under 5 μm in size, even though such material is only about 14 percent of total solids.

The classifications of particle size have general usefulness but fail to recognize the paramount biological and physical importance of subclasses, especially those between 0.5 μm and 20 μm (Faisst, 1980). Due to the complexity of sludges, it is not possible to find a general correlation between particle size distribution and filterability (Olboter and Vogelpohl, 1993; Lotito *et al.*, 1993).

In sludge dewatering, particle density is also a highly important factor. It affects settling velocity, and is also is a major factor in determining the achievable cake solids concentration by various dewatering methods (Huang, 1979). The amount of water in a floc due to strong water binding forces results in a low density of sludge floc (Olboter and Vogelpohl, 1993).

In simplest terms, water in sludge can be differentiated as either "free" or "bulk" water or as "bound" water. The latter is held by the solid either through sorption on specific

sites (i.e. functional groups of the proteins and other macromolecules and/or restricted within pores and capillaries) (Katsiris and Kouzeli-Katsiri, 1987). Others have proposed more detailed models of water distribution of sludge. Vesilind (1978) proposed a model with four types of water: (1) *free water* which is not associated in any way with sludge particles and can be removed by gravitational thickening; (2) *floc water* which is trapped in the flocs and may be removed by mechanical methods; (3) *capillary water* which is attached to the particle lattice by capillary forces and cannot be removed by mechanical means unless extreme pressures are used; and (4) *particle water* which is bound chemically to the individual particles and can be removed only by chemical or thermal means, and only if the particle is altered (e.g. a microorganism is killed). The amount of water in each category can be determined by centrifugation with the centrifugal force up to 20,000 gravity. A typical activated sludge has 75% free water, 20% floc water, 2% capillary water, and 2.5% particle water. Vesilind's model is the most widely accepted (Karr, 1976; Huang, 1979; Robinson and Knocke, 1992). Huang (1979) proposed a model with six types of water: free water, interfloc water, floc-adsorbed water, inter-particle water, particle-adsorbed water, and particle water. However, a technique capable of characterizing all of these six types of water does not exist, and such classification is mostly of theoretical value.

Of these different types, bound water is the most difficult to remove. In addition, particles with high bound water content tend to have the most surface water. Therefore, much of research focus has been on bound water. The term bound water in most cases includes both physically and chemically bound water. It can be defined in many ways, depending on investigator's definition and the tests used (Vesilind, 1995). The methods

of determination include high speed centrifugation, drying, dilatometry (freezing), sorption isotherm method, and differential thermal analysis (DTA). Different methods may give different results for bound water content (Lee and Hsu, 1995). For digested sludge, a drying test was reported to give 30 % more bound water than a dilatometric method (Robinson and Knocke, 1992).

Conditioning of sludge, thermal conditioning, and freeze-thaw were reported to release bound water (Katsiris and Kouzeli-Katsiri 1987). Polymer conditioning also released bound water even in high gravitational centrifugation (Robinson and Knocke, 1992). Tsang and Vesilind (1990) reported that surface bound and chemically bound water of anaerobically digested sludge were not significantly affected either by polymer conditioning or mechanical dewatering. The discrepancy may result from different definitions and the corresponding test methods.

2.2 SLUDGE DIGESTION

2.2.1 Sludge Composition

The composition of sludge depends on its origin and subsequent treatment. Primary sludge designates the product obtained after liquids have been removed by purely physical means (gravity sedimentation, or flotation). It consists of solid particles, mainly organic in nature. WAS designates the end product of aerobic biological treatment of the primary tank effluent and consists of biomass. Material from the anaerobic digestion of primary sludge or/and WAS is designated digested sludge. Anaerobic digestion results

in cellular destruction and a decrease in volatile solids content, but it still consists predominantly of biomass. The major types of organics in municipal sludges are proteins, lipids, and carbohydrates (Table 2-1).

Table 2-1. Basic organic composition of sludge (% volatile solids).

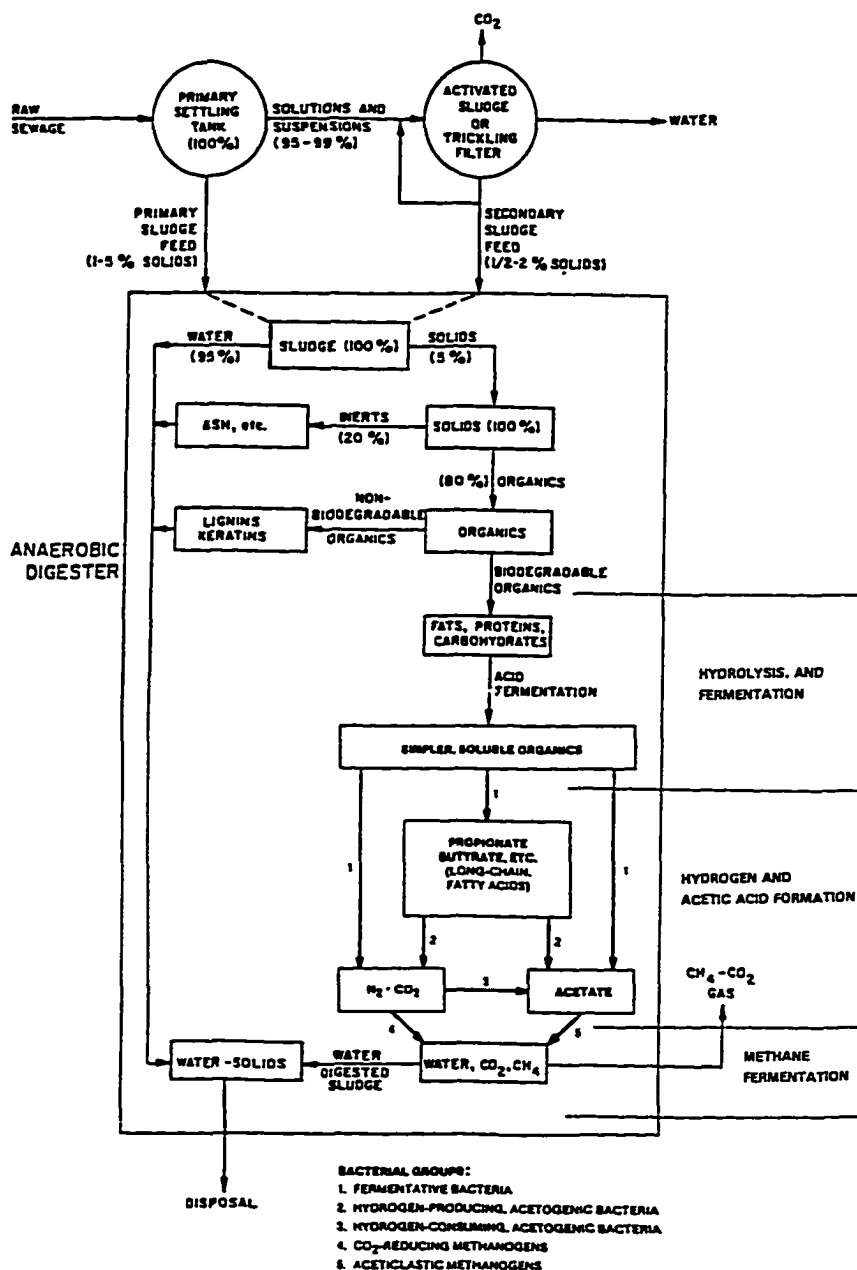
Sludge	Protein	Lipids	Carbohydrate	Source
PS	17.5	29.6	48.2	Teletzke <i>et al.</i> , (1967)
WAS	57.4	10.2	15.9	Wang <i>et al.</i> , (1988)
WAS	63.8	9.3	10.8	Shimizu <i>et al.</i> , (1993)
PDS	40	20	20	Garzon-Lopez, (1987)

2.2.2 Anaerobic Digestion

Anaerobic biological waste treatment has been practiced since the beginning of this century. It is in use throughout the world today, either alone or in combination with other processes, for the treatment of domestic, industrial, and agricultural liquid wastes. The primary purpose of anaerobic digestion is the stabilization of organic matter and the concurrent reduction of odor, pathogens, and organic materials. This is accomplished through biological conversion of organics to methane and carbon dioxide in an oxygen-free environment (Parkin and Owen, 1986). Anaerobic digestion in sewage treatment plant is presented schematically in Figure 2-5. It is a complex microbiological process which involves, perhaps, five groups of bacteria (Figure 2-5). Current common belief is that it is a three-stage process consisting of hydrolysis, acidogenesis, and

methanogenesis (Metcalf & Eddy, Inc., 1992; Parkin and Owen, 1986; Winfrey, 1984).

The rate-limiting step in the overall process depends on the nature of the substrate, process configuration, temperature, and loading rate (Speece, 1983).



(After Klass and Ghosh, 1973; Parkin and Owen, 1986; and MetCalf & Eddy, Inc., 1991).

Figure 2-5. Schematic representation of anaerobic digestion in sludge digester.

2.2.2.1 Hydrolysis. Most constituents of wastewater sludges are organic in nature and particulate in form. Hydrolysis of complex insoluble organics is necessary to reduce their size and convert them to a form in which they are able to pass through bacterial cell walls and serve as an energy or nutrient source (Parkin and Owen, 1986). During hydrolysis, facultative microorganisms attack organic matter. Polymers are transformed into soluble monomers through enzymatic hydrolysis. These monomers are the substrate for microorganisms in the second stage where soluble organics are converted into organic acids (Cheremisnoff *et al.*, 1980). The hydrolysis reactions of carbohydrates, proteins and lipids are following:

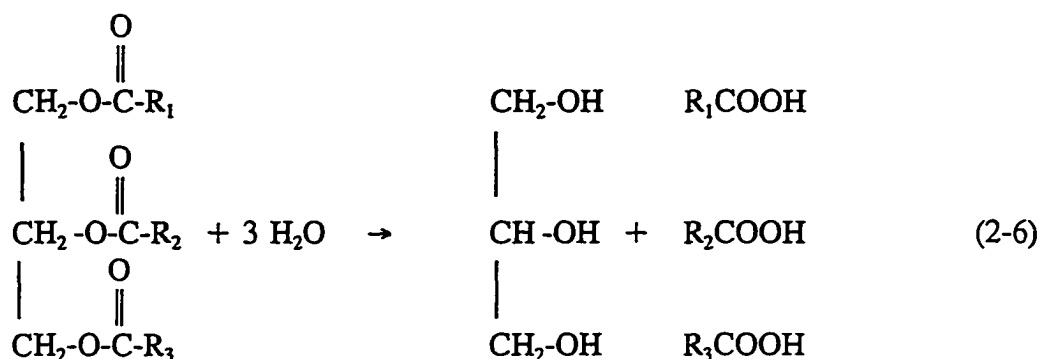
(1) Hydrolysis of cellulose to glucose



(2) Hydrolysis of proteins



(3) Hydrolysis of lipids



Proteins are hydrolyzed to amino acids, and lipids to fatty acids and alcohols. Carbohydrates hydrolyze by molecular disruption to disaccharides and monosaccharides.

It is important to recognize that digestion cannot occur unless the hydrolysis step functions properly. In other words, hydrolysis can be the rate-limiting step for digestion. Furthermore, not all organics are hydrolyzable to simple compounds which can be utilized by bacteria. This may be because of structure, inaccessibility, or complex non-hydrolyzable linkages. The amount of such non-biodegradable or refractory components in municipal wastewater varies from a low of 35-40% up to 70-80% of the volatile matter content (Parkin and Owen, 1986). For WAS, the hydrolysis of compounds produced from death and lysis of WAS bacteria is believed to be the rate-limiting step in the overall anaerobic digestion process (Li and Noike, 1992; Gossett and Belser, 1982). Proteins and cellulose degrade much more rapidly than lipids (O'Rourke, 1968 in Parkin and Owen, 1986). On the other hand, Cheremisnoff *et al.*, (1980) believe that cellulose hydrolysis is rate limiting.

2.2.2.2 Acidogenesis Once complex organics are hydrolyzed, they are fermented to organic acids, sugars, amino acids, and eventually to smaller organic acids such as propionic-, butyric-, and valeric-acid. Amino acids are deaminated to acids. These acids are oxidized by H_2 -producing acetogens to acetic acid, hydrogen, and carbon dioxide. Soluble organic acids, consisting primarily acetic acid, form the substrate for the methanogenesis stage (Parkin and Owen, 1986; Cheremisnoff *et al.*, 1980).

Hydrogen inhibits many acid-forming bacteria. However, it is an energy source for

some methanogenic bacteria and is rapidly consumed in the reduction of carbon dioxide to methane (Wilkie and Colleran, 1988; Parkin and Owen, 1986). The population of bacteria responsible for acid production may be facultative anaerobes, and/or strict or obligate anaerobes.

2.2.2.3 Methanogenesis In the last stage of digestion, methanogenic bacteria generate methane by two routes. In one route, acetic acid is fermented to methane and carbon dioxide. In the other, carbon dioxide is reduced to methane by hydrogen gas or formate generated by other bacterial species (Cheremisnoff *et al.*, 1980). Approximately 72% of the methane comes from the first route, acetic acid cleavage by acetoclastic bacteria (Parkin and Owen, 1986):



The remaining 28% results from reduction of carbon dioxide using hydrogen as the energy source by CO_2 -reducing methanogens,



In the stages of hydrolysis and acidogenesis, organic material is simply changed in form, but essentially no stabilization occurs. Waste stabilization, or COD reduction occurs only in methanogenesis. Methane, insoluble in water, readily separates from sludge and leaves the system as part of the exit gas (Parkin and Owen, 1986). Carbon dioxide produced either escapes as gas or is converted to bicarbonate alkalinity. The methane

content of gas from digesters operating on municipal wastewater sludges is typically 65%(Metcalf & Eddy,1991). The remaining gas mostly is carbon dioxide, plus trace amount of hydrogen, nitrogen, and hydrogen sulfide. Ammonia is also formed from degradation of urea or proteins (Cheremisnoff *et al.*, 1980).

One of the most important characteristics of the methanogenic stage is that very few substrates can act as energy sources for methane bacteria. These are presently known to be only formic acid, acetic acid, methanol, methylamines, hydrogen plus carbon dioxide, and carbon monoxide. Of these, acetic acid and hydrogen serve as the major substrates for methane formation in the anaerobic digestion of wastewater sludge (Metcalf & Eddy,1991; Parkin and Owen, 1986).

2.2.2.4 Toxicity The effect of toxic (inhibitory) substances in anaerobic digestion is that they alter the kinetics of organic matter decomposition. Its extent depends on the nature and concentration of the toxic materials. Only soluble materials are toxic to microorganisms. Alkali and alkaline-earth metal salts (e.g., sodium, potassium, calcium, or magnesium salts) are toxic above certain threshold. In addition, low but soluble concentrations of heavy metals (e.g., from copper, zinc, or nickel salts) are also toxic. Ammonia is toxic at high concentrations. A variety of organics also inhibit anaerobic digestion, these include organic solvents, alcohols, long-chain fatty acids, and pesticides (Cheremisnoff *et al.*, 1980). Thermally treated nitrogenous compounds are reported to be toxic (Stuckey and McCarty, 1984). The method of using serum bottles to evaluate the effect of toxicity on anaerobic digestion was initiated by Owen *et al.*, (1979) and has been accepted by many investigators (Tang *et al.*, 1991; Stuckey and McCarty, 1984).

2.3 THERMAL CONDITIONING OF SLUDGE AND OTHER SUBSTRATES

2.3.1 Thermal Conditioning Processes

In this context, thermal conditioning refers to the application of high temperature and pressure to substrates of biological origin for a defined length of time. Under such conditions solubilization and hydrolysis of the substrate take place. The basic complex polymeric substrates that make up the organic fraction of sludge are initially degraded to their simple constituent compounds (Teletzke *et al.*, 1967). After conditioning, chemical and physical properties of the sludge are both altered. The hydrolysis of sludge can be divided into three forms: autohydrolysis, catalytic hydrolysis, and oxidative hydrolysis, corresponding to the addition of nothing, catalysts, or oxidants. Common catalysts in thermal conditioning are acids and bases.

Thermal conditioning, as a process for pretreatment of sludge, has a long history. The full scale application of the Porteous process can be traced at least as far back as the 1930's (Lumb and Barnes, 1944). It has always been an option for sludge treatment and many modifications have been made during past decades. In addition to the Porteous process, wet air oxidation (WAO) process, an oxidative hydrolysis process, has also been developed to commercial scale by Zimpro Inc. However, its popularity is limited because of its sophistication in comparison to conventional treatment processes, operational problems, odor concerns, and higher costs.

In past decade, supercritical water oxidation(SCWO) has emerged as an aqueous waste treatment technology. It is able to achieve highly efficient destruction of organic compounds. Commercialization of SCWO has only been on the way since 1994 (Caruana, 1995). Although SCWO applications currently emphasize government hazardous waste sites, this process has also been applied to municipal and industrial sludge treatment.

As to the conditions of thermal processing, except SCWO, the temperatures mostly range from 170 to 250°C (Everett, 1974; Brook, 1970; Haug *et al.*, 1983; Lumb and Barnes, 1944), with some ranging from 60 to 80°C (Hiraoka *et al.*, 1984; Garelli *et al.*, 1992). Retention times range from 15 minutes to 60 minutes. In some cases, additives are employed. Oxygen addition, as in the Zimpro process, was used to partially oxidize sludge and increase temperature (Friedman *et al.*, 1988). The addition of acids or alkalis prior to or during thermal conditioning has been used to enhance solubilization (Everett, 1974). Injected carbon dioxide forms carbonic acid which reacts with free hydroxide ions to lower pH making this an acid hydrolysis. In addition to improvement of sludge dewaterability, acid conditions eliminate the formation of struvite which deposits on vessel walls and blocks piping (Garelli *et al.*, 1992). SCWO is operated above the critical temperature of water (374°C), ranging from 400 to 600°C. Oxygen, air, or hydrogen peroxide, are used as oxidants. Because water becomes completely miscible with oxygen and most organic compounds above its critical point, retention times as short as minutes or seconds can be used for the reaction (Gloyne and Li, 1993).

Initially, thermal conditioning was used to improve the dewaterability of sludge, and the decant of thermally conditioned sludge was subjected to aeration or an aerobic filter for further treatment. Other methods for treatment of thermally conditioned sludge have also been proposed. They include activated carbon and coal, solvent extraction, additives and evaporation (Brook, 1970b). Currently, anaerobic digestion is most commonly used, and different kinds of reactors such as packed beds, fluidized beds, rotating biological contactors, among others, have been tested. Anaerobic digestion of thermally conditioned sludge is believed to improve the control of odor, reduce the biological strength of the discharge and reduce energy consumption (Haug, 1978). It also produces digestion gas. On the other hand, SCWO efficiently converts organic compounds to CO₂ and water. A total organic carbon destruction efficiency of 99.3 percent was reported for SCWO treatment of pulp mill sludge (USEPA, 1992). However, it is also noted that acetic acid is the most refractory byproducts of SCWO (USEPA, 1992). In recent years, an innovative process, rapid thermal conditioning (RTC) was studied for sludge treatment application, and it will be discussed in Section 1.3 (Garzon-Lopez, 1987; and Pierides, 1994).

The critical factors involved in thermal conditioning have been suggested to be pH, temperature and retention time (Alsop and Conway, 1982). High temperature and minimum retention time are necessary for a significant improvement in sludge dewaterability. However, an increase in specific resistance was observed when retention time was longer than 30 minutes with a temperature higher than about 200°C (Brook, 1970a). Also, high temperature was reported to result in refractory or toxic materials which reverse anaerobic digestibility (Haug *et al.*, 1978; Stuckey and McCarty, 1984;

Friedman *et al.*, 1988; and Leuschner and Laquidara, 1988). Leuschner and Laquidara (1988) also found that oxidative hydrolysis is disadvantageous since it improved methane production less than autohydrolysis.

There are two most important improvements in sludge properties resulting from the thermal conditioning process. One is in dewaterability. Solids and liquor are more easily separated and more concentrated sludge cake is obtained. The second is in biodegradability. More methane gas is produced from anaerobic digestion of the thermally conditioned sludge. Several operating parameters such as temperature, retention time and pH, affect these improvements. Of these parameters, the most decisive are temperature and retention time.

2.3.2 Rapid Thermal Conditioning

Rapid thermal conditioning (RTC) was initiated by McParland and Grethlein (1982). This process was characterized by the use of rapid heating to reduce retention time while maintaining a high conditioning temperature. Typically, heating time was 10 seconds and conditioning temperature 220°C. To accomplish rapid thermal conditioning, substrate was mixed with steam in a plug flow reactor and temperature was raised "instantaneously". The practical temperature limit in this apparatus was 240°C. The effluent from the reactor was flashed through an orifice, whereby the reaction temperature was reduced instantaneously to the boiling point of the effluent. Reaction retention time was only 1 to 30 seconds. After flashing, the effluent could be further cooled through a heat exchanger.

The RTC process was initially developed for hydrolysis of cellulosic material. Since the formation of glucose from the breakdown of cellulose and its subsequent decomposition is a chain reaction, the selectivity of glucose is time dependent. It was found that rapid thermal conditioning resulted in high glucose yield (McParland *et al.* 1982). Church and Wooldridge (1981) used a plug flow reactor system, similar to that of Grethlien, to acid-hydrolyze biomass. Sawdust, newspaper, straw, and bagasse at 35% solid input were hydrolysed at 200-225°C to produce glucose and furfural. To overcome difficulties in control and mixing, which they believed to be associated with short retention time, Church and Woodridge increased residence time to 4.5 minutes.

Garzon-Lopez (1987) adopted the rapid thermal process for sludge conditioning. It had been suggested that a long retention time at high temperature results in the formation of refractory material which inhibits methanogenic bacteria when thermally conditioned sludge is subjected to anaerobic digestion. The new process, RTC, proved to improve sludge biodegradability more than traditional thermal conditioning. Pierides (1994) found that RTC significantly improves biodegradability of WAS and PDS, especially during the first several days of anaerobic fermentation. A preliminary design was made for implementation of the RTC process by Garzon-Lopez (1987). In that design, however, a series of heat exchangers was used to raise the temperature of sludge, prolonging retention time and losing the benefits of the rapid heating process.

Although the effect of RTC on biodegradability of sludge has been studied by several workers, a search of the literature shows that its effect on sludge dewaterability has not

so far been investigated. Yet, dewaterability is an important consideration in any application of a thermal conditioning process.

2.3.3 Factors Affecting Sludge Dewaterability

Thermal conditioning ruptures bacterial cells, changes the gel-like structure of sludge to discrete solids, and releases bonded water, thereby increasing the dryness of the sludge. Thirty percent of the bound water in activated sludge and digested sludge was removed at 130°C thermal conditioning for 30 to 60 min. (Katsiris and Kouzeli-Katsiri, 1987). The amount of polymer coagulant could be greatly reduced or even eliminated. The dewaterability of thermally conditioned sludge is associated with solubilization of sludge solids. Solubilization of solid organic material is the most general result of thermal conditioning, but it is not necessarily directly related to dewaterability. It is discussed in dewatering because it reduces the amount of suspended solids that would be captured during dewatering and must eventually be disposed of.

For both slow and rapid thermal conditioning, increasing either temperature or retention time increases sludge solubility (Everett, 1972; Haug *et al.*, 1978; Garzon-Lopez, 1987). However, Everett (1972) noticed that when temperature exceeded 170°C, retention times, longer than 30 minutes had little further effect on solubilization. A Similar effect was observed by Haug *et al.* (1978). At 225°C, the solubilization was less than that predicted by extrapolation of low temperature data. Possible causes suggested were, first, the formation of insoluble humic substances and, second, the presence of a fixed percentage of organic material that cannot be solubilized during thermal conditioning. Data from

Wang *et al.*, (1988) also show that temperature is the dominant factor in sludge solubilization, and that the effect of retention time is marginal.

Garzon-Lopez (1987) gave the following data: Partially digested sludge had an average of 9% solubilization ($VDS/TVS \times 100 \%$). When it was conditioned at 200°C for 10 seconds, auto-hydrolysis yielded an average value of 30%. Alkaline hydrolysis yielded solubilization from 44 to 58%, in which higher solubilization corresponded to higher pH. All acid hydrolysis, at all levels of sulfuric acid addition tested, yielded a similar degree of solubilization, around 33%. Reviewing all data at conditioning temperatures between 140°C and 260°C for 10 seconds, alkaline hydrolysis always produced higher solubilization.

The improvement of sludge dewaterability was the initial and is still the prime concern of all kinds of thermal conditioning process. The effect of these thermal conditioning factors on sludge dewaterability is discussed in more detail in the following sections.

2.3.3.1 Sludge Characteristics Haug *et al.*(1978) have shown that the dewaterability of primary sludge is greatly improved by thermal conditioning. For waste activated sludge, higher temperature or longer retention time is needed to reach the same conditioning effect as for primary sludge. For a mixture of primary and activated sludge, as expected, improvement is between that of its components. Brooks (1970) found that digested sludge is conditioned at lower temperature for a given holding time than activated and primary/activated sludge. He also concluded that the more mineralized is a particular type of sludge, the more easily it is conditioned. A well-

digested sludge is more difficult to condition than a badly digested one containing a high concentration of volatile acids (Everett, 1972).

2.3.3.2 Temperature and Retention Time The conditioning temperature range for most sludges is 100°C to 350°C. Batch reactors are most often used in research studies because they are much easier to handle under high pressure and temperature and cost less. For this type of reactor the heating process is slow. Typically, it takes 20 to 90 minutes (Haug *et al.*, 1978) to reach conditioning temperature, holding for 15 to 60 minutes before cooling down (Brook, 1970a; Haug *et al.*, 1978; Everett, 1972).

The improvement in sludge dewaterability depends on temperature and retention time. Brooks (1970a) found that the specific resistance of all sludges deteriorated at low temperature, particularly with zero retention time (in slowly heating processes). High temperature and long retention time favor reduction of filtration resistance. Brooks (1970a) set a maximum tolerable level of sludge SRF of 40×10^7 (s²/g). To lower SRF to this level, a retention time of 15 minutes and a temperature 200°C was required for activated sludge and primary/activated sludge, 180°C and 170°C for humus and digested sludge respectively. For activated sludge at the temperature above 200°C or retention time above 30 minutes, longer retention time or higher temperature caused a slight increase in specific resistance. The explanation is that the first deterioration is a result of the initial release of colloidal material from cells as their walls are broken down and from the disintegration of sludge flocs. As the temperature was raised further, the remaining suspended solids became finer. The second deterioration could be caused by a decrease in voidage of the filter cake due to the dominance of such fine particles.

Brooks (1970a) noticed that the filterabilities of thermally conditioned primary and activated sludge were similar. Generally speaking, in all cases higher temperature improved filterability. However, the settleabilities differed considerably. Over the whole range, 150 to 190°C and 0 to 60 minutes retention time, higher conditioning temperatures made the settleability of digested sludge worse. Similar phenomena were seen in primary/activated sludge. Retention time seemed to have little impact on settleability of digested and primary/ digested sludge. It was suggested that fine organic particles, as in activated sludge, control filterability and coarse inorganic particles, as in primary sludge, control settleability.

2.3.3.3 The pH Value. The pH value has a profound effect on the dewaterability of thermo-chemically conditioned sludge. Since neutralization of thermally conditioned sludge was found to have no effect on its specific resistance (Everett, 1972), it could be concluded that any obvious change in sludge dewatering characteristics would be achieved only by adjusting pH prior to or during conditioning.

Everett (1974) found that, with his experiment of 3% solids sludge at 190°C and 30 minutes retention time, high pH was associated with high specific resistance to filtration, and vice versa. Over the pH range of 10 to 2, SRF varied from 1×10^{15} to 1×10^{11} m/kg, and the relation was linear. However, in one set of experiments, at 180°C and 30 minutes retention time, minimum specific resistance was found at pH 3.5. Further lowering pH would increase the resistance. Leuschner and Laquidara (1988) also reported that the partially digested sludge exposed to acid hydrolysis showed substantially improved dewaterability, compared with either auto or alkaline hydrolysis. Acid

hydrolysis was chosen in a pilot scale thermal conditioning unit to improve sludge dewaterability (Gober and Boyle,1992).

Everett (1974) noted that the pH value of sludge, 7.5, rose to 9.35 after auto-hydrolysis at 190°C. He suggested that neutralization of well-digested sludge, which is alkaline, would be beneficial for conditioning. However, Leuschner and Laquidara (1988) reported a contrary result. That is, the pH value of the sludge could be depressed below 4 after thermal conditioning, caused by organic acids from refractory volatile materials during the conditioning process. This discrepancy could be ascribed to a difference in sludge characteristics.

There was a hypothesis put forward that solubilization of sludge is responsible for the reduction in SRF brought about by thermal conditioning. Experimental data between pH 2 and 8 seemed to support this hypothesis. However, for a pH higher than 8, it was untrue (Everett, 1974).

The solids concentration of sludge cake after acid hydrolysis and pressure filter dewatering might be as high as 65 -70 % (Gober and Boyle,1992), the highest found in this literature review. In this process, sludge was first thickened by filters or centrifuges to reach a solids concentration of 15 to 25 %, then conditioned at 165°C and finally dewatered using a press filter. The pH for the sludge was adjusted before thermal conditioning to between 2 and 5. Retention time was between 30 and 200 minutes according to the pH value for thermal conditioning, where the low pH corresponded to shorter retention time, and vice versa. This retention time served as a minimum to

produce a sludge with improved dewaterability which yet would not become worse during shearing occurring later in the dewatering process.

2.3.3.4 Other Factors. Brooks (1970a) found that the settleability of thermally conditioned sludge improved with increasing solids concentration (between 1 and 6% solids) of feed, due to the compressibility of sludge. This filterability of thermal conditioned sludge decreased with increase in feed solids concentration. However, this could be explained by the effect of solids concentration, rather than thermal conditioning, on filtration.

Using a continuously stirred fermentor with 15 days retention time, Haug *et al.* (1978) found that for WAS, digestion had little effect on sludge filterability except with treatment at 175°C where some decrease in the filterability was noted. For primary sludge, digestion decreased dewaterability more than for WAS. However, it still exhibited better dewaterability than raw primary sludge. Using a batch reactor, Leuschner and Laquidara (1988) found in all cases that the dewaterability of thermally conditioned PDS was enhanced by anaerobic digestion.

2.3.4 Thermal Conditioning Effect on Biodegradability

2.3.4.1 Solubilization and Hydrolysis of Solids Thermal conditioning has been found to promote sludge solubilization, splitting complex nitrogen polymeric substrates that make up the organic fraction of sludge into their simpler and more degradable constituent compounds (Teletzke *et al.*, 1967). Heat ruptures the walls of bacterial cells, releasing

mainly proteinaceous protoplasm. These proteins and zoogloal slime are further broken down to form a liquor consisting of soluble polypeptides, ammonia nitrogen, volatile acids and carbohydrates. The solids left behind would be mineral matter and wall debris which are mainly composed of polysaccharides (Brooks, 1970b; Wang *et al.*, 1988). Sludge solubilization is promoted with an increase in temperature of thermal conditioning, but COD solubilization is significant only if temperature is higher than 140°C (Wang *et al.*, 1988). In WAS, more than half of volatile solids are proteins, and their solubilization controls the COD solubilization. The increase in solubilization of major organic compounds in WAS by thermal conditioning varies, and is in the following order: carbohydrates, proteins and lipids (Li and Noike, 1992).

Acid hydrolysis of sludge was reported most effective in producing material containing volatile solids of less than 500 molecular weight in either a slow (30 seconds) or a rapid heating (10 seconds) process. Alkaline hydrolysis is slightly less effective than auto-hydrolysis (Leuschner and Laquidara, 1988). The choice of a molecular weight of 500 was based on the observation that volatile solids of less than 500 molecular weight showed greater conversion to volatile acids and methane gas than those above 500 molecular weight.

Products of low temperature sludge oxidation include free amino acids, fatty acids, and simple sugars. As the degree of oxidation increases, such as at temperature above 200°C, these products disappear rapidly (Teletzke, *et al.*, 1967).

