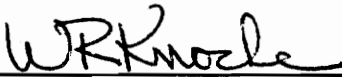


# CHARACTERIZATION OF WATER DISTRIBUTION IN SLUDGES

by  
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Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of  
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in  
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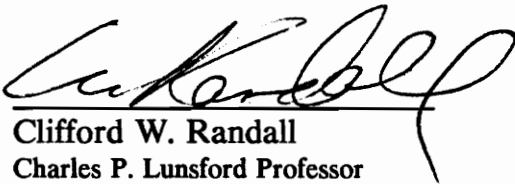
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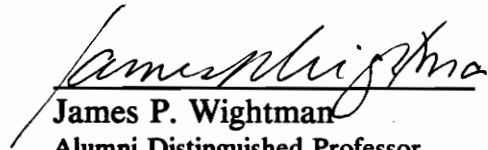
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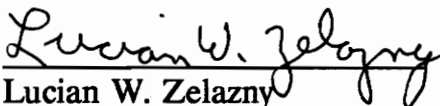
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# CHARACTERIZATION OF WATER DISTRIBUTION IN SLUDGES

by

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(ABSTRACT)

Knowledge of water distribution in sludges is important in developing a better understanding of the mechanisms by which various fractions of water are bound to the sludge matrix as well as the extent to which sludges may be dewatered in an economic manner. Various models have been proposed in the literature to describe the types or fractions of water present in sludges, both before and after dewatering. Likewise, there exist a variety of measurement techniques to quantify the fractions of water believed to be present in sludges.

The major objective of the research reported herein was an attempt to develop a more rational basis for defining the various fractions of water present in sludges, as well as to apply and develop feasible analytical techniques to characterize moisture distribution in sludges and determine if there was any correlation between these techniques. Secondary objectives included investigation of polymer addition, mechanical dewatering, and the effect of freeze-thaw cycles to different water fractions in sludge samples, and measuring or estimating various densities (bulk, floc, dry) and specific surface areas of sludge particles in an attempt to predict the dewatering performance of various sludge samples. The matrix of sludges included various water treatment plant/inorganic chemical sludges and bio-solids.

The sludge moisture characterization techniques used or developed in this study were the thermo-gravimetric analysis (TGA), differential scanning calorimetry (DSC), and dilatometric methods. The TGA method developed used the drying curve rate technique whereby changes in the drying (water removal) rates would

provide information on moisture distribution in sludges. The DSC and dilatometric methods used the property of the free water fraction to freeze by  $-20^{\circ}\text{C}$ , as compared to the bound water fraction that is thought not to freeze until well below  $-20^{\circ}\text{C}$ .

It was found that there were uncertainties in the determination of different sub-fractions of sludge water. In an effort to better rationalize these various sub-fractions, it has been proposed in this study that water in sludges be considered to be in two major fractions: bound and unbound. For the TGA, the demarcation point between these two fractions was indicated by the onset of the first critical/inflection point on the drying rate curve. The DSC and dilatometric methods determined the amount of bound water by first measuring the amount of unbound water that froze by  $-20^{\circ}\text{C}$ , and subtracting this value from the total water present in the dry solids analysis. While the DSC measured the calorimetric (enthalpic) changes, the dilatometer measured the expansion of the unbound water. The three DSC instruments evaluated in this study were not able to measure the rapid exothermic change of the freezing of unbound water, but was able to measure the amount of unbound water that melted. Freezing point depression (supercooling) phenomena was also observed for various samples using this technique. Due to these effects, the sludge moisture characterization method developed for the DSC measured the amount of unbound water from the endothermic changes upon melting.

The three different analytical techniques used to determine moisture in sludges were found to provide different quantities of the bound water fraction. Other sludge characteristics evaluated included the bulk, floc, and dry density values, as well as the specific surface area of dry sludge particles. Correlations were attempted to determine if there were any meaningful relationships in the results obtained.



## ACKNOWLEDGEMENTS

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maze of the literature that helped explain (or attempt to) some of the "interesting" observations of this study. Dr. Zelazny has also been a great teacher and was always available to guide me through unfamiliar territory. He has been magnanimous in allowing me to use his laboratories for both the initial development of the differential scanning calorimeter as a method to characterize moisture distribution in sludges, as well as in introducing me to the EGME-specific surface measurement. Dr. May was instrumental in arranging for my summer research co-op assignment at the Nalco Chemical Company Scientific Laboratories at Naperville, Illinois, including providing for accommodations for much of my sojourn there.

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for a vacuum pump at a moment's notice. Julie helped me find my way around the department on many occasions, and kept numerous pieces of equipment "alive" for my research, over and beyond her responsibilities as the Laboratory Manager. Numerous colleagues and friends have made my sojourn here so warm and pleasant. Faculty members have been excellent teachers, and always been happy to assist me whenever needed. Special mention also goes to Pat Furey, Vickie Graham, Judy Dumin, and Betty Wingate to handling efficiently and smoothly all the necessary logistics and details of administration.

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## LIST OF ABBREVIATIONS AND NOMENCLATURE

$A$	cross-sectional area of sample material
$\text{\AA}$	angstrom ( $1\text{\AA} = 10^{-3} \mu\text{m} = 10^{-1} \text{nm}$ )
ANOVA	one-way analysis of variance (a statistical test)
APHA	American Public Health Association
AWWA	American Water Works Association
cal	calorie(s)
$c_b$	reduced specific heat of liquid phase
$^{\circ}\text{C}$	degrees celsius (centigrade)
$\text{CaCO}_3$	calcium carbonate
CST or cst	capillary suction time(r)
DMRT	Duncan's multiple range test (another statistical test)
D.S. or d.s.	dry solids
DSC	differential scanning calorimeter
DTA	differential thermal analyzer
$E$	energy of activation
EGME	ethylene glycol monoethyl ether
EPA	<i>see USEPA</i>
f.p.	freezing point
$f(r)$	differential curve for distribution of pore sizes by radius $r$
g	gram(s)
g/mL	gram(s)/milliliter
J	joule ( $1\text{J} = 4.18 \text{cal}$ )
$J_l$	capillary-liquid flux
$K_H$	unsaturated hydraulic conductivity
$K_l$	surface (liquid)-diffusion coefficient
$K_{l0}$	diffusion coefficient at saturation state, or initial value
$K_{mT}$	overall thermal moisture diffusivity
$K_m$	overall isothermal moisture diffusivity (total moisture diffusion coefficient)
$K_v, K_l$	diffusion coefficients (diffusivity)
$K_{iT}, K_{vT}$	thermal moisture diffusivities
L	liter
$L_v$	specific heat of evaporation
$M$	moisture content (dry basis)
mg	milligrams
mL	milliliter
m.p.	melting point
$n$	number of moles
nm	nanometers
NMR	nuclear magnetic resonance

**LIST OF ABBREVIATIONS  
AND NOMENCLATURE  
(Continued)**

$P$	pressure
PACl	polyaluminum chloride
QA/QC	quality assurance/quality control
$r_0, r_1$	minimum, maximum values of radii of capillaries
$R$	radius
rpm	revolutions per minute
$S$	entropy
$\text{SiO}_2$	silicon dioxide
sp gr	specific gravity
$t$	time
$T$	absolute temperature
TBP	twin belt press
TGA	thermo-gravimetric analyzer
$U$	circumference of pores or internal energy
USEPA	United States Environmental Protection Agency
$V$	volume
WEF	Water Environment Federation
WTP	water treatment plant
WWTP	wastewater treatment plant
$Z$	vertical ordinate
$\alpha$	level of significance for statistical testing
$\delta$	thermal gradient coefficient
$\epsilon$	tortuosity factor for diffusion of gases in porous media
$\eta$	dynamic viscosity
$\theta$	wetting angle (in capillaries) or moisture-transfer potential
$\mu$	chemical potential
$\rho$	density
$\rho_b$	bulk density
$\rho_k$	dry solid density
$\rho_s$	density of solid skeleton or body surface
$\rho_w$	density of water (g/mL)
$\sigma$	entropy production per unit volume and unit time or surface tension $d_i S/dt$
$\psi$	capillary potential
$\nabla$	nabla operator

# CHAPTER 1

## INTRODUCTION

### BACKGROUND

Water in sludges is believed to exist in a free (or bulk or unbound) form and a bound form. The latter has been further divided into various other forms, depending on the analytical methods and materials used. These may be the interstitial, capillary, immobilized, physically-adsorbed, chemically-bound, surface, bound, or vicinal water. There seems to be no well-distinguishing demarcation between the various "forms" of water, as well as little agreement as to the drying (or moisture loss) mechanisms involved. Classification of the different forms of water in solids, colloids, etc., appears to depend on the method or technique used, and in some cases, upon the investigator(s) conducting the research.

There is also currently no standard method or procedure to define and measure moisture distribution in sludges. In general, the various methods cited in the literature indicate that water in these materials may be divided into two main categories: free water and bound water (the latter being more difficult to remove). The more popular methods involve demarcation of the water fractions based on the freezing of water (while "free" water freezes at or near 0 °C, "bound" water is thought not to freeze at temperatures as low as -20 °C). Water freezing fraction methods include: (i) dilatometric, (ii) dielectric, (iii) differential scanning calorimetry (DSC), and (iv) differential thermal analysis (DTA). Controlled drying methods appear to further differentiate other (more than two) forms of bound water. Additional methods reported include the vapor pressure depression method, the centrifugation technique, and the nuclear magnetic resonance (NMR) method.

Due to the different methods available, there seems to be no convention to the nomenclature used in classifying the differently perceived forms of water. There

is also no agreement on whether moisture in solids move up to the drying surface (i.e. diffusional moisture movement) due to a moisture content gradient or a vapor pressure gradient, or a combination of the two mechanisms. Table 1 summarizes briefly the various methods to determine bound water in a variety of materials, presenting the different categories of water and characterization techniques used. Of all the above techniques, those most applicable to sludges appeared to be the dilatometric, DSC, and drying rate method. These methods were selected for the moisture characterization studies reported herein.

## **RESEARCH OBJECTIVES**

The major objective of this dissertational research was an attempt to develop a more rational basis for defining the various fractions of water present in sludges, as well as to apply and develop feasible analytical techniques to characterize moisture distribution in sludges and determine if there is any correlation between these techniques. Secondary objectives included investigation of polymer addition, mechanical dewatering, and freeze-thaw conditioning to different water fractions in sludge samples. and measurement or calculation of the various densities (bulk, floc, dry) and specific surface areas of sludge particles in an attempt to predict the dewatering performance of various sludge samples.