2.3.4.2 Digestion of Thermally Conditioned Sludge Solubilization of solid organic material by thermal conditioning renders these compounds more readily attacked by bacteria, and more easily transformed to methane under anaerobic conditions. In early years, the supernatant liquid from dewatering of thermally conditioned sludge was simply recycled to the influent of the wastewater treatment plant (Lumb and Barnes, 1944). This increased COD loading on secondary facilities by 30 percent (Haug *et al.*, 1978). Beginning in the 1970s, the anaerobic digestibility of thermally conditioned sludge was studied to make effective use of the improvement in biodegradability brought about by conditioning. In the WAO process, the organics are directly oxidized to water and carbon dioxide, hence, solids are reduced. The product stream is still high-strength and must be further treated to meet discharge regulations.

Li and Noike (1992) evaluated the digestibility of thermal conditioned WAS. In the matrix of experiment conditions, temperature was varied from 62 to 175°C, and retention time from 15 to 120 minutes. An optimum condition was found at 170°C for 60 minutes. When WAS, treated at such conditions, is subjected to anaerobic digestion for 5 to 10 days, 60% COD can be removed; this is double that of the control. It is noticed that their data shows less gas produced from WAS conditioned at 175°C than from WAS conditioned at 170°C.

For the RTC process, at temperatures up to 230°C, an increase in temperature resulted in a noticeable increase in biodegradability, and gas production from anaerobic digestion with auto-hydrolysis increased up to 43 percent over that of the control. Over the test range of retention times, 10 to 30 seconds, ultimate biodegradability increased slightly.

Overcooking was not reported (Garzon-Lopez, 1987). Further study revealed that RTC not only increases ultimate gas production, but also increases the rate of reaction especially during the first several days of digestion (Pierides, 1994). The significance of this improvement is that short retention times can be used for digestion. Higher yields of methane gas also mean higher destruction of organics in the sludge.

2.3.4.3 Toxicity of Thermal Conditioning Products Generally, the products of hydrolysis are biodegradable. However, toxic or refractory substances can be produced during thermal conditioning of biomass. At high temperature, such as 200°C, a significant portion of these organics, even in the soluble form, are not susceptible for microbial to attack. The creation of substances toxic and/or refractory to biological methane production are implicated. To avoid their formation, and to obtain more methane gas production, the optimum treatment temperature for slow heating process was suggested to be 175°C (Haug, *et al.*, 1978; Stuckey and McCarty, 1984). It has also been suggested that there is a general trend at long retention times at high temperature to form refractory materials, which inhibit the methane forming bacteria when thermally conditioned sludge is subjected to anaerobic digestion. Leuschner and Laquidara (1988) reported that batch conditioning of partially digested sludge proved ineffective in promoting digestion. The long retention time used in batch conditioning could cause conditioned material to be less biodegradable. Therefore, it has been suggested that thermal conditioning would be limited to continuous reactors with short retention time.

Baugh and McCarty (1988) studied thermochemical conditioning of lignocellulose to enhance fermentation to methane. The major identified soluble products from staged

thermochemical conditioning of white fir, which are monosaccharides, 2-furfural, and 5-hydroxymethyl-2-furfural (5-HMF), are all highly biodegradable to methane. However, the products resulting from their decomposition during thermochemical conditioning are much less biodegradable. At high temperature exceeding 200°C, hydrolysis product, free glucose, can be repolymerized (Church and Wooldridge 1981), or form dehydration products (Gossett and McCarty, 1976), both of which are non-biodegradable.

In order to understand, at a more fundamental level, the refractory nature of thermally conditioned sludge, Stuckey and McCarty (1984) used pure nitrogenous organic compounds present in sludge to see if the observed behavior of sludge could be explained from the behavior of its simple constituents. A large fraction of bacterial cell mass in WAS is protein. With thermal conditioning, it is hydrolyzed to amino acids (as indicated in Table 2-2, after Teletzke *et al.*, 1967). Therefore, 20 naturally synthesized L-amino acids were subjected to thermal conditioning, and then tested by bioassay. In most cases, thermal conditioning of these amino acids resulted in decreased bioconvertibility and increased toxicity. However, the reason for toxicity was not clearly given.

In the area of food processing, to investigate heat damage to nutrients, a so called "model" experiment method has been used for decades, i.e., using pure individual constituents of food and their mixtures instead of food itself. Many test results have been compiled by Harris and Loesecke (1960). Excessive heat was found to change the structure of protein in such a manner that some amino acids, especially lysine, aspartic acids, and glutamic acid, become resistant to enzymatic action.

Table 2-2. Amino acids in primary sludge.

Amino acids	mg/L total as N
Aspartic	97.6
Glutamic Acid	250.0
Serine	87.5
Glycine	112.0
Threonine	88.4
Alanine	277.0
Arginine	90.5
Tyrosine	0.0
Histidine	0.0
Valine	85.2
Methionine	148.2
Isoleucine	51.6
Leucine	91.4
Proline	40.8
Unknown	11.5

(After Teletzke *et al.*, 1967)

With the exception of glycine, all amino acids obtained from a natural source are optically active since each contains at least one optically active carbon atom. In certain procedures in the laboratory the optical form of the amino acids may in part be converted to its isomer. When equal quantities of the two isomers are present in solution, a racemic mixture is formed, which exhibits no optical activity. The conversion of an optical isomer into equal amount of its antipodes is the procedure of racemization.

The naturally occurring amino acids generally belong to the L-series. Only a few metabolic products of lower organisms and particular animals contain D-amino

acids(Jakubke and Jeschkeit, 1977). It is usually assumed that all amino acids in intact proteins are of the L-configuration, and D-amino acids present in hydrolysates are products of racemization (Greenburg, 1951). High temperature, long retention time, and especially alkaline condition cause increased racemization (Schmidt 1938; Greenburg, 1951). It was also reported that free amino acids are easily racemized in the neutral solution at 150-250°C (Chibata *et al.*, 1973, cited in Hayase *et al.*, 1975).

The biological reactions of D- and L-form amino acids are different. In general, only the optical form occurring in nature is the one which can be attacked by living organisms (Schmidt 1938). The nutritive value of D- or racemized amino acids is known to be very low (Gilberson and Wiseman, 1951 cited in Hayase *et al.*, 1975). However, D-form amino acids can be transformed to the L-form series though α -epimerisation, and are then available to the metabolic pathway (Rydon, 1976).

Hayase *et al.*, (1975) studied decomposition of amino acids during the roasting of proteins. They noted a study by Bajarnason and Carpenter in 1970, which showed that the heating of bovine plasma albumin at 145°C for 27 hours resulted in a partially racemized isoleucine residue. They thought that it was reasonable to consider that racemization of amino acids occurs simultaneously with their decomposition during food heat processing, and this they subsequently proved experimentally. They roasted casein and several L-amino acids (alanine, glutamic acid, and lysine) at 180-300°C for 20 minutes in an atmosphere of air or nitrogen with the results shown in Table 2-3.

Table 2-3. Degree of racemization of amino acid residue on roasting for 20 min.

Material	Amino acid	Treatment conditions				
		Control	180°C, air	230°C, air	250°C, air	250°C, N ₂
Casein	Ala	3.0		24.0(85)	66(30)	66
	Val	0.0		8.8(82)	28(31)	26
	Ile	0.0		7.6(66)	32(17)	24
	Leu	3.8		14.0(76)	32(24)	26
	Pro	0.0		2.0(76)	15(25)	0
	Asp	6.2		62.0(70)	100(18)	88
	Phe	0.0		0.0(76)	38(28)	28
	Glu	0.0		32.0(72)	72(19)	64
Casein	Ala	4.0	6.8(92)	24.0(89)		48
	Val	2.8	2.6(92)	5.0(86)		26
	Ile	0.0	2.8(95)	7.0(80)		20
	Leu	3.6	7.2(92)	15.0(73)		46
	Pro	0.0	0.0(90)	0(64)		0
	Asp	4.3	17.0(91)	64(70)		96
	Phe	0.0	0.0(98)	13(66)		0(0)
	Glu	0.0	0.0(90)	36(69)		50
Poly-L-amino acid	Poly-L- α -Ala	4.0			8(82)	
	Poly-L-Glu	0.0	20		100(48)	86
	Poly-L-Lys	2.0		88		

(After Hayase *et al.*, 1975)

Note: The number in parentheses is the remaining ratio (%) of amino acids.

The degree of racemization is defined as twice the D-amino acid derivative/(D-amino acid derivative+L-amino acid derivative) x 100%, and it varies from 0 to 100. At 180°C, more than 90 percent amino acids remained, and only aspartic acid residue was racemized more than 10 percent. As temperature increased, the remaining ratio of amino

acid decreased with the concurrently remarkable increase in degree of racemization. At 250°C under air, the degree of racemization was close to 100% for aspartic acid, and 15% for proline which shows the strongest resistance to racemization. With air replaced by nitrogen, racemization was reduced slightly. The order of racemization of amino acid residue is as follows: Asp > Glu > Ala > Phe, Leu, Ile, Val > Pro. With further analysis, it was found that lower molecular peptides and free amino acids were racemized more rapidly than higher molecular peptides. The cause of racemization is assumed to be that the dissociation of α -hydrogen atom occurs mostly by heat and other factors such as acids produced by the degradation of proteins. In another later paper, Hayase *et al.*, (1979) reported that glucose and/or methyl linoleate promote both decomposition and racemization of amino acids under roasting conditions. They also concluded that there was a close correlation between the remaining ratio and degree of racemization of amino acids.

Because severe heat treatment of proteins had induced extensive racemization, Gandolfi *et al.*, (1992) studied D-amino acid formation during the heating of milk with short retention time. D-amino acids comprise 2-4% of the total amino acids in milk. With sterilization at 148°C for 3 seconds, the ratio of D-amino acids to total amino acids was not appreciably affected. They concluded that relatively high temperature conditions for short periods does not induce racemization.

It is quite understandable that in the area of food science there has been long standing interest in the study of thermal treatment. It is, after all, the most popular method of treating food. In contrast, much less attention has been paid to the thermal treatment of

sludge which is also food but for bacteria. Although it was realized that there is some analogy between human and bacterial digestion (Parkin and Owen, 1986), valuable research results in food science were ignored by researchers in sludge treatment. So far, no literature has been found to mention racemic reactions in sludge thermal conditioning. However, a great deal of literature in food science provides a basis for the speculation that racemic reaction is one possible reason that thermally conditioned sludge is toxic and refractory to digestion. That is, the formation of D-form amino acids during hydrolysis of sludge under high temperature and long retention time would delay or even prevent methane-forming reactions.

2.4 SUMMARY

The foregoing review was concentrated on those aspects of the literature relevant to this research. The first two sections focused on two major sludge processes: dewatering and digestion. It established a frame of reference for the third section which mainly introduced the effect of thermal conditioning on sludge dewaterability and biodegradability and is the most pertinent to the goal of this study. The review shows that very little work has been done either on assessing the dewaterability of rapid thermally conditioned sludge or on the cause of toxic effects in digestion resulting from traditional thermal conditioning. The later might provide a clue to explain the findings of others that RTC improves sludge biodegradability more than traditional thermal conditioning process. This work therefore, is an effort to contribute to these aspects of importance in sludge thermal conditioning.

CHAPTER THREE

LABORATORY SCALE RTC TEST FACILITY

3.1 CONFIGURATION AND PRINCIPLES

Rapid thermal conditioning (RTC) was initially proposed for hydrolysis of cellulosic material and a system was designed and built by McParland and Grethlein (1982). For the work carried out here, a laboratory scale RTC system was designed and constructed at the City College of New York along the same lines, but with several modifications. It is the major item of equipment for this study of the RTC process.

The configuration of the laboratory scale system is shown in the Figure 3-1. At the heart of the system are three identical reactors R1, R2, and R3, which provide the flexibility to operate the system at three different HRTs but at identical flow rates and reaction temperatures. The three reactors provide an HRT range from 10 to 180 seconds. HRT is changed by adjusting the sludge feed flow rate (ranging from 1.5 to 0.5 l/min) and by using one, two, or three of the reactors in series.

Sludge is held in a storage tank while high pressure steam is generated in a boiler. Steam and sludge are continuously combined in a high intensity mixing zone at the entrance to the first tubular reactor; this provides an extremely high heating rate. The mixture then passes through one, two or three reactor sections in series having a

residence time of 10 seconds each in most tests. Temperatures are monitored by thermocouples which are placed at each end of each reactor. The reaction is quenched when the mixture flashes through a pressure let-down valve to atmospheric pressure. After further cooling in a plate-and-frame heat exchanger, the product is collected in a holding tank. The pH adjustment, when used, is made in the storage tank prior to RTC.

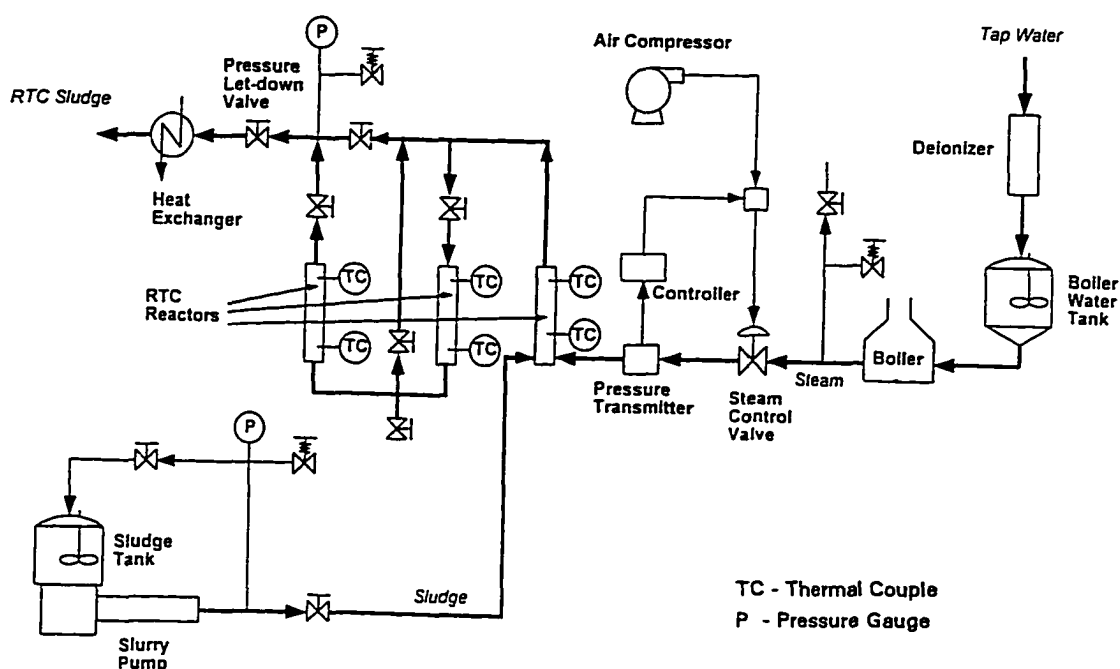


Figure 3-1. Laboratory scale RTC test facility

The equipment can be grouped into four functional categories: steam supply, sludge supply, control, and reactor. The major components comprising the RTC process are detailed as follows:

3.1.1 Steam Supply

Deionizer. A deionizer, model PS300 by Philadelphia Scientific, is used to remove hardness from tap water. Its resin is a mixture of cation exchanger and anion exchanger in an activated state, which retains the foreign ions in water, replacing them with hydrogen and hydroxyl ions.

Boiler Feed Water Tank. A 200 liter tank, made of polyethylene, is used to store as well as chemically treat boiler feed water. Chemicals are added to the water to remove oxygen and raise pH to prevent corrosion and scaling inside the boiler. An agitator of 1550 rpm and 0.033 hp is installed to mix the water during chemical treatment.

Steam Boiler. A 3.6 hp electrically heated horizontal steam boiler, model 36AF by Lattener, is used to produce saturated steam. The pressure of boiler can be preset to up to 900 psig, which corresponds to a saturation temperature of 288°C. A plunger pump, model SF20E by CAT with 1.5 hp motor, is used to pump the feed water to the boiler running at high pressure. A bypass line is installed for the venting of steam, and a blow-down separator is provided for separation of steam from discharged hot water in boiler blowdown before shutoff.

3.1.2 Sludge Supply

Sludge Tank with Agitator. A 200 liter tank made of polyethylene was mounted above the inlet of sludge pump and directly connected to it through a bottom coupling. It is

used to store and prepare the feed to the sludge pump. An agitator with 0.25 hp and 1,725 rpm motor is used to prevent settling of solids and to keep the feed uniform. When pH adjustment is required, the acids or alkalies are added to and mixed with sludge in this tank.

Sludge Pump. The sludge pump is a 12-stage progressing cavity pump, model 12P2SSQAAA by Robbins & Myers. It is capable of pumping slurry at a rate of up to 2.3 liters per minute against a pressure of 900 psig. The flow rate of the pump has been tested and determined to be independent of back pressure; it can be adjusted continuously. A recycle line is set up, allowing the measurement of the flow rate of the pump effluent as well as returning of the sludge to the storage tank during the intervals between feeding to the reactor. Provision is made to adjust the pH of sludge in the storage tank before sludge enters the rapid thermal reactor.

3.1.3 Control

Steam Control Valve. Control valve, model V1D1S3H00V by Foxboro, is operated pneumatically by a diaphragm actuator, which requires an air supply at the pressure of 20 psi.

Controller. The controller model 760 CNA-AT by Foxboro, is a self-contained, single-loop microprocessor-based, with standard proportional, integral and derivative (PID) functions. It can be operated from either a computer station or from the front of its panel, and can be configured to continuously monitor and control the process.

Convertor. The convertor, model E69F by Foxboro, transforms a DC input signal ranging from 4 to 20 mA, to a proportional pneumatic output signal ranging from 3 to 27 psi. The output signal controls the actuator of the steam control valve.

Transmitter. The transmitter, model 841GM-DI1 by Foxboro, allows a pressure input from 1 to 1000 psi., and produces an output 2 to 20 mA accordingly. It transfers the pressure signal from the sensor in the reactor steam input line to the controller.

3.1.4 Reactors

RTC Reactors. Three plug flow reactors, made of 304 stainless steel, are identical in size: inch internal diameter, 0.12 inch wall thickness, and 31 inch length. The first reactor is provided with bottom inlets for sludge and steam located on opposite sides and tangential to the inner wall of the reactor to provide good mixing. The reactors are interconnected to allow one to three of them to be connected in series. This allows residence time to be doubled or tripled without changing volumetric flowrate. All reactors are wrapped with Siltemp woven tape 0.125 inch thickness (Janos Inc.), bead heaters and a ceramic fiber blanket of 6 lb/cuft density (Janos, Inc.). The current to the bead heaters is adjusted with variable transformers to maintain the reaction temperature.

Temperature Indicator. In order to monitor the temperature in the reactors, six temperature indicators, model DP701 by Omega, are mounted on a control panel. These indicators have 0.05% reading accuracy with a 0.1°C resolution for K type thermocouple.

Thermocouple. Three pairs of type K thermocouples, TJ36-CASS-14-12 (Omega) are inserted into and mounted at the entrance and exit of each of the three reactors to monitor the temperature of thermal conditioning.

Pressure Letdown Valve. A half inch gate valve, Swagelock model SS-12NBS8, is connected to the exit of the reactor assembly. Pressure in the thermal reactor is controlled by adjusting this valve.

Heater/Variable Transformers. Three insulation layers are used to wrap the tubing and valves from the steam outlet of boiler to the entrance of the thermal reactor to prevent the condensation of steam. They are, in the order from inside to outside, Siltemp woven tape 0.125 inch thickness (Janos, Inc.) beaded heaters, and a ceramic fiber blanket of 6 lb/cuft density (Janos, Inc.). Four heating sections of beaded heaters are each controlled by a variable transformer with 0-140 V output and 1.4 kW, type 3NP116C, by the Superior Electric Co.

Heat Exchanger. A plate heat exchanger, model PO1-VG by Alfa-Laval Inc., is connected to the pressure letdown valve to cool the thermally conditioned sludge to near room temperature. The heat exchanger, made of stainless steel AISI 316, has 26 effective plates and a total of 8.96 square feet heat transfer area. Tap water is used as coolant at the rate approximately one liter per second.

Half-inch stainless steel SS-316 tubing was used to connect boiler, sludge pump, reactor, and heat exchanger, and valves together. The manually controlled valves used in this

unit are Swagelock 0.5 inch stainless steel valves.

3.2 BOILER WATER TREATMENT

Feed water specifications for prevention of corrosion in the high pressure boiler, as recommended by Eric Dlugosz of Dexter Corp (1990), are listed in Table 3-1. The first three are met by laboratory tap water without treatment. Therefore, concern is with total phosphate, pH and sulfite, with the ratio of phosphate to pH being kept within a certain range. Di-sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$), and tri-sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) are used to adjust both pH and total phosphate, and sodium sulfite (Na_2SO_3) is added to remove oxygen. Tests were performed to determine the optimum dosage. An Orion meter was used to measure dissolved oxygen, and a digital meter to measure pH. A colorimetric method, ascorbic acid method of 4500-P E of ASTM Standard Methods (1989), was used to determine phosphate concentration. The optimum dosages are listed in Table 3-2. With these dosages, the following measurements were obtained: pH=9.8, $\text{PO}_4=20$ ppm, and DO=0.08 ppm, $\text{SO}_3=15.7$ ppm.

Table 3-1. Specifications for boiler feed water.

Parameter	Value
Total dissolved solids, ppm max	500
Silica, ppm max	10
Iron, ppm max	2.0
Total phosphate, ppm	15.0-25.0
pH	9.8-10.2
Sulfite, ppm	10.0-20.0

Table 3-2. Dosage for boiler water treatment.

Parameter	Value
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, g/L	0.63
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, g/L	0.1
Na_2SO_3 , g/L	1.0

3.3 OPERATION OF THE RTC UNIT

Tap water is first introduced through the deionizer, to fill boiler water feed tank. Di-sodium phosphate and tri-sodium phosphate are added to water and mixed using the stirrer. Sodium sulfite must be added last, and stirring is stopped when it is dissolved and mixed well. Otherwise, the dissolved oxygen which is removed by sodium sulfite will again be built up by oxygen influx through the surface between water and air. The treated water is pumped into boiler until it reaches the required level. The boiler heater and steam line heaters are then energized.

The storage tank is filled with sludge, and mixed with both mixer and pumping through recycle line. The flow rate of the pump is set and checked it by taking a timed sample from the recycle line. Acid or base is added to the sludge tank according to the requirements of the experiment.

When the boiler pressure reaches its preset value, the sludge recycle valve is closed, and steam control valve is opened. Sludge and steam are injected into the reactor. As it mixes with steam, sludge is rapidly heated to a reaction temperature as high as 220°C.

The reaction temperature is maintained throughout the plug flow reactor. The reaction temperature is determined by the selected ratio of steam to sludge. In this RTC system, the retention time at high temperature can be as short as 10 seconds. As the sludge exits the reactor, it passes through a pressure let-down valve. The pressure drop to nearly atmospheric pressure causes the thermally conditioned sludge to vaporize partially, resulting in a temperature of about 100°C, thus quenching the reaction. The sludge is cooled further against cooling water in a heat exchanger to about room temperature. A three-way valve is used to switch thermally conditioned sludge either to a collection tank or drain.

In operation, the RTC unit meets all design criteria. It is able to treat sludge up to 1.5 L/min at 220°C with retention times from 10 seconds to 3 minutes. Intermittent plugging of the pressure let-down valve by sludge particles occurred. This caused intermittent fluctuation of pressure, even resulting in the opening of the safety relief valve during high pressure surges. This problem was solved by manual operation of the pressure let-down valve.

CHAPTER FOUR

DEWATERABILITY OF THERMALLY CONDITIONED SLUDGE

This chapter is devoted to assessing the dewaterability of thermally conditioned sludge by its centrifugeability and filterability. A mathematical model for batch centrifugation is developed. Sludge properties related to dewaterability, namely particle size distribution, density, and effect of polymer additive, are examined.

4.1 OBJECTIVE

Although an increase in biodegradability of PDS after RTC has been reported (Pierides, 1994; Garzon-Lopez, 1987), the effect of the RTC on dewaterability has not yet been investigated. This is true even though sludge dewaterability in most circumstances is of greater concern than biodegradability. Therefore, an investigation of dewaterability is a necessity for development of the RTC process. The objectives of this research are:

- (1) To determine the effect of thermal conditioning factors on sludge dewaterability.
- (2) To investigate the mechanism by which thermal conditioning affects sludge dewaterability.
- (3) To provide design criteria and performance data for sludge dewatering to be used in the implementation of the RTC process.

At present, the most prominent mechanical dewatering processes in wastewater treatment plants are filtration and centrifugation. In New York City WPCPs, only solid bowl centrifugation is used. Therefore, it is the primary focus of this study. Reliable sludge characterization methods are needed which can be used to predict the performance of plant centrifuges for different sludges as well as different operating conditions.

4.2 EXPERIMENTAL CONDITIONS

4.2.1 Sludge Source and Sample Processing

PDS (partially digested sludge), commonly known as digested sludge, was used for this study. It is the end product of biological treatment in New York City WPCPs, and the RTC process has the potential for being added to an existing plant to further treat it. PDS from Wards Island WPCP was mostly used. Some additional tests were made with PDS from the Newtown Creek and Rockaway plants.

Sludge was collected at the WPCP and transported in carboys to the City College laboratory within hours. Because fibers and coarse particles contained in the sludge cause plugging in the laboratory scale RTC system, sludges were sieved through a 20 mesh screen using a vacuum pump. Because PDS contains active bacterial cells, it must be processed quickly to avoid spontaneous alteration. Sludge samples were processed on the same day as collection or, at most, on the following day. Thermal conditioning was usually carried out in the continuous RTC reactor described above. Tests requiring a residence time in excess of several minutes were conducted in a batch reactor.

4.2.2 Rapid Thermal Conditioning (RTC)

For rapid heating and short retention time (usually 10 seconds), the continuous RTC unit shown in the Figure 3-1 was used. A total of 22 runs was made at the following conditions:

- (1) Thermal treatment temperature: room temperature, 100, 130, 160, 190, 220°C.
- (2) Retention time: 10 to 30 seconds.
- (3) pH: neutral, and 2 to 12.

In the RTC unit, continuously pumped sludge was heated by direct mixing with high temperature steam injected at a rate to achieve the target temperatures. When applicable, the pH values were adjusted in the sludge tank just before thermal conditioning. Most experiments were done in the RTC unit because of the associated improvement in sludge biodegradability.

Table 4-1. Ratio of steam to untreated sludge in laboratory RTC unit.

RTC temperature, °C	100	130	160	190	220
Ratio of steam to PDS	0.18	0.24	0.33	0.41	0.47

The temperature of the saturated steam from the boiler was about 250°C. The ratio of steam to PDS was adjusted as shown in Table 4-1 to achieve the target temperature. This results in different dilutions for each temperature tested. To eliminate this variation, all sludge samples were adjusted to the same water content as sludge conditioned at 220°C, which has the greatest dilution among treated samples.

4.2.3 Batch Thermal Conditioning

In addition to the RTC process, a slow heating batch conditioning process was used for comparison with retention times of 10 and 20 minutes. The batch thermal conditioning unit consists of a batch reactor and a fluidized bed heater. The reactor of 1 inch o.d.(outer diameter), 14 inches length, and 11 cubic inches (120 milliliters) volume is made of stainless steel SS-316. Considering expansion during heating, the reactor holds a maximum of 80 ml of sample. A K-type thermocouple was inserted and sealed into one end of the reactor. The other end is a threaded Swagelock cap which is easily removed for sample loading or unloading. The fluidized bed heater, Techne IFB-200, has a bath 20 by 9 inches with 12 inches working depth. The bath medium is aluminum oxide sand. It is heated electrically to a preset temperature and maintained at this temperature by a thermocouple actuated controller (Eurotherm type 101) within a limit of $\pm 5^{\circ}\text{C}$. The turbulence of fluidization assures uniformity of temperature in the bath.

When the reactor is submerged in the bath, the temperature of the sample inside the reactor rises quickly because of the high heat transfer coefficient in the fluidized medium. It takes about 2 minutes for sludge to reach a preset temperature of 100°C , and 4 minutes for 220°C . Reaction time is counted after the reactor temperature reaches its preset value. In order to reduce uneven temperature distribution in the reactor and to prevent local overheating, the reactor was shaken during the test. Thermal conditioning was terminated by lifting the reactor out of the bath and cooling it quickly in a water bath.

4.3 DEWATERABILITY TESTS

Thermal conditioning dissolves solids, and reduces the quantity of solids cake requiring dewatering. The dewatering properties of the remaining solids are also altered. Three methods are used to measure sludge dewaterability: The centrifugation test is for centrifugeability. The capillary suction time (CST) and pressure filtration tests are for filterability. These filtration tests have been widely used and comparatively mature. However, the centrifugeability test has not been developed. Although CST is sometimes used for this purpose, it may inadequately forecast sludge dewaterability by centrifugation. For this reason, a laboratory scale centrifugation test is necessary to measure sludge dewaterability at conditions which simulate the real processes.

Unconditioned PDS was tested to set a baseline, and sludges treated at a variety of conditions were examined. These are compared in terms of dewaterability, particle size distribution and density. Dewatering tests were performed the same day as thermal conditioning where possible. In case time was not sufficient, thermally conditioned sludge was preserved over night in a refrigerator set at 4°C to suppress biological activity. All dewatering tests were performed at room temperature, about 25°C.

4.4 MATHEMATICAL MODEL FOR CENTRIFUGEABILITY ASSESSMENT

4.4.1 Derivation of the Model

The purpose of the proposed model is to quantitatively describe centrifugation in a liquid-

solids system using a limited number of parameters. With a valid mathematical model, the prediction of centrifugeability in a commercial installation from measurements made on a desk-top centrifuge becomes possible.

In a centrifugation process, solids first settle and then compact. Cake is formed with a structure capable of supporting compression. Suppose equilibrium is reached after the centrifuge has been spinning at constant angular speed Ω , for some time. This means that the compaction of cake has ended, and there is no further flow of either solids or liquid. A force balance over an element of cake in cylindrical coordinates, shown in Figure 4-1, gives

$$d(rp_L) d\theta + d(rp_S) d\theta - 2(p_L + k_0 p_S) dr \sin\left(d\frac{\theta}{2}\right) - [\rho_L \epsilon + \rho_S \delta] r \Omega^2 dr d\theta = 0.$$

(4-1)

Where, p_L = hydraulic pressure, Pa

p_S = compressive pressure, Pa

δ = solidosity, solids volume fraction

ρ_L = density of liquid, kg/m³

ρ_S = density of solids, kg/m³

Ω = angular speed, rad/s

k_0 = ratio of lateral stress to normal compressive pressure of solids phase

r = radial distance, m

θ = angle, rad

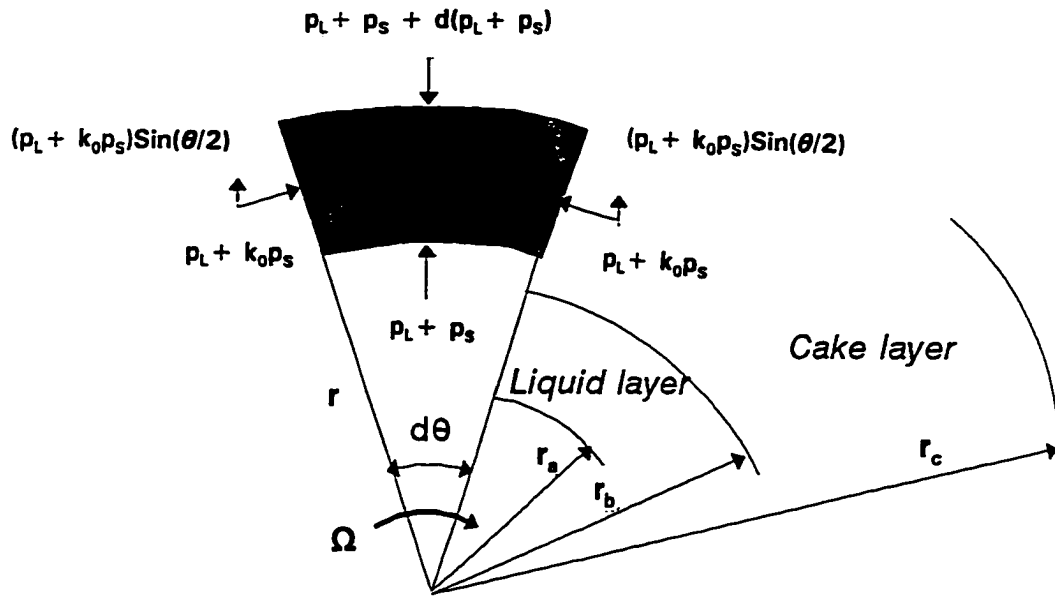


Figure 4-1. Forces on an element of centrifuged cake

Noting that $\sin(d\theta/2) \approx d\theta/2$, Equation (4-1) can be transformed to

$$\frac{dp_L}{dr} + \frac{dp_s}{dr} + (1 - k_0) \frac{p_s}{r} - (\rho_s \epsilon + \rho_L \delta) r \Omega^2 = 0. \quad (4-2)$$

The range of k_0 is between zero and 1, and is suggested to be between 0.4 to 0.6 (Sambuichi *et al.*, 1987). Equation (4-2) is for combined liquid and solid phases. To obtain a force balance for the liquid phase, let $p_s = 0$, $\epsilon = 1$, and $\delta = 0$ in Equation (4-2).

This gives

$$\frac{dp_L}{dr} - \rho_L r \Omega^2 = 0. \quad (4-3)$$

Subtracting Equation (4-3) from Equation (4-2) results in a force balance for the solids phase,

$$\frac{dp_s}{dr} + (1-k_0) \frac{p_s}{r} - (\rho_s - \rho_L) \delta r \Omega^2 = 0. \quad (4-4)$$

Equation 4-1 to 4-4 are a special case of the equations derived by Sambuichi *et al.*, (1987).

Analysis of the magnitude of the terms in Equation (4-4) leads to a simplification. In the range of $r_b \leq r \leq r_c$, the magnitudes of the parameters in Equation (4-4) are: $dp_s \sim p_c$, $dr \sim (r_c - r_b)$, $p_s \sim p_c$, $r \sim r_c$, and $(1-k_0) \sim 1$, where, p_c is the compressive pressure at the interface between cake and wall of centrifuge where radius $r = r_c$. Then the magnitude of first two terms of Equation (4-4) can be obtained by simply substituting for each parameter the equivalent magnitude parameter; they are $p_s/(r_c - r_b)$ and p_s/r_c . The third term of Equation (4-4) needs more work to evaluate. Considering that r_c is very large, the weight of cake is the normal stress at $r = r_c$, or

$$(\rho_s - \rho_L) \delta_a r_c \Omega^2 (r_c - r_b) = p_s. \quad (4-5)$$

Where δ_a is an average solidosity. From Equation (4-5), it can be seen that the third term in the Equation (4-4), $(\rho_s - \rho_L) \delta_a r_c \Omega^2$ has a magnitude of $p_s/(r_c - r_b)$, which is the same magnitude as the first term. Because the thickness of cake is much less than the radius of centrifuge, or $(r_c - r_b) \ll r_c$, the magnitude of the second term is much smaller than that of first and third term, and can be neglected. Therefore, Equation (4-4) becomes

$$\frac{dp_s}{dr} - (\rho_s - \rho_L) \delta r \Omega^2 = 0. \quad (4-6)$$

In Equation (4-6), cake solids fraction, δ , is a function of compressive pressure. For compressive filtration, Tiller *et al.* (1980) selected an empirically formulated revised power function, among several functions such as polynomial, power and exponential one.

$$\delta = \delta_0 \left(1 + \frac{p_s}{p_0}\right)^\lambda \quad (4-7)$$

Where, δ_0 = dimensionless compressibility coefficient

λ = dimensionless compressibility exponent

p_0 = constant, Pa

Substituting Equation (4-7) in (4-6) results in

$$\frac{dp_s}{dr} - (\rho_s - \rho_L) \delta_0 \left(1 + \frac{p_s}{p_0}\right)^\lambda r \Omega^2 = 0. \quad (4-8)$$

Equation (4-8) is a first order differential equation. It has one boundary condition which is that the compressive pressure equals zero at the cake surface, e. g., $p_s = 0$ at $r = r_b$.

The analytical solution of Equation (4-8) can be obtained. Two cases, for λ equal to or not equal to one, must be considered separately. Consider first the general case where λ is not unity. The solution is

$$p_s(r) = p_0 \left[\left[1 + \frac{1}{2p_0} (1-\lambda) (\rho_s - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2) \right]^{\frac{1}{1-\lambda}} - 1 \right]. \quad (4-9)$$

Substitution of Equation (4-9) into (4-7) gives the solids volume fraction as a function of radius,

$$\delta(r) = \delta_0 \left[1 + \frac{1}{2P_0} (1-\lambda) (\rho_s - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2) \right]^{\frac{\lambda}{1-\lambda}}. \quad (4-10)$$

The solids volume fraction averaged over the cake is

$$\delta_{ave} = \frac{2 \int_{r_b}^{r_c} \delta(r) r dr}{r_c^2 - r_b^2}. \quad (4-11)$$

To substitute Equation (4-10) into (4-11), and to use operating parameter $\Psi = \Omega^2(r_c^2 - r_b^2)$ lead to

$$\delta_{ave}(\Psi) = \frac{2P_0 \left[\left(1 + \frac{1}{2P_0} (1-\lambda) (\rho_s - \rho_L) \delta_0 \Psi \right)^{\frac{1}{1-\lambda}} - 1 \right]}{(\rho_s - \rho_L) \Psi}. \quad (4-12)$$

Operating parameter can be written as $\Psi = \Omega^2 \tau (2r_c - \tau)$, where cake thickness $\tau = r_c - r_b$. It represents all centrifugation process parameters: centrifuge diameter, rotation speed, and cake thickness. It is clear that cake solids concentration not only simply depends on g force, which is $\Omega^2 r_c$, but also on cake thickness. In the laboratory test, centrifuge rotation speed and cake solids concentration are dependent. Fortunately, we are able to group them together to reduce to a single variable.

For a liquid-solids system where voidage can be easily measured, either Equation (4-10) or (4-12) can be used to fit data, obtaining model constants through regression. However, for sludge, cake solids concentration is easier to measure than solids voidage; furthermore, it is the most important concern of dewatering. Therefore, a solids concentration distribution is more convenient to use. By definition, solids concentration of cake, γ , is the solids mass fraction of cake, or

$$\gamma = \frac{\delta \rho_s}{\rho_c} . \quad (4-13)$$

The cake density ρ_c can be expressed as

$$\rho_c = \delta \rho_s + (1 - \delta) \rho_L . \quad (4-14)$$

Combination of Equation (4-13) and (4-14) results in

$$\gamma = \frac{1}{1 + \frac{\rho_L}{\rho_s} (\delta^{-1} - 1)} . \quad (4-15)$$

Substitution of Equation (4-10) into (4-15) leads to the distribution of cake solids mass fraction,

$$\gamma(r) = \frac{1}{1 + \frac{\rho_L}{\rho_s} \left[\frac{1}{\delta_0} \left[1 + \frac{1}{2P_0} (1 - \lambda) (\rho_s - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2) \right]^{-\frac{\lambda}{(1-\lambda)}} - 1 \right]} . \quad (4-16)$$

The average cake solids mass fraction of the cake is

$$\gamma_{ave} = \frac{2 \int_{r_b}^{r_c} \gamma(r) r dr}{r_c^2 - r_b^2} . \quad (4-17)$$

If Equation (4-16) is substituted into Equation (4-17), a general analytical solution is not available. However, γ_{ave} can be expressed approximately in a simple way. To apply Equation (4-13) and (4-14) to the overall cake, three parameters in these equations, ρ_c , γ and δ can be replaced by average values. Then, an equation similar to Equation (4-15) is obtained as

$$\gamma_{ave} = \frac{1}{1 + \frac{\rho_L}{\rho_S} (\delta_{ave}^{-1} - 1)} . \quad (4-18)$$

Substitution of Equation (4-12) into (4-18) results in

$$\gamma_{ave}(\psi) = \frac{1}{1 + \frac{\rho_L}{\rho_S} \left[\frac{(\rho_S - \rho_L) \psi}{2p_0 \left[\left(1 + \frac{1}{2p_0} (1-\lambda) (\rho_S - \rho_L) \delta_0 \psi \right)^{\frac{1}{1-\lambda}} - 1 \right]} - 1 \right]} . \quad (4-19)$$

Either Equation (4-16) or Equation (4-19) may be used for regression of experimental data to obtain the three parameters of the model. The former is used for the data of solids mass fraction verses radial distance at a fixed angular speed. The later is used for average solids mass fraction as a function of angular velocity. Also, the former is exact while later is an approximation.

The case of $\lambda = 1$ is a special case almost impossible to obtain from a regression of test data unless it is set to unity in some cases as an approximation. In that case, the solution of Equation (4-8) is

$$p_S(r) = p_0 \left(e^{\frac{1}{2p_0} (\rho_S - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2)} - 1 \right) . \quad (4-20)$$

Then, substitution of Equation (4-20) into (4-7) gives

$$\delta(r) = \delta_0 e^{\frac{1}{2p_0} (\rho_S - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2)} . \quad (4-21)$$

And, substitution of Equation (4-21) into (4-11) gives

$$\delta_{ave} = \frac{2p_0}{(\rho_s - \rho_L) \Psi} (e^{\frac{1}{2p_0} (\rho_s - \rho_L) \delta_0 \Psi} - 1) . \quad (4-22)$$

Substitution of Equation (4-21) into (4-15) leads to the distribution of cake solids mass fraction,

$$\gamma(r) = \frac{1}{1 + \frac{\rho_L}{\rho_s} \left[\frac{1}{\delta_0} e^{-\frac{1}{2p_0} (\rho_s - \rho_L) \delta_0 \Omega^2 (r^2 - r_b^2)} - 1 \right]} . \quad (4-23)$$

Unlike the case of λ not unity, Equation (4-17) now admits an analytical solution. Because of its length, it is not listed here. By the same method as used to derive Equation (4-19), substituting Equation (4-22) into (4-18) gives a simple form of γ_{ave} ,

$$\gamma_{ave}(\Psi) = \frac{1}{1 + \frac{\rho_L}{\rho_c} \left[\frac{(\rho_s - \rho_L) \Psi}{2p_0 (e^{\frac{1}{2p_0} (\rho_s - \rho_L) \delta_0 \Psi} - 1)} - 1 \right]} . \quad (4-24)$$

4.4.2 Determination and Interpretation of Model Parameters

Three parameters, δ_0 , λ , and p_0 , which relate to sludge compressibility, are contained in the model. Equation (4-19) or (4-16) can be used first to regress experimental data from centrifugation tests to obtain these parameters. The case of $\lambda=1$ being met by experimental data is highly improbable. However, it may be used in an approximation or simplification of the model.

The physical meaning of the parameter δ_0 is that it is the solidosity of the cake at zero

compressive pressure, as may be seen in equation (4-7) when p_s equals 0, δ equals δ_0 (though zero compressive pressure upon cake is never a reality). Parameters λ and p_0 depict the cake's sensitivity to compaction. Cake with a higher λ and lower p_0 is more sensitive to compressive pressure.

As the model involves empirical parameters, it has certain limitations. The parameters are strictly valid only within the range from which they are obtained through regression. In other words, the parameter may only be valid piecewise.

4.4.3 The Effect of Thermal Conditioning on Sludge Cake

The cake solids concentration is the most important index of the dewatering process. From equation (4-19), the parameters affecting cake solids concentration are:

- Centrifuge radius, r_c
- Operating parameters, Ω and τ
- Characteristics of liquid, ρ_L
- Characteristics of solids, ρ_s
- Characteristics of cake, δ_0 , λ , and p_0

Thermal conditioning of sludge can only affect the last two groups of parameters, which are solids density and cake compressibility. This means that the combination of these two kinds of factors, solids density and cake compressibility determines the cake solids concentration.

Typical parameters for centrifugation in wastewater treatment plants are 2500 g (gravitational acceleration) force and 15 to 30 minutes of solids retention time (Trionfetti, 1992). These conditions can be simulated using a desk-top centrifuge. The major difference between plant scale and desk-top centrifuges is the process of conveyance used in the former one, which compacts the cake and dries product (Reif and Stahl, 1989). Therefore, results on cake solids concentration obtained from a desk-top centrifuge are conservative.

4.5 MEASUREMENT APPARATUS AND PROCEDURES

4.5.1 Solids Distribution

Solids measurements were made according to Standard Methods for the Examination of Water and Wastewater, APHA, (1992). Total solids were determined gravimetrically for samples after drying overnight at 103°C. Filtration has been used to classify solids into suspended solids and dissolved solids. Solids passing a filter with average approximately 1 μm pore size are classified with dissolved solids. Solids remaining on the filter are called suspended solids. Each category of solids is then classified into volatile solids and fixed solids. Solids that volatilize at 550°C are called volatile solids, and those remaining are fixed solids.

4.5.2 Specific Resistance to Filtration (SRF)

A Baroid Low Pressure Filter Press (Figure 2-3) was used to perform the filtration test.

The filter cylinder has a diameter of 3 inches and height of 3½ inches. The effective area of filter is 7.1 square inches. The filter paper is 3½ inches specially hardened filter paper for the Baroid Low Pressure Filter Press manufactured by Fann.

The test is started by pouring a 25 ml sludge sample into the filter chamber. After tightening the cap of the filter cylinder, compressed nitrogen or carbon dioxide gas (at the pressure usually of 100 psig, controlled by a gas regulator) is introduced to force the filtrate out of the sludge sample. The volume of filtrate is recorded at selected intervals until the pressure breaks. These are used to calculate SRF defined in Equation 2-1.

Among the parameters needed in Equation 2-1 is the viscosity of filtrate. This was measured using a Gilmont Falling Ball Viscosimeter. However, as an approximation, it can be set equal to the viscosity of water.

4.5.3 Capillary Suction Time (CST)

The CST unit is a Triton CST Filterability Tester Model 200 schematically shown in the Figure 2-2. The stainless steel collar that serves as a reservoir for the sludge has an inner diameter of 1.8 cm, and a height of 2.5 cm. The absorbent filter paper that is put underneath the collar is 7 cm by 9 cm. The test is started by pouring a sludge sample into the collar. The capillary suction pressure of the filter paper drives the filtrate from sludge. The time required for the filtrate to pass across two probes is recorded as CST time.

4.5.4 Centrifugation

A Marathon 10K model centrifuge (Fisher Scientific) was used for the centrifugation test which, in this study, is considered to be a tentative method for the evaluation of a sludge's susceptibility to dewatering by this means. It has a spin diameter of 32 cm and maximum speed of 9,200 rpm. The centrifugal force is established by setting the appropriate rotation rate. Sludge samples were first put in plastic bottles, then the bottles were placed into the holders in the centrifuge.

There are two parameters of interest in centrifugation, the concentration of compacted solids cake and the clarity of centrate (Vesilind, 1995). Accordingly, two indices can be established. The first is sludge solids concentration of the cake. This is a measure of cake solid compressibility and would affect the disposal cost. The second is suspended solids recovery, the mass ratio of suspended solids in the cake to that in original sample. It is a measure of solids removal efficiency and would affect the quality of the liquor discharge. The suspended solids recovery, R , is calculated by Equation 4-25 derived from a mass balance of suspended solids over the centrifuge.

$$R = \frac{C_s (C_f - C_c)}{C_f (C_s - C_c)} \quad (4-25)$$

where, C_s = suspended solids concentration of cake, percent
 C_f = suspended solids concentration of feed, percent
 C_c = suspended solids concentration of centrate, percent
 R = suspended solids recovery, percent SS

During centrifugation tests, 150 ml sludge samples were put in plastic bottles of 5-cm diameter and centrifuged for 20 minutes. Centrifugal force and duration time have to be set first to provide a standard conditions. They are chosen to be reasonably similar to those occurring in the wastewater treatment plant, 2,500 gravity force and 15 to 30 minutes retention time for the sludge cake (Trionfetti, 1992).

After centrifugation, centrate was carefully poured out, and the last part of centrate drained from the bottle discarded since it contained solids resuspended into the centrate form disturbance of the cake. Among the suspended solids concentrations in Equation (4-25), C_r and C_c were measured by the methods described in the Section 4.5.1. While C_s is approximated by total solids in the cake. This would overestimate cake solids concentration, but underestimate solids recovery rate according to Equation (4-25). However, since C_s is much higher than C_c or C_r , the error caused by the approximation can be ignored.

In testing the mathematical model, thicker and larger cake layers were needed to ensure parameter accuracy. Sludge samples were pre-thickened with a g force less than that set for the test; the cakes were then combined for the centrifugation test, in which 200-ml sludge samples were put in plastic bottles of 250 ml. The g force was changed and used as a variable.

4.5.5 Particle Size Distribution

Particle size distribution was measured using a Malvern System 2600 laser particle size

analyzer, which operates on the principle of laser ensemble light scattering. This system employs conventional Fourier optics shown diagrammatically in Figure 4-2. Light from a low power helium-neon laser is used to form a collimated and monochromatic beam. Any particles present within the analyzer beam will scatter this light. The scattered light and unscattered remainder fall onto a receiver lens. A detector, in the form of 31 concentric annular sectors, gathers the scattered light over a range of scattering angles. The unscattered light is brought to a focus on the detector and passes through a small aperture in the detector and out of the optical system; this is monitored to determine sample volume concentration. When a particle scatters light, it produces a unique light intensity variation with angle of observation. Particle size is determined by relating the measured peak at an established scattering angle. Large particles have peak energies in small angles of scatter, and vice versa, as shown in Figure 4-2. The detector thus provides an electrical output signal proportional to light energy measured over 31 separate angles of collection. The computer reads those signals and performs time averaging to give particle size distribution as well as other statistical data. A schematic of the laser particle analyzer is shown in Figure 4-3.

It should be noted that the mean particle size will be computed only using particles measurable to the particle analyzer. They range from 1.2 to 1880 μm . This upper limit covers the maximum particle size in sludge passing a 20-mesh sieve (which has an opening size of 840 μm). However, the lower limit, 1.2 μm , excludes "dissolved solids" in this study. These dissolved solids can be further classified as colloidal solids (1 $\text{m}\mu\text{m}$ to 1 μm) and soluble solids ($< 1 \text{ m}\mu\text{m}$).

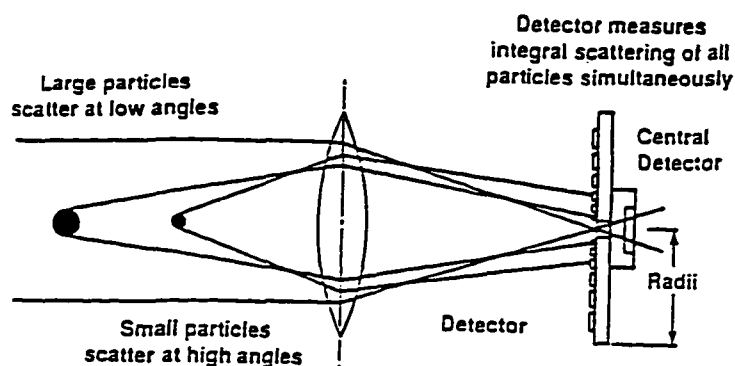


Figure 4-2. Properties of scattered light

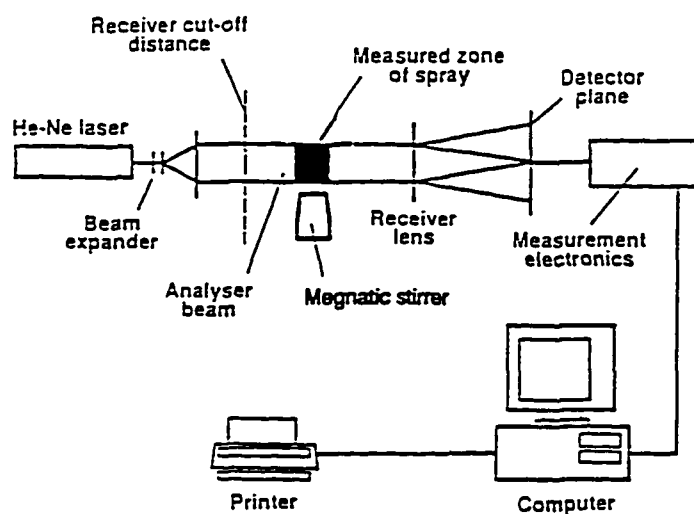


Figure 4-3. System scheme of laser particle size analyzer

4.5.6 Solids Density

By Archimedes' principle, if a submerged object has the same density as the fluid medium, it will keep its original state of motion in the medium. This principle was applied to the measurement of sludge particle density. An aqueous solution of cesium chloride (CsCl) was made to have a specific density varying from 1.2 to 1.9, in 0.1

intervals. To prevent further dilution of the CsCl solution, sludge was first thickened by centrifugation before taking sludge samples. To avoid rupture of the solids being thickened, a low g force of 100 was used for 5 minutes centrifugation time. The thickened sludge was collected and stirred to obtain an evenly mixed sample. Then about 0.2 ml of sample was injected slowly into 14-ml tubes that contained 6 ml of CsCl solution and were set vertically in a rack. Observations were made within 10 minutes in order to determine the sludge particle density. Longer contact time might cause errors of measurement due to diffusion of CsCl into sludge particles and flocs, giving erroneously high densities.

4.5.7 Sludge Settling Velocity

The basic principle of sludge settling in a centrifuge is similar to that of sludge thickening using a gravity thickener. In gravity thickening, the driving force is gravity acceleration while in centrifugation the gravity force is replaced by centrifugal force. As suspended solids in the sludge are concentrated into a cake in a centrifuge, the solids undergo not only settling but also compression. Therefore, both settleability and compressibility of sludge must be investigated. To assess settling of suspended solids, polymethylpentene tubes with a volume of 15 ml and an inner diameter of 14.5 mm were used. A 14-ml sludge sample was placed in each tube, and centrifuged in a Marathon 10K centrifuge as described in Section 4.5.4. The g force was changed by progressive increments. At intervals during the test, the tubes were taken out of the centrifuge to record the position of the interface between the supernatant fluid and the sludge blanket. The acceleration period, i.e., the time for the centrifuge to reach a preset speed, was as

short as 10 to 20 seconds. The deceleration time, the time for the centrifuge to stop, was much longer, but was not counted as part of centrifugation time.

4.5.8 Jar Test

The effect of polymer on the dewaterability of thermally conditioned sludge was further investigated in a jar test apparatus. Polymer conditioned sludge was prepared using 500 ml of thermally conditioned PDS with a solids concentration of 1.6 percent placed in each of six jars. According to the instructions from Percol polymer's manufacturer, Allied Colloids, polymers were diluted to 1 percent active solution and then applied to sludge. Sludge samples were put in 100-ml beakers and stirred by magnetic stirrer while polymer solutions were added slowly. Sludges were mixed rapidly for 1 minute to ensure complete dispersion of the polymers, then mixed slowly for 15 minutes to aid the formation of flocs. The sludge was next allowed to settle for about 20 minutes before the dewatering test.

4.6 RESULTS AND DISCUSSION

4.6.1 Solubilization

Sludge solids are commonly categorized into four types: volatile suspended solids (VSS), volatile dissolved solids (VDS), fixed suspended solids (fixed SS), and fixed dissolved solids (fixed DS) (Standard Methods, 1989). Dewatering processes are designed to capture suspended solids, while leaving the dissolved solids in the supernatant liquid.

Reduction of suspended solids through solubilization will lead to a reduction (in weight and volume) of the dewatered cake. With thermal conditioning, suspended solids solubilize, becoming dissolved solids. Solubilization of sludge solids during thermal conditioning is characterized by the solids distribution shown in Figure 4-4. In PDS, dissolved solids consists of 7 percent total solids (TS), and VDS approximately 3 percent TS. Solubilization of solids increases with conditioning temperature. At 220°C, 47 percent of the solids in PDS are dissolved, a six-fold increase. Volatile dissolved solids increase more than 10 times, while fixed dissolved solids increase less than one time. Solubilized solids come predominantly from volatile solids, leaving the fixed suspended solids relatively intact. Volatile solids are considered biodegradable, and can be further reduced by digestion. When, at 220°C, the RTC time is extended to 30 seconds from 10 seconds, solubilization of solids increases slightly to 49 percent from 44 percent, as shown in Figures 4-5. If dewatering occurs immediately after thermal conditioning, a significant reduction in sludge cake would be realized at the expense of a higher strength side stream, which would need further treatment.

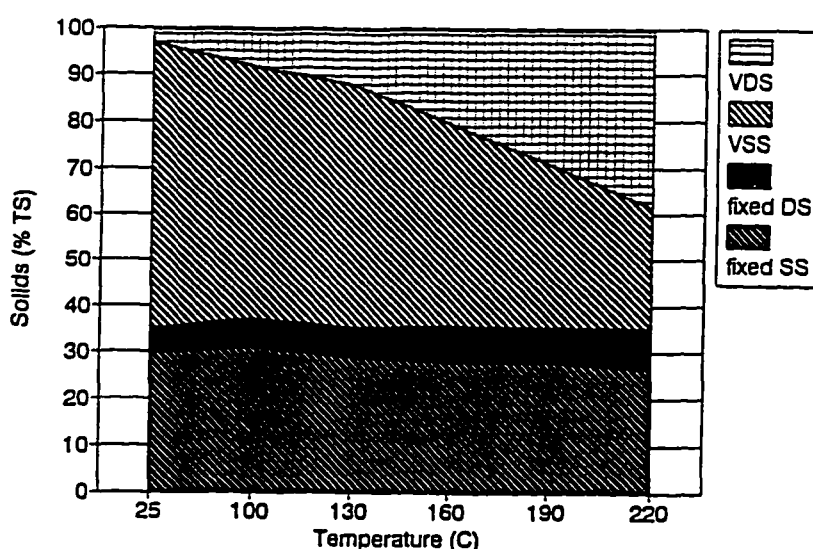


Figure 4-4. Solids distribution of rapid thermally conditioned PDS (10 seconds)

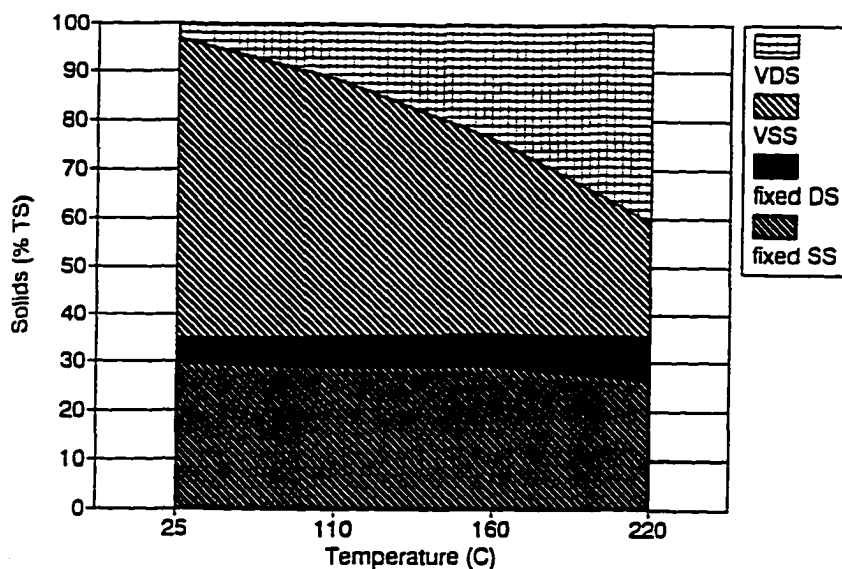


Figure 4-5. Solids distribution of rapid thermally conditioned PDS (30 seconds)

Figures 4-6 and 4-7 show the solubilization of volatile solids and fixed solids of PDS respectively from three WPCPs with various solids concentrations from 1.4 to 4.9 percent. The characteristics of sludge solids at room temperature serve as a baseline. The difference between the amount of suspended solids and baseline is the solubilization resulted from RTC. These figures show that solubilization occurs predominantly from volatile solids. It is a function of the operating temperature of the RTC reactor. Figure 4-6 and 4-7 also show that solubilization of suspended solids is independent of solids concentration in the tested range. However, solubilization depends on the characteristics of PDS. With the same thermal conditioning, PDS from the Newtown Creek plant showed much less solubilization than PDS from either the Wards Island plant or the Rockaway plant. Solubilization for WAS due to RTC at 220°C reached 55 percent of TS, higher than that for PDS.

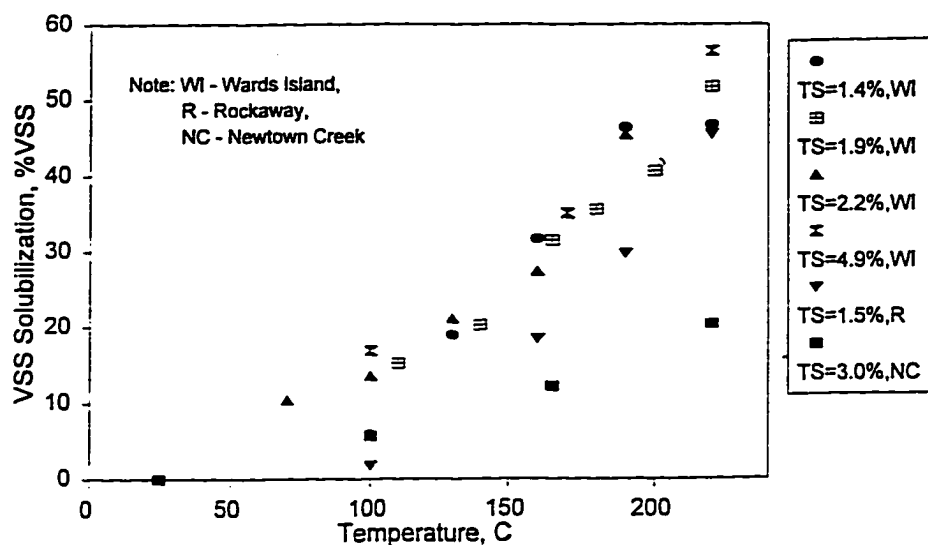


Figure 4-6. Solubilization of VSS of rapid thermally conditioned PDS

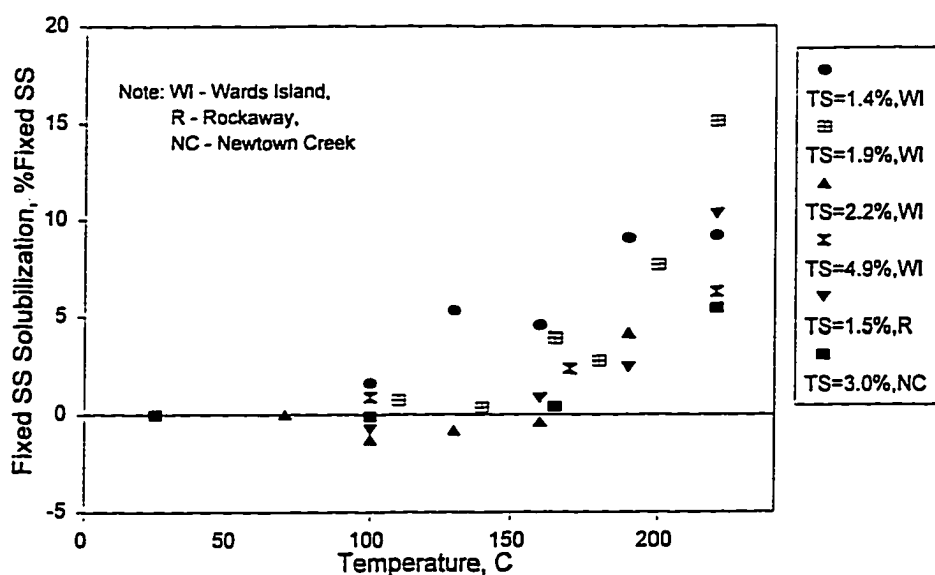


Figure 4-7. Solubilization of fixed SS of rapid thermally conditioned PDS

Acids and alkalis can act as catalysts in hydrolysis processes. The effect of addition of acids and alkalis during rapid thermal conditioning was also evaluated. For acid conditioning, hydrochloric acid was used to adjust pH to 2. Figure 4-8 shows that solubilization of PDS increased substantially even at room temperature. Lower pH resulted in higher solubilization. Higher temperature also favored higher solubilization.