To summarize, the specific objectives of the dissertational research undertaken were to:

- (i) review the methods for determining bound water content as well as their removal and quantification methods in various other disciplines, with a view to adapting these techniques to sludge characterization,
- (ii) further define free and bound water in sludges as well as review the available models of water distribution,



TABLE 1  
METHODS TO DETERMINE "BOUND" WATER

METHOD	"FORMS" OF WATER	SAMPLE	INVESTIGATOR(S)
Vapor Pressure Depression	Free and Capillary	Biological Sludges	Novak, <i>et al</i> (1982) <sup>68</sup>
Dielectric	Free and Bound	Soils	Oliphant (1985) <sup>69</sup>
Dilatometric	Free and Bound	Elastic & non-elastic gels (gelatin, egg white, activated silicates, ferric hydroxide, etc.) Biological Sludges Biological & Chemical Sludges	Jones & Gortner (1932) <sup>41</sup> Henkelejian & Wesburg (1956) <sup>38</sup> Robinson (1989) <sup>79</sup> Robinson & Knocke (1992) <sup>80</sup>
DTA (Differential Thermal Analysis)	Free and Bound	Clay	Anderson & Tice (1971) <sup>2</sup>
DSC (Differential Scanning Calorimeter)	Free and Bound Free and Bound Free and Bound	Clay Liquid Foods Biological Sludges	Katsiris & Kouzeli-Katsiris(1987) <sup>68</sup> Anderson & Tice (1973) <sup>3</sup> Kumagai, <i>et al</i> (1985) <sup>50</sup> Rha (1987) <sup>78</sup>
Centrifugal	Free, Flocc, Capillary, and Bound Free, Interfloc, Flocc-adsorbed, Inter-particle, Particle-adsorbed, & Particle	Biological Sludges Biological Sludges Biological Sludges	Vesilind (1979) <sup>93</sup> Huang (1979) <sup>40</sup>
Drying Rate	Free (drainable), Capillary-held, Flocc (particle), & Chemically-bound Interspace (drainable), Interstitial capillary, Adsorption and adhesion, & Internal Free, Immobilized, Bound, Chemically Bound	Biological Sludges Biological Sludges Biological Sludges	Coackley & Allos (1962) <sup>19</sup> Möller (1983) <sup>63</sup> Smollen (1986) <sup>85</sup>
NMR (Nuclear Magnetic Resonance)	Free, Interstitial, Surface, & Bound Free and Bound	Biological Sludges Alum Sludges Food & Agricultural Industries	Tsang & Vesilind (1990) <sup>89</sup> Sato, <i>et al</i> (1982) <sup>82</sup> Others
	Free and Bound	Alum Sludges Food & Agricultural Industries Coal Minerals	Sato, <i>et al</i> (1982) <sup>82</sup> Yakubu, <i>et al</i> (1990) <sup>98</sup> Mraw & Silbernagel (1981) <sup>66</sup>

- (iii) based on (i), to apply the dilatometric, DSC, and thermo-gravimetric analyzer (TGA)/drying rate curve techniques to characterize bound water in sludges,
- (iv) investigate the effect of conditioning (polymer, freeze-thaw, and mechanical dewatering) on the different fractions of water present in sludge samples; and
- (v) attempt to correlate water distribution data to the dewatering performance and other characteristics of various sludge samples.

## WORK PLAN

Based on an initial extensive review of the literature, a preliminary work plan was drawn up for the summer session in 1991 to learn to use and apply the TGA using the drying curve rate technique to determine moisture distribution in sludges. In addition, techniques used by the industry to optimize (flocculant and/or coagulant) polymer dosages for removal of free water, as well as the simulation of twin belt press mechanical dewatering devices (for the characterization of sludge water through the various zones in the device) would be learnt. Field trips were also arranged to a number of pulp and paper mills in the region to characterize this particular sludge.

In the following periods, the research continued in an attempt to characterize moisture distribution using the DSC and dilatometric methods. The former was carried out in various laboratories on the Virginia Tech campus in Blacksburg and involved the development of the technique to characterize sludge moisture distribution using the DSC instrument.

The matrix of sludges studied included:

- (i) artificial silicon dioxide slurry (made from *Min-U-Sil 30*, supplied by U.S. Silica, with a predetermined amount of distilled water added),
- (ii) biological sludges (municipal anaerobically digested wastewater treatment plant sludges),

- (iii) water treatment plant alum and lime sludges,
- (iv) pulp and paper mill sludge, and
- (v) chemical sludges/slurries [ $\text{Al}(\text{OH})_3$  ppt from alum and sodium hydroxide, as well as  $\text{CaCO}_3$  (s) from calcium carbonate and water] made in the laboratory.

Certain properties of sludges, including their bulk and floc densities, based on previous research by Knocke, *et al*<sup>47</sup>, as well as the specific surface areas of sludge particles (an application of a method used widely in soil mineralogy), were also determined in an effort to quantify their vicinal or bound water content, and determine any correlations between these characteristics.

In addition, the change, if any, of sludge moisture distribution due to chemical and mechanical dewatering techniques (including polymer addition, freeze-thaw conditioning, belt presses, centrifuges) were also investigated briefly in an attempt to predict the dewatering performance of sludges.

## CHAPTER 2

### LITERATURE REVIEW

#### GENERAL

A review of the literature indicates that there is currently no standard method or procedure to define and measure moisture distribution in sludges. A wide variety of methods to determine bound water content in materials ranging from spinach leaves to sludges are cited in the literature. These include and are not limited to differential scanning calorimetry (DSC), differential thermal analysis (DTA), nuclear magnetic resonance (NMR), thermo-gravimetric analysis (TGA), dielectric method, dilatometric techniques, drying techniques, centrifuge method, vapor pressure depression, aggregate volume index (AVI), etc.

The results obtained from the above methods indicate water content in the materials tested can generally be divided into two main categories: free water and bound water (the latter being more difficult to remove). Some measuring techniques (e.g., the drying rate method in particular) hypothesize an ability to further classify water content into interstitial, adsorbed, capillary, and chemically bound fractions. However, there appears to be no convention as to the nomenclature used in classifying the differently perceived fractions of water.

Research into the drying of solids began to be reported in the literature in the 1930s. Moisture in solids was thought to move up to the drying surface by diffusion. However, Ceaglske and Hougen<sup>18</sup> pointed out in 1937 that the term diffusion was misleading as the flow of moisture is induced by gravitational and interfacial forces. They stated that diffusion properly refers to "the spontaneous change induced by molecular motion in the intermingling of two different gases without the aid of mechanical action or as in the equalization of temperature within a solid." Earlier reports by researchers<sup>83,84</sup> used the term diffusion to describe moisture movement or

flow during drying. Further research indicated that heat and mass transfer appear to be the major mechanisms of drying.

Six theoretical models for heat and moisture transfer in capillary porous bodies have been widely quoted in the literature<sup>30</sup>: diffusion, capillary, vaporization-condensation, Krischer's, Luikov's, and Philip and De Vries' theories. The controversy is still not resolved as to whether diffusional moisture movement is caused by a moisture-content gradient or a vapor-pressure gradient<sup>49,53,92</sup>.

This chapter begins with a brief review of the properties of water and discusses the concept of vicinal water, followed by an introduction to the methods to determine bound water and the various water distribution models. This includes an overview of the published literature pertaining to the determination of bound water in hygroscopic capillary-porous media (sludges do not easily "fit" in any category but water treatment plant or chemical sludges can probably be classified here), summarizing the various methods to determine bound water, water distribution models, and the development of the theory of drying (i.e. moisture removal mechanisms). A review of recent research on sludges using the dilatometric and drying techniques is presented, followed by an overview of techniques of thermal analysis in the determination of water fractions.

## **PROPERTIES OF WATER**

For a research study characterizing water (moisture) distribution in sludges, it may be prudent to present an overview of the properties of water. Water is the only inorganic liquid that occurs naturally on this planet. It is also the only chemical compound that occurs naturally in all three physical states: solid, liquid, and vapor. It has so far been impossible to reconcile all the known physical properties and arrive at a molecular description of water which can account correctly for its behavior over the whole liquid range from the supercooled state to the critical point (Franks,

1983)<sup>32</sup>. Indeed, one of the most comprehensive attempts to compile many of the aspects of the chemistry of water and aqueous solutions into a single referenced source has been that undertaken over a decade by Professor Felix Franks at the University of Cambridge, U.K., in the seven volume series entitled *Water - A Comprehensive Treatise* (published over the period 1972-1982)<sup>31</sup> incorporating chapters by various eminent scholars and researchers.

To understand the properties of water and other aqueous solutions, one should be familiar with the smallest unit of the compound water, i.e. the H<sub>2</sub>O molecule. As both Buckingham and Everett have pointed out in *Water and Aqueous Solutions*<sup>67</sup>, paraphrased here: "... while we know a great deal about water, much remains to be learnt. While we know a great deal about the structure of a single water molecule, we do not know enough. For example, if we knew how to break down water into hydrogen and oxygen in sunlight, the world's energy problems would be solved. While we seem to know a lot about the structures of the many forms of ice, we know far too little about liquid water. Electrolyte solutions present still greater challenges, whereas biological systems are even more challenging."

Most water molecules have a molecular weight of 18. However, since hydrogen and oxygen each have 3 isotopes, there exist 18 possible molecular weights for water<sup>87</sup>. Both hydrogen atoms are located on the same side of the oxygen atom. The hydrogen atoms carry a positive charge while the oxygen atom is negatively charged, making this molecule strongly dipolar. The water molecule dipoles attract each other to form aggregates through hydrogen bonds; and it is believed that many of the seemingly anomalous (in comparison to dihydrides of elements in the same family of the periodic table) properties are caused by hydrogen bonding between water molecules. These anomalous properties include its naturally occurring physical state (liquid at room temperature, 25 °C and 1 atmosphere), "universal" solvent powers, relatively higher density as a liquid than as a solid (with a maximum near 4 °C), surface tension and dielectric properties<sup>87</sup>.

A water molecule measures 0.5 nm or 5 Å across. It contains two protons, one oxygen nucleus, and 10 electrons. In its ground state the water molecule has  $C_{2v}$  symmetry, so the two protons are equivalent. High resolution spectroscopy have shown that the OH bonds at equilibrium have lengths of 0.957 Å and that the HOH bond angle is 104.5°. The maximum density of water at 1 bar occurs at 3.98°C where the molar volume is 18.01 cm<sup>3</sup>. If the charge density of a molecule is known, then the potential energy surface could be evaluated. Although this has not been accurately determined for the water molecule, there have been a number of fairly sophisticated experiments to determine it, and our understanding of water is advancing fairly rapidly.

Some of the other known properties of bulk or free water (as opposed to the bound or vicinal water referred to in the next section) are briefly summarized in Table 2 on the following page.

## **VICINAL WATER**

Vicinal water is distinct and different from the "polywater" or "anomalous" water that spawned so much controversy over 30 years ago (an eloquent overview of the events of those years has been presented by Everett in Reference 67). It had been suggested that water condensed on to silica or glass surfaces takes up a form which has a different structure and very different properties from ordinary water and that it retains this form when removed from the surface. Although its unusual properties are now generally attributed to the presence of impurities, the study of anomalous water has greatly stimulated the development of techniques for examining surface water and thinking about its structure.

Vicinal water is defined as interfacial water (usually near a "solid" surface) with properties that differ from the corresponding bulk water due to structural differences induced by proximity to the surface. Drost-Hansen<sup>24</sup> refers to studies that

TABLE 2  
PROPERTIES OF WATER

<u>Property</u>	<u>Value</u>
Molecular weight	18 amu (other isotopes have additional H atoms: 19, 20, 21, 22; but are much less abundant)
Boiling point	373 K (100 °C or 212 °F) at 1 atm
Melting point	273.2 K (0 °C or 32 °F)
Specific gravity	1.000 (at 4 °C)
Weight per gallon	8.337 lbs/gallon at 15 °C
Density, kg/m <sup>3</sup> :	
Liquid	997
Solid	920
Latent heat of fusion	5.98 kJ/mol
Latent heat of vaporization	40.5 kJ/mol
Heat capacity, J/mol K:	
Liquid	75.2
Solid	37.6
Liquid range	100 K
Isothermal compressibility, (N m <sup>2</sup> ) <sup>-1</sup> :	
Liquid	4.9
Solid	2
Surface tension	72 mJ/m <sup>2</sup> (for liquid)
Viscosity	0.01 Poise (= 10 <sup>-1</sup> kg/m s)
Self-diffusion coefficient, m <sup>2</sup> /s:	
Liquid	2.2 x 10 <sup>-9</sup>
Solid	10 <sup>-14</sup>
Thermal conductivity, J/(s m K):	
Liquid	0.58
Solid	2.1

(Literature Sources for above values include Water,  
by Felix Franks, 1983, © The Royal Society of Chemistry)



appear to show the existence of water structure modifications, probably due to the polar nature of water molecules, which decay (possibly exponentially) from the surface with a characteristic decay length of the order of one (or at most a few nanometers) from the surface (i.e. a decay distance of the order of 4 to 10 water molecular diameters). In contrast to such estimates, Drost-Hansen believed that subtle structural effects may be observed over distances of the order of 0.01 to 0.05  $\mu\text{m}$  (i.e. 20 to 100 molecular diameters). Such vicinal water appears to exist near most solid surfaces regardless of the specific chemical nature of the surface. "Local" water-surface interactions will also exist due, for instance, to ion-dipole or dipole-dipole interactions; such interactions, however, are all relatively highly energetic and of relatively short range.

Vicinal water, on the other hand, appears to exist regardless of specific surface interactions, and to extend far beyond the range of these specific effects. It appears also that vicinal water occurs independently of the existence and effects of electrical double layers.

Drost-Hansen<sup>24</sup> reviewed a few relatively recent (circa 1981) measurements to obtain estimates for the thickness of vicinal water. This appeared to range from 0.02 to 0.05  $\mu\text{m}$  depth; with the difference in energy between bulk and vicinal water to be very small, of the order of 10 to 100 cal/mol. Vicinal water appears to have some measurable properties, of which two seem to have the potential for sludge dewatering (and that make it distinct from free or bulk water), viz. lower density (about 0.965  $\text{g}/\text{cm}^3$ ) and higher viscosity (about 2 to 10 times). The "properties" of vicinal and bulk water are summarized in Table 3.

Vesilind in a recent paper<sup>94</sup> discussed the role of water in sludge dewatering, mentioned some of the more recent work described by Drost-Hansen and other researchers regarding vicinal water, and pointed out that the determination of the various fractions of these waters could lead to a better understanding of mechanical sludge dewatering. In his review he discussed the results of sludge "bound water" reported by various researchers and drew the fairly reasonable conclusion that the

TABLE 3  
SELECTED PROPERTIES OF VICINAL WATER

	<u>Bulk Water</u>	<u>Vicinal Water</u>
Density (g/cm <sup>3</sup> at 25 °C)	1.000	0.965
Viscosity (cP)	1.00	2 - 10
Heat Capacity (cal/g-°C)	1.00	1.25
Freezing Point (°C)	0	< -20
Distance from "Solid" Particle (μm)	≥ 0.05	≥ 0.01 - 0.05

Data from Drost-Hansen (1982)<sup>24</sup>

term "bound" water may actually be a gross estimate of several forms of water.

Vesilind indicated<sup>94</sup> that in classical sludge dewatering, it had been assumed that the water continuum surrounding the sludge particles had the physical properties of bulk water. He suggested that such an assumption may be invalid and attempted to demonstrate (from the literature in various disciplines) the existence of vicinal water, consisting of ordered and layered water molecules on the surfaces of submerged solids. For the review he cited the two interesting physical properties (discussed above) that relate to the potential for sludge dewatering - density and viscosity. With increased temperatures, the relatively higher viscosity of vicinal water appears to decrease until it completely disappears at about 70 °C, suggesting that the higher temperature destroys the vicinal water boundary water layers<sup>94</sup>. Vesilind also cited some other studies that indicated the loss of these vicinal water properties at elevated temperatures, and suggested that the effectiveness of heat in sludge conditioning may be due to the destruction of vicinal water.

The author<sup>94</sup> also presented an overview of the fractions of water in sludges cited in the literature and discussed later in this chapter. These fractions include:

- (i) *free (or bulk) water*: water not associated with and not influenced by the suspended solids particles,
- (ii) *interstitial water*: water trapped in crevices and interstitial spaces of the flocs and organisms,
- (iii) *vicinal water*: multiple layers of water molecules held tightly to the particle surface by hydrogen bonding (note that Vesilind suggested from his review of the literature that the major distinction between vicinal water and interstitial water is that the latter is free to move when the physical confinement, e.g. cell structure, is eliminated, whereas the former adheres to solid surfaces), and
- (iv) *water of hydration*: water chemically bound to the particles and removable only by the expenditure of thermal energy.

The role of vicinal water in sludge thickening and dewatering was also discussed<sup>94</sup>. It was indicated that in gravitational thickening, the presence of vicinal water, with its higher viscosity and layered shells around fine particles, would greatly affect the hindered settling or thickening of sludge, as well as the cake solids concentrations after mechanical dewatering. An accurate measurement of the distribution of water in sludge would enable prediction of the highest possible cake solids concentration that can be achieved for a given sludge. An important inference that Vesilind<sup>94</sup> suggested as one of the reasons sludge dewatering is often unsuccessful is that some of the water tends to be attached to particle surfaces as vicinal water, and this can only be removed by changing the amount of surface that the water can adhere to.

## **OVERVIEW OF BOUND WATER DETERMINATION METHODS AND WATER DISTRIBUTION MODELS**

### **Models Hypothesizing Two Water Fractions**

In 1932, Briggs<sup>15</sup> presented a review of the existing methods to determine bound water in colloids, and pointed out that bound water results varied in relation to the method utilized. He defined "bound water" as that portion of the water in a system containing colloid and crystalloid which is associated with the colloid, together with those ions which form a part of the colloid complex. Bound water was thought not to be a fixed quantity of water associated with the colloid, but to vary with the activity of the water in a manner consistent with the vapor pressure of the isotherm. Briggs also outlined a theoretical basis for bound water determinations in colloid systems in terms of the relative vapor pressure-water content curve (vapor pressure isotherm) of the colloid.

Novak, *et al*<sup>68</sup>, have used these changes in vapor pressure depression to estimate free and capillary water.

Jones and Gortner<sup>41</sup> reviewed the work prior to 1932 in determining free and bound water in elastic and non-elastic gels. They also reported the results of their pioneering investigations using dilatometric techniques (to measure bound water at temperatures below freezing, from 0 °C to -50 °C based on the hypothesis that at temperatures as low as -20 °C, bound water would not freeze) on various gels. The behavior upon repeated freezing at low temperatures of certain organic hydrosols and hydrogels was also compared with that of certain inorganic colloidal systems. Elastic type gels used in their study were gelatin and egg white. Inelastic gel materials included activated silicates and colloidal ferric hydroxide. Water binding in gelatin-water system was observed to be an adsorption reaction. A logarithmic relationship was found to exist between the concentration of the gelatin gel and the mass (in grams) of water which were bound per unit mass (gram) dry gelatin.

Measurements of bound water in sludges was first reported by Heukelekian and Weisburg in 1956<sup>38</sup>. They used the dilatometric method, based on the theory (cited also in Jones and Gortner's<sup>41</sup> work) that bound water does not freeze at temperatures below the freezing point of free water. By noting the expansion of a sludge sample due to freezing, the amount of free water can be estimated and the bound water content calculated as the difference between total moisture content (obtained by oven-drying a similar sample at or above 103 °C for a specific period, usually 12 hours, until there is no more weight loss) and free water. Robinson<sup>79</sup> developed part of his thesis experimental work based on the dilatometric technique, and obtained consistent free and bound water fractions for sludge samples.

Bound water measurements using the DTA for clay samples were undertaken by Anderson and Tice<sup>2</sup>. The different intensity peaks observed during the freezing of clay indicated the existence of several types of moisture which froze at different temperatures. The authors subsequently verified their findings using the DSC<sup>3</sup>.

Katsiris and Kouzeli-Katsiris<sup>43</sup> used the DTA technique to study free and bound water content of biological sludges in relation to filtration and dewatering.

The DSC is based on a similar theory, and is believed to be faster and more accurate than the DTA. The use of DSC to determine waters of hydration (as well as other characteristics, viz. glass transition temperature, heats of enthalpy and fusion) is fairly well documented in the literature in the food<sup>50,98</sup>, pharmaceutical, textile/fiber industry, and in research on coal<sup>64-66</sup>, soils and clays<sup>3,4</sup>, polymers<sup>7,8</sup>, etc.

Kumagai, *et al*<sup>50</sup>, reported on the use of the DSC to measure frozen and unfrozen (signifying free and tightly bound) waters in liquid foods in the context of its influence on the performance of freeze-drying. The amount of unfreezable water in milk was found to be constant irrespective of the initial water content. In freeze-drying liquid foods, they observed an almost constant rate period, followed abruptly by a decreasing drying rate. This was attributed to the transition from the sublimation of ice to the evaporation of water unfrozen and bound in the concentrated amorphous solution (during the freezing of liquid foods, the aqueous solution was believed to separate into ice crystals and the concentrated amorphous solution).