For base conditioning, sodium hydroxide was used to adjust pH to 12. Sodium hydroxide, being nonvolatile, contributes to the total fixed solids in the sample and cake. Therefore, the data was processed to subtract the mass of sodium hydroxide from the solids. Figure 4-9 shows that base conditioning also enhanced the solubilization of sludge solids at the room temperature. Solubilization also increased with temperature.

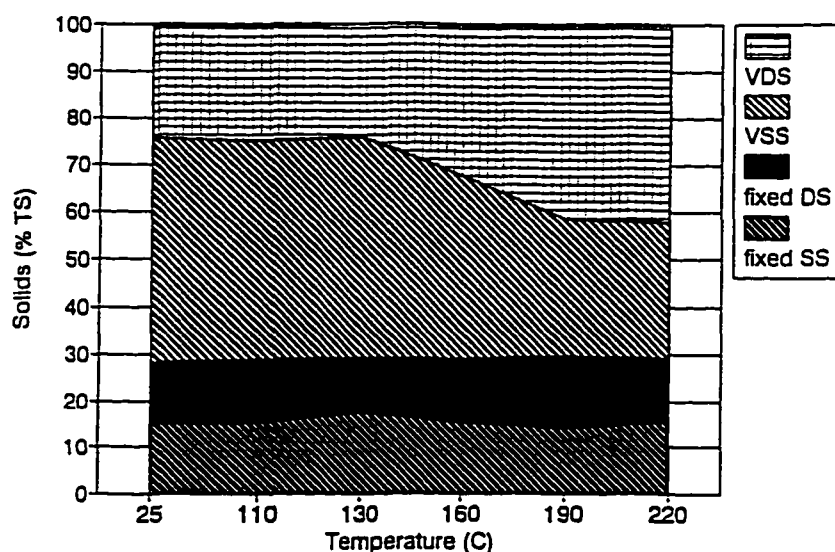


Figure 4-8. Solids distribution of rapid thermally conditioned PDS (pH=2)

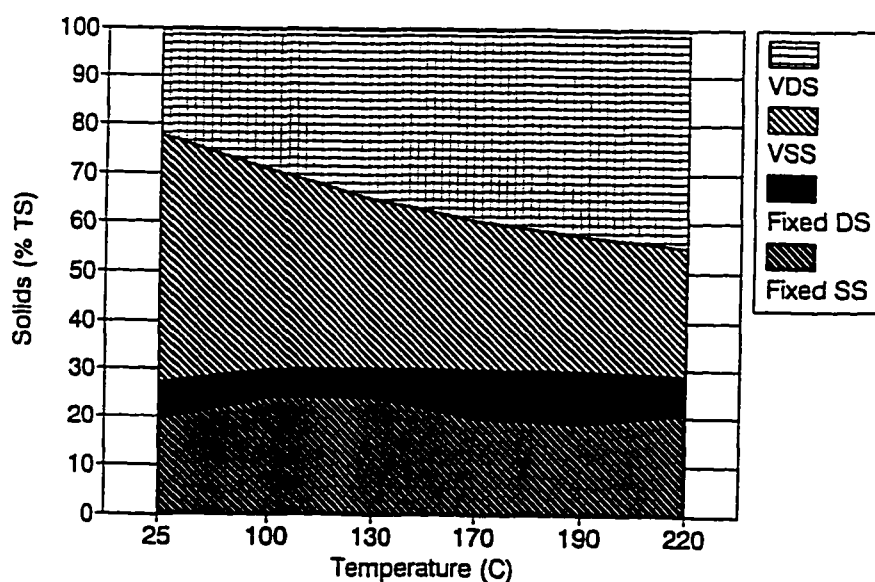


Figure 4-9. Solids distribution of rapid thermally conditioned PDS (pH=12)

The difference in solubilization between neutral pH and base or acid conditioning diminished as conditioning temperature increased, and was eventually insignificant at 220°C. This suggests an upper limit for solids solubilization.

4.6.2 Filterability of RTC Sludge

4.6.2.1 CST Test

Essentially, CST is the travel speed of filtrate in the filter paper, which depends largely on the dewaterability of sludge. Sludges with shorter CSTs are supposed to be more readily dewaterable. The results of the CST test for the sludge with an unmodified pH (pH=7.4) are shown in Figure 4-10, along with results for other pH values. High temperature conditioning of PDS with neutral pH resulted in longer CST, indicating a poor dewaterability with capillary suction. The explanation is that thermal conditioning produces fine particles that block the flow passages.

The pH also affected CST tests. At room temperature, a decrease in pH alone would reduce the CST. In addition, and in contrast to the results for sludge with unmodified pH, thermal conditioning reduced the CST of sludge with pH adjustment. However this reduction occurred only at temperatures above 130°C. At high temperature, sludge with unmodified pH has the longest CST. Over the range of temperature tested, acidified sludge always has shorter CST than sludge with unmodified pH and alkalized sludge (see Figure 4-10). Acid addition may effectively destroy the gel-like structure of sludge solids during RTC, resulting in improved filterability.

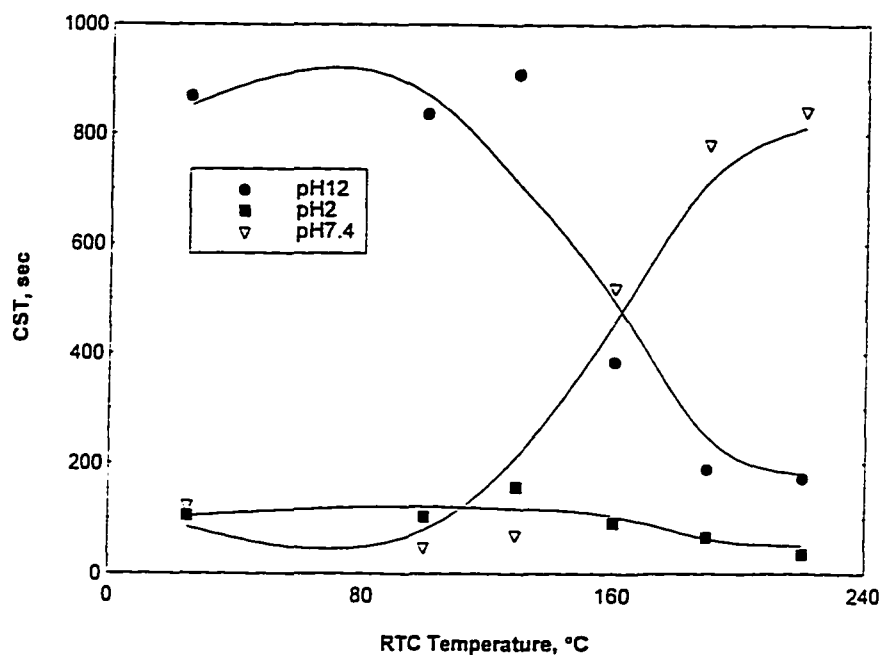


Figure 4-10. CST of rapid thermally conditioned PDS

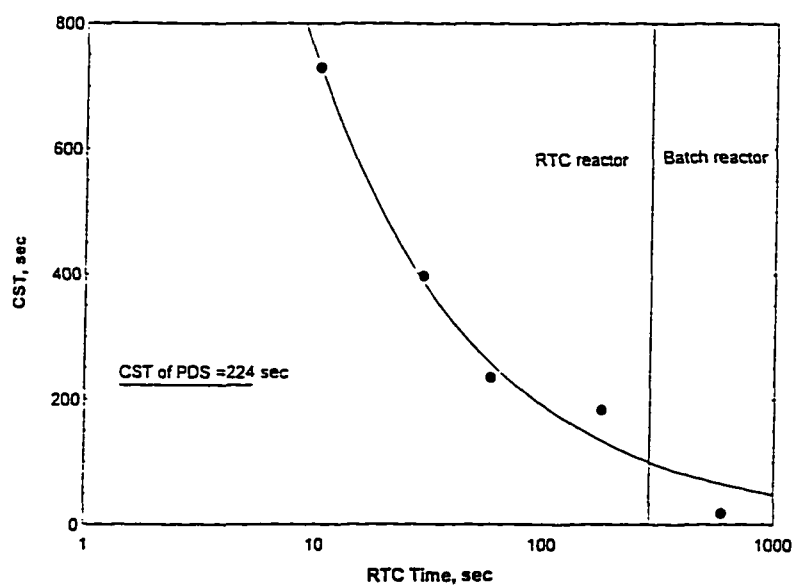


Figure 4-11. CST of thermally conditioned PDS

Figure 4-11 shows the CST test results of PDS thermally conditioned at 220°C. Only when retention time is longer than one minute does the CST drop below that of unconditioned PDS. Batch thermal conditioning at long retention time results in much lower CST than RTC.

4.6.2.2 SRF Test

The filtration curves of t/V versus V for unmodified PDS are shown in Figure 4-12. It reveals a nonstandard filtration cycle. A straight line of t/V versus V is the standard model of filtration. The curve in Figure 4-12 does not conform to that model.

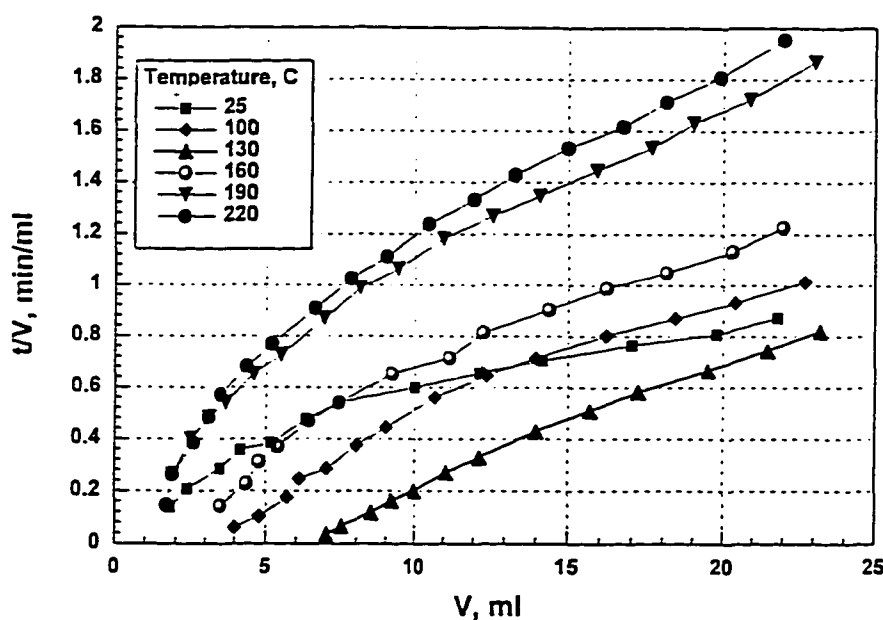


Figure 4-12. Filtration test of rapid thermally conditioned PDS

Cake can be formed by sedimentation or/and filtration. According to Christensen and Dick (1985), a steeper initial slope reflects sedimentation, and a following straight line represents pure filtration. For unconditioned PDS, the initial slope is not steep, and sedimentation is comparable to filtration. This suggests the a concomitant sedimentation and filtration. For PDS conditioned at 130°C, drainage of liquid took place prior to the formation of cake. This is due to the formation of particle agglomerates at that temperature, which makes it easier for the inter floc water to drain. However, the water within agglomerates is more strongly held. For PDS conditioned at 190 and 220°C, the

initial stage of filtration shows a steeper slope. This pattern is caused by sedimentation prior to filtration. The centrifugal settling tests confirm that higher temperature RTC result in more rapid sedimentation. The results of filtration tests for rapid thermally conditioned sludge at pH2 and pH12 are shown in Figure 4-13 and 4-14 respectively.

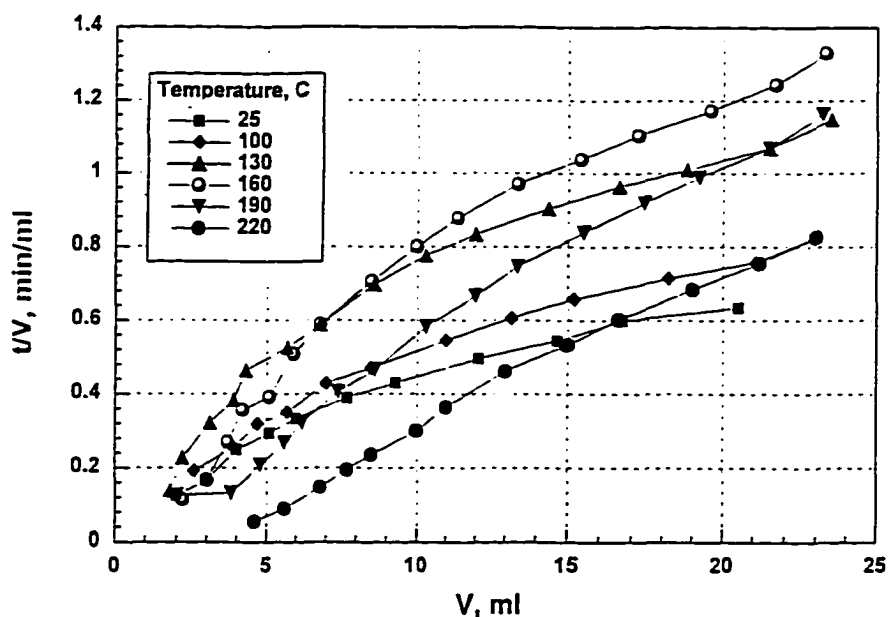


Figure 4-13. Filtration test of rapid thermally conditioned PDS (pH=2)

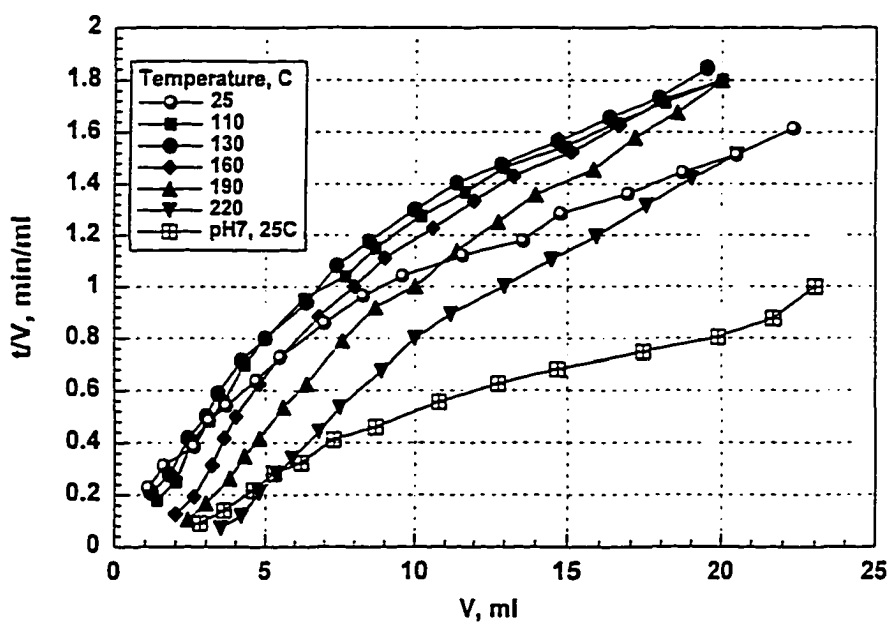


Figure 4-14. Filtration test of rapid thermally conditioned PDS (pH=12)

The SRFs are obtained by linear regression of the curves in Figure 4-12, 4-13 and 4-14. They are average values, and are shown in Figure 4-15. Rapid thermally conditioned sludge with unmodified pH always had a higher SRF than untreated sludge. Higher temperature results in higher SRF, which was caused by fine particles produced by RTC.

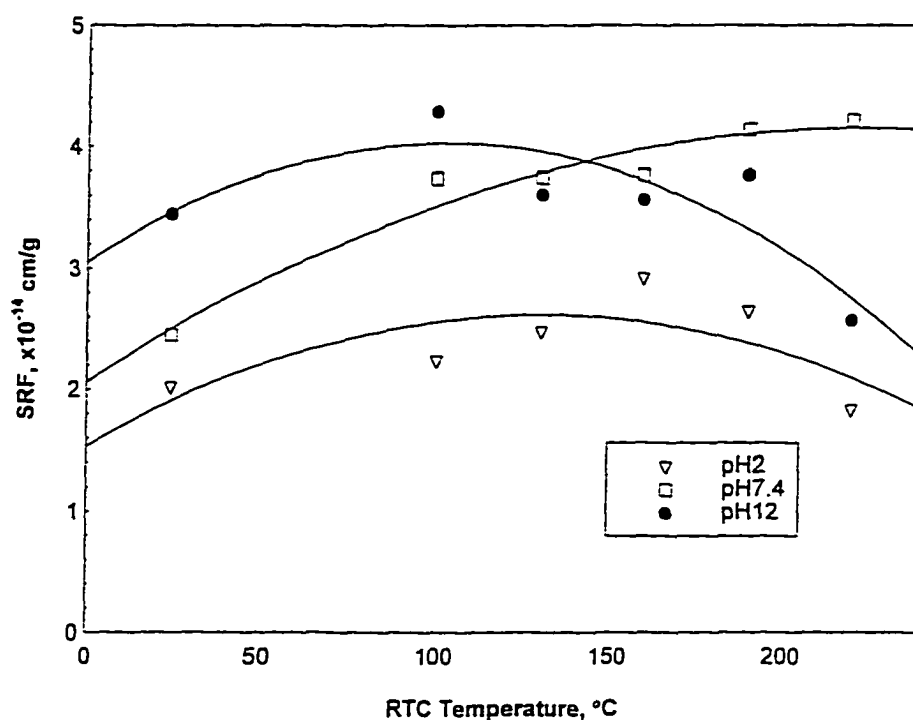


Figure 4-15. SRF of rapid thermally conditioned PDS

Generally speaking, for the sludge with pH of 2 and 12, high pH caused higher SRF; and higher RTC temperatures below 190°C also result in higher SRF. However, when RTC temperature goes above 190°C, SRF decreases. Figure 4-16 shows that batch thermal conditioning at long retention time results much in lower SRF than RTC. All of these results qualitatively support those from CST (see Figure 4-10). Since the CST and filtration depend on the same mechanism, filtrate passing through a solids cake medium, it is not surprising to see this agreement of results.

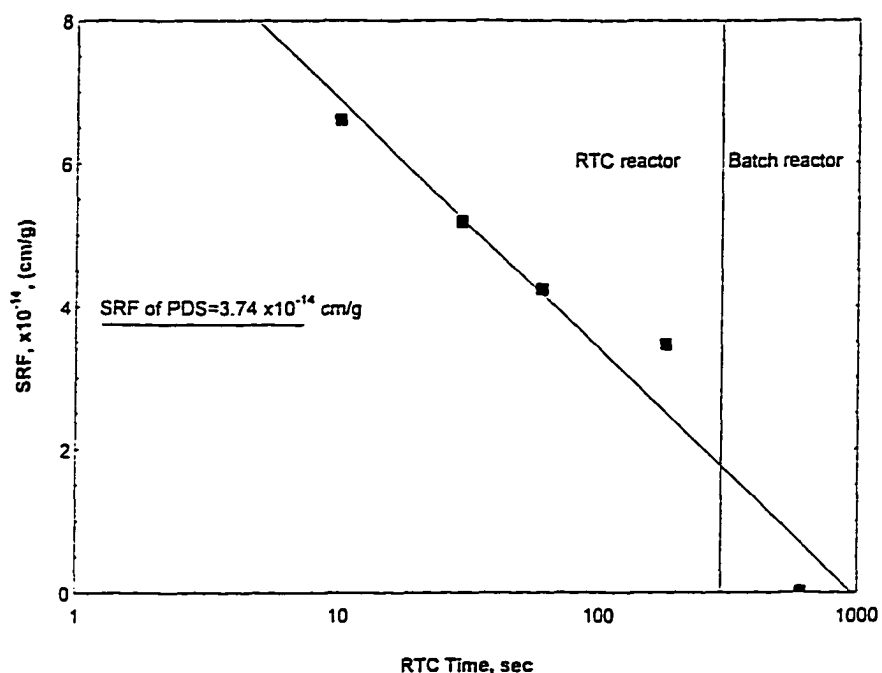


Figure 4-16. SRF of thermally conditioned PDS

Table 4.2. Viscosity of filtrate of rapid thermally conditioned PDS, 25°C.
(Units: centipoise)

Temperature (°C)	25	100	130	160	190	220	25 (pH=7.4)
pH=2	1.00	1.06	1.24	1.08	1.12	1.22	1.14
pH=7.4	1.00	1.10		1.05		1.14	1.00
pH=7.4	1.17	1.06	1.06	1.06	1.02	1.03	1.17
pH=12	1.14	1.14	1.28	1.24	1.17	1.35	1.26

The results of the viscosity test are shown in Table 4-2. The viscosity data are average values of two measurements. The measurement error of the instrument could be as high as 20 percent. Although the viscosity variation of sludge filtrate samples is not great and

just falls within the range of measurement error, a slight increase in viscosity with increasing temperature of thermal conditioning can still be seen. The reason for this may be that higher temperature causes more material to be dissolved in the liquid phase. However, the changes in sludge filtrate viscosity under the conditions of this test are minor and have negligible effect on either filtration or centrifugation.

4.6.3 Centrifugation Dewatering Test

4.6.3.1 Suspended Solids Recovery and Cake Solids Concentration

In a centrifuge, four types of forces are involved: centrifugal body force, frictional drag force due to the relative motion of the liquid with respect to solids, an arching effect caused by radial geometry, and inter-particle stress resisting compaction (Tiller and Hsyung, 1993). These are basic forces existing in all types of centrifuge. Differences in dewatering are due to several circumstances. First, the conveying process in full-scale centrifuges compacts the cake and results in a drier product (Reif and Stahl, 1989). Second, at the discharge point of a field centrifuge, where sludge cake is gradually pushed up along a conical section, it emerges from centrate and centrifugal force further drains water from the matrix of sludge cake solids. However, in the laboratory test, sludge cake always remains immersed in liquid, and inter-floc water cannot be drained. This increases the water content of sludge cake. Third, probably most important, is that cakes formed in the bottom of the bottle are thin, varying approximately from 5 to 20 mm, much thinner than that in a plant centrifuge. This results in a low average solids concentration in the cake.

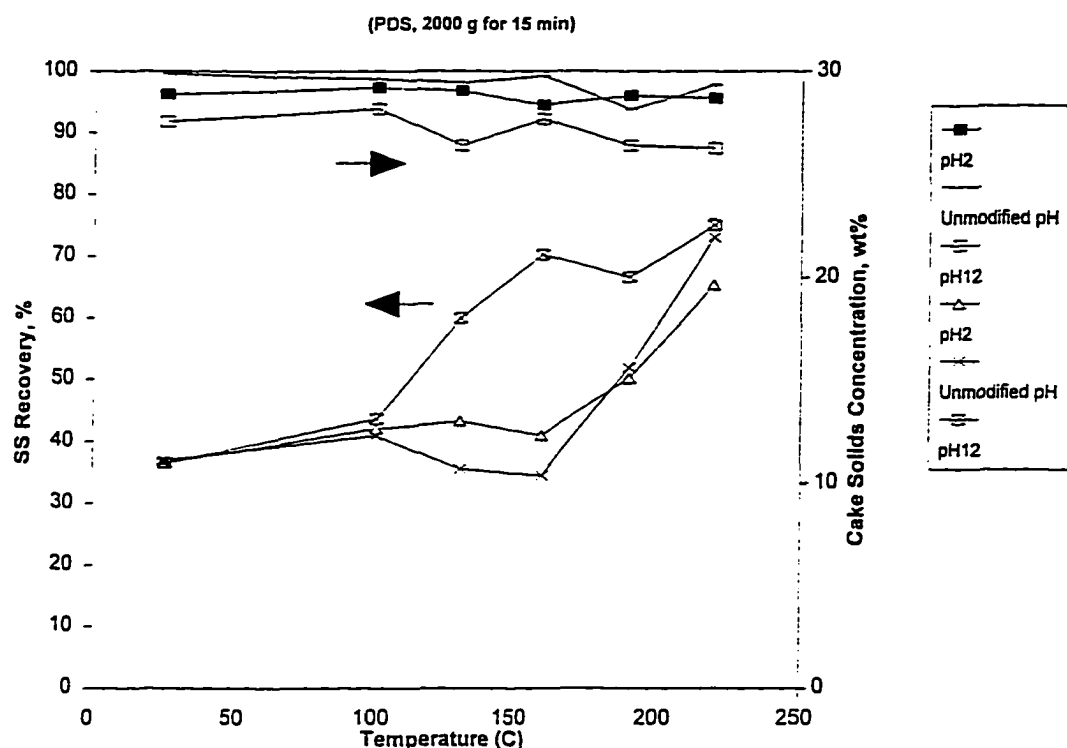


Figure 4-17. Solids recovery and cake solids concentration of centrifugation test for rapid thermally conditioned PDS

Figure 4-17 shows the results of laboratory centrifugation tests: the recovery rate of suspended solids and cake solids concentration. For thermally conditioned PDS with unmodified pH, the suspended solids recovery was always greater than 95 percent; this is satisfactory, although at higher temperatures the recovery was less. TS recovery decreased at the higher temperature because of the increase in the solubilization of the suspended solids, which results in lower amount of cake. As to sludge compressibility, low temperatures, such as 100°C, had little effect in all cases. Solids concentration is in the range of 10 to 13 percent by weight. As the conditioning temperature approached 220°C, cake solids concentration increased drastically. Table 4-3 shows that the concentration of cake solids remained relatively constant over a retention time range of 10 seconds to 3 minutes.

Table 4-3. Cake solids concentration of thermal conditioned PDS, 220°C.

Retention time	10 sec	20 sec	30 sec	1 min	2 min	3 min
Cake solids, %	25.1	24.2	27.2	28.1	26.0	27.5

The results of centrifugation tests for PDS with pH 2, 4, and 12 (Figure 4-17) indicate that the suspended solids recovery ratios for acidified PDS at all temperatures remain above 95 percent, while the recovery ratios for PDS at pH12 are around 90 percent.

For both acid and base conditioning, the solids concentration of sludge cake from centrifugation tests is very close to that for the conditioning at unmodified pH. This reveals that thermal conditioning temperature affects sludge compressibility more than pH value. At 220°C for 10 sec, regardless of pH, thermal conditioning significantly improves sludge dewaterability by centrifuge.

4.6.3.2 Sludge Settling Velocity

The results of sludge settling tests are shown in the Figure 4-18. Initial settling velocities, derived From Figure 4-18, are given in the Table 4-4. These were calculated from the change in the interface position divided by the centrifugation time and are the slopes of curves in Figure 4-18. It is evident from Figure 4-18 that the initial slope of line for sludge treated at 220°C changes very quickly and is probably much higher than the calculated value.

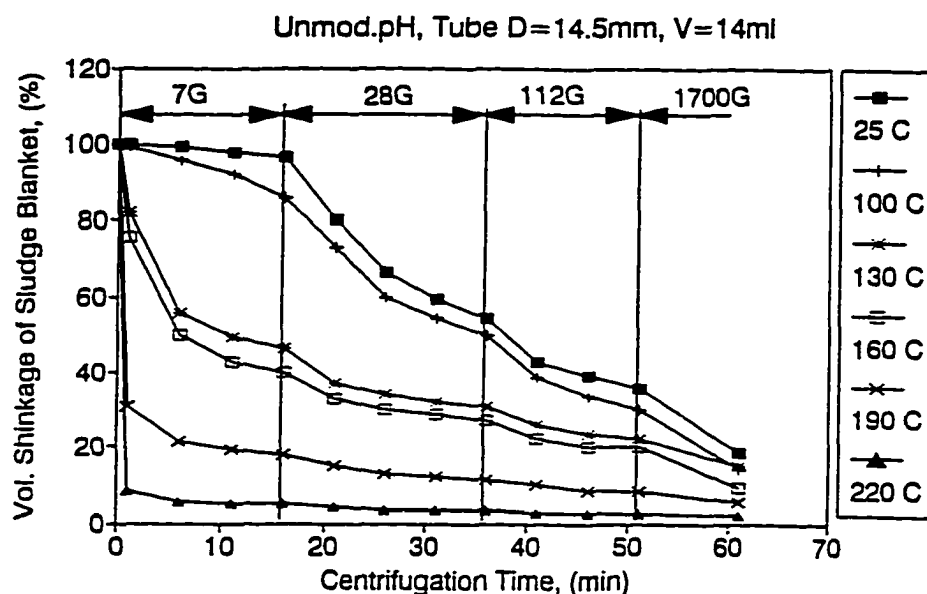


Figure 4-18. Solids settling test of rapid thermally conditioned PDS

Table 4-4. Initial settling velocity of centrifugal settling test.

(Without TS adjustment, time interval for initial settling velocity 1 minute)

RTC Temperature, °C	25	100	130	160	190	220
Initial Settling Velocity, $V \times 10^{-4} \text{ m/sec}$	0.02	1.7	4.17	5.67	16.2	21.3
Settling Coefficient, $S \times 10^{-5} \text{ sec}$	0.028	2.4	5.96	8.1	23.1	30.4

For the temperature range tested, higher thermal conditioning temperatures increased the initial settling velocity and settling coefficient. Figure 4-18 also shows that at higher temperature thermal conditioning resulted in less cake. Thermal conditioning at 220°C gave the best settleability and compressibility for PDS. Improvement in PDS settleability by RTC probably results from the dissolution of volatile suspended solids, leaving higher density solids which have better settling characteristics.

Taken together, the data for centrifugal settling and compaction show that thermal conditioning improves sludge settleability throughout the temperature range tested, but improves sludge compressibility only at high temperatures. Thermal conditioning at 220°C for 10 seconds produces the best dewatering results, i.e., satisfactory recovery with maximum cake dryness.

4.6.3.3 Parameters of the Centrifugation Model

The three parameters of the proposed centrifugation model (Table 4-5) were determined by regression of the experimental data using Equation 4-19. A comparison of the model, using these values of the parameters, with the test data is shown in Figure 4-19. Although the variable used in Figure 4-19 is $\Omega^2(r_c^2 - r_b^2)$, in experiments angular velocity, Ω , and radius of cake surface, r_b , are independent. However, they can be grouped into a single parameter representing the operating condition. Such treatment also greatly reduces the difficulty of regression. The model calculation shows an excellent fit to the test data.

Table 4-5. Sludge compressibility parameters.

Parameter	PDS	PDS, RTC at 220°C for 10 Second
p_0	3170	0.00546
λ	0.4255	0.2336
δ_0	0.0494	0.00616

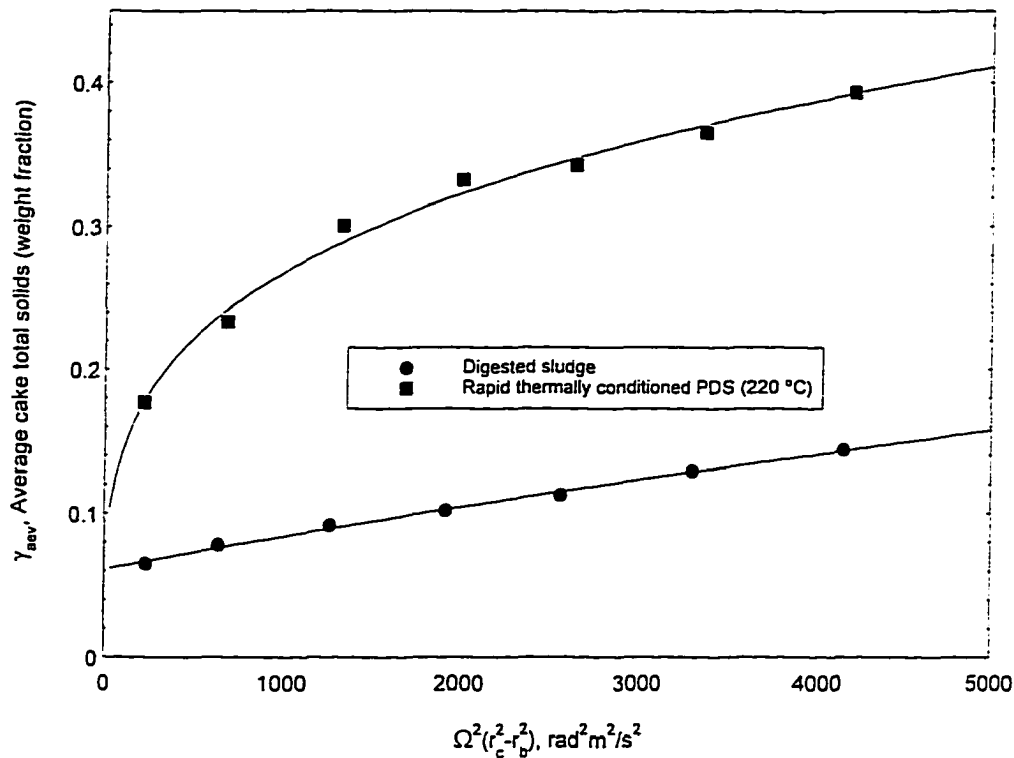


Figure 4-19. Comparison of centrifugation model and test data

The significance of this model is that it can be used to quantitatively describe the centrifugeability of a slurry. The two most important properties of centrifugation are solids recovery ratio and solids concentration in the cake. The results showed that solids recovery, over 95 percent at all tested conditions, is satisfactory. The major difference in centrifugeability turns out to be only in solids concentration, which can be fully correlated by this model. Furthermore, it can be used to predict the performance of a centrifuge used for dewatering. However, more work is needed to establish the correlation between the performance of a plant scale and a laboratory desk-top centrifuge.

As seen in Figure 4-19, RTC significantly improves centrifugeability of sludge; but CST and SRF tests show a deterioration in its filterability. On this point, it can be concluded

that CST and SRF, traditional tests for sludge dewaterability, are unable to assess sludge centrifugeability.

4.6.4 Other Sludge Dewatering Properties

Tests were conducted to measure some additional properties related to sludge dewatering in order to better understand its mechanism. The focus is on particle size distribution together with particle density. Other properties, such as viscosity, were also measured.

4.6.4.1 Polymer Conditioning

The addition of a polymer coagulant is a common method of sludge conditioning for dewatering. In the Wards Island plant, centrifuges are used to dewater PDS with the addition of polymer as coagulant. Percol 788N polymer by Allied Colloids was used until 1992, at a ratio of 20 lb polymer per ton dry sludge solids. Centrifugation dewatering of PDS with polymer resulted in a cake with a solids concentration in the range of 20 to 30 percent (Wards Island WPCP Operation Data, 1992). However, the laboratory centrifugation tests gave a much lower solids concentration. Applying the same dosage of polymer Percol 788N on PDS, and using a 2000 g force and 15 minutes, equivalent to full-scale operating conditions, resulted in a cake of 10 percent solids compared to 8 to 9 percent without polymer. The reasons for this have been discussed above (Section 4.6.3.1.).

There are three types of polymer: cationic, anionic and non-ionic. Several polymers of

Percol 700 series by Allied Colloids were tested for both PDS and thermally conditioned PDS. Visual observation indicated that the cationic polymer, Percol 788N and 728, coagulated the particles of PDS; the anionic polymers, Percol 712 and 710, and non-ionic polymer, Percol 720, did not. This is explained in part by negatively charged sludge particles. However, for thermally conditioned PDS, both cationic and non-ionic polymer coagulated the particles. This suggests that after thermal conditioning reduces the negative charge on the particles.

Table 4-6. Polymer effect on rapid thermally conditioned PDS.

Polymer (Percol #)	Dosage Polymer/sludge (lb/ton TS)	Floc Size (mm)	CST (sec)	Cake Solids Concentration (% w)
None	0	N/A	325	23.5
728N	0.5	0.1 - 0.5	360	23.1
728N	1.25	0.1 - 2	389	23.7
728N	1.95	0.1 - 5	287	23.5
720	0.25	2 - 5	257	23.7
720	0.5	2 - 4	200	23.6
720	1.98	5 - 20	52	22.2

Jar test results are shown in Table 4-6. The table shows that the amount of polymer required to produce flocs of a noticeable size with thermally conditioned PDS is less than 2 lb/ton dry solids, much less than that needed for untreated PDS which is about 20 lb/ton dry solids. For unconditioned PDS, addition of polymer reduces CST drastically and agglomerated particles offer almost no resistance to water flow. For sludge conditioned at high temperature, polymer addition increases CST, possibly because

excess free polymer molecules increase liquid viscosity. The data also show that non-ionic polymer Percol 720 is better than cationic polymer Percol 728 in terms of floc size and CST. However, the addition of polymer has no effect on sludge cake. In all cases, cake solids concentrations were about 23 percent in the centrifugation test. Therefore, thermally conditioned PDS requires little polymer for dewatering, and the use of polymer may, in fact, be eliminated.

4.6.4.2 Sludge Particle Size Distribution

It has been suggested that the single factor which most influences sludge dewaterability is particle size (Karr, and Keinath 1978). However, its relation to thermal conditioning had not been previously studied. Such a study provides an approach for better understanding the dewatering mechanism. Here, a Malvern 2600 particle size analyzer is used to measure the particle size distribution, especially in the range of 1 to 100 μm , which are believed to cause bad dewaterability of sludge (Karr and Keinath, 1978).

The general form of mean particle diameter is, by definition,

$$D[m, n] = \left[\frac{\int D^m N(D) dD}{\int D^n N(D) dD} \right]^{\frac{1}{m-n}} = \left[\frac{\sum V_i d_i^{m-3}}{\sum V_i d_i^{n-3}} \right]^{\frac{1}{m-n}} \quad (4-26)$$

where, $D[m, n]$ = mean diameter over the surface area distribution

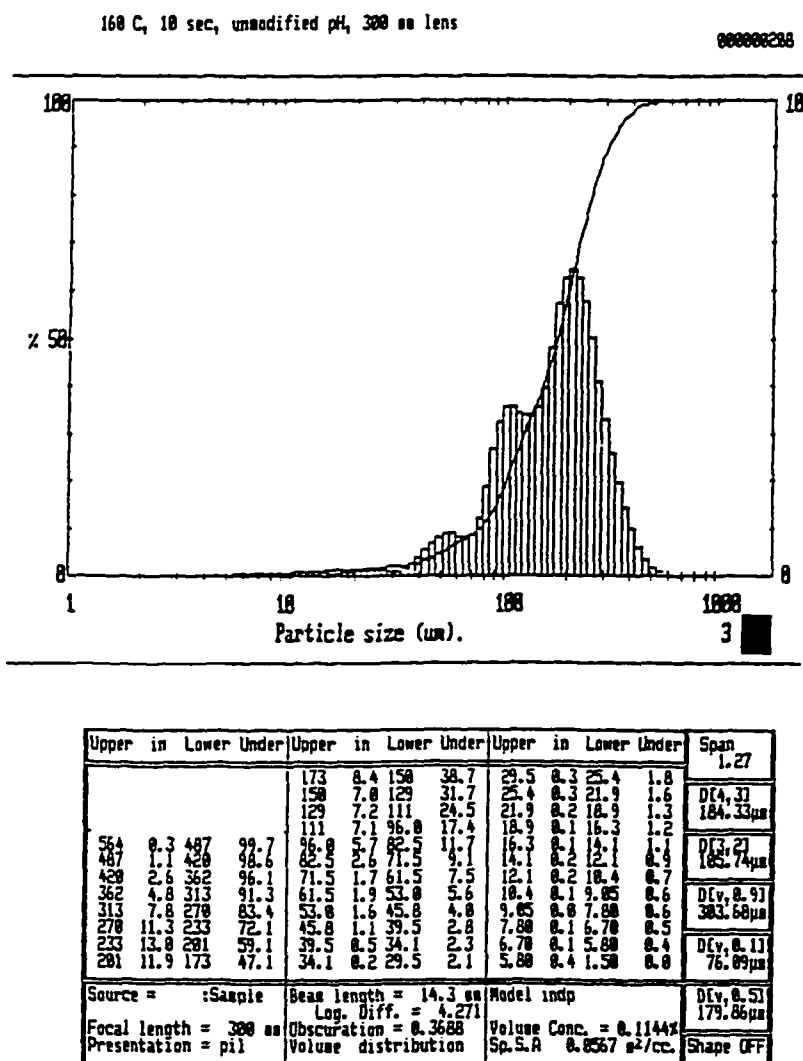
V_i = volume in size band i

d_i = mean diameter of size band i

$N(D)$ = the number of particles of size D

D = particle size

$D[4,3]$ is the mean diameter over the volume, and $D[3,2]$ over surface area known as Sauter mean diameter. These are the two mean diameters of interest. $D[4,3]$ is the natural result of a size measurement. $D[3,2]$ is important because in both settling and filtration the particle cross-sectional area is of prime importance.



Malvern Instruments

Figure 4-20. An example of particle size distribution report

A typical particle size distribution report generated by Malvern 2600 laser particle size analyzer is shown in Figure 4-20. It gives the particle size distribution in both tabular and graphical form and lists the mean particle sizes $D[4,3]$ and $D[3,2]$. A summary of test results is given in Table 4-7.

Table 4-7. Particle size distribution of rapid thermally conditioned PDS.

RTC temperature °C	Cumulative particle size distribution (over volume)						
	Volume % of particles of 1-1000 μ m						
Diameter, μ m	< 10	< 50	< 100	< 200	< 500	$D[4,3]$	$D[3,2]$
Unmodified pH							
25	8.3	62.8	88.7	97.0	100	50.8	22.6
100	0.3	6.0	24.5	72.3	100	157.4	77.8
130	0.7	4.5	13.5	45.1	98.4	189.2	100.3
160	0.6	3.3	12.2	46.6	99.5	184.3	105.7
190	2.0	17.6	53.9	88.6	98.9	99.2	49.0
220	3.4	20.4	49.3	92.9	99.6	97.2	41.1
pH=2							
25	5.5	42.1	77.8	96.8	100	60.9	26.7
110	6.4	44.2	78.8	95.0	100	54.7	23.5
130	1.4	13.3	37.3	79.7	99.3	95.1	50.1
160	0.8	9.6	25.5	63.4	99.8	151.1	77.4
190	0.6	7.1	24.9	74.5	98.5	119.8	71.0
220	1.6	25.5	71.4	97.0	100	72.2	42.5

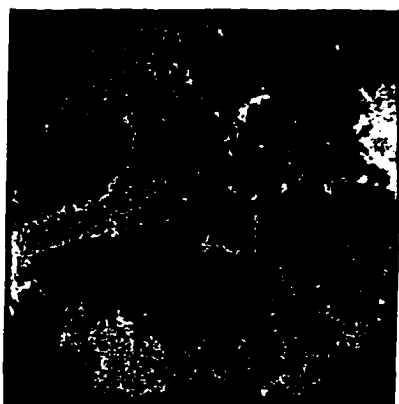
The particle size distribution of sludge with unmodified pH after 10-second thermal conditioning shows interesting characteristics. The mean particle diameter of PDS, $D[3,2]$ is only 22.6 μ m (Table 4-7). As the conditioning temperature is increased to a mild level, 130 to 160°C, mean particle size increased to 190 μ m. However, further

increase of temperature reduced particle size to about 30 μm at 200°C. Figure 4-21 (a)-(c) are photos through a Nikon microscope showing the size and structure of PDS and thermally conditioned PDS.



(a) PDS

Amplification: 1:35



(b) Thermally Conditioned PDS

130°C for 10 Seconds

Amplification: 1:72



(c) Thermally Conditioned PDS

220°C for 10 Seconds

Amplification: 1:35

Figure 4-21. Microscopic structure of rapid thermally conditioned PDS

In this figure, the particles of unconditioned PDS are well dispersed. The darkest spots are believed to be inorganic (or fixed) solids, and gray spots to be biomass. Fibers were also visible. At 130°C, particle agglomeration is observed. At 220°C, the gray spots tend to disappear while these dark ones remain. This corresponds to the pattern of sludge solubilization, suspended volatile solids being solubilized and suspended fixed solids mostly remaining unchanged.

The particle agglomerates observed at 130 to 160°C tend to be loose and fragile, as suggested by the following observation. In the measurement sample cell of the particle analyzer, a magnetic stirrer runs continuously to keep the solids in suspension and, consequently, exerting a shear force on the particles. The shear force reduced the area-mean particle size of sludge conditioned at 160°C from 189 μm to 112 μm within 11 minutes of stirring time. In contrast, the particle size distribution of 220°C conditioned sludge remained at 27 μm after 4 minutes of stirring time. For the PDS with pH 2, solids particle size also reached a peak as conditioning temperature increased, but it is lower than that of PDS with unmodified pH.

The experimental data were plotted on several forms commonly used to display particle size distribution including lognormal, Gaudin-Schuhmann, and Rosin-Ramler. The PDS particle size distribution fits Rosin-Ramler distribution well, for which the undersize volume distribution $Q(D)$ has the form

$$Q(D) = 1 - \exp \left[- \left(\frac{D}{x'} \right)^n \right] \quad (4-27)$$

where, D is particle diameter, and n and x' are constants. Figure 4-22 shows the comparison of measured data for PDS and Equation (4-27) with constant $n=1.33$ and $x'=53.4 \mu\text{m}$.

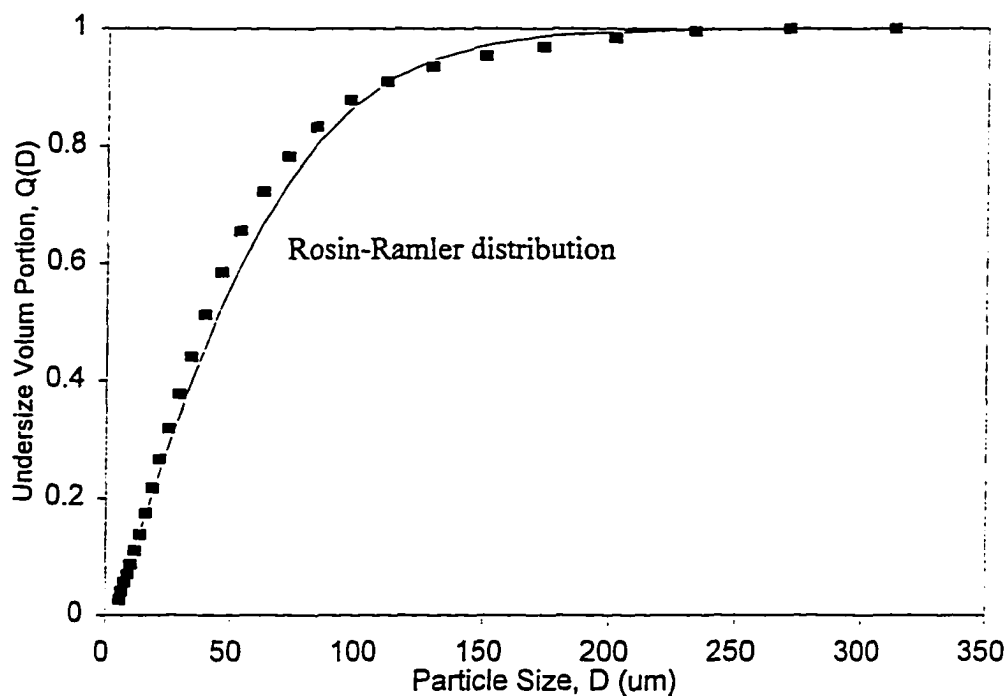


Figure 4-22. Particle undersize distribution of PDS

Generally, the change of particle size can explain the change in settleability of thermal conditioned sludge, but it fails to correlate with filterability tests including SRF and CST. Because only solids with a diameter larger than $1 \mu\text{m}$ can be measured by the laser particle size analyzer, it is possible the particles with size less than, or close to, $1 \mu\text{m}$ play an important role regarding sludge filterability.

4.6.4.3 Density of Sludge Particles

The results of sludge solids density tests, Figure 4-23, indicate that sludge particle density increases with thermal conditioning temperature. This is supported by the results shown in Figure 4-4, which shows that solubilization is mainly associated with the organic component. The remaining solids are primarily inorganic and thus have higher densities. Increased particle density enhances settling and compaction in centrifugation.

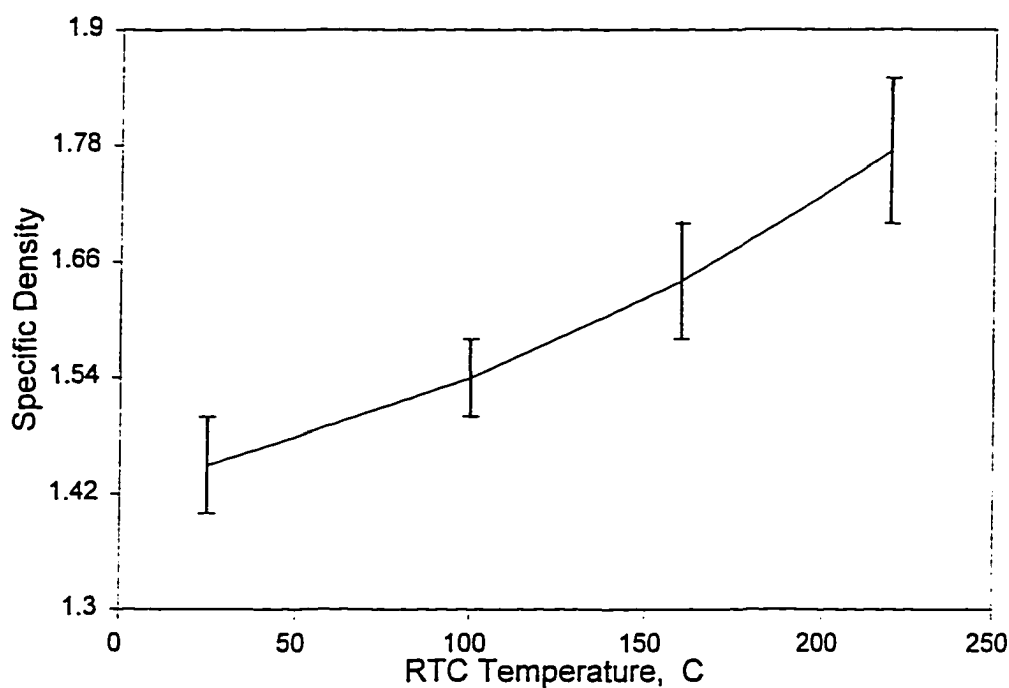


Figure 4-23. Solids specific density of rapid thermally conditioned PDS

4.7 SUMMARY

(1) RTC at 220°C dissolves approximately 40 percent of the suspended solids in PDS. Approximately 90 percent of these dissolved solids are volatile solids. In the tested range of solids concentration from 1.4 to 4.9 percent, the percentage of total solids solubilized

is independent of their initial concentration. The density of the remaining suspended solids increases.

(2) RTC improves the centrifuge dewaterability of PDS, especially at a conditioning temperature of 220°C. With RTC, solids density increases, settling rate increases, and a drier cake is obtained.

(3) For centrifugal dewatering of rapid thermally conditioned PDS, polymer addition can be eliminated without affecting the solids concentration in cake.

(4) In contrast to centrifugeability, RTC deteriorates the filterability of the PDS. The thermal conditioning retention time affects filtration much more than centrifugation. For thermal conditioning with long retention times, either centrifugation or filtration can be applied. However, for RTC of PDS, centrifugation is recommended as an effective dewatering process and filtration processes should be avoided.

(5) RTC of PDS adjusted to alkaline pH will achieve slightly better filterability and centrifuge dewaterability than at either neutral or acidic pH.

CHAPTER FIVE

BIOCONVERTIBILITY OF L-, D-, AND THERMALLY CONDITIONED L-AMINO ACIDS

5.1 OBJECTIVES

The objectives of this part of the study are:

- (1) To obtaining an understanding of the effect of retention time in thermal conditioning on sludge biodegradability.
- (2) To test substances for their possible role in the formation, during thermal conditioning, of compounds toxic or refractory to anaerobic digestion.

Although thermal conditioning of sludge has been practiced for decades, there is still a lack of knowledge of the toxicity produced in thermal conditioning and its relation with sludge biodegradability. In order to better understand possible effect on biodegradability of sludge by thermal conditioning, a study at a fundamental level is necessary. This chapter describes an effort to understand the formation of compounds during thermal conditioning which are refractory in anaerobic digestion. L-amino acids were used to study the effect of retention time of high-temperature thermal conditioning on their anaerobic digestibility in terms of reaction rate and ultimate digestion gas production. It is hypothesized that racemization causes the observed decrease in biodegradability.

As a first step toward verifying this hypothesis, D-amino acids are used as model compound to compare their biodegradability with L-amino acids. Glucose and PDS were also tested in this study.

Protein is a major constituent of sludge as indicated in Table 2-1. Amino acids are the products of its hydrolysis, and certainly have a major influence in subsequent digestion of sludge. As suggested in Section 2.3.4.3, racemization of amino acids takes place during thermal conditioning of protein at high temperature and long retention time. L- (levorotary) amino acids are converted into D- (dextrorotary) isomers which may explain the decrease in biodegradability of the amino acids. This is a new hypothesis which has not been found in the prior literature of sludge conditioning. To investigate this hypothesis, D- and L- amino acids were used as model compounds and their behavior studied during anaerobic digestion. Sludge is a complicated system in terms of its composition. The study of the representative components isolates single factors and simplifies the problem. It is an approach to understanding the behavior of the system containing those individual components.

In addition to amino acids, glucose and PDS were also used for this study. Glucose is the product of carbohydrate hydrolysis. How thermal conditioning affects its biodegradability was also of interest to this study. PDS was used for comparison with the model substance in regard to the relation between thermal conditioning and biodegradability.

5.2 EXPERIMENTAL CONDITIONS

5.2.1 Materials and Processing

(1) Amino Acids

A total of 32 D- and L- forms of 17 amino acids were selected from among the 20 commonly present in protein: glycine, 16 L-amino acids, and 15 D- form isomers. Amino acids were purchased from Aldrich Chemical Company Inc. with a purity of at least 98%, mostly 99% or higher. Because of their low solubility, 1.0 g/L solutions were made for all samples except 0.816 g/L for L-Glutamic acids and 0.5 g/L for L-Lysine, which have solubilities lower than 1.0 g/L. Amino acid samples were in weighed aluminum foil pans and then transferred to a beaker. Deionized water was used to rinse the pan twice then added to the beaker. Deionized water was added into the beaker to make the desired volume of solution. This eliminated the loss of amino acids during transfer.

(2) Sewage Sludge

PDS was collected from the Wards Island Water Pollution Control Plant and stored at 4°C to prevent biological deterioration.. This sample had total solids 2.6%, of which 60% were volatile, a total COD of 26,000 mg/L, and a dissolved COD of 500 mg/L.

(3) Glucose

(3) Glucose was purchased from Aldrich Chemical Company Inc. An aqueous solution of 1.0 g/L was prepared using the same procedures as that for amino acids.

5.2.2 Thermal Conditioning

Thermal conditioning was performed with a batch reactor unit, which is described in Section 4.2.3. In order to avoid oxidative reactions with air during thermal conditioning, the reactor containing the sample was flushed with nitrogen for about one minute.

The temperature for thermal conditioning was 220°C, and the retention times were 20 seconds and 20 minutes to simulate both rapid and long time thermal conditioning. Thermal conditioning was applied only to L-form amino acids, glucose and PDS. The D-form amino acids were not subjected to thermal conditioning, as they are thought to be produced from the L-form during this process.

5.2.3 Bioconvertibility Test Procedure

Biodegradability was assessed by the Biochemical Methane Potential (BMP) assay (Owen *et al.*, 1979) in terms of methane production. When organic material is anaerobically digested, 75 to 98 percent is converted to digestion gas and the remainder to cell mass (Stuckey and McCarty, 1984). BMP assay counts only the first and dominant product. The simplicity of this method allows dozens of samples to be tested simultaneously at the same condition, which is important for the comparison of different samples.

Serum bottles of 160 ml served as batch reactors, and total gas production was measured as a function of incubation time. The samples consisted of two components, seed (microbial culture) and feed (substrate). PDS was used as seed as well as to provide

trace nutrients and enough alkalinity necessary for digestion. Seed viability was confirmed by Pierides (1994). The feed was the substrate to be studied for its kinetics of digestion.

Each serum bottle contained a mixture of 25 ml sample feed and an appropriate volume of seed (25 or 50 ml). This lower ratio of seed to feed avoids large gas production fluctuations (Pierides, 1994). During the preparation of serum bottles, seed was stirred by a magnetic stirrer to keep the contents well mixed. All samples were prepared and tested in duplicate. Before the serum bottle was closed by a butyl robber stopper and then sealed by a crimped aluminum seal, nitrogen gas was injected for 2 minutes to replace air in the head space of bottle providing anaerobic conditions.

Both seed and feed contribute to gas production. In order to exclude the gas produced from seed, a seed sample was also set. In this sample, 25-(or 50-)ml deionized water, the same volume as the amino acids solution, was mixed with seed. Since the deionized water produced no digestion gas, the total gas resulted only from seed.

The bottles then were incubated mesophilically in an environmental chamber maintained at a constant temperature of 35°C. The incubation period lasted over 75 days, which was longer than the 30 days of Owen *et al.*'s BMP assay (1979), in order to obtain a reliable measure of ultimate biodegradability.

5.2.4 Analytical Methods

The gas production was measured volumetrically by a water displacement system at ambient pressure and incubation chamber temperature of 35°C. The interval for gas measurement started with 12 hours of incubation and then was lengthened due to decreased gas production rate over time. The gas production data were averaged for each pair of duplicate samples.

```

File : 57___01.D01          D-Serine room          John
Run : 01                      Type : Sample
Path : C:\CHROM\GAS1\JO
Collection : 19:33:33 Sep 21 1993  Method : GAS1    [ 19:31:35 Sep 21 1993 ]
Integration: 19:33:35 Sep 21 1993  Method : GAS1    [ 19:31:35 Sep 21 1993 ]
Report   : 19:51:35 Sep 21 1993  Method : GAS1    [ 19:31:35 Sep 21 1993 ]

Dilution: 1.00000e+0

```

NORMALIZATION (AREA)						
RT	Area	BC	ExpRT	RF	Area %	Name
			1.300	3.28836e-6		Hydrogen
5.667	6795	T	5.500	1.71225e-5	0.1212	Oxygen
6.260	607753		5.900	1.55796e-5	7.8734	Nitrogen
			8.400	1.55722e-5		CO
11.806	342238	J	12.000	1.91701e-5	68.3283	Methane
14.327	1759470		14.400	1.18294e-5	21.6767	Carbon Dioxide

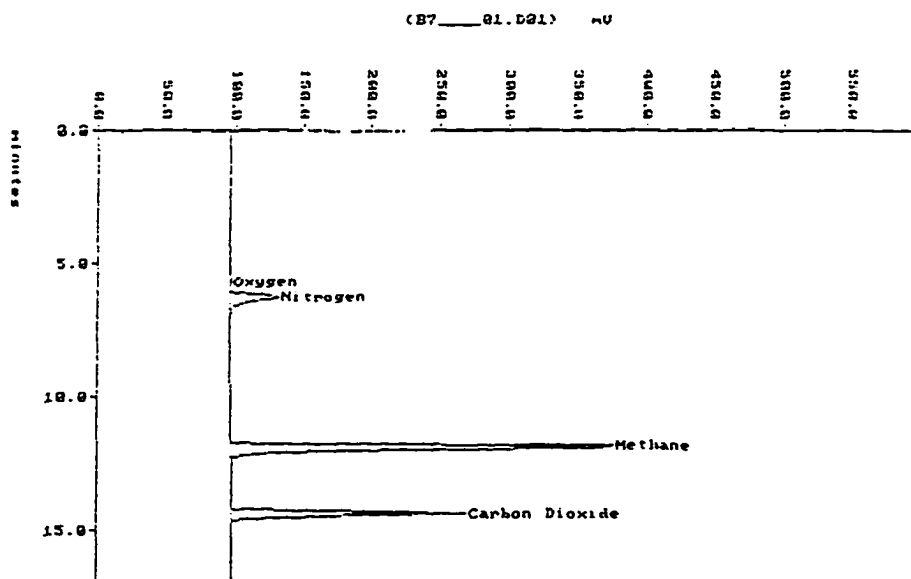


Figure 5-1. A report of digestion gas composition by gas chromatograph.

5.2.5 Bioconvertibility Evaluation

Gas composition was analyzed by a gas chromatograph, Perkin-Elmer Sigma 2000. Gases of primary concern were methane and carbon dioxide. Nitrogen, residual purge gas, was also measured. Oxygen was checked to ensure an anaerobic atmosphere. A sample test report is shown in Figure 5-1. The pH was measured by a Orion digital pH meter. Color and odor of sample were judged by observation and smelling.

The gas production data were used to compare the different feed substances and different conditions of thermal processing. The following items were calculated:

Gas Production. To obtain the net gas production from feed, the separately measured seed gas production was subtracted from total gas production for the sample of seed plus feed. The accumulated gas production (AGP) at time n is the summation of the total gas production (GP) measured at time i minus summation of the gas production of seed sample (GP_s)

$$AGP_f = \sum_{i=1}^n (GP_t - GP_s)_i \quad (5-1)$$

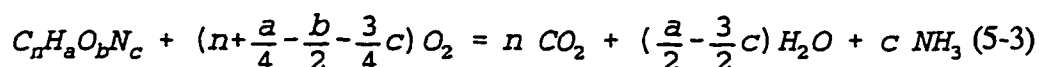
Where, the subscript f indicates feed, t indicates total, and s indicates seed.

Bioconvertibility to Methane. Bioconvertibility to Methane (BTM) is COD of methane gas produced, y , divided by COD of feed in each serum bottle, y_s :

$$BTM = \frac{y}{y_s} \times 100\% \quad (5-2)$$

BTM is a function of digestion time. Gas volumes, measured at 35°C, are calculated to standard conditions, 1 atmospheric pressure and 0°C, using the perfect gas law. Digestion gas was assumed to consist of methane, carbon dioxide and water vapor. The ratio of methane to carbon dioxide was taken as 75 percent based on gas chromatograph measurements as shown in Table 5-2. Water, as saturated vapor, was about 5 percent. Therefore, methane content was taken as 70 percent of digestion gas, and then transformed into its corresponding feed COD, COD_f .

The COD of an organic compound can be represented by the following generalized reaction equation (Sawyer and McCarty, 1978):



The COD of methane, individual amino acids, and glucose can be calculated by Equation 5-3. For PDS, COD must be measured.

Material with BTM higher than 83 percent is regarded as highly biodegradable, between 50 and 83 percent as medium biodegradable, and lower than 50 percent as refractory (Stuckey and McCarty, 1984). Material with negative BTM is regarded as toxic, since it not only resists digestion, but also inhibits the digestion of seed.

Ten, 30, and 75 days are used to define short, medium, and long-term BTM of substrates. For anaerobic digestion, HRT of 10 days is commonly the upper limit. Test results show that for more than 90 percent of the samples, gas production curves were flat after 75 days of digestion. This means the methane producing biological processes

no longer significant either because nutrients were exhausted or the remaining organics were indigestible.

BTM for a sample represents its ultimate biodegradability, and the time to reach such a level of conversion represents the biological reaction rate. The combination of these two factors determines the order of bioconvertibility of samples. The judgement of bioconvertibility was reached as follows: First the level of BTM was determined, e.g. high, medium, low BTM and toxic. Then within the same level of BTM, the time required to reach this level was determined. A higher BTM at shorter term means a higher biodegradability and vice versa.