Very little work has been reported with respect to sludge characterization using the DSC. Rha<sup>78</sup>, as cited by<sup>88</sup> used the DSC technique to determine freezable portions of water in sludges down to -30 °C. The sludge was subsequently warmed to 40 °C and the ice-melting endotherm was reviewed to evaluate the amount of freezable water. Water unfrozen at -30 °C was assumed to be bound water. Since this work was reported to a private agency, there appears to be no published information on the results and applicability of the method for sludges.

All of the methods mentioned above can only differentiate two forms of water: free and bound, generally based on the assumption that the free water fraction freezes by -20 °C, while the bound water fraction freezes only at a much lower temperature. This classification does not recognize other forms of water bound by

different mechanisms (e.g. capillary, adsorption, etc.), as hypothesized by the methods described in the following section.

### **Models Hypothesizing Additional Water Fractions**

Vesilind<sup>93</sup> measured sludge water by subjecting sludge samples to gravitational settling and subsequent centrifugal settling at increasing acceleration. He found that for many sludges, the moisture content is constant over a range of acceleration followed by a sudden transition to a lower moisture content. These transitions were attributed to the removal of different forms of water. Vesilind classified the sludge water into four categories: (a) free, (b) floc, (c) capillary, and (d) bound waters. Huang<sup>40</sup> also studied sludge water using a high-speed centrifuge. The author hypothesized that water in sludges could be classified into: (a) free, (b) inter-floc, (c) floc-adsorbed, (d) inter-particle, (e) particle-adsorbed, and (f) particle waters. However, Huang doubted that the various types of water in sludges could be characterized completely by the centrifugation technique. Vesilind also acknowledged in a later paper<sup>94</sup> that these reductions in sludge volume may not necessarily indicate the release of different fractions of water.

As described later in this section, investigations into drying of materials, including lumber and foodstuff, showed that bound water content could be measured by characteristic drying curves. This method involves drying in a controlled environment (at a constant low temperature [e.g. 35 °C] and specific humidity and air flow) a mechanically dewatered sludge sample, with weight measured at timed intervals. The hypothesis of the method is that the rate of water removal is constant as long as the free water is being removed. The point at which the drying rate begins to decline is termed the critical point and signifies the commencement of bound water removal. The difference in the mass of the sample at this point and the constant mass after drying at this temperature is thought to represent the bound

water fraction. A second characteristic is quantified by taking the mass at which no further moisture is removed at 35 °C less the mass of the dry solids upon drying in a 103 °C oven. This value is defined as the chemically bound fraction<sup>79</sup>. Inorganic sludges with a definite crystal structure (e.g. alum sludges) may show a definite critical point<sup>79,88</sup>. The critical point for biological sludges appeared to be not as well defined and subject to the interpretation of the operator<sup>79,85,86,88</sup>. The method also appeared to take longer than the previously described techniques<sup>79</sup>.

Coackley and Allos<sup>19</sup> studied the characteristic drying rate curves for sewage sludges in 1962 and differentiated four types of water in sludges: (a) free or drainable, (b) capillary-held, which is removed between the first and second critical moisture contents, (c) floc or particle, which is water held within the individual sludge particles represented by the moisture below the second critical moisture value, and (d) chemically bound, which is water held at a moisture content below the equilibrium moisture content. Sludge particle size was found to have a considerable effect on the drying process<sup>19</sup>. Coackley and Allos fractionated sludges into various size ranges and found that filterability decreased with decreasing particle size.

Möller<sup>63</sup> distinguished internal and external sludge water and suggested that the binding mechanisms include capillarity, adhesion, adsorption and chemical binding by primary valences. The intensity of the binding forces was found to vary according to these mechanisms and the separation of sludge water occurred according to the intensity of the binding forces. Möller categorized moisture in sludges into four fairly distinct types: (a) interspace (drainable), (b) interstitial capillary, (c) adsorption and adhesion, and (d) internal (including cell fluid, water of hydration, and internal capillary) waters.

Using similar techniques (vacuum filtration and drying at 30 °C and 105 °C) in 1986 (and in a later study<sup>86</sup> with controlled vacuum drying), Smollen<sup>85</sup> found a linear relationship between cake moisture content and immobilized moisture fraction. No apparent relationship was found to exist between the immobilized and bound moisture fractions. The author categorized the moisture content of biological sewage



sludges into the following four fractions: (a) free, (b) immobilized, (iii) bound, and (iv) chemically bound waters. Higher free moisture fraction was found to correspond with lower specific resistance to filtration (SRF) and capillary suction time (CST) measurements.

More recently, Tsang and Vesilind<sup>88,89</sup> studied drying curves and classified moisture in sludge into four categories: (a) free water, (b) interstitial water, (c) surface water, and (d) bound water. Halde<sup>35</sup> had suggested using a vacuum drying technique instead of convective drying to overcome some of the potential problems of drying at atmospheric pressure (e.g. effect of microorganisms altering the sludge characteristics if drying is to take place over a long period of time). Similar drying curves were obtained and the critical moisture contents were used to classify the different types of water in sludge.

Sato, *et al*<sup>82</sup>, modified the drying curve experiment to minimize shrinkage effects for alum sludges. Their experimental work involved slowly drying a vacuum filtered 2mm thick, 35mm diameter sludge disc at 30°C and constant humidity (similar to TGA experiments). They found that the gravimetric moisture content of mechanically dewatered cake increased linearly with an increase in the amount of bound water. The drying experiment results were found to correlate well with NMR data. Only one critical moisture content was seen and, hence, the sludge water was classified as free and bound water. There was some concern about iron in the alum sludges interfering with the NMR<sup>82</sup> technique but this was not detailed.

NMR has been used to measure bound water in a variety of food industry products including potato starch<sup>98</sup> and in studies on coal<sup>66</sup>. However, due to its very nature, NMR is affected by paramagnetic compounds and some transitional elements, including iron and manganese<sup>72</sup>. This may be the reason that only a limited number of references to the use of NMR techniques in sludge water (which may contain trace to significant quantities of these elements or in compound form and would potentially interfere with the NMR signals) determinations were found in the literature search.

## **DRYING THEORIES (THEORIES OF MOISTURE MIGRATION IN SOLIDS)**

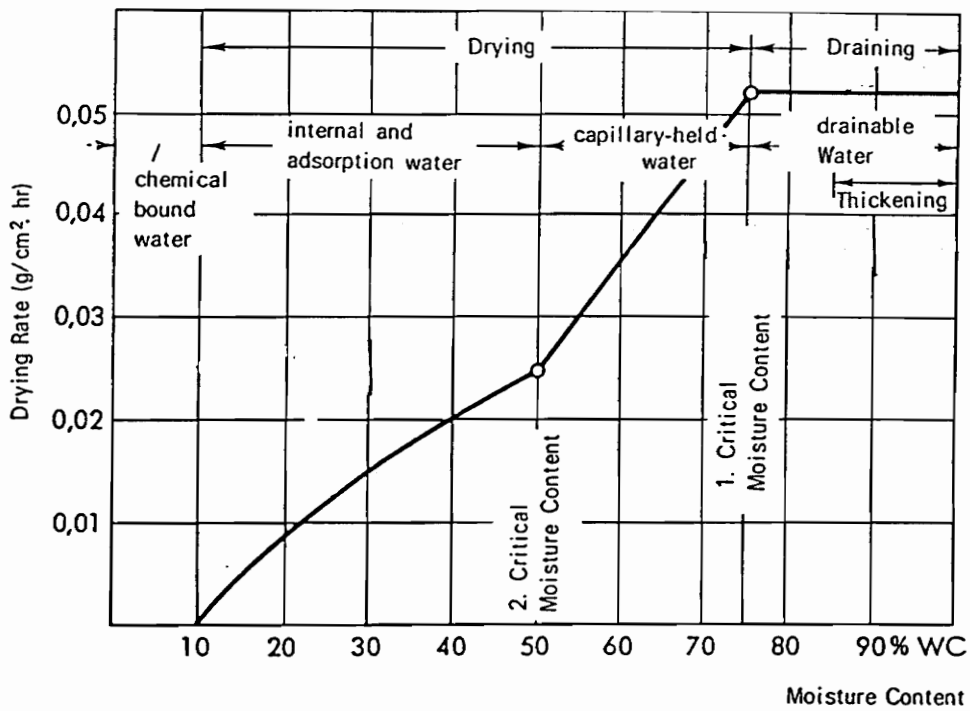
Drying theories rely on a number of different mechanisms for moisture movement in solids, some of which are applicable in some form or another to hygroscopic capillary porous media. Fortes and Okos<sup>30</sup> have presented an excellent review of the various theories including characterizations of the various drying curves obtained using the drying technique.

### **Characteristics of Drying Curves**

Data on drying are usually available as a plot of the average moisture content (dry basis) or moisture ratio against time, or drying rate versus relative moisture content. Previous work by Sherwood<sup>83,84</sup> and many others<sup>18,19,27,60,61,92</sup> indicated that the process of drying can be divided into a "constant rate" period and one or two "falling rate" periods.

Figure 1 is a representative diagram of a characteristic drying curve. In the constant rate period, the material remains at the wet-bulb temperature and the rate of surface evaporation is determined by the rate of diffusion of water vapor through the stationary film of air surrounding the material, which is proportional to the difference between the partial pressure of the water vapor at the surface of the material (wet-bulb temperature) and that in the drying air. The rate of diffusion increases with increasing air velocity. The magnitude of the constant-rate period depends upon the heat- and mass-transfer coefficients, area exposed to the drying medium, geometry of the sample, and difference in temperature and humidity between the gas stream and the wet surface of the solid. The internal mechanism of moisture flow does not affect the drying rate.