BTM can also be expressed analytically. If digestion is treated as a first order reaction, the COD of methane gas (y) produced at time t , in Equation (5-2), is

$$y = y_t (1 - e^{-kt}) \quad (5-4)$$

Where, y_t = ultimate COD converted to methane gas, mg/L

k = reaction constant, days⁻¹

t = digestion time, days

Substitution of Equation (5-4) into Equation (5-2) gives

$$BTM = \frac{y_t}{y_s} (1 - e^{-kt}) \times 100\% \quad (5-5)$$

When $t \rightarrow \infty$, BTM becomes the ultimate BTM, BTM_u .

$$BTM_u = \frac{y_t}{y_s} \times 100\% \quad (5-6)$$

Substitution of Equation (5-6) in to Equation (5-5) gives

$$BTM = BTM_u (1 - e^{-kt}) \quad (5-7)$$

If the experimental data fit the pattern of Equation(5-7), BTM_u and k can be obtained by regression.

5.3 RESULTS AND DISCUSSION

The general formula for protein amino acids is $R-CH(NH_2)-COOH$, and these differ only in the nature of side chain R . The classification of amino acids is shown in Table 5-1. The 17 amino acids used in this study cover all categories.

The composition of digestion gas was measured for 7 amino acids of both the L- and D-form (Table 5-2). These show that the anaerobic digestion of the tested samples was normal. A higher residual nitrogen gas content corresponds to a lower methane production. The ratio of methane to methane plus carbon dioxide varies from 67 to 83 percent. The same type of amino acid, regardless of its L- or D- form and its thermal conditioning, produces digestion gas with nearly the same composition. However, the quantity of gas produced strongly depends on the form of the amino acid and its thermal conditioning.

Table 5-1. Classification of amino acids.

Side chain	Amino acids
Aliphatic natural	glycine, alanine, valine, leucine, isoleucine
Aliphatic -OH containing	serine, threonine
Aliphatic -S containing	cysteine, cystine, methionine
Aliphatic -NH- containing	lysine, arginine
Basic	lysine, arginine, histidine
Acid and mono amides thereof	aspartic acid, asparagine, glutamic acid, glutamine
Aromatic and heteroaromatic	phenylalanine, tyrosine, tryptophan
Heterocyclic	proline, hydroxyproline, histidine, tryptophan

(After Jakubke and Jeschkeit, 1977; Encyclopedia of Chemical Technology, 1992)

Table 5-2. Composition of digestion gas (% Volume)

Amino Acids	TC Time min.	CH ₄	CO ₂	O ₂	N ₂	<u>CH₄</u> (CH ₄ +CO ₂)
L-serine	20	67.5	19.7	0.08	12.8	77.4
	2	67.3	21.7	0.08	10.9	75.6
	no	67.0	22.4	0.09	10.5	74.9
D-serine	no	68.3	21.7	0.12	9.9	75.9
L-alanine	20	70.3	19.4	0.31	9.9	78.4
	no	71.4	19.7	0.06	8.9	78.4
D-alanine	no	72.1	19.4	0.13	8.4	78.8
L-threonine	20	66.6	17.2	0.09	16.1	79.5
	no	70.9	21.6	0.10	7.4	76.7
D-threonine	no	69.4	23.2	0.12	7.2	74.9
L-valine	20	73.4	20.6	0.12	5.8	78.1
	2	73.4	20.5	0.12	5.8	78.1
	no	73.4	20.5	0.10	5.5	77.9
D-valine	no	78.2	16.8	0.06	5.0	82.3
L-arginine	20	71.6	14.8	0.09	13.5	82.8
	2	82.7	17.2	0.0	0.11	82.8
	no	72.1	14.8	0.09	13.0	83.0
D-arginine	no	72.4	15.3	0.11	12.2	82.6
L-tyrosine	20	52.6	22.1	0.28	25.0	70.5
	2	59.8	28.6	0.18	11.3	67.7
	no	59.5	27.6	0.61	12.4	68.3
D-tyrosine	no	30.1	10.1	0.48	58.6	75.3
L-Tryptophan	20	27.5	10.5	1.37	60.6	72.4
	2	24.5	2.26	10.3	63.0	70.5
	no	24.6	10.3	2.43	63.2	71.5
PDS	20	31.3	10.7	0.22	57.8	74.5

The BTM results are shown in Table 5-3. The BTMs for some samples are higher than 100 percent. This was also reported by Stuckey and McCarty (1984). One possible reason for this is that substrate stimulates and interacts with seed, resulting in extra gas production (Pierides, 1995).

Table 5.3. Bioconvertibility to methane of amino acids and glucose.

Amino Acid	TC Time (min.)	BTM, %		
		10 days	30 days	75 days
L-threonine	25	-2	33	39
	2	59	93	99
	no	71	97	103
D-threonine	no	23	48	103
L-arginine	25	33	60	57
	2	39	60	55
	no	36	66	61
D-arginine	no	31	68	66
L-valine	25	39	68	82
	2	48	88	92
	no	51	91	94
D-valine	no	1	8	47
L-serine	25	76	79	80
	2	104	106	105
	no	109	112	111
D-serine	no	109	111	111
L-alanine	25	84	87	87
	2	88	93	91
	no	90	96	94
D-alanine	no	86	94	96
L-phenylalanine	25	1	1	1
	2	8	19	26
	no	7	18	25
D-phenylalanine	no	-1	-2	-2
L-methionine	25	12	22	35
	2	18	46	45
	no	14	47	48
D-methionine	no	1	-2	-2
L-aspartic acid	25	101	108	109
	2	109	118	119
	no	116	121	122
D-aspartic acid	no	114	132	133
L-tyrosine	25	14	31	35
	2	20	71	98
	no	20	79	105
D-tyrosine	no	-2	-2	-1

Table 5.3. (Continued)

Amino Acid	TC Time (min.)	BTM, %		
		10 days	30 days	75 days
L-tryptophan	25	4	1	-1
	2	6	2	1
	no	6	4	3
D-tryptophan	no	-1	-2	-3
L-asparagine	25	68	74	75
	2	40	62	65
	no	85	88	90
D-asparagine	no	13	54	78
L-histidine	25	62	68	67
	2	62	65	64
	no	69	72	71
D-histidine	no	48	80	80
L-lysine	25	32	43	42
	2	62	72	71
	no	63	75	74
D-lysine	no	62	70	70
Glycine	25	68	78	77
	2	72	82	82
	no	70	82	80
L-leucine	25	18	46	49
	2	20	68	75
	no	20	72	82
D-leucine	no	0	-1	-2
L-glutamic acid	25	98	103	102
	2	96	101	101
	no	104	108	108
D-glutamic acid	no	62	105	105
L-Isoleucine	25	34	55	61
	20	50	88	88
	no	48	91	91
Glucose	25	3	34	59
	5	23	76	98
	no	112	120	120

5.3.1 L-amino Acids

Among 17 L-amino acids (include glycine), 11 had high BTM (5 high short-term. BTM, 4 high medium-term BTM, 2 high long-term BTM), 3 medium BTM, and 3 low BTM. L-amino acids with high short-term BTM include all three acidic amino acids and their monoamides tested: aspartic acid, asparagine and glutamic acid, as well as serine and alanine which belong to the aliphatic amino acids. Four L-amino acids, threonine, isoleucine, glycine and valine, all in the aliphatic amino acids group, showed high medium-term BTM. Leucine, another member of the aliphatic amino acids group, showed high long-term BTM. Among the three L-amino acids containing a benzene ring, only tyrosine showed high long-term BTM. The other two, tryptophan and phenylalanine, appeared to be refractory. Another refractory L-amino acid, methionine containing sulfur, may be toxic to digestion. All three basic L-amino acids tested, lysine, arginine, histidine, show medium BTM. Generally, the order of BTM for different groups of amino acids is: acidic > aliphatic > basic > heterocyclic, aromatic and heteroaromatic, sulfur containing.

5.3.2 Thermally Conditioned L-amino Acids

A comparison of the BTM for unconditioned amino acids and amino acids with two-minutes of thermal conditioning at 220°C (Table 5-3) shows that the two are very close, about 10 percent difference, except asparagine. Nine of the 17 treated samples still showed high BTM, only one had less. The other 5 had medium BTM, and 3 had low

BTM. However, when thermal conditioning time was increased to 25 minutes, only 4 samples had high BTM, 7 medium BTM, and 6 low BTM.

With thermal conditioning, the BTMs of amino acids mostly dropped to different extent, some were maintained. No increase in gas production took place after thermal conditioning. Even the three amino acids with lowest BTM, phenylalanine, tryptophan and methionine, did not change their refractory nature. The five amino acids which have high to medium BTM were highly resistant to thermal conditioning. Among them, aspartic acid and glutamic acid belong to the acidic group, the other three: arginine, alanine, and glycine, to the aliphatic group.

Six substrates experienced significant deterioration in BTM at the thermal conditioning time of 25 minutes. Among them, threonine, serine, lysine, leucine, isoleucine, belong to the aliphatic group. Another, tyrosine, is the only one in the aromatic and heteroaromatic group which shows high long term BTM without thermal conditioning. The decrease in BTM of amino acids due to thermal conditioning is in the following order: acidic, aliphatic natural > aliphatic other than natural > aromatic and heteroaromatic.

Samples of L-amino acids thermally conditioned at 220°C for 20 minutes were analyzed to the amount unreacted using an amino acid analyzer (Zhang, 1994). The results are shown in Table 5-4. Zhang also noticed that ammonia was present in all thermally conditioned amino acid samples. This is an indication of break-down of the amino group or deamination.

Table 5-4. Characteristic of thermally conditioned amino acids and other substrates

Amino acid or other substrates	TC time (min)	pH	Color	Odor	Amino acid remaining, %
Glycine	no	5.81	None	None	
	2	6.91	None	None	
	25	7.74	Light yellow	Slight	44.3
D-glutamic acid	no	N/A	None	None	
L-glutamic acid	no	3.17	None	None	
	2	2.57	None	None	
	25	2.48	None	Medium	
D-valine	no	N/A	None	None	
L-valine	no	5.4	None	None	
	2	7.06	None	None	
	25	7.18	None	None	75.4
D-threonine	no	N/A	None	None	
L-threonine	no	5.72	None	None	
	2	5.91	None	None	
	25	8.32	Brown	Medium	4.7
D-alanine	no	N/A	None	None	
L-alanine	no	5.85	None	None	
	2	6.66	None	None	
	25	7.44	None	Slight	46.1
D-serine	no	N/A	None	None	
L-serine	no	5.23	None	None	
	2	6.44	None	None	
	25	8.68	Brown	Medium	25.9
D-leucine	no	N/A	None	None	
L-leucine	no	5.86	None	None	
	2	6.88	None	None	
	25	7.31	Light yellow	Medium	90.5
D-phenylalanine	no	N/A	None	None	
L-phenylalanine	no	5.58	None	None	
	2	7.31	None	None	
	25	7.39	L. yellow, turbid	None	100.3
D-arginine	no	N/A	None	None	
L-arginine	no	5.46	None	None	
	2	6.28	None	None	
	25	8.08	None	Slight	22.8

Table 5-4. (Continued)

Amino acid or other substrates	TC time (min)	pH	Color	Odor	Amino acid remaining, %
D-tyrosine	no	N/A	None	None	
L-tyrosine	no	6.06	None	None	
	2	3.65	Turbid	None	
	25	7.61	Suspension	None	1.7
D-tryptophane	no	N/A	None	None	
L-tryptophane	no	5.92	None	None	
	2	7.13	Light yellow	Slight	
	25	7.29	L. yellow, turbid	Slight	87.7
D-asparagine	no	N/A	None	None	
L-asparagine	no	2.94	None	None	
	2	3.42	None	None	
	25	3.59	Light yellow	None	0
D-methionine	no	N/A	None	N/A	
L-methionine	no	5.69	None	Medium	
	2	6.68	None	Medium	
	25	7.39	Light yellow	Strong	60.2
D-aspartic acid	no	N/A	None	None	
L-aspartic acid	no	2.94	None	None	
	2	3.42	None	None	
	25	3.59	Light yellow	None	6.1
D-histidine	no	N/A	None	None	
L-histidine	no	3.73	None	None	
	2	4.36	None	None	
	25	4.70	Light yellow	None	23.9
D-lysine	no	N/A	None	None	
L-lysine	no	9.54	None	None	
	2	9.69	None	None	
	25	8.85	Light yellow	Medium	23.2
D-glutamic acid	no	N/A	None	None	
L-glutamic acid	no	3.17	None	None	
	2	2.57	None	None	
	25	2.38	Light yellow	None	
Glucose	no	4.46	None	None	
	2	4.47	Light yellow	None	
	25	2.89	Dark brown	None	
PDS	no	7.54			
	2	8.58			
	25	8.23			

Smells were judged on a relative scale and shown in Table 5-4. The aqueous solution of all 17 amino acids tested, except methionine are without odor. With thermal conditioning at 220°C for 2 minutes, two samples had odor. Thermal conditioning at 220°C for 25 minutes, resulted in 10 amino acid solutions with odor. This indicates that long retention time is needed for deamination.

Sample colors were judged by observation (Table 5-4). Aqueous solution of all 17 L-amino acids tested were transparent. With thermal conditioning at 220°C for 2 minutes, one sample showed a light yellowish color. When retention time was increased to 25 minutes, twelve samples showed colors from yellow to brown. Suspensions were also observed for 3 samples. These results indicate that long retention time in thermal conditioning is the major reason for the strong yellow-brownish color also observed in traditional thermal conditioning process.

5.3.3 D-amino Acids

Of the 15 tested D-amino acids (Table 5-3), 6 had high BTM, 3 medium BTM and 6 low BTM. Five of the 6 D-amino acids with low BTM were indigestible, producing no gas up to 75 days. These indigestible D-amino acids include all of the members of the aromatic, heteroaromatic, and sulphur containing D-amino acids tested: tyrosine, tryptophan, phenylalanine, methionine. D-leucine was also indigestible. In total, 10 D-amino acids were digestible and 5 were not. All tested D-amino acids except leucine in acidic and aliphatic groups were digestible.

In comparison with L-amino acids, D-amino acids as whole are much less biodegradable. Several D-amino acids produce slightly higher amounts of digestion gas than L-amino acids, but the amount is insignificant, less than 10 percent. Among the 10 digestible D-amino acids, 5 had gas production curves coinciding with those of the corresponding L-amino acids, arginine, serine, alanine, aspartic acid, and lysine, all of which except aspartic acid belong to their aliphatic group. From the point of view of reaction kinetics, these D- and L- amino acids have the both same reaction rate and conversion rate.

Five D-amino acids show an initial time-delay behavior, but as digestion progresses, their cumulative gas production approaches, or even equals, that of the D-amino acid. This group includes threonine, histidine, glutamic acid, asparagine, and valine. The ultimate BTM of this group of substrates seems to be almost the same as that of their L-form isomers. Valine and threonine yield no gas for 20 and 16 days respectively. Three D-amino acids, threonine, histidine, and glutamic acid, have the same ultimate BTM after a period of 30 days incubation, while asparagine takes 50 days. The digestion of D-valine has the longest period of time-delay. L-valine is depleted only after 20 days. However, for D-valine, even when testing was terminated after 98 days, significant amount of gas was still being produced. By extrapolation, it is estimated take 150 days are required for D-valine to reach the ultimate BTM of its L-isomer.

All L-form isomers of the 5 non-digestible D-amino acids, except tryptophan, are digestible. However, they have either a low BTM (L-phenylalanine, and L-methionine) or a relatively low reaction rate (L-tyrosine, and L-leucine). The general tendency is that the lower the BTM of an L-amino acid, the more refractory is its D-form isomer.

In this exploratory investigation, no attempt was made to analyze D-amino acids formed in the thermally conditioned L-amino acids. But the work of others (Hayase *et al.*, 1975) shows that such transformation does take place under high temperature treatment (Table 2-3). They give the order of racemization of several amino acids as Asp > Glu > Ala > Phe, Leu, Val. The higher order of racemization means a higher ratio of D-amino acids is formed in the product amino acid. What is the order of methane convertibility of these D-amino acids? And if there is any relation between racemization ability of an L-amino acid and the BTM of its D- form isomer? From Table 5-3, The order of these 6 D-amino acids for BTM is Asp, Ala > Glu > Val, Phe, Leu. The order of racemization is, thus, rather similar to that of BTM. Generally, the more easily an L-amino acid is racemized, the less refractory is its D-form isomer to digestion. This tendency offsets the impact of thermal conditioning to digestion. This conclusion is based on a comparison of only seven amino acids, and more data are needed to make this a firm conclusion. Nevertheless, because of racemization, thermal treatment always reduces bioconvertibility of L-amino acids.

D- and L- amino acids are interchangeable. Consequently, D-amino acids can also be used in the control of metabolic pathways involving L-amino acids. This conclusion seems to be supported by the similarity of gas composition for L- and D- amino acids (Table 5-2).

5.3.4 Other Substrates

Glucose aqueous solution is colorless, odorless, and shows high short-term BTM. Its

biodegradability is very sensitive to retention time in thermal conditioning, dropping sharply with increasing retention time. A delayed first stage of digestion is recorded, reaching as long as 20 days for glucose with a thermal conditioning time of 25 minutes. This shows that both conversion rate and reaction rate are decreased. An observed dark brown color is believed to be carbon produced by glucose dissociation. Such inorganic carbon is not digestible, and it is at least one reason for reduced ultimate bioconvertibility.

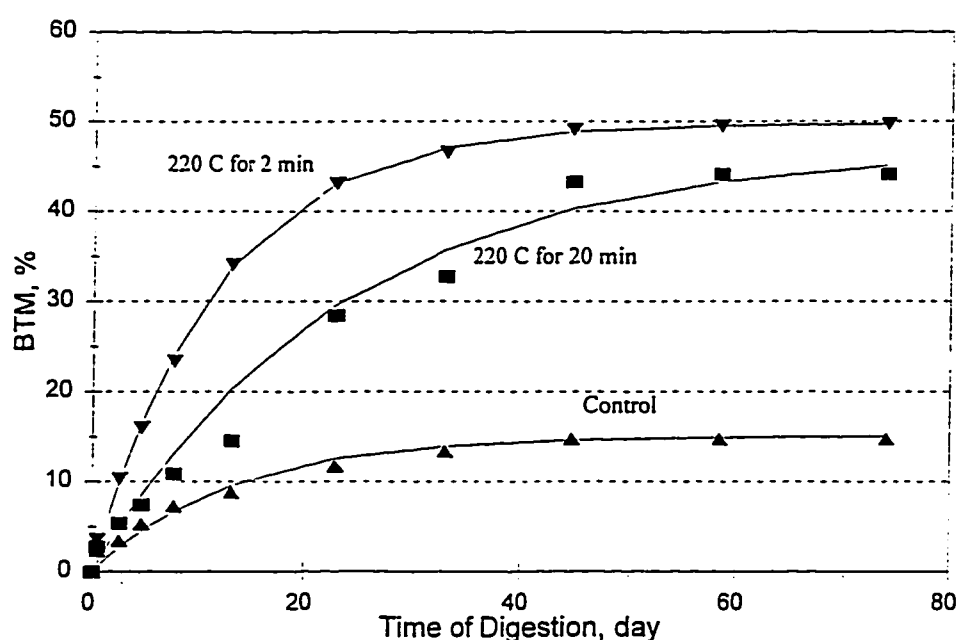


Figure 5-2. BTM of thermally conditioned PDS.

The BTM of PDS is significantly increased by thermal conditioning, the ultimate BTM being triple that of the raw material (Figure 5-2). The effect of thermal conditioning time is illuminated by a comparison of the kinetic parameters in Equation 5-5 for PDS conditioned at 220°C for 2 and 20 minutes. By regression, ultimate BTM is 49.8 percent for the former and 45.1 percent for the later sample, and rate constant k is 0.088

day⁻¹ for the former and 0.044 day⁻¹ for the later. Thus, longer retention time results not only in lower ultimate bioconvertibility but also in lower reaction rate constant. The resultant loss in gas production occurs most significantly at the first two weeks of digestion. Because retention time for digestion processes is generally less than two weeks, the delayed phase at the beginning of digestion is especially disadvantageous for process efficiency.

This phenomenon of a delayed phase for PDS is in agreement with the results for its major constituents, amino acids and glucose. Also, from the test results for amino acids and glucose, two reasons may be offered for the reduction in biodegradability by thermal conditioning. Decomposition of highly biodegradable materials is one reason. Another is the formation of D-amino acids by racemization. Although, the work of others strongly supports the later reason, further experimental work is required for proof. In order to increase sludge biodegradability, short retention times of seconds or minutes should be used.

5.4 SUMMARY

L-amino acids are highly biodegradable, but the extent varies according to structure. At 220°C and 2 minutes retention time, biodegradability is slightly reduced. However, when retention time is increased to 25 minutes, biodegradability of L-amino acids as whole dropped significantly. A yellow-brownish color, as well as an odor, was produced.

Some D-amino acids have the same high biodegradability as their L-form isomers. Most D-amino acids are less biodegradable than their isomers in two ways: lower reaction rate or ultimate conversion. In comparison with other studies(Hayase *et al.*, 1975), it is concluded that highly biodegradable D-amino acids are more easily produced by racemization reactions. D-amino acids produced by racemization reactions are highly likely contributors to the loss of sludge biodegradability by thermal conditioning.

For high-temperature thermal conditioning, short retention time favors sludge biodegradability.

CHAPTER SIX

IMPLEMENTATION OF THE RTC PROCESS

In this chapter, the feasibility of incorporating the RTC process into an existing wastewater treatment plant is assessed by drawing up suitable flow sheets and cost estimates. The Wards Island Water Pollution Control Plant in New York City is the selected target plant. Design criteria for this installation are based on the bench-scale studies described above. Engineering design, including development of flow sheets, equipment selection and design, and economic analyses are performed with process design software, ASPEN PLUS. Economic analyses include capital and operating costs of the proposed alternatives, and the comparison of their operating costs with that of the current process.

As a result of these studies, two promising alternatives for the commercial implementation of RTC into an existing WPCP have been identified and are reported here. In addition, a possible modification for ammonia removal is evaluated.

6.1 BACKGROUND

6.1.1 RTC Application Objective

Rapid thermal conditioning (RTC) can be incorporated in either a new or existing sludge

treatment facility employing anaerobic digestion. The process offers several benefits:

- (1) Volatile suspended solids are solubilized. This results in a decrease in the solids output of the wastewater treatment plant requiring land disposal.
- (2) The dewaterability characteristics of the sludge are improved, so that a drier cake is obtained by centrifugation even without polymer addition.
- (3) The resulting soluble organic substances stimulate biological activity. This results in increased gas yields in subsequent anaerobic digestion. The methane gas released may be used as the fuel for the thermal conditioning process, making the overall process thermally self-sufficient.
- (4) The high temperatures of RTC destroy pathogens, making it possible to meet requirements for Class A sludge as defined in the US EPA Sewage Sludge Use and Disposal Regulations. This allows widespread land application of the residual biosolids.
- (5) It was noticed during dozens of tests that RTC did not increase the unpleasant odor of sludge. This is a significant improvement over traditional thermal conditioning processes. Evidently, the short retention time avoids formation of new odoriferous compounds.

The objectives of this design are, first, to develop methods for the application of RTC technology to municipal wastewater facilities, and, second, to assess the economics of

possible implementation options. To optimize the design of a sludge treatment and disposal system, several factors must be analyzed; these usually include sludge dewaterability, biodegradability, energy balance, and process reliability. However, cost is most important and dominates the optimization process.

6.1.2 Current Operation of the Wards Island Water Pollution Control Plant

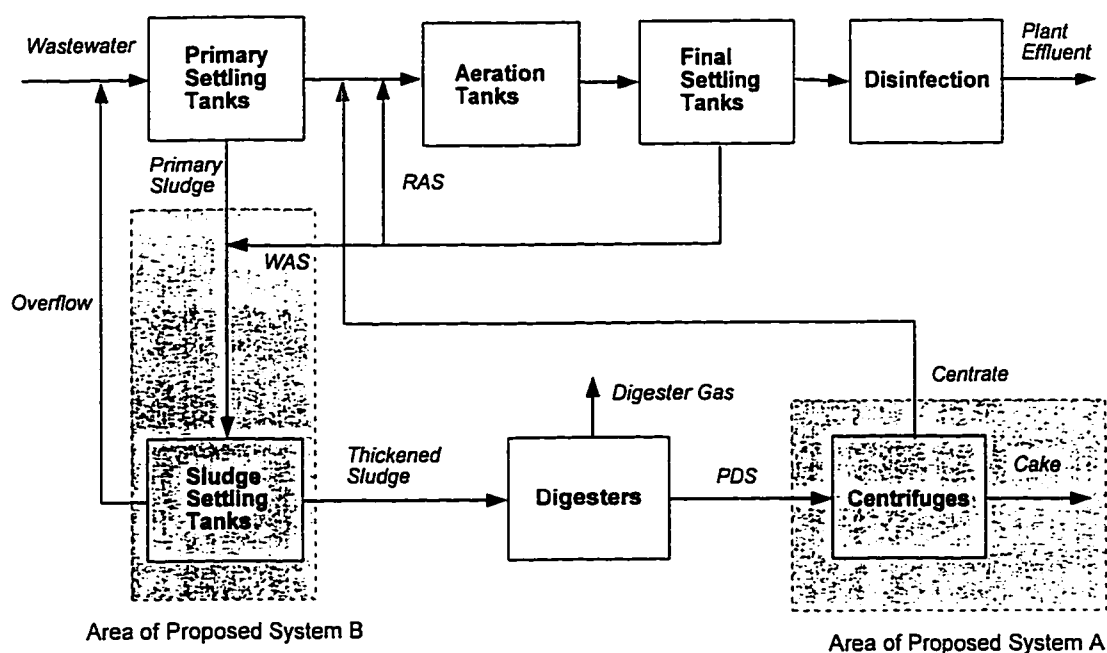


Figure 6-1. Wards Island WPCP process flow diagram

The Wards Island WPCP is the second largest of the 14 WPCPs in the five boroughs of New York City (Figure 6-1). Operating data, averaged over 12 months from July 1991 to June 1992, are shown in Table 6-1. During the fiscal year ending June 1992, this plant treated municipal wastewater at an average rate of 268 million gallons per day (MGD), 16.8 percent of the total amount treated in New York City. Digested sludge

from the plants was disposed of at a designated site in the ocean until December 31, 1991. Since then, digested sludge has been dewatered in centrifuges for land disposal at a rate of approximately 80 dry tons of dewatered sludge per day. Centrate is returned to the head of the aeration tanks.

Table 6-1. The operating parameters for the Wards Island WPCP, Fiscal year 1991-1992.

Parameter	Value	Note
Sewage flow rate, Mm ³ /day	1.01	268 MGD
Aerated flow rate, Mm ³ /day	1.01	268 MGD
SS of raw sludge, mg/L	87	
SS of primary effluent, mg/L	66	
TS of thickened sludge, % by weight	3.7	
VS of thickened sludge, % TS	78.5	
Flow rate of PDS, m ³ /d	2525	0.67 MGD
TS of PDS, %	2.6	
VS of PDS, % TS	69	
Digester gas, m ³ /day	48,810	1,723,000 cuft/d
Digester gas wasted, m ³ /day	18,690	660,000 cuft/d
Sludge cake, dry metric ton/d	73	77.8 dry ton/d

Digestion gas is sent to the Manhattan Psychiatric Center in exchange for steam to heat the plant's buildings and to maintain the temperature of the digesters within the mesophilic range. Of the total gas produced, 38 percent is wasted. Dewatered sludge cake may be transported to other states for land application and disposal. Because of the long distances, transportation of the sludge cake represents a major cost item. Any process that reduces the amount of cake produced without affecting its quality would have a significant impact on the overall operating cost.

6.2 IMPLEMENTING THE RTC SYSTEM

The development of design criteria is based on the Ward Island WPCP operational data, laboratory test results, and engineering principles. Although major tests for development of RTC have been done, there may still be needs for more experiment. In some case, extrapolations of test results were used with cautious consideration.

6.2.1 RTC Effect on Sludge Biodegradability

The major laboratory tests on RTC process are focused on the dewaterability and biodegradability of thermally conditioned sludge. The work on the sludge dewaterability of RTC process is presented in Chapter Four. The work on sludge biodegradability was performed by Pierides (1993), which is summarized in this section.

The anaerobic biodegradability of thermally conditioned sludge was first tested using 160 ml serum bottles as batch reactors for periods exceeding 60 days. The results of these tests were used to select the best conditions for RTC. More extensive anaerobic digestion tests, using sludge treated at the optimal RTC conditions, were made in a 6.5-liter continuous stirred tank reactor (CSTR) and a hybrid packed bed reactor. The packed bed reactor has an inside diameter of 11 cm and a height of 1.83 m, packed with 1.5 cm diameter pall-ring media. For the CSTR and packed bed tests, an optimum hydraulic retention time was selected. All tests were conducted in an environmental chamber maintained at 35°C.

The RTC process increases sludge anaerobic digestibility giving higher yields of methane gas and leaving correspondingly less organics in the residue. RTC not only increases ultimate gas production, but also increases the rate of reaction especially during the first several days of digestion. For WAS in serum bottle tests, RTC at 220°C for 10 to 30 seconds results in 200 percent increase in gas production during the first one to two days, compared to unconditioned sludge. Over a period of 20 days, the average gas production improvement is 80 percent, a value which is maintained even after 60 days. Anaerobic packed bed tests show that 80 percent VDS in RTC PDS can be removed with 2 days HRT. The significance of this improvement is that shorter retention times can be used in anaerobic digestion.

Both WAS and PDS consist mainly of bacterial cells and multiple tests show increased biodegradability and dewaterability of these substrates. In contrast, primary sludge, which contain inorganic and non-living organic matter, show considerably less response to RTC (Pierides 1994). Consequently, thermal conditioning is considered only for WAS and PDS.

6.2.2 Rapid Thermal Conditioning System

The RTC system consists in all cases of a positive displacement pump, boiler, rapid thermal reactor and flash tank all operating under high temperature and pressure. A positive displacement pump is required to transport sludge to the thermal reactor against its operating pressure of 2,320 kPa (336 psi). Saturated steam at 220°C is provided by

a boiler fueled with methane from digestion or an external source if additional fuel is needed.

The streams of sludge and steam each enter the reactor through a static mixer to reach the mixing temperature of 220°C nearly instantaneously. The liquid retention time in the reactor is 30 seconds. The pressure in the reactor is maintained above vapor pressure of water at the reaction temperature to prevent vaporization of the mixture. The presence of vapor in the reactor shortens retention time and deteriorates the performance of thermal conditioning. The maintenance of pressure is achieved by an automated control valve, and the suspension is discharged into a flash tank.

Flashing of the treated suspension serves two objectives: First, it quenches reaction. When the hot suspension enters the flash tank, partial vaporization of the water content occurs. The temperature instantaneously drops from 220°C to the saturation temperature of thermally treated sludge which will be about 100°C if the pressure in the flash tank is atmospheric. This sudden drop in temperature results in a drastic decrease in reaction rate. A second objective is to separate the water from the sludge to reduce the load on both dewatering and digestion equipment which follows. About one fourth of the influent suspension is vaporized. Since vapor contains volatile organics, it is recycled to the aeration section of the plant. Except in the size of its various components, this RTC subsystem is the same in each proposed implementation alternative.

6.2.3 Thickening of Sludge Prior to Thermal Conditioning

The major cost of operating an RTC system is that associated with the supply of thermal energy to achieve the operating temperature. In some circumstances the increased gas production could be less than the additional fuel needed for the RTC process. Therefore, strategies to reduce energy consumption must be considered.

Heat recovery by using hot product streams to preheat feed sludge, as has been used in other processes such as Porteous and Zimpro, is not considered here because through-the-wall heat transfer results in slow heating. If this approach is used, the benefits of rapid thermal conditioning are lost. There are, nevertheless, several ways to recover the heat from this RTC process:

- (1) Preheat the boiler feed water using heat exchangers.
- (2) Preheat sludge entering the digesters to compensate heat loss from this equipment.
- (3) Use the heat content of thermally conditioned sludge to compensate for heat loss from the digester used to treat RTC sludge.

However, even with such heat recovery the RTC and digestion system would not be self-sufficient in thermal energy. The digester gas can provide less than 40 percent of the boiler fuel requirement for conditioning of PDS. A calculation shows that extra fuel cost alone would then make the RTC process more expensive than current processes to handle and dispose of sludge.

Thickening the sludge reduces the steam required to heat it to operating temperature, and the proposed flow sheets incorporate thickening of sludge prior to the RTC step. It is assumed here that thickening does not affect the solubilization of volatile suspended solids. Support for this assumption comes from tests with sludge solids concentration lower than 4.9 percent. Its application to sludge with higher solids concentration, though accepted for the present, will need experimental verification. Sludge thickening appears to be a practical and effective way to reduce the energy required without affecting the basic mechanism of solubilizing the volatile suspended solids.

Centrifugation is taken as the preferred method of thickening because it has a high processing capacity and a high suspended solids recovery rate. With polymer addition, Humboldt centrifuges at the Wards Island WPCP are able to achieve a solids concentration of 30 percent for dewatered PDS, which is an upper limit achieved for PDS thickening. In laboratory centrifuge tests without polymer addition, 10 percent is typical for solids concentration and can be considered the lower limit of PDS thickening. This substantial reduction in flow rate decreases the required capacity of the RTC reactor, pump, and digester for conditioning of PDS by about three-fourths, resulting in both lower capital and operating costs.

6.2.4 Digestion of Thermally Conditioned Sludge

There are two options for digestion of thermally conditioned sludge. One is that the entire product of thermal conditioning, both suspended and soluble solids, be subjected to anaerobic digestion in a completely mixed suspended-growth reactor. The

disadvantage of this method is that the hydraulic and solids retention time cannot be controlled independently, requiring a larger reactor. However, a larger volume of gas can be produced and more volatile solids can be destroyed since both soluble and remaining suspended solids will be subject to biological degradation. This would take full advantage of the effect of thermal conditioning on sludge biodegradability.

An alternative approach is to separate the soluble from the suspended solids and digest only the soluble organics. An attached growth reactor is more appropriate in this case, resulting in high efficiency and short hydraulic retention time. It requires a digester of small volume; an attractive feature in New York City plants where land is scarce. However, the potential of an attached growth system for gas production may be lower than that for a suspended growth system.

6.2.5 Use of Existing Equipment

Existing equipment, which includes digesters, centrifuges, grinders, pumps, and piping, would be used in implementing the RTC system. Of these, digesters and centrifuges represent the most expensive items in the RTC-digestion system configuration. Their utilization offers significant savings in capital cost. Their configuration in the system may have to be changed depending on the operating alternative selected. Existing dewatering centrifuges may also be operated as thickeners and handle almost twice the flow rate of sludge as that of dewatering centrifuges. To ensure the reliability of rotating machinery, such as pumps and centrifuges, standby units are purchased. Also for the same reason, two boilers are used for each system.

6.3 DESIGN OF SELECTED ALTERNATIVES

Two alternatives for implementing rapid thermal conditioning of sludge at the Wards Island plant have been devised. In the first scheme (System A), thickened sludge is subjected first to RTC, and then attached growth anaerobic digestion. For the second (System B), WAS is subjected to RTC, mixed with primary sludge and then digested in a suspended growth anaerobic reactor.

6.3.1 Software and Computation

ASPEN PLUS release 8.5-3 (Aspen Technology, Inc., 1987), a well-developed computer software for chemical engineering process design, was used to simulate the proposed system and perform the following computations: mass balance, energy balance, equipment specification, cost, and economic analysis.

To facilitate the use of ASPEN PLUS model, RTC system units were coded and incorporated as model units. The Unit Operation Model of ASPEN PLUS was used to calculate the mass and energy balance. Next, equipment sizing criteria such as surface areas of heat exchangers and power requirements of individual items of equipment were established. To simplify the calculation, sludge was treated as pure water permitting the use of the ASME Steam Tables available in ASPEN. The solids part of sludge and the biochemical reactions were calculated separately as a supplement to the calculations by ASPEN PLUS.

ASPEN PLUS Costing (Aspen Technology, Inc., 1990) was used to estimate the capital costs and evaluate the economics of the designs. ASPEN PLUS Costing consists of four steps: (1) Equipment sizing and costing, (2) Fixed capital cost estimation, (3) Operating cost estimation, and (4) Economic evaluation. These four steps can be all or partially executed. This design stops at operating cost estimation, and economic evaluation is handled off line. ASPEN PLUS can either retrieve the information from the Unit Operation Model or receive information from data entry. ASPEN PLUS has its own built-in data bank. Defaults are provided in many cases.

ASPEN PLUS Costing uses a factor method to generate cost estimates: The base costs of major process equipment are the bases to which a series of key factors is applied to estimate the cost of installation of equipment and total fixed capital cost. This factor method is used throughout the economic analysis. All prices, material, and labor costs are adjusted for inflation using the cost indexing system. The required data input can be placed into three categories: no default, adequate default and inadequate default. For the first category, data must be entered reliably. For the second category, the most likely one, default data are used. For the third case, adjustment must be performed on an individual basis.

Fixed capital cost can be broken down into depreciable capital costs and nondepreciable costs. The hierarchical structure of fixed capital cost with detailed content of each item is shown in Table 6-2. The hierarchical structure of operating cost, with detailed content of each item, is shown in the Table 6-3. Among utility costs, the costs for electricity and water were provided by New York City DEP. The cost of chemicals for water

Table 6-2. The hierarchical structure of fixed capital cost.

Item	Cost
Total fixed capital cost	
Depreciable capital cost	
Direct cost	
Equipment purchased cost	
Major pieces of equipment	ASPEN, or vendors quote
Unlisted equipment	0.15 \$/\$ total equipment base cost (default)
Commodity cost	
Commodity material cost	0.3 to 0.9 \$/\$ unit equipment cost
Commodity labor cost	0.05 to 0.06 hr/\$ unit commodity material
Capitalized spares	0.02 \$/\$ unit equipment base cost (default)
Process building	
Material	0.12 \$/\$ unit equipment and material cost)
Labor	0.05 hr/\$ building material cost
Service items	
Service buildings	
Material	0.038 \$/\$ total process units
Labor	0.025 hr/\$ service building material
Service system	
Material	0.03 \$/\$ total process units, service building
Labor	0.01 hr/\$ service system material
Site cost:	
Site preparation	
Material	0.01 \$/\$ total direct material, equipment cost
Labor	0.02 Hr/\$ site preparation material
Freight	0.02 \$/\$ total direct equipment, material cost
Sales taxes	0
Indirect cost:	
Contractor's field cost:	
Material	0.27 \$/\$ total direct labor, site cost
Labor	0.73 \$/\$ total direct and site labor
Contractor's home office cost	0.12 \$/\$ total direct cost and contractor's field indirect cost
Owner's home office cost	0.056 \$/\$ total direct, contractor's field indirect
Various fees, permits and insurance	0.08 \$/\$ total direct cost and contractor's field indirect cost
Additional depreciable costs	\$1,000,000
Contingency allowance	0.1 \$/\$ total director and indirect costs
Nondepreciable costs:	
Land	0
Royalty	0

Note:

1. The wages rate for construction labor is \$30/hr.

Table 6-3. The hierarchical structure of operating cost.

Item	Cost
Operating cost:	
Utility:	
Electricity	\$ 0.03/kWh
Water	No cost incurred
Chemicals for boiler water treatment	\$1.02/1000 gal water
Fuel	\$5.00/MMBtu
Labor:	
Operating labor:	
Availability	365.5 days/year
Number of operators per shift	2 persons
Average operator wage rate	\$20/hr
Maintenance labor	0.036 \$/\$ total depreciable cost
Supervision	0.02 \$/\$ operating and maintenance labor cost
Fringe benefits	0.4 \$/\$ operating labor, maintenance labor, and supervision costs
Supplies:	
Operating supplies	0.1 \$/\$ operating labor cost
Maintenance supplies	0.024 \$/\$ total depreciable cost
Laboratory charges	0.1 \$/\$ operating labor cost
General work:	
General and administration	0.1 \$/\$ operating labor cost, maintenance labor cost, and supervision cost
Property Tax	0
Insurance	0.008 \$/\$ total depreciable cost
Depreciation	Life span of 15 years

treatment was provided by Metro Group Inc., a Long Island City based consulting company. The natural gas price was provided by the Public Affairs Department of Con Edison. Project start date was specified as January 1994. As no data were entered for project duration or cost index, ASPEN PLUS will estimate the project duration based on the labor hours required and generated indexes at the default centroid dates based on the default escalation rate 7 percent per year. At the end of these calculations, the operating costs due to the incorporation of the RTC process were generated.

6.3.2 System A

A flow sheet for System A is shown in Figure 6-2, its design basis in Table 6-4, and its major streams in Table 6-5. PDS is thickened first using centrifuges, to increase the solids concentration to 10 percent. The PDS centrate has low BOD and is of little value for thermal conditioning and digestion. Therefore, it is returned to the aeration tanks, following current practice at the Wards Island Plant. The mass flow rate of thickened PDS is reduced to 27 percent of that of the feed. (Although an experimental RTC test with thickened PDS of 10 percent solids has not been done, it is assumed that the fraction solubilized, 47 percent on a dry basis, is unchanged by thickening). This substantial reduction in flow rate reduces the required capacity of the RTC unit, the pump, and the digester for conditioned PDS by about 75 percent. This results in both a lower capital cost and a lower operating cost.

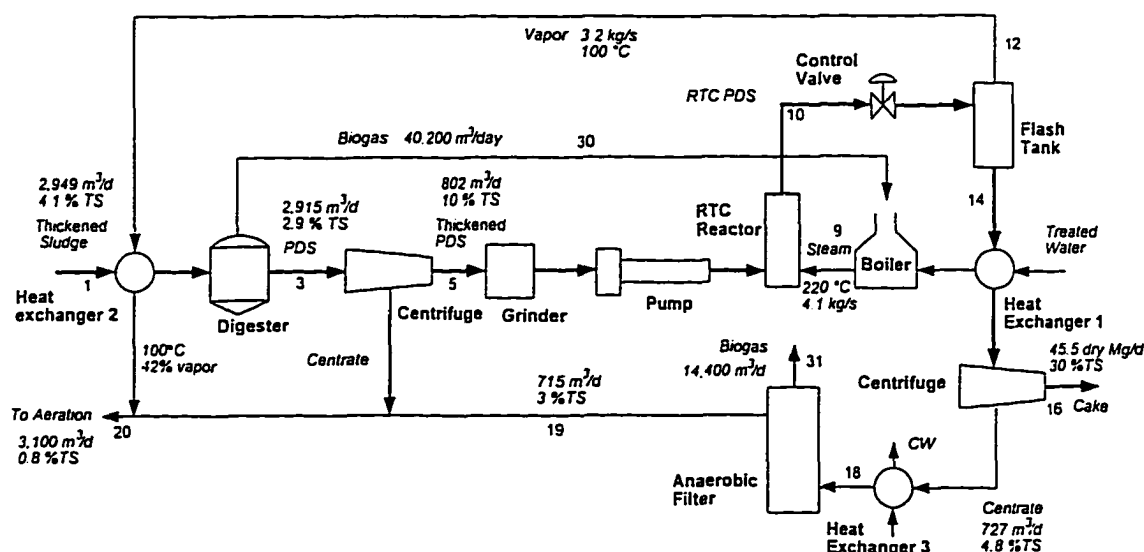


Figure 6-2. Flow diagram of System A, RTC of thickened PDS

Table 6-4. Design basis for System A.

Parameters and units	Value	Note
Flow rate of thickened sludge, m ³ /d	2,949	0.78 MGD
TS of thickened sludge, % by weight	4.1	
VS content of thickened sludge, % TS	79	
Temperature of thickened sludge, °C	15	
VS reduction of thickened sludge by digestion, % VS	40	
Gas production, m ³ /kg VS destroyed	1.06	17.0 ft ³ /lb
Lower heating value of digester gas, kJ/m ³	22,400	600 Btu/ft ³
TS of thickened PDS, % by weight	10	
Digestion temperature, °C	35	
RTC temperature, °C	220	
RTC time, sec	30	
TS solubilization of PDS due to RTC, % TS	47	
VDS content, % DS	80	
SS recovery rate by centrifuge, % SS	96	
Cake solids concentration, % by weight	30	
VDS removal rate by anaerobic filter, % VDS	50	

Centrifuges are a major investment. Though a centrifuge thickening process is added, the total number of centrifuges does not necessarily increase beyond what is now used in the current sludge dewatering process. Thickening achieves a lower solids concentration in the cake than does the dewatering process. When a centrifuge is used for thickening, its capacity can be 50 percent higher than for dewatering. Therefore, as long as the thickening ratio is less than 1/3, rearrangement of the centrifuges currently in use is able to meet the requirements of both thickening and dewatering. Additional units of this costly item are not be required in System A.

Table 6-5. Stream summary, System A.

Stream number	Flowrate Mg/d	State	Temperature °C	TS %	DS %
1	2,949	liquid + solids	15	4.10	0.15
3	2,912	liquid + solids	35	2.90	0.19
5	803	liquid + solids	35	10.00	0.18
9	354	vapor	220	0.00	0.00
10	1,157	liquid + solids	220	6.94	3.26
12	277	vapor	100	0.00	0.00
14	881	liquid + solids	100	9.12	4.29
16	152	liquid + solids	69	30.00	3.00
18	729	liquid + solids	45	4.78	4.55
19	716	liquid + solids	37	3.01	2.50
20	3,101	liquid + solids	35	0.83	0.71
30	42,200 m ³ /d	gas			
31	14,400 m ³ /d	gas			

For this flow sheet, an up-flow anaerobic filter is selected for digestion of thermally conditioned sludge. To provide the filter with soluble feed, suspended solids must be separated and excluded using a dewatering centrifuge preceding digestion. This configuration has an advantage in that the higher temperature of thermally conditioned PDS, close to 70°C, reduces the viscosity of the sludge and improves its settleability. As was done previously, the filter effluent is recycled to the head of the aeration process.

For the dewatering of thermally conditioned thickened PDS, suspended solids concentration is as high as 6 percent. Higher solids concentration of centrifuge input results in a dewatered cake of higher solids concentration. This is an additional advantage of thickening.

The resulting design of System A is shown in Table 6-6.

Table 6-6. Major equipment for System A.

Equipment name	Size	Quantity	Design basis
Digester	7140 m ³	8	Existing, operation in same manner
Thickening centrifuges	68 m ³ /hr	2	Existing, model: Humboldt 450F Flowrate: 2,900 m ³ /d
Dewatering centrifuges	46 m ³ /hr		Existing, model: Humboldt 450F
Positive displacement pump, MOYNO 6P10	26 m ³ /hr	2*	Flowrate: 800 m ³ /d 30 kW, Inlet pressure: 100 kPa Outlet pressure: 2,320 kPa
Boiler	6 MW	2	Output: 220°C vapor 4.08 kg/sec Feed: 90°C water Efficiency: 0.8 Fuel: digester gas
Reactor	0.4 m ³	1	Retention time: 30 sec. Pressure: 2,320 kPa
Flash tank	D 0.8 m, H 1.6 m	1	Retention time 1 min. Inlet: 220°C, 2,320 kPa outlet pressure: 100 kPa
Anaerobic filter	1755 m ³	1	Retention time 2 days TS: 5%, DS:90% TS Flowrate 727 m ³ /d Total COD 60,000 mg/L Soluble COD 15,000 mg/L
Heat exchanger 1	45.7 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 15°C Cold stream outlet temperature 90°C
Heat exchanger 2	72.1 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 15°C Cold stream outlet temperature 45°C
Heat exchanger 3	55.9 m ²	1	Heat transfer coefficient 450 W/m ² K Hot stream inlet temperature 70°C Hot stream outlet temperature 40°C

* One unit is standby.

6.3.3 System B

System B is designed for the treatment of WAS in the Wards Island WPCP. Although the flow rates of primary sludge and WAS in this plant were not separately listed in the available operating data (Table 6-1), they could be calculated from this information. Table 6-7 shows the design basis, and Table 6-8 is a summary of the major streams of System B.

Table 6-7. Design basis for System B.

Parameters and units	Value	Note
Flow rate of WAS, m ³ /d	4,011	1.08 MGD
TS of WAS, % by weight	2.47	
VS content of WAS, % TS	83	
Temperature of WAS, °C	15	
TS of thickened WAS, % by weight	7.1	
RTC temperature, °C	220	
RTC time, sec	30	
TS solubilization of WAS due to RTC, % TS	55	
Flow rate of primary sludge, m ³ /d	500	
TS of primary sludge, % by weight	6	
VS content of primary sludge, % TS	62	
Temperature of primary sludge, °C	15	
VS reduction digestion, % VS	66	
Cake solids concentration, % by weight	30	
Gas production, m ³ /kg VS destroyed	1.06	
Lower heating value of digester gas, kJ/m ³	22,400	
Digestion temperature, °C	35	
SS recovery rate by centrifuge, % SS	96	
Cake solids concentration, % by weight	30	

Table 6-8. Stream summary, System B.

Stream number	Flowrate Mg/day	State	Temperature °C	TS %	DS %
3	4,011	liquid + solids	15	2.47	0.10
5	1,288	liquid + solids	15	7.12	0.10
9	587	vapor	220	0.00	0.00
10	1,875	liquid + solids	220	4.89	2.69
12	423	vapor	100	0.00	0.00
14	1,452	liquid + solids	100	6.31	3.47
17	499	liquid + solids	69	6.00	0.20
18	1,951	liquid + solids	45	6.23	2.63
19	1,889	liquid + solids	35	3.15	0.55
20	160	liquid + solids	35	30.00	0.41
21	1,729	liquid + solids	35	0.67	0.56
22	4,452	liquid + solids	23	0.43	0.28
25	69,000	m ³ /d gas			
26	177,000	MJ/d gas			

In System B (Figure 6-3), WAS with a solids concentration of 2.47 percent is thickened by centrifugation to 7.1 percent in order to reduce the size of the RTC unit. The lower degree of thickening used in this case, as compared to System A, is a result of the nature of WAS, which is more difficult to thicken and dewater than PDS. Moreover, thickening of WAS requires a different type of centrifuge from that used for PDS, and these must be purchased. The centrate is returned to the influent of the aeration process, and thickened WAS is pumped to the RTC system.

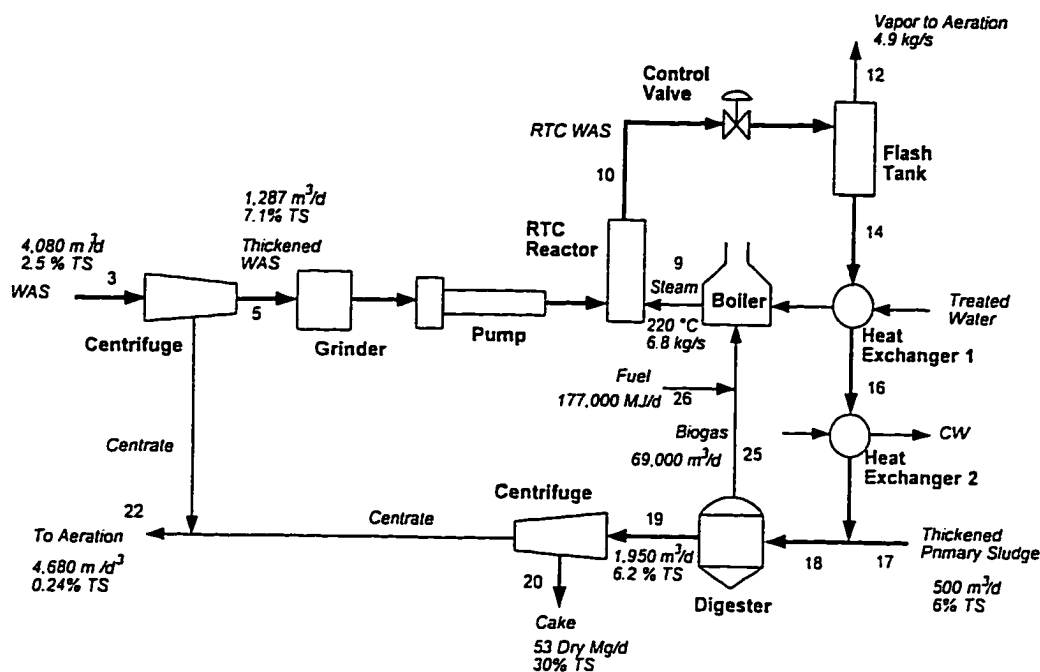


Figure 6-3. Flow diagram of System B, RTC of WAS

Thermally conditioned WAS is first cooled, and then mixed with thickened primary sludge. The mixed sludge is at 45°C before being pumped into digesters. The solids concentration of thickened primary sludge is assumed to be 6 percent. Thermal conditioning is limited to WAS because experiments with primary sludge showed negligible improvement of both biodegradability and dewaterability. The digested sludge is dewatered by centrifuge and the centrate returned to the head of the aeration process. Additional fuel of 177,000 MJ/d, 13 percent of the total, is needed for this flow sheet. However, this requirement can be eliminated if WAS can be thickened to a solids concentration of 8.0 percent.

Design results for System B are shown in Table 6-9. Digestion in System B takes place in one step, making separate digesters for thermally conditioned PDS, as in System A,

unnecessary. Two-thirds of the dewatering centrifuges must be replaced by thickening centrifuges specifically for WAS.

Table 6-9. Major equipment for System B.

Equipment name	Size	Quantity	Design basis
Digester	7140 m ³	5	Existing, operation in same manner
Thickening centrifuge Humboldt BL5-2	83 m ³ /hr	3*	Flowrate: 4,000 m ³ /d (1.08 MGD)
Dewatering centrifuges	46 m ³ /hr	2	Existing, model:Humboldt 450F
Positive displacement pump MOYNO 6P10	26 m ³ /hr	3*	Flowrate 800 m ³ /d 30 kW, Inlet pressure: 100 kPa Outlet pressure: 23,200 kPa
Boiler	12.5MW	2	Output:220°C vapor 6.83 kg/sec Feed: 90°C water Efficiency: 0.8 Fuel: digester gas, and natural gas
Reactor	0.65 m ³	1	Retention time 30 sec. Pressure 23,200 kPa
Flash tank	D 1.0 m, H 2.0 m	1	Retention time 1min. Inlet: 220°C, 23,200 kPa outlet pressure: 100 kPa
Heat exchanger 1	96.7 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 15°C Cold stream outlet temperature 90°C
Heat exchanger 2	39.7 m ²	1	Heat transfer coefficient 450 W/m ² K Hot stream inlet temperature 69°C Hot stream outlet temperature 53°C

* One unit is standby.

6.4 ECONOMIC COMPARISON

Economics analyses were performed with ASPEN PLUS 8.3-5 which was used to size the equipment, and estimate cost. However, the cost of major items of equipment, such

as centrifuges and boilers were based on prices quoted by suppliers. The itemized costs of the new equipment for each system are shown in Tables 6-10 and 6-11. Based on the cost of new equipment, the fixed capital costs, as estimated using ASPEN PLUS, are \$11,893,000 for System A and \$18,034,000 for System B. The itemized fixed capital costs are shown in Table 6-12. As a rough check, it is reasonable for fixed capital cost to be approximately five times the cost of new equipment. Amortized total fixed capital (linear depreciation for a life time of 15 years) is included in operating costs. Utilities include electricity, fuel, and chemicals to treat boiler water. Six additional operating personnel are estimated to be required for the operation of either System A or B. Operating costs (Table 6-13), ascribable to the additional RTC process equipment is \$2,490,000 per year for System A and \$4,031,000 per year for System B. These operating costs are to be compared with the costs of current (unmodified) system operation.

New York City favors those methods which prepare sludge for various land application alternatives that include composting, agricultural land spreading, land reclamation, land filling and manufacture of soil conditioner. Currently, three private companies, New York Organic Fertilizer Company (NYOFCO), MERCO and Chambers Service, Inc, are contracted to handle 400 dry tons of sludge cake daily produced in New York City. Dewatered sludge cake with 70 percent moisture may be transported to Arizona, Colorado, Pennsylvania, Texas, and Virginia for composting, land application and reclamation. Charges to New York City vary from \$101.4 to \$261.2 per wet metric ton (\$92 to \$237 per wet ton) of sludge, because of differences in subsequent treatment methods and disposal locations (Merco \$92/wet ton, NYOFCO \$215/wet ton, and

Table 6-10. Purchasing cost of major items of equipment for System A.

Equipment name	Quantity	Purchased cost
Digester	8	existing
Grinder	2	existing
Thickening centrifuge	2	existing
Positive displacement pump	2	\$106,400
Boiler	2	\$232,000
Reactor	1	\$4,700
Flash tank	1	\$5,300
Dewatering centrifuge	1	existing
Anaerobic filter	1	\$1,489,600
Heat exchanger 1	1	\$49,100
Heat exchanger 2	1	\$65,600
Heat exchanger 3	1	\$56,000
Unlisted		\$301,000
Total		\$2,310,000

Table 6-11. Purchasing cost of major items of equipment for System B.

Equipment name	Quantity	Purchasing cost
Digester	5	existing
Grinder	2	existing
Thickening centrifuge	3	\$2,568,000
Positive displacement pump	3	\$160,500
Boiler	2	\$402,600
Reactor	1	\$4,700
Flash tank	1	\$7,400
Dewatering centrifuge	2	existing
Heat exchanger 1	1	\$78,600
Heat exchanger 2	1	\$31,300
Unlisted		\$488,100
Total		\$3,741,200

Table 6-12. Fixed capital cost summary.

	(Unit: \$)	
System	A	B
Equipment Cost	2,310,000	3,741,200
Commodity Material Cost	1,127,900	1,260,700
Commodity Labor Cost	1,100,100	1,246,800
Capitalized Spare	46,500	75,300
Building Material	81,300	605,300
Building Labor	78,900	586,200
Service Building	202,000	323,000
Service System	117,000	187,000
Site Development	69,000	110,000
Freight	76,000	122,000
<i>Total Direct Cost</i>	<i>5,209,000</i>	<i>8,258,000</i>
Contractor's Field Cost	1,278,000	1,992,000
Contractor's Home Office Cost	779,000	1,230,000
Owner's Home Office Cost	363,000	574,000
Fees, Permits and Insurance	519,000	820,000
Additional Depreciable	1,000,000	1,000,000
<i>Total Indirect Cost</i>	<i>3,939,000</i>	<i>5,616,000</i>
<i>Project Contingency</i>	<i>915,000</i>	<i>1,387,000</i>
<i>Progress Contingency</i>	<i>1,830,000</i>	<i>2,775,000</i>
Total Fixed Capital	11,893,000	18,034,000

Table 6-13. Annual operating cost summary.

	(Unit: \$/year)	
System	A	B
Utilities		
Electricity	31,800	161,100
Chemical for Boiler Water	23,200	65,100
Natural Gas	0	425,500
Labor		
Operating	351,000	351,000
Maintenance	428,000	649,000
Supervision	16,000	20,000
Fringe Benefits	318,000	408,000
Supplies		
Operating	35,000	35,000
Maintenance	285,000	433,000
General Work		
General & Administration	79,000	102,000
Insurance	95,000	144,000
Laboratory Charge	35,000	35,000
Depreciation	793,000	1,202,000
Net Annual Operating Cost	2,490,000	4,031,000

Note: Totals are rounded to nearest 1000.

CHAMBERS \$117 - 237/wet ton). Because of the long distances, transportation of the sludge cake represents a major cost item on which water content has a significant impact. In order to reach target dewatering levels at the Wards Island WPCP, present practice

requires the addition of polymer at the rate of about 10 kg/dry metric ton (20 lb/dry ton). The price of this polymer is approximately \$4.4/kg (\$2/lb).

Savings resulting from the introduction of RTC into the WPCP include:

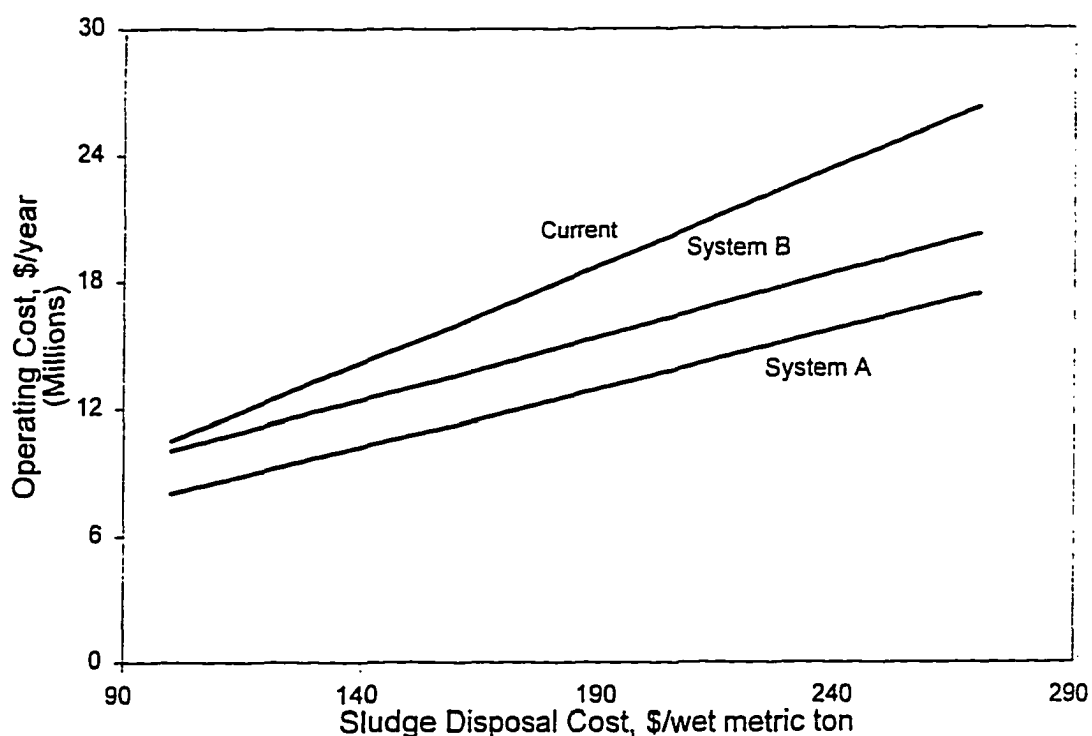
- (1) Reducing the amount of sludge cake requiring disposal,
- (2) Elimination of polymer cost, and
- (3) Elimination of polymer addition operating costs.

Annual operating costs for the different alternatives are given in Table 6-14. Only operating costs related to differences resulting from implementation of the RTC processes are shown. For current practice, the relevant operating costs are the costs of polymer and disposal of sludge cake. For the latter, a range of values is given. For plants incorporating the RTC process, the total operating cost will be the charge to handle the sludge cake plus an operating cost attributable to the RTC system. A charge of \$101.4/wet metric ton(\$92/wet ton) serves as the lower limit for sludge cake disposal cost and \$237/wet ton (\$261.2/wet metric ton) as the upper limit. The results in Table 6-14 are also plotted in Figure 6-4, where the operating costs for the different processes are shown as a continuous function of average cake disposal cost.

From Table 6-14, System A has the lowest operating cost. One important reason is that System A makes full use of the existing facilities. Another reason is that thickening the sludge reduces required size of the RTC system. At this small scale, the RTC system is not only self-sufficient in terms of fuel, it even produces a surplus of digestion gas.

Table 6-14. Comparison of total operating and cake disposal costs.