When the departure from the constant-rate period is first noticed, the falling rate (period of drying) starts. The point at which this departure is first seen (i.e. the



Source: Möller, 1983

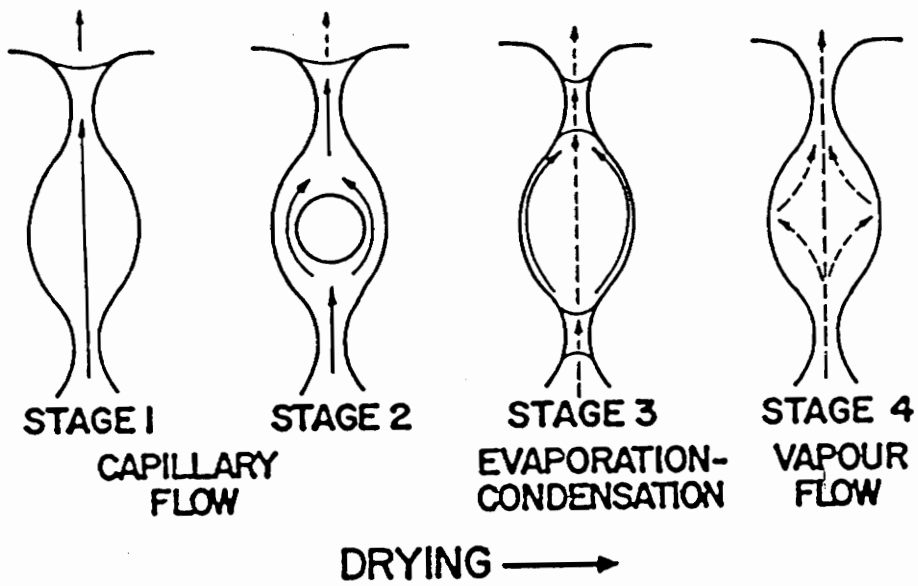
FIGURE 1: CHARACTERISTIC DRYING RATE CURVE FOR SLUDGES

inflection on the curve) is called the critical point. In the first falling-rate period, the evaporating surface decreases and consequently, the total surface evaporation rate decreases. In the second falling-rate period, the plane of vaporization moves into the solid, and the drying rate is then governed by the rate of internal moisture movement. Air velocity, temperature, and humidity have less effect on the progress of drying during this state.

Fortes and Okos<sup>30</sup> have given the following description of the main physical events that may occur during food drying:

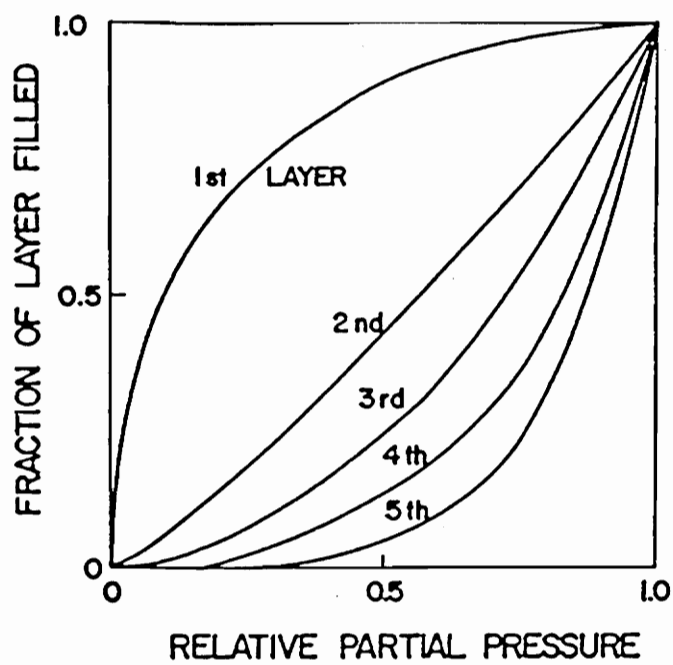
*Constant-rate drying period.* If, at the start of drying, the material is completely wet, liquid flow may occur under a hydraulic gradient<sup>45</sup>, as in stage 1 in Figure 2. Moisture is then unbound, exerting its full vapor pressure (if the effects of solutes is negligible) and held on the surface and the largest capillaries. Gradually, air pockets can be formed, replacing the moisture lost (stage 2 in Figure 2). The air temperature at the surface is approximately the wet-bulb temperature. There is a decrease in the diameter of the pores and capillaries, and the volume shrinkage is approximately equal to the volume of the water evaporated<sup>92</sup>.

*First drying period.* The moisture still exerts its full vapor pressure and is transferred mainly by capillary forces. Inner friction restrains shrinkage of the outer layers, which tend to dry more quickly<sup>33</sup>. With further drying, the moisture content decreases, and the liquid water bridges particles in the solid skeleton. A simultaneous vapor movement can start. This vapor transfer may take place even at high pore saturation, in the presence of temperature gradients<sup>51</sup> of the order of 1 °C/mm. Rounsley's<sup>81</sup> theory of sorption gives further support to this transfer by predicting that even at high relative partial pressures, a fraction of the first and second layers of water molecules adsorbed by the solid are unfilled (Figure 3), and vapor transfer may take



Source: Fortes and Okos, 1980; citing Keey, 1973

FIGURE 2: MOISTURE MOVEMENT IN DRYING OF A POROUS MATERIAL



Source: Fortes and Okos, 1980; citing Rounsley, 1961

FIGURE 3: BUILD-UP OF INDIVIDUAL LAYERS DURING WATER SORPTION

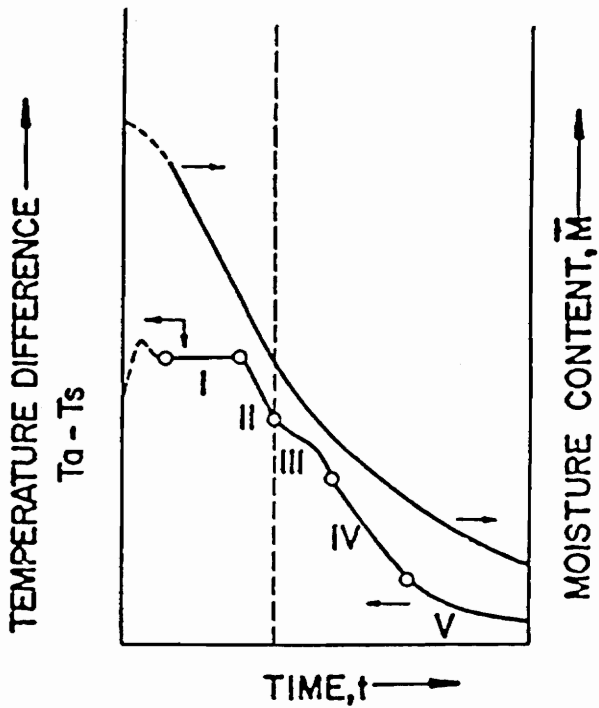
place. This drying stage corresponds to the funicular state (unsaturated surface zone). The temperature rises above the wet-bulb temperature. It is common to assume that water, then, also moves by diffusion.

*Second drying period.* The drying rate decreases sharply. Moisture is held in the finest capillaries and can migrate by creeping along the capillary walls or by successive evaporation and condensation between liquid bridges (stage 3 in Figure 2). This is the liquid-assisted vapor transfer as described by Philip and De Vries<sup>74</sup>. The partial pressure of the water vapor decreases. Shrinkage still takes place, but to a much lesser extent.

*Third drying period.* Drying takes place in all inner portions of the material<sup>33</sup>. Moisture is initially held in multimolecular layers and finally in a monolayer. An equilibrium is attained when the amount of water that vaporizes equals the amount that condenses (stage 4 in Figure 2). A thermogram (record of the mean temperature difference between the ambient and the product versus time, during drying) such as that in Figure 4 can show the different stages described above.

## **Moisture-Movement Mechanisms**

As mentioned previously, Fortes and Okos<sup>30</sup> presented excellent insights into the theories of drying, pointing out their restrictions and usefulness as applied to food and grain drying. Seven different mechanisms of moisture-movement are discussed by the authors. Of these, four primary mechanisms that can be applied to sludge drying are paraphrased as follows:



Thermogram for clay. Region I, moisture unbound, on the surface and largest capillaries; region II, moisture bridging particles in solid skeleton; region III, moisture in multimolecular layers; region IV, moisture in a monomolecular layer.

Source: Fortes and Okos, 1980; citing Luikov, 1964, citing Kazansky, 1949

FIGURE 4: THERMOGRAM FOR CLAY



- (i) Liquid diffusion due to concentration gradients.
- (ii) Vapor diffusion due to partial vapor-pressure gradients (caused by temperature gradients).
- (iii) Liquid movement due to capillary forces.
- (iv) Liquid or vapor flow due to differences in total pressure, caused by external pressure, shrinkage, high temperatures, and capillarity.

The following three are not usually taken into consideration for reasons indicated below:

- (v) Effusion (Knudsen) flow: This exists when the mean free path of the vapor molecules is of the order of the diameter of the pores. This is important only in high-vacuum conditions (as in freeze drying). Luikov<sup>56-58</sup> takes into account effusion and other mechanisms by lumping them into a single diffusion equation.
- (vi) Liquid movement due to gravity: This is often neglected, especially in food drying as it is not significant when the pore dimensions are very small.
- (vii) Surface diffusion: This is not taken directly into consideration by any of the existing theories. Philip and De Vries<sup>74</sup> suggest that it seems unlikely that diffusion in the adsorbed phase will significantly affect the total heat-and mass-transfer process. Their reasoning is that part of the vapor that evaporates from or condenses on the surfaces may recirculate in a single air-filled pore through the process of surface migration.

Keey<sup>46</sup> has also reviewed the recent literature on the drying of particulate and loose solids under commercial conditions. In his text, he presented useful information on the kinetics of drying and on moisture in particulate solids, including a section on the measurement of moisture content.

Theories of drying are usually limited to the falling-rate period as the constant-rate period is amenable to simple calculations. A brief review of the prevalent theories of moisture migration in solids is abstracted from Fortes and Okos<sup>30</sup>, and presented as follows:

### **Liquid-Diffusion Theory**

Probably the most popular theory, many researchers (including Sherwood and Comings<sup>83</sup>) have proposed the movement of moisture by liquid diffusion as the principal mechanism in a drying solid. Fick's equation,

$$\frac{\delta M}{\delta t} = \nabla (K_l \nabla M) \quad [1]$$

where:

$M$  = moisture content (dry basis)

$t$  = time

$K_l$  = surface-diffusion coefficient

$\nabla$  = nabla operator

has been used with various assumptions such as constant diffusion coefficients, isotropy, or first-order boundary conditions. The liquid-diffusion theory has gained the preference of food and grain researchers, many of them using the solution of diffusion equations, either for a sphere or a parallelepiped.

In his recent dissertational work on sludges, Tsang<sup>88</sup> also applied the liquid-diffusion theory to develop a theoretical model for the drying of sludges. However, he also indicated that the model had obvious limitations related to the lack of knowledge of the pore structure and temperature effects. The author attempted to develop the model in an effort to simplify the concept of drying to allow identification of the free, interstitial, and surface water fractions in sludges<sup>88</sup>.

The diffusion coefficient is generally assumed to be a constant, or linearly dependent on temperature and/or concentration, or of a temperature Arrhenius-type dependency:

$$K_t = K_{t0} \exp \left\{ - \frac{E}{RT} \right\} \quad [2]$$

where:

$K_t$  = surface-diffusion coefficient

$K_{t0}$  = diffusion coefficient at saturation state, or initial value

$E$  = energy of activation

$R$  = radius

$T$  = absolute temperature

Liquid diffusion, as the only mechanism for moisture movement, has been subject to severe criticism. Hougen, *et al*<sup>39</sup> (as cited by 30), stated that the condition for the validity of a model is that it should predict the correct moisture gradient in the solid during drying. There appeared to be discrepancies between calculated (based upon diffusion coefficients corresponding to average experimental values of moisture content) and experimental values for the drying of soap and paper when applying liquid diffusion as the only mechanism for moisture movement. Nevertheless, Hougen, *et al*<sup>39</sup>, pointed out that the results could have been better if, for some cases, variable diffusion coefficients were used. They concluded that diffusion coefficients could be applied to the drying of:

- (a) Clays, starches, flours, textiles, paper, and wood, restricted to the equilibrium moisture content below the point of atmospheric saturation.
- (b) Soaps, glues, gelatin, and pastes, i.e., single-phase solid systems in which water and solid are mutually soluble.

Babbitt<sup>10</sup> stated that the driving force in diffusion through solids is pressure and not concentration. The relationship between pressure and concentration is seldom linear, owing to the complexities of adsorption and desorption (including hysteresis effects). Equations in terms of concentration should be avoided, since they fail to distinguish diffusion from other flow mechanisms that may occur simultaneously. Using a piece of fiberboard, Babbitt<sup>10</sup> showed experimentally that moisture can flow in response to a vapor gradient and against a moisture-concentration gradient. Sherwood<sup>84</sup> commented that the apparent success of the diffusion equations was due to the fact that the calculations were made by integration techniques, which compensate for the error caused by assuming wrong distributions.

Moisture movement through liquid diffusion cannot be denied. More sophisticated theories take Fick's law as representative for liquid and vapor movement. The criticism lies in the assumption that liquid movement is the only mechanism for moisture transfer in all stages of drying. The diffusion theory, as well as most of the recent theories, also does not take into account shrinkage, case hardening, or sorption isotherms.

### Capillary Theory

Capillarity refers to the flow of a liquid through the interstices and over the surface of a solid due to molecular attraction between the liquid and the solid<sup>39</sup>. This phenomenon was first analyzed by Buckingham<sup>16</sup>, who introduced the concept of "capillary potential" as the driving force for unsaturated capillary flow, i.e. the pressure difference between the water and the air at the curved air-water interfaces present in a capillary. The interface curvature is produced by the surface tension of the water. The equation for capillary-liquid flow is

$$J_l = -K_H \nabla \psi \quad [3]$$

where:

$J_l$  = capillary-liquid flux

$K_H$  = unsaturated hydraulic conductivity

$\psi$  = capillary potential

For isothermal conditions the capillary potential is usually assumed to be proportional to the gradient of moisture concentration, and Equation 3 becomes<sup>57</sup>

$$J_l = -K_H \rho_s \nabla M \quad [4]$$

where:

$$K_H = \frac{\sigma \cos \theta}{4 \eta r^2 f(r)} \int_{r_0}^{r_1} r^2 f(r) dr \quad [5]$$

$\rho_s$  = density of the solid skeleton or body surface

$f(r)$  = differential curve for distribution of pore sizes by radius  $r$

$r_0$   $r_1$  = minimum, maximum values of radii of capillaries

$\eta$  = dynamic viscosity

$\theta$  = wetting angle (in capillaries) or moisture-transfer potential

Ceaglske and Hougen<sup>18</sup> pointed out that in the drying of granular solids, the water flow is determined entirely by capillary forces and hence is independent of water concentration. They showed experimentally that moisture flow may be in the direction of increasing concentration. Miller and Miller<sup>60,61</sup> explained this by stating that the driving force is a tension gradient. Their argument is that both surface tension and viscous flows are based on pressure. Only for homogeneous media and negligible body forces is tension proportional to moisture content, and Equation 4 holds. Water held in the interstices of solids, as liquid covering the surface and as

free water in cell cavities, is subject to movement by gravity and capillarity, provided passageways for continuity of flow are present. Thus, Hougen, *et al*<sup>39</sup> (as cited by 30), concluded that, in drying, the capillary-liquid equation applies to:

- (a) Water not held in solution and all water above the saturation point, as in textiles, paper, and leather.
- (b) All water above the equilibrium moisture content at atmospheric saturation, as in fine powders and granular solids, such as paint pigments, mineral, clays, soil, and sand.

Krischer<sup>49</sup>, as cited by 30 stated that the first stage of drying of foods is controlled by capillarity and used a slightly modified form of Equation 4:

$$J_l = - K_l A \nabla M \quad [6]$$

where:

$K_l$  = liquid conductivity

$A$  = cross-sectional area of sample material

### **Evaporation-Condensation Theory**

In his investigation on the uptake of moisture by cotton bales in 1939, Henry<sup>37</sup> studied the diffusion of one substance through another in the pores of a solid body, which may adsorb (or desorb) and immobilize some of the diffusing substance. Even though his theory was not limited to vapor as an exclusive diffusing substance, in his work and in all modified models based on it, moisture was assumed to migrate entirely in the gaseous phase. His theory took into account the simultaneous diffusion of heat and mass, and he assumed the pores to be a continuous network of

spaces included in the solid. He further assumed, for mathematical convenience, that the amount of vapor in the solid varied linearly with the concentration of vapor and temperature. The diffusion coefficient was taken to be constant. Moisture movement in the vapor phase was substantiated by Gurr, *et al*<sup>34</sup>, and Kuzmak and Sereda<sup>51</sup>, who experimentally found that, in an unsaturated porous material such as soil, there was no flow in the liquid phase when water moved due to a temperature gradient. Thus, the flow occurred entirely in the vapor phase. However, when there was a pressure gradient, moisture flow occurred entirely in the liquid phase.

A further refinement of Henry's model was made by Harmathy<sup>36</sup>, who developed a theory for simultaneous mass and heat transfer during the pendicular state (i.e. the internal moisture control zone when the evaporating surface is unsaturated) of porous systems. He based his model on the assumptions of the evaporation-condensation theory and on the assumption that the phases of a porous system are so finely distributed that, from a macroscopic standpoint, the system is a quasi-one-phase system. A system of equations was obtained that yielded the complete moisture-content, temperature, and pressure history of the system. He concluded that the capillary flow mechanism is not the only one present at the beginning of the falling-rate period, but that vapor transfer by diffusion also occurs.

Hougen, *et al*<sup>39</sup>, stated that moisture may move by vapor diffusion through a solid, provided that a temperature gradient is established, thus creating a vapor-pressure gradient toward the drying surface. Vaporization and vapor diffusion may be applied to any solid where heating is taking place at one surface and drying from the other, and when water is isolated between granules of solids.

Based on Henry's theory, a number of researchers, cited by Fortes and Okos<sup>30</sup>, developed slightly different models for moisture migration in cereal grains. A linear dependency among pressure, moisture content, and temperature was assumed, although no physical evidence for such an assumption was given. Young<sup>99</sup> defined a modified Lewis number that could be used to determine the significance of considering the heat-transfer equations in drying problems. For a modified Lewis

number greater than 60, the mass-transfer equation alone is sufficient to describe the drying process. Below this number, heat transfer becomes critical.

### Luikov's Theory

Luikov is credited with discovering, in 1934, the phenomenon of moisture thermal diffusion and with establishing that temperature gradient is also a factor causing moisture transfer in materials<sup>53</sup>. Since then, much use has been made of Luikov's theory. In the development of his theory, Luikov<sup>56-58</sup> employs the principles of irreversible thermodynamics. The basic equation of the thermodynamics of irreversible processes:

$$\sigma = \frac{d_i S}{dt} = \sum_i J_i \cdot x_i > 0 \quad [7]$$

where:

$\sigma$  = entropy production per unit volume and unit time or surface tension

relates the rate of entropy production  $d_i S/dt$  to the fluxes  $J_i$  (heat and diffusion fluxes, etc.) and the thermodynamic forces  $X_i$  giving rise to these (temperature gradient, concentration gradient, etc.). Equation 7 may be derived from the Gibb's equation<sup>22</sup>:

$$T dS = dU + P dV - \sum_i \mu_i dn_i \quad [8]$$

where:

$T$  = absolute temperature

$S$  = entropy



$U$  = circumference of pores or internal energy

$P$  = pressure

$V$  = volume

$\mu$  = chemical potential

$n$  = number of moles

The above equations assume that the entropy of the system, which is not in the equilibrium state, is determined by the same independent variables as in the equilibrium state. This is a rather good approximation when deviations from equilibrium are not large<sup>22,53</sup>. Fortes and Okos<sup>30</sup> present the development of Luikov's theory, including a review of its basic ideas and restrictions. Luikov's basic equations are as follows:

$$\frac{\delta M}{\delta t} = \nabla \cdot [K_m (\nabla M + \delta \nabla T)] \quad [9]$$

$$c_b \rho_s \frac{\delta T}{\delta t} = \nabla \cdot (K_T \nabla T) + L_v \epsilon \rho_s \frac{\delta M}{\delta t} \quad [10]$$

where

$$K_m = K_l + K_v = \text{total moisture diffusion coefficient} \quad [11]$$

$$\delta = \frac{K_{lT} + K_{vT}}{K_l + K_v} = \text{thermal gradient coefficient} \quad [12]$$

$L_v = h_v - h_l$  = specific heat of evaporation

$K_v, K_l$  = diffusion coefficients (diffusivity)

$K_{lT}, K_{vT}$  = thermal moisture diffusivities

$c_b$  = reduced specific heat of liquid phase

$\rho_s$  = density of solid skeleton or body surface

$\epsilon$  = tortuosity factor for diffusion of gases in porous media

The transfer coefficients  $K_m$ ,  $K_T$ ,  $c_b$ , and  $\delta$  are variable.

Considerable work was carried out by Luikov to determine experimentally, for a number of different materials, the values of the parameters required in the theory and to validate the theory as far as possible<sup>53,54</sup>.

### **Philip and De Vries' Theory**

Philip and De Vries<sup>74</sup> derived a set of equations describing moisture and heat transfer in porous bodies under combined moisture and temperature gradients. Their approach is a mechanistic one that, basically, assumes that water moves by both vapor diffusion and capillarity. The model was originally developed for application to soil moisture migration problems and has not been extended to more general application<sup>54</sup>. The general partial differential equation describing moisture movement in porous materials under combined temperature and moisture gradients can be stated as follows<sup>30</sup>:

$$\frac{\delta M}{\delta t} = \nabla \cdot (K_{mT} \nabla T) + \nabla \cdot (K_m \nabla M) + \frac{\delta K}{\delta Z} \quad [13]$$

where:

$K_{mT} = K_{IT} + K_{vT} =$  overall thermal moisture diffusivity

$K_m = K_l + K_v =$  overall isothermal moisture diffusivity [14]

$Z =$  vertical ordinate

Fortes and Okos<sup>30</sup> indicated that a major limitation of Philip and De Vries' theory is the use of certain assumptions which hold only for the capillary region of the isotherms, since only then is there liquid continuity in the pores and capillaries.

## Krischer's and Berger and Pei's Theories

Krischer<sup>49</sup> analyzed heat and mass transfer in a variety of porous media. His model was based on the assumption that, during drying, some combination of capillary flow of liquid and diffusion of vapor controlled the internal moisture transfer. According to Berger and Pei<sup>14</sup>, however, there were difficulties in applying Krischer's work. This arose from his simplifying assumption that the sorption isotherm could be used as a coupling equation over a whole range of moisture contents. Berger and Pei proposed a new model which employed two coupling equations between the three dependent variables,  $u$  (volumetric moisture content, i.e. volume of water per volume of dry solid),  $\rho_v$  (density of the vapor phase), and  $T$  (absolute temperature). These two equations are the Clausius-Clapeyron equation in the region where the liquid content is larger than the maximum sorptional region of liquid content. Their theory, however, is not verified by any experimental investigations<sup>54</sup>. While Berger and Pei's model has not been applied to biological materials, Krischer's has been applied to a variety of food materials<sup>30</sup>.

## REMARKS ON THE ABOVE DRYING THEORIES

From the thermodynamics of irreversible processes, it was shown<sup>22</sup> that the actual driving forces for mass transport are chemical potential and temperature gradients. Fortes and Okos<sup>30</sup> state that "the chemical potential of water in a food material could be expressed, in terms of the difference between the chemical potential of water at a point in question in the food material and water in its reference state, by

$$\Delta\mu = \Delta\mu_s + \Delta\mu_p + \Delta\mu_o + \Delta\mu_F \quad [15]$$

where  $\Delta\mu_s$  denotes the component of the chemical potential due to surface tension and radius of curvature of the water-air interface;  $\Delta\mu_p$ , that due to the hydrostatic pressure of the moisture adjacent to the food-particle surface caused by the adsorptive forces surrounding the food particle (excluding that due to surface tension and radius of curvature of the water-air interfaces), as well as due to any pressure transmitted from external sources;  $\Delta\mu_o$ , that due to the osmotic pressure of the dissolved material; and  $\Delta\mu_F$ , the chemical potential of water due to its position in the adsorptive field surrounding the food interstitial particles as well as the gravitational field".

In view of the above expression, and the already accepted experimental fact that water can migrate in either the liquid or vapor phase or both, it can be ascertained that the liquid-diffusion, capillary, or vaporization-condensation theory lacks of a valid physical meaning when applied to a whole drying process. These theories are complementary to each other and should be taken as such. Philip and De Vries<sup>74</sup> assumed the modified Kelvin equation to cover the whole range of moisture content. The Kelvin equation is applicable only to the capillary condensation region. Even for soils, Philip and De Vries' model should be used with some caution, since at low moisture contents, adsorptive forces may play an important role<sup>27</sup>. Luikov<sup>58</sup> lumped together all the components of the total chemical potential and created a new driving force for mass transfer (moisture-transfer potential). The concept of moisture-transfer potential has been subjected to criticism. Luikov's original equations are very similar to Philip and De Vries', and both models should furnish similar results when applied to biological materials. Berger and Pei's approach, an extended version of Krischer's basic ideas, does not offer much innovation over Luikov's and Philip and De Vries' models, except for the fact that Berger and Pei take into consideration the isotherm equation (empirically obtained) as a coupling equation among liquid, vapor, and heat transfer<sup>30</sup>. Experimental confirmation of this model is needed to ensure its validity.

Real solids are usually very different from the conceptual solids referred to in drying theories. The conceptual solids can best be classified as follows<sup>92</sup>:

(a) *Capillary-porous media.* Possible examples are packings of sand, crushed minerals, nonhygroscopic crystals, polymer particles, some ceramics. The defining criteria are:

1. There is a clearly recognizable pore space which is filled with liquid if the medium is completely saturated, and filled with air when completely dry.
2. The amount of physically bound water is negligible, i.e. the medium is nonhygroscopic.
3. The medium does not shrink during drying.

(b) *Hygroscopic-porous media.* Possible examples are clay, molecular sieves, wood, and textiles. The defining criteria are:

1. There is a clearly recognizable pore space.
2. There is a large amount of physically bound liquid.
3. Shrinkage often occurs in the initial stages of drying.

This category might be further classified into (i) hygroscopic capillary-porous media (micropores and macropores, including bidisperse media; for example, wood, clays, and textiles), and (ii) strictly hygroscopic media (only micropores: silica gel, alumina, zeolites).

(c) *Colloidal (nonporous) media.* Possible examples are soap, glue, and some polymers (e.g. nylon), and various food products. The defining criteria are:

1. There is no pore space (evaporation can take place only at the surface).
2. All liquid is physically bound.

The above classifications apply only (if at all) to homogeneous media, which can be considered as continua for transport. Many practical systems do not meet this criterion<sup>92</sup>.

Few attempts have been made to classify the different types of drying characteristics. Figure 5 presents a provisional classification of the characteristic drying curves reported in the literature (after van Brakel<sup>92</sup>). Classes I-VIII are for capillary- and hygroscopic-porous media. Classes IX and X are for colloidal media, and classes XI and XII give examples of special cases.

## **REVIEW OF RECENT RESEARCH AND TECHNIQUES**

### **Drying Rate Curve Studies**

In his dissertational research, Tsang<sup>88</sup> built on the classical drying experiments by Sherwood<sup>84</sup>. By applying Fick's Law to model the rate of evaporation from the free water surface, Tsang related the evaporative flux to the molecular and convective fluxes. His solution of diffusion equations assumed cylindrical (capillary) pore structures. He distinguished three stages of drying: Stage I describing the drying of free moisture, Stage II the drying of interstitial moisture, and Stage III the drying of surface moisture. This represents an ideal condition and, in reality, not all stages may be apparent during the drying of some materials, with the critical points being difficult to detect. This is one of the limitations of the model, i.e. the differentiation of the inflection points where evaporation changes from wide to small capillaries. The selection of inflection points from the drying curve appears to be operator sensitive, relying upon the individual's judgement. In addition, the model applies only to non-hygroscopic materials as no bound moisture is considered. The drying process is defined purely by the evaporation of moisture from the liquid surface, and it is assumed that mass transfer is by diffusion only. The temperature

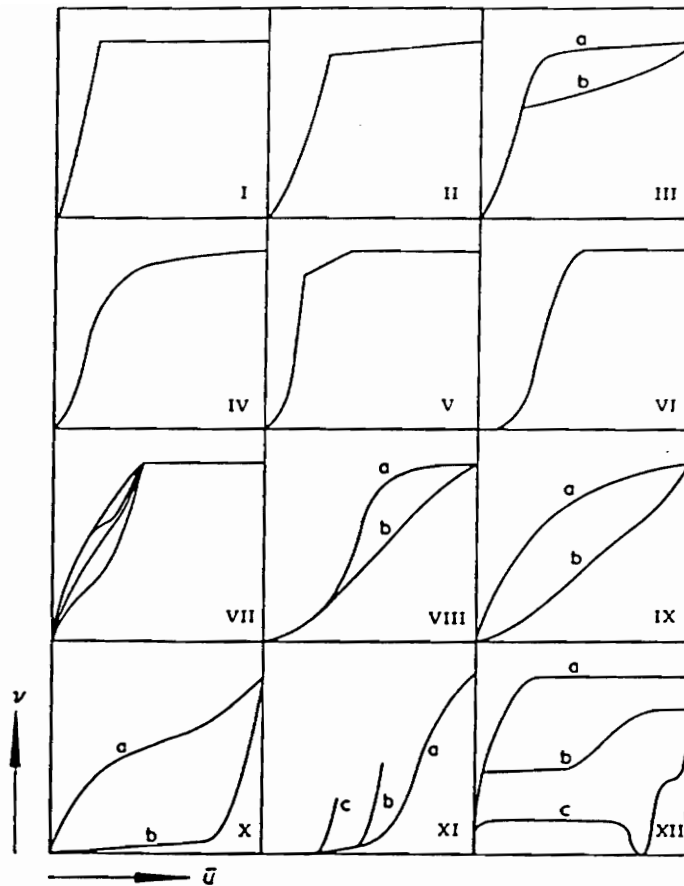


Figure 1 Examples of normalized drying-rate curves  $v(\bar{u})$  for different types of media. Unless noted otherwise, the evaporating liquid is water. For comparison all curves extend from (1,1) to (0,0). Class I: glass beads,<sup>86,100</sup> sand,<sup>17</sup> clay,<sup>47,62,104</sup> mixtures of sand and clay,<sup>47</sup> calcium carbonate,<sup>104,120</sup> silica gel,<sup>23</sup> paper pulp,<sup>47</sup> leather,<sup>59,62</sup> pig manure,<sup>8</sup> Class II: glass beads,<sup>58</sup> ceramic tiles,<sup>23,28</sup> clay,<sup>42</sup> silica gel.<sup>23</sup> Class III: organic liquids in glass beads<sup>74,86</sup>; for example, (a) benzene and *n*-propanol, (b) *n*-pentanol. Class IV: glass beads,<sup>2,9</sup> polystyrene beads.<sup>3</sup> Class V: sand,<sup>17</sup> plastic-clay mix,<sup>105</sup> silica-brick mix,<sup>105</sup> whiting slab,<sup>105</sup> ceramic plate,<sup>10</sup> leather,<sup>59,62</sup> lactose granulation.<sup>13</sup> Class VI: special case of class I; Schlünder reports that for molecular sieves  $v(\bar{u})$  is independent of  $T^*$ . Class VII: class I with different curvatures during the period of decreasing drying rate, aluminum silicate particles as a function of air temperature temperature,<sup>102</sup> and sand<sup>17</sup> and paper pulp<sup>42</sup> as a function of thickness of the sample. Class VIII: (a) fir wood; (b) cypress wood.<sup>42</sup> Class IX: (a) paper,<sup>104</sup> wool,<sup>125</sup> aluminum stearate,<sup>134</sup> dough<sup>62</sup>; (b) potatoes,<sup>24</sup> tapioca tuber, and rice flour (this laboratory). Class X: (a) rye bread,<sup>42</sup> yeast<sup>110</sup>; (b) butter and margarine.<sup>98</sup> Class XI: (a) wheat corns; (b) and (c) the same for lower  $X_0$ , normalized to the initial drying rate for (a).<sup>45</sup> Class XII: limestone granules saturated with (a) water, (b) 0.05-M NaCl, (c) 0.35-M NaCl.<sup>96</sup> Similar behavior, due to crust formation, has been observed for plaster tiles<sup>134</sup> and for clay.<sup>22</sup>

Source: van Brakel, 1980

FIGURE 5: CLASSIFICATION OF DRYING CURVES

effect on the rate of evaporation was not considered as all tests were done under a constant temperature.

Tsang<sup>88</sup> investigated sludge drying results over the range 22.9 to 38 °C with relative humidity values ranging from 32 to 45%; these being the limits of the experimental set-up. The results indicated maximum variation in replicate tests of less than 4%. Tsang used Min-U-Sil (a silicon dioxide slurry) to prepare "control" sludges. Properties of this compound are presented in Table 4. Particle size did not appear to have a significant effect on the observed drying characteristics (this is unlike previous studies<sup>19,42</sup> that appeared to show that particle size distribution affected the dewatering and drying). Similar to the experimental method discussed by Sato, *et al*<sup>82</sup>, Tsang used samples of 2mm depth and 45mm diameter to minimize rate limiting mass transport mechanisms and optimize his drying results. In addition, he used a high molecular weight cationic polymer (Nalco 7148) to determine how this would change the moisture distribution of sludge, and how this change affected the dewaterability of sludge. He found that free moisture content was significantly reduced when the polymer was added prior to mechanical dewatering, and that the amounts of surface and (chemically) bound water were not markedly affected.

### **Dilatometric Studies**

Robinson and Knocke<sup>79,80</sup> investigated constant temperature (35 °C) drying and dilatometric techniques for quantifying the free and bound water content of various chemical (alum and lime water treatment sludges) and biological (anaerobically and aerobically digested) sludges. The dilatometric method was preferred and investigated in more detail in their study as it was thought to be more reproducible and less prone to interpretational error in comparison to the drying technique<sup>79</sup>. Dilatometric test units were fabricated from standard taper ground glass joints. The total volume of each dilatometer was approximately 50 mL. A suitable measuring



TABLE 4  
PROPERTIES OF MIN-U-SIL

Min-U-Sil #	<u>30</u>	<u>15</u>	<u>10</u>	<u>5</u>
<i>Chemical Analysis %</i>				
SiO <sub>2</sub>	99.62	99.58	99.55	99.25
Fe <sub>2</sub> O <sub>3</sub>	0.022	0.025	0.025	0.064
Al <sub>2</sub> O <sub>3</sub>	0.124	0.139	0.163	0.143
TiO <sub>2</sub>	0.015	0.015	0.02	0.051
MgO	<0.01	<0.01	<0.01	<0.01
pH	7.7	7.7	7.7	8.0
Average size (μm)	3.5	2.3	1.7	1.1
Specific area (cm <sup>2</sup> /g)	6660	9840	13300	21500
Bulk density (lb/ft <sup>3</sup> )	48.5	46.0	42.7	35.7

Source: Data provided by U.S. Silica to Tsang<sup>88</sup>

fluid was selected; hydraulic oil was chosen after testing various fluids. Standard cooling and freezing curves were developed for the hydraulic oil alone and distilled water so that the unit amount of expansion and contraction for each fluid could be quantified.

This information was used to calculate the average volume expansion associated with the freezing of free and interstitial water. The researchers found that bound water content decreased following polymer or freeze-thaw conditioning of the sludges. Mechanical dewatering produced a significant decrease in bound water content and corresponding increase in dewatered cake solids concentration. Interstitial water was found to have a key role in defining dewatered cake solids concentration<sup>80</sup>.

### **Floc Density Measurements**

Knocke, *et al.*<sup>47</sup> (see also 9,20,23,48,62&95) developed an isopycnic centrifugation procedure to estimate the characteristic floc density present in several chemical sludges. Analytical centrifugation has been successfully used in biological and medical sciences for isolating and characterizing various biological particles. The premise of isopycnic (or density gradient) centrifugation is that particles will migrate through a varying density liquid until they reach a point where their density equals that of the specific liquid layers, defined as the isopycnic point. Measurement or knowledge of the gradient density at many locations allows for the particle density to be estimated. Separation of particles by isopycnic sedimentation is independent of particle settling rates or particle size and is a function of particle density only. Knocke, *et al.*<sup>47</sup>, found that increases in sludge floc density corresponded to an increase in cake solids concentration following mechanical dewatering. Most sludge water removal during dewatering was hypothesized to be external to the floc

structure. The floc density measurement technique is described in greater detail in the following chapter.

## **THERMAL ANALYSIS**

Thermal analysis is broadly defined as the measurement of changes in chemical or physical properties of a sample as a function of temperature. It includes various techniques including TGA, DTA, and DSC. These methods have long been used in analytical chemistry of a diverse group of materials including polymers<sup>7,8,11</sup>, coal<sup>61,62</sup>, clays<sup>2,3,5</sup> and other geological samples, forest products, pharmaceutical products, foodstuff<sup>50</sup>, etc. The samples are usually analyzed as to the relative quantities of their various constituents, the latter confirmed by the use of other analytical instruments including, but not limited to: Atomic Adsorption (AA), Fourier transformation infra-red (FTIR) spectrometry, high pressure liquid chromatography (HPLC), nuclear magnetic resonance (NMR), etc.

Following are typical definitions<sup>75,97</sup> of three of the thermal analysis techniques used in the current research:

- The *TGA* is a dynamic-mass change method in which the mass of a sample is measured as a function of temperature while the sample is subjected to a controlled temperature program.
- The *DTA* method is based on temperature change, where the difference in temperature between a substance and a reference material is measured while both are subjected to a controlled temperature program.
- The *DSC* is an enthalpy change method in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while both materials are subjected to a controlled temperature program.

Pope and Judd (1977)<sup>75</sup> provide an excellent overview of the techniques and applications of the DTA and the DSC, as well as a discussion of their relative advantages and disadvantages, and factors that can affect the instrument detection limits and measurements. A more recent text by Wunderlich<sup>97</sup> also discusses the theory and applications (including instrumentation) of various thermal analytical techniques, including the TGA and DSC, to analyze a variety of materials.

A fairly widely used property of bound water is used to differentiate between the "free" and "bound" fractions of water. Bound water is operationally defined as that fraction of water that does not freeze even at temperatures down to -20°C. Since free water is thought to freeze at temperatures near or slightly below 0°C, the difference between the total water present (as determined by drying representative samples at 105°C) and that fraction frozen by -20°C is supposed to be the bound water fraction. The DSC and the DTA both rely on this property to characterize moisture distribution; the DSC by recording the change in enthalpy and the DTA by change in temperature.

## **CLOSING REMARKS**

Water is ubiquitous in sludges, making up a huge volume and weight portion of the total sludge. Various dewatering methods abound to reduce the portion of water, usually by chemical and mechanical methods. However, most of these methods are able to only remove a portion of water, usually known as the "free" fraction. The "bound" fraction is usually much more difficult to remove as it appears tenaciously bound to the sludge particles. Knowing more about the bound fraction ultimately could lead to the development of (or significant improvements to current) techniques to remove this fraction, thereby minimizing the amount and costs of sludge to be ultimately disposed off.

Based on the fairly extensive review of the literature as presented in this chapter, it was determined that some of the methods that have been used in other disciplines to characterize moisture could be applied to sludges. For this dissertational research two thermal analysis techniques were chosen: the DSC and the TGA. The two methods utilize different properties of water to differentiate the various fractions, and these are explained in the following chapter.

For environmental engineers, the application of thermal analysis techniques appeared to be a useful, albeit currently expensive, tool in the characterization of moisture in biological and chemical solids. The current research reported herein appears to be among the first to utilize such techniques.

As indicated previously, there appear to be a number of nomenclatures for the various fractions, although there recently appears to be some consensus that the fractions (in order of increasing difficulty of removal) and for bio-solids are: free, interstitial, surface, and bound. In addition, the term vicinal water is beginning to be used to describe some of the surface and much of the interstitial water (all of this assumes, of course, that such waters actually exist in distinct regions around the sludge particles).

The concept of vicinal water appears to be reflected in the various forms of water in sludges indicated earlier in this literature review, especially in the drying techniques. Thus, vicinal water could include surface (physically and chemically bound), interstitial, and some capillary water(s). In other words, some of the "bound" water fractions of sludge water could be considered to be vicinal water. This may be a matter of different terminologies. There can be little doubt that "bound" or "vicinal" water exists. There is, however, a great deal of uncertainty as to its extent, structure, and energetics.

## **CHAPTER 3**

### **METHODS AND MATERIALS**

#### **OVERVIEW**

This chapter describes the rationale for the dissertational research undertaken in an effort to better characterize moisture distribution in sludges, and to gain a better understanding of those properties that may affect moisture distribution. Sludges generally contain an extremely high proportion of water, bound by various mechanisms (not currently fully understood) to the sludge particles. A better understanding and removal of as much of the water as economically and technically feasible could conceivably lead to greater cost savings in the ultimate disposal of the remaining fractions.

As indicated in the preceding literature review chapter, the research methodology built in part upon work undertaken by various researchers in other disciplines and further explored the characterization of moisture in various sludges of interest to the environmental engineering discipline. Various techniques used in other disciplines were studied and those deemed most applicable to use to analyze bio-solids and chemical sludges were chosen for this study.

This chapter presents the methodology used in the current study that have been used by other researchers to characterize sludges, and includes the dilatometric technique for moisture characterization. It describes the techniques chosen, methods and materials used, and precautions taken in the study. The initial section of this chapter provides an overview of the rationale for choosing the techniques, followed by descriptions of the matrix of sludges chosen, dewatering methods adopted, and the analytical techniques used to determine certain sludge particle characteristics.

The following chapter presents the results and discussion of the method development effort to utilize two other analytical techniques, viz. the thermo-

gravimetric analyzer and the differential scanning calorimeter, to characterize moisture distribution in sludges.

## **NATURE OF SLUDGES**

Sludges, by their very nature, are extremely difficult to analyze; even samples from the same treatment plant/source can exhibit differing characteristics at different times on the same day. However, with continued and additional research, time, and effort, it should eventually be possible to make some general characterizations that would lead to a better understanding of sludges in general for waste management and disposal (with its associated economics).

In a very broad manner, depending on their origin, sludges