System	Current	A	B
Sludge, dry Mg/d	84.0		
Cake produced, dry Mg/d	76.2	42.5	49.4
Cake produced, wet Mg/d	254.0	151.7	164.8
Polymer cost (\$MM/yr)	1.23	0	0
Cake disposal cost			
minimum(\$MM/yr)	9.40	5.61	6.10
maximum(\$MM/yr)	24.22	14.46	15.71
RTC operating cost(\$MM/yr)	0	2.49	4.03
Total operating cost			
minimum(\$MM/yr)	10.63	8.10	10.13
maximum(\$MM/yr)	25.45	16.95	19.74
Saving due to RTC			
minimum(\$MM/yr)	N/A	2.53	0.50
maximum(\$MM/yr)	N/A	8.50	5.71

**Figure 6-4. Comparison of operating cost for sludge conditioning and disposal**

System B uses less of the existing plant equipment. Three of the eight existing digesters cannot be used. The savings in operating costs arising from a reduction in the size of the existing digestion facility have not been estimated. System A uses two-step digestion, i. e., digestion both before and after thermal conditioning. System B uses only one-step digestion plus thickening before digestion. Therefore, System B has both the lowest capital and operating costs for the digestion. System B requires additional fuel because WAS is difficult to thicken, and so can only be thickened to solids concentration of 7.1 percent, while PDS can be thickened PDS to a solids concentration of 10 percent. Although System B is not the most economic option for incorporation into an existing facility, it would become so if the digestion capacity of an existing plant is to be expanded or a new plant is to be constructed.

6.5 MODIFICATION FOR NITROGEN REMOVAL

It is attractive to combine ammonia removal with RTC when the latter is incorporated into an existing wastewater treatment plant. The Wards Island WPCP is again used as the target facility for an engineering design and economic analysis. Engineering design includes development of a system flow sheet and identification of individual equipment items. Economic analysis includes capital and operating costs.

6.5.1 Background

In addition to effectively reducing sludge production, and eliminating polymer use, the RTC process could be modified to deal with other problems, such as nitrogen removal.

The removal of these nutrients ranks as a major new issue for WPCPs because of recently promulgated regulations. The U.S. Environmental Protection Agency's new approach to implementing water-based ammonia limits has promoted great interest in cost-effective technologies for ammonia removal.

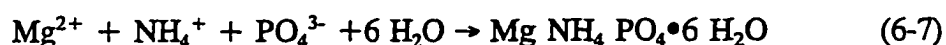
In New York City, since the termination of sludge ocean dumping, the production of ammonia containing centrate from dewatering facilities has presented an additional load for existing plants. Moreover, these plants were not designed for nitrogen removal. In view of the "no net increase" policy of the New York State Department of Environmental Conservation (NYSDEC), nitrogen (in all its chemical forms) has become the contaminant of concern in the centrate discharge. Integration of nitrogen removal must be considered in any upgrading of WPCPs.

In the Wards Island WPCP, ammonia nitrogen was found to increase from 219 mg/L in thickened sludge, to 889 mg/L in digested sludge. Similarly, phosphate phosphorous increased from 48 mg/L to 93 mg/L. Such increases are attributed to re-solubilization of bound ammonia and phosphate by digestion of bacterial cells (Philips, 1993). The characteristics of centrate from the Wards Island WPCP are shown in Table 6-15. More than 80 percent of the nitrogen is in the form of ammonia. The remaining portion of TKN is mostly organic nitrogen. The removal of free ammonia is significant in reducing nitrogen discharge by centrate.

Table 6-15. Characteristics of centrate in Wards Island WPCP dewatering facility (average from March to June, 1993).

Parameter	Value
TS, mg/L	3,180
DS, mg/L	1,340
TCOD, mg/L	2,097
DCOD, mg/L	415
NH ₃ -N, mg/L	950
NO ₂ -N, mg/L	0.11
NO ₃ -N, mg/L	0.15
TKN, mg/L	1,176
Alkalinity, as CaCO ₃ mg/L	3,200
pH	7.8

The combination of ammonium, phosphate and magnesium ions in sludge or dewatering centrate may result in the precipitation of struvite, $\text{Mg NH}_4 \text{ PO}_4 \cdot 6 \text{ H}_2\text{O}$, a troublesome compound which causes scaling of equipment and piping blockage.



There are many methods to remove ammonia, from physicochemical to biological. Four categories have been identified: chemical oxidation of ammonia, chemical precipitation of ammonia, ammonia separation from centrate, and biological nutrient removal. The later two categories are considered to be both economically and ecologically practical (Fillos and Diyamandoglu, 1994). Air stripping at elevated temperature and steam distillation belong to the group of ammonia separations from centrate. These two processes, especially steam distillation, involve high temperature. High temperature

shifts the equilibrium between ammonia and ammonium ion toward ammonia, increases mass transfer rates, and decreases the solubility of ammonia in the liquid phase. All these favor the separation of ammonia at the cost of high thermal energy consumption. However, since RTC is a high temperature process, heat from RTC can be effectively utilized for distillation or air stripping by proper configuration of the heat exchange network. Thus, additional heat may not be needed. Consequently, the integration of RTC and ammonia separation process can be more economic.

In order to shift equilibrium to transform ammonium ion to ammonia, an elevated pH above 9 is necessary. The addition of alkali will also precipitate phosphate, and other solids.

6.5.2 Proposed RTC with Distillation

Because high temperature streams are available from the RTC process, distillation has been selected as a companion process for ammonia removal. For the situation where System A is the preferred configuration, a design and economic study has been carried out for the case where ammonia removal by distillation is integrated into the plant. This arrangement is referred to as System C. Test data show that higher pH improves digestion gas production and slightly increased solids concentration in centrifuge dewatering. Fillos and Diyamandoglu (1994) estimated the increase in settleable suspended solids in centrate due to pH adjustment to be approximately 5 dry tons per million gallons; this figure is used here. Design criteria for System C are given in Table 6-16 and the flow sheet in Figure 6-5.

Table 6-16. Additional design basis for System C.

Parameters and units	Value
Flow rate of thickened sludge, m ³ /d	2,949
TS of thickened sludge, % by weight	4.1
VS content of thickened sludge, % TS	79
Temperature of thickened sludge, °C	15
pH of PDS	7.8
Adjusted pH	9.5
Ammonia in feed as N, mg/L	940
VS reduction of thickened sludge by digestion, % VS	40
Gas production, m ³ /kg VS destroyed	1.06
Lower heating value of digester gas, kJ/m ³	22,400
TS of thickened PDS, % by weight	10
Digestion temperature, °C	35
RTC temperature, °C	220
RTC time, sec	30
TS solubilization of PDS due to RTC, % TS	47
VDS content, % DS	80
SS recovery rate by dewatering centrifuge, % SS	96
Cake solids concentration, % by weight	30
VDS removal rate by anaerobic filter, % VDS	50

The configuration of the RTC part of the process in this case is similar to that of System A, except that a two-stage flash separation is used rather than a single stage. This two-stage operation releases ammonia from the thermally conditioned sludge. Only this concentrated ammonia vapor is fed to the distillation column. The remaining liquid, which contains suspended solids, is discharged from the bottom of the second stage flash tank and sent to a dewatering centrifuge. Reflux is used to obtain concentrated ammonia solution from the top of the distillation column.

(6-10) to (6-12) reflect the alkalinity and acidity in the model, since they affect pH. An experimental curve of pH versus concentration of NaOH in centrate at ambient temperature from the Wards Island WPCP, provided by D. Kathesis (1995), is used as reference. The concentration of HCO_3^- and H^+ in the feed for the model is adjusted to match the experimental curve. As a result, the model feed has the same pH response to NaOH addition as centrate. The following reactions are used to model the behavior of PDS:



The ammonia removal efficiency depends on pH, the configuration of the separation units and their operating conditions. The pH can be elevated by addition of alkali, such as sodium hydroxide, whereby reaction (6-9) is shifted toward the formation of ammonia gas which can be separated from the liquid phase.

Thermal conditioning is carried out at 220°C, and a retention time of 30 seconds. The pressure in the first flash tank is 718 kPa, and the temperature is 166°C. This stream provides the heat for reboiling in the distillation column through a heat exchanger. After

cooling, it is fed into the top of a 13-stage distillation column, because it has the highest ammonia concentration of any stream into the unit. Vapor from the second flash tank contains less ammonia and has a temperature of 100 °C. It is mixed with centrate directly to raise the temperature of the mixture to the bubble point which is 99°C. The mixture is then fed to the fifth stage of the distillation column. In this way, the heat content of the low temperature steam from the second flash tank can be fully utilized, and there is no need for a heat exchanger. The distillation process is a continuous distillation, operated at about atmospheric pressure, with reflux. Heat from the reflux condenser is used to raise the temperature of PDS centrate.

In this design, the pH of PDS is raised to 9.33. The pH of centrate from thermally conditioned PDS must be reduced to about neutral before being fed to the anaerobic filter in order to satisfy the requirements for digestion. This is achieved by addition of sulfuric acid. The effluent from the anaerobic filter is raised to pH 9.33 by addition of sodium hydroxide. Digestion breaks down organic nitrogen and makes it available for removal by distillation.

Detailed stream data are given in Table 6-18. Distillation column overhead removes 85 percent of the feed ammonia. The system is thermally self-sufficient, and all required boiler fuel is provided by digester gas. Design results for major items of equipment are shown in Table 6-19.

Table 6-18 Stream summary, System C.

Stream N number	Flowrate Mg/d	State	Temperature °C	TS %	DS %	pH	NH ₄ ⁺ kmol/hr	NH ₃ kmol/hr	NH ₂ CO ₂ ⁻ kmol/hr	Total Ammonia as kmol/hr	mg/L
1	2,949	liquid + solids	15	4.10	0.15	neutral				8.21	
3	2,912	liquid + solids	35	2.90	0.19	9.31	2.72	5.25	0.24	8.21	947
4	2,109	liquid + solids	35	0.20	0.19	9.31	1.98	3.83	0.18	5.99	955
5	803	liquid + solids	35	10.00	0.19	9.31	0.73	1.42	0.06	2.22	927
7	354	liquid	15	0.00	0.00	N/A	0	0	0	0	0
9	354	vapor	220	0.00	0.00	N/A	0	0	0	0	0
10	1157	liquid + solids	220	6.94	3.26	7.85	0.014	2.20	0.001	2.22	644
11	142	vapor	166	0	0	N/A	0	1.57	0	1.57	3707
12	1015	liquid + solids	166	7.91	3.72	8.58	0.004	0.64	0	0.65	215
13	124	vapor	100	0	0	N/A	0	0.50	0	0.50	1361
14	891	liquid + solids	100	9.01	4.24	9.40	0.002	0.15	0	0.15	55
16	152	liquid + solids	70	30.00	2.97	9.73	0	0.02	0	0.02	55
18	739	liquid + solids	38	4.70	4.50	10.19	0	0.12	0	0.12	55
19	744	liquid + solids	35	3.01	2.50	9.29	0.70	1.28	0.06	2.04	920
21	2853	liquid + solids	81	0.93	0.79	8.29	2.16	5.77	0.10	8.03	946
22	2977	liquid + solids	99	0.89	0.74	7.96	2.14	6.32	0.07	8.53	963
23	16	vapor	89	0	0	N/A	0	8.30	0	8.30	174,191
24	3103	liquid	100	0.86	0.72	9.25	0.03	1.77	0.004	1.80	195
26	3103	liquid	54	0.86	0.72	9.75	0.11	1.69	0.01	1.80	195
28	16	liquid	57	0	0	9.05	3.68	2.50	2.12	8.30	174,791
30	42,200 m ³ /d	gas									
31	14,400 m ³ /d	gas									

Table 6-19. Major equipment for System C.

Equipment name	Size	Quantity	Design basis
Digester	7140 m ³	8	Existing, operation in same manner
Thickening centrifuges (C2)	68 m ³ /hr	2	Existing, model: Humboldt 450F Flowrate: 2,900 m ³ /d
Dewatering centrifuges (C1)	46 m ³ /hr		Existing, model:Humboldt 450F
Positive displacement pump, MOYNO 6P10	26 m ³ /hr 30 kW	2*	Flowrate: 0.28 m ³ /min Inlet pressure: 100 kPa Pressure: 3,100 kPaOutlet pressure: 2,320 kPa
Boiler	6 MW	2	Output: 220°C vapor 4.08 kg/sec Feed: 90°C water Efficiency: 0.8 Fuel: digester gas
Reactor	0.4 m ³		1Retention time: 30 sec. Pressure: 2,320 kPa
Flash tank 1	D 1 m, H 1.12 m	1	Retention time 1min. Inlet: 220°C, 2,320 kPa outlet pressure: 896 kPa
Flash tank 2	D 1.34 m, H 0.27 m	1	Retention time 1min. Inlet: 166°C, outlet pressure: 100 kPa
Anaerobic filter	1755 m ³		1Retention time 2 days TS: 5%, DS:90% TS Flowrate 727 m ³ /d Total COD 60,000 mg/L Soluble COD 15,000 mg/L
Heat exchanger 1	45 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 15°C Cold stream outlet temperature 90°C Hot stream inlet temperature 100°C
Heat exchanger 2	122 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 22°C Cold stream outlet temperature 45°C Hot stream inlet temperature 76°C
Heat exchanger 3	214 m ²	1	Heat transfer coefficient 450 W/m ² K Hot stream inlet temperature 100°C Cold stream inlet temperature 54°C Cold stream outlet temperature 81°C
Distillation condenser (HX4)	123 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 35°C Hot stream inlet temperature 100°C Duty 2.23 MW
Reboiler (HX5)	107 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream temperature 100°C Hot stream temperature 166°C Duty 2.64 MW
Distillation Column	H 16.5 m, D 1.8 m 26 trays, and 13 stages	1	Atmospheric pressure Tray efficiency: 0.5
NH ₃ solution condenser (HX6)	28 m ²	1	Heat transfer coefficient 450 W/m ² K Cold stream inlet temperature 15°C Hot stream inlet temperature 89°C Hot stream outlet temperature 54°C
Heat exchanger 7 (HX7)	34 m ²	1	Heat transfer coefficient 450 W/m ² K Hot stream inlet temperature 73°C Cold stream inlet temperature 15°C Cold stream outlet temperature 22°C

* One unit is standby.

An alternative design might also be considered: The pH adjustment could be made for PDS centrate instead of PDS. Cake then has a neutral pH, and pH would not require adjustments at the influent and effluent of the anaerobic filter. However, a larger settling tank would be needed to separate settleable solids from centrate after pH adjustment.

6.5.3 Economic Evaluation

Table 6-20. Purchasing cost of major items of equipment for System C.

Equipment name	Quantity	Purchased cost
Digester	8	existing
Grinder	2	existing
Thickening centrifuge	2	existing
Positive displacement pump	2	\$107,000
Boiler	2	\$239,400
Reactor	1	\$4,700
Flash tank 1	1	\$6,700
Flash tank 2	1	\$7,900
Dewatering centrifuge	1	existing
Anaerobic filter	1	\$1,498,000
Distillation system (including condenser, reboiler, pumps)	1	\$425,200
Heat exchanger 1	1	\$48,100
Heat exchanger 2	1	\$90,000
Heat exchanger 3	1	\$127,800
Heat exchanger 6	1	\$30,900
Unlisted		\$392,100
Total		\$2,977,800

The estimated costs of major equipment items are given in Table 6-20. The fixed capital

cost is \$14,415,000 and the annual operating cost is \$4,792,000. Fifty percent sodium hydroxide costs \$265 per metric ton, and daily consumption is 19.2 metric tons per day. Sulfuric acid cost \$17.4 per metric ton, and daily consumption is 2.5 metric tons. The details of fixed capital and operating costs are shown in Tables 6-21 and 6-22.

Table 6-21. Fixed capital estimate summary.

(Unit: \$)		
System	C	Existing plant plus air stripping
Equipment Cost	2,977,800	1,603,100
Equipment Setting Cost	83,600	0
Commodity Material Cost	1,299,000	839,100
Commodity Labor Cost	1,288,300	943,300
Capitalized Spare	85,000	32,100
Building Material	60,300	0
Building Labor	82,000	0
Service Building	252,000	139,000
Service System	147,000	80,000
Site Development	85,000	47,000
Freight	95,000	53,000
<i>Total Direct Cost</i>	<i>6,455,000</i>	<i>3,737,000</i>
Contractor's Field Cost	1,577,000	1,011,000
Contractor's Home Office Cost	964,000	570,000
Owner's Home Office Cost	450,000	266,000
Fees, Permits and Insurance	643,000	380,000
Additional Depreciable	1,000,000	700,000
<i>Total Indirect Cost</i>	<i>4,634,000</i>	<i>2,927,000</i>
<i>Project Contingency</i>	<i>1,109,000</i>	<i>667,000</i>
<i>Progress Contingency</i>	<i>2,217,000</i>	<i>1,333,000</i>
Total Fixed Capital	14,415,000	8,664,000

An alternative to distillation for ammonia removal is hot air stripping. A process of this type was designed by Katehis(Fillos and Diyamandoglu, 1994) for the Wards Island WPCP, with a centrate flow rate of 1 MGD. With this as a basis for cost estimation, a lower limit on fixed cost for the same process with capacity as in System C is estimated to be \$8,8664,000 (Table 6-2). The annual operating cost is \$3,580,000 (Table 6-22).

Table 6-22. Annual operating cost summary.

(Unit: \$/year)

System	C	Existing plant plus air stripping
Raw Material		
NaOH	1,890,000	1,191,000
H ₂ SO ₄	16,000	303,000
Utilities		
Electricity	31,400	110,000
Chemical for Boiler Water	32,100	0
Heat	0	339,000
Labor		
Operating	351,000	175,000
Maintenance	519,000	312,000
Supervision	17,000	10,000
Fringe Benefits	355,000	199,000
Supplies		
Operating	35,000	18,000
Maintenance	346,000	208,000
General Work		
General & Administration	89,000	50,000
Insurance	115,000	69,000
Laboratory Charge	35,000	18,000
Depreciation	961,000	578,000
Net Annual Operating Cost	4,792,000	3,580,000

Note: Totals are rounded to nearest 1000.

The economic comparison is shown in Table 6-23. The method of comparison is the same as in Section 6.4, where only the differences in operating costs resulting from implementation of the RTC and ammonia removal processes are shown. For current practice, the operating costs are the costs of polymer, disposal of sludge cake, and hot air stripping. For plants incorporating RTC and distillation, the total operating cost will be the charge to handle the sludge cake plus an operating cost attributable to the RTC and distillation system. The results show that System C saves 3.8 to 10.0 million dollars annually over current practice plus hot air stripping.

Table 6-23. Comparison of sludge conditioning, ammonia removal, and cake disposal costs.

System	Current plus air stripping	C
Cake produced, dry Mg/d	76.2	42.5
Cake produced, wet Mg/d	254.0	151.7
Polymer cost (\$MM/yr)	1.23	0
Cake disposal cost		
minimum(\$MM/yr)	9.40	5.61
maximum(\$MM/yr)	24.22	14.46
NH ₃ removal operating cost (\$MM/yr)	3.58	4.79
Total operating cost		
minimum(\$MM/yr)	14.21	9.70
maximum(\$MM/yr)	27.41	17.44

6.6 SUMMARY

Several important conclusions can be drawn from this work on the implementation of RTC process.

1. The rapid thermal conditioning process is feasible technically. It is both environmentally and economically beneficial in comparison with other methods for handling sludge.
2. Thickening sludge to raise the solids concentration prior to thermal conditioning is crucial to significantly reducing the cost of thermal conditioning and subsequent digestion.
3. System A is the most attractive option for use in an existing facility. By integrating System B into the Wards Island WPCP, the cost of handling dewatered sludge would be reduced between 2.5 to 8.5 million dollars per year, which is 24 to 33 percent of the current disposal cost.
4. For the design of a new WPCP, or the expansion of the digestion capacity of an existing plant, implementation of System B is preferred. It does not use enough of the existing equipment to be useful in an existing plant, but if incorporated into the initial system design it is the most efficient and cost-effective option.
5. Ammonia removal by distillation shows promise for integration with a rapid thermal

conditioning process. Heat available from the RTC process is easily used to drive ammonia removal. In the design presented here 85 percent ammonia removal is achieved. Higher removal ratios can be reached by raising the reboiling ratio and/or pH.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the research and conclusions reached from this study. Directions for further research are recommended.

7.1 SUMMARY OF RESEARCH

This research was concerned with several important aspects in the development of the RTC process for treatment of municipal wastewater. At the start of this work, no prior literature on the effect of RTC on dewaterability had been found. The refractory effect of thermal conditioning on sludge biodegradability was poorly understood. These obscure areas of sludge treatment required exploration to help RTC become a mature technology. Experimental testing with municipal wastewater sludges was needed to show feasibility and to establish effective conditions for the treatment. In addition, design and economic studies were needed to examine how RTC might be incorporated into a new or existing wastewater treatment plant and what the costs might be.

The laboratory work was carried out in the Departments of Chemical and Civil Engineering, at the City College of New York, during the period of 1990 to 1993. A continuous laboratory-scale RTC apparatus was designed and constructed for the study.

Sludges from several WPCPs in New York City were conditioned in RTC apparatus at a range of temperature of 100 to 220°C, pH 2 to 12, and retention time 10 seconds to 3 minutes. Dewaterability of rapid thermally conditioned sludges was evaluated by SRF, CST and a centrifugation test. The properties of these sludges related to their dewaterability, particle size distribution, solids setting test, and solids densities, were also examined. A mathematical model was derived for the evaluation of sludge centrifugeability and tested with experimental data.

In research related to the effect of thermal conditioning on substrate biodegradability, model compounds L- and D- amino acids, glucose, as well as PDS were used. L-amino acids, glucose, and PDS were conditioned in a batch reactor at 220°C for 2 and 25 minutes, and then subjected to anaerobic digestion at 35°C for over 75 days. Thus, the effect of retention time on substrate biodegradability was examined. A hypothesis is proposed that racemization of amino acids causes the decrease in biodegradability of nitrogenous sludge. As a first step in the verification of this hypothesis, D-amino acids were digested to compare the pattern of their digestion kinetics with that of L-amino acids.

Laboratory test data provided a basis for the design of a full scale RTC plant. Digestion kinetics was available from the work of Pierides (1994). Two options for integrating RTC in to an existing wastewater plant, and an additional scheme with ammonia removal were drawn up and evaluated.

7.2 CONCLUSIONS

This study demonstrates that RTC:

- Improves sludge centrifugeability,
- Improves sludge biodegradability, and
- Can be integrated into a water pollution control plant with great economic advantage.

Compared with traditional thermal conditioning processes, RTC may not achieve better dewaterability, especially filterability because of its short retention time. The main advantages of RTC over traditional methods are better biodegradability, less odor, and less color of the thermally conditioned product. More detailed conclusions are provided below.

7.2.1 Dewatering Characteristics of Rapid Thermally Conditioned Sludge

(1) Solubilization. Solubilization during RTC occurs almost entirely from the volatile fraction of sludge solids, and it increases with RTC temperature. RTC at 220°C dissolves approximately 40 percent of the suspended solids in PDS, and approximately 90 percent of these are volatile solids.

(2) Centrifugeability. RTC improves the centrifugeability of PDS, especially at a 220°C RTC temperature. With RTC, the density of the remaining suspended solids increases, solids settle faster, and a drier cake is obtained. Also, at least the same solids

concentration, about 30 percent, can be achieved without polymer addition as is now achieved with polymer addition but no conditioning. Therefore, for RTC of sludge, centrifugation is the dewatering process of choice.

(3) Filterability. RTC increases both CST and SRF, indicating a deterioration of filterability. Longer thermal conditioning retention time, of about one minute can significantly improve filterability. It is thought that long retention time solubilizes small organic particles released by thermal conditioning. These small organic particles may block the filtration passages. Filtration process following RTC should not be considered.

(4) Solids Size Distribution. Solids size distribution measurement shows agglomeration takes place at medium RTC temperatures (130 to 160°C), indicating the breakup of bacterial cells. However, solids size distributions alone fail to correlate with sludge dewaterability. The chemical characteristics of solids may be more important than size distribution.

(5) Effect of pH Adjustment. Both acid and base addition increase solubilization. However, at high temperature, its effect becomes marginal. RTC of PDS adjusted to alkaline pH will achieve slightly better filterability and centrifuge dewaterability than at either neutral or acidic PDS.

(6) Mathematical Model for Batch Centrifugation. The mathematical model proposed for batch centrifugation is able to describe the distribution of sludge cake solids concentration which is the most important characteristic of centrifugeability. Unlike CST

or SRF which only judge filterability on a relative scale, this model is able to not only judge centrifugeability but also to predict the solids concentration of the cake. This model has generality and can be applied to other liquid-solids centrifuge separations.

7.2.2 Digestibility of Organic Substrates and the Other Sense Effect

(1) L-amino Acids. L-amino acids are highly biodegradable, but the extent of biodegradability depends on structure. Amino acids with ring structures or containing sulfur have poor biodegradability. The biodegradability of L-amino acids all decrease as thermal conditioning retention time increases. At 220°C, 2 minutes retention time reduces their biodegradability only slightly. However, at 25 minutes, the reduction in biodegradability can be significant.

(2) D-amino Acids. Most D-amino acids are less biodegradable than their L-isomers in two ways: lower reaction rate or ultimate conversion rate to digestion gas. The former is more likely, and it means D-amino acids require more retention time for digestion than L-amino acids. D-amino acids containing an aromatic ring or sulfur are either not or slightly biodegradable.

(3) Racemization Effect. D-amino acids are among substances likely to reduce the biodegradability of thermally conditioned sludge if they are formed by racemization. However, the D-amino acids more easily produced by racemization are found to be more easily biodegradable. This offsets the impact of racemization to digestion.

(4) Glucose. Glucose is highly biodegradable. Its biodegradability is reduced with thermal conditioning, and this reduction is very sensitive to retention time. At 220°C, even 2 minutes retention time significantly reduces the rate of digestion gas production.

(5) PDS. Thermal conditioning increases the biodegradability of PDS. However, at high temperature (220°C) the effect is reduced at longer retention times. The intermediate products of sludge hydrolysis, such as amino acids, and simple sugars are highly biodegradable but the end products, as indicated previously, are not. Therefore, selectivity toward such highly biodegradable intermediate products requires an appropriate retention time. For high-temperature thermal conditioning of sludge, such as 220°C, retention time at the order of seconds or several minutes is appropriate in order to maximize the improvement in sludge biodegradability.

(6) Color and Smell. The thermal conditioning of amino acids and glucose shows that long retention times at high temperature give rise to a yellow-brownish color as well as an odor. The color and odor of the products are disadvantages of traditional thermal conditioning methods. They are circumvented by the RTC process.

7.2.3 Implementation of RTC in a Water Pollution Control Plant

(1) Incorporation of the RTC Process. The rapid thermal conditioning process is feasible technically and beneficial economically. Of the two proposed systems, System A is the more attractive option for use in an existing facility. The integration of RTC into the Wards Island WPCP using flowsheet A would reduce wastewater treatment and

disposal costs by 2.5 to 8.5 million dollars per year. This is a saving of 24 to 33 percent of current costs. For the design of a new WPCP or the expansion of the digestion capacity of an existing plant, flowsheet B provides the more efficient and cost-effective alternative.

(2) RTC with Ammonia Removal. Distillation can be advantageously integrated with the RTC process to recover ammonia from dewatering centrate. Heat available from the RTC process is then fully utilized and 85 percent of ammonia removal is achieved. This removal ratio can be increased by raising the reboiling ratio and/or pH. The former requires additional fuel, and later requires additional alkali consumption. The total savings realized in wastewater treatment using RTC are increased when ammonia removal requirements are taken into account, thus making RTC all the more attractive.

(3) Future of RTC. RTC will be more attractive in two cases. First, the economics of RTC process mainly depends on the cost of sludge disposal. As environmental consciousness rises, public opposition and legislation will make disposal of sludge to other states more difficult, and disposal costs higher. In such a scenario, RTC is an attractive way to reduce sludge local production. Secondly, as more restrictions are imposed on the WPCP discharge of ammonia and phosphorous, the integration of distillation into RTC increasingly attractive since the combination achieves good energy utilization, in addition to the benefits of RTC.

7.3 RECOMMENDATIONS

Although this research has answered several important questions related to thermal conditioning of sludge, several new and interesting questions have been opened up. These have not been addressed due to the limitations of research scale and time. Research on these questions will advance the understanding of the overall process.

(1) RTC and Digestion of Thickened Sludge. Thickening of sludge before RTC is crucial to making RTC economically attractive. RTC and subsequent digestion of thickened PDS with a total solids content of about 10 percent and WAS with a solids content of about 6 percent should be tested in the laboratory.

(2) Racemization of Thermally Conditioned Sludge. Measurement of amino acids in thermally conditioned sludge can be found in literature. However, there has not been any differentiation between L- and D-amino acids. In this study it has been found that D-amino acids are less biodegradable than L-amino acids. However, the formation of D-amino acids has not been examined. The hypothesis proposed in this study regarding the racemization effect can be firmly established only after a significant portion of D-amino acids is identified in thermally conditioned sludge.

(3) Correlation between Plant and Laboratory Scale Centrifuge Performance. The model for centrifugation developed here makes it possible to use a laboratory batch centrifuge to quantitatively assess slurry centrifugeability. Using parameters determined in the laboratory the model is able to predict the minimum performance of a plant

centrifuge. However, more accurate prediction requires correlations between the two types of centrifuge. Differences between laboratory and plant-scale centrifuge performance arising from the method of operation (batch or continuous) can be corrected by experiment.

LIST OF ABBREVIATIONS

AGP	= average gas production
BMP	= biochemical methane potential
BOD	= biological oxygen demand
BTM	= bioconvertibility to methane
COD	= chemical oxygen demand
CST	= capillary suction time
CW	= cooling water
CSTR	= continuous stirred tank reactor
DEP	= department of environmental protection
DS	= dissolved solids
GP	= gas production, cm ³
HRT	= hydraulic retention time
MGD	= million gallons per day
PDS	= partially digested sludge
RTC	= rapid thermal conditioning
RA	= returned activated sludge
SCWO	= supercritical water oxidation
SRF	= specific resistance to filtration
SS	= suspended solids
TKN	= total Kjeldahl nitrogen
TS	= total solids
TVS	= total volatile solids
USEPA	= The United States Environmental Protection Agency
VDS	= volatile dissolved solids
VS	= volatile solids
VSS	= volatile suspended solids
WAO	= wet air oxidation
WAS	= waste activated sludge
WPCP	= water pollution control plant

NOMENCLATURE

A	= filter area, cm^2
b	= slope of filtration curve t/V verses V , s/cm^6
C	= mass of solids deposited per unit volume of filtrate, g/cm^3
C_c	= SS concentration in cake, percent
C_f	= SS concentration in feed, percent
C_s	= SS concentration in centrate, percent
D	= particle size, μm
d_i	= mean diameter of particle size band i , μm
k	= reaction constant, day^{-1}
k_0	= ratio of lateral stress to normal compressive pressure of solids phase
n	= constant
p	= pressure across the filtration cake, Pa
p_0	= compressibility constant, Pa
p_L	= hydraulic pressure, Pa
p_s	= compressive pressure of cake, Pa
Q	= particle undersize distribution
R	= suspended solids recovery, percent SS
r	= radius, m
r_a	= radius of liquid surface, m
r_b	= radius of cake surface, m
r_c	= radius of centrifuge wall, m
r_s	= specific resistance to filtration (SRF), cm/g
S	= settling coefficient, sec
t	= filtration time, sec; digestion time, day
V	= volume of filtrate, cm^3
V_i	= volume of particle in size band i , m^3
v	= settling velocity, m/sec
x'	= constant, μm
y	= COD of methane gas produced, mg/L
y_s	= COD of feed, mg/L

γ	= local solids concentration of cake
γ_{ave}	= average cake solids mass fraction of cake
δ	= solidosity, solids volume fraction
δ_0	= dimensionless compressibility coefficient
δ_{ave}	= average cake solids volume fraction of the cake
θ	= angle, rad
ϵ	= voidage, liquid volume fraction
λ	= dimensionless compressibility coefficient
μ	= viscosity of filtrate, pois
ρ_c	= density of cake, kg/m ³
ρ_L	= density of liquid, kg/m ³
ρ_s	= density of solids, kg/m ³
τ	= cake thickness, m
Ψ	= centrifuge operating parameter, m ² /sec ²
Ω	= angular speed, rad/sec

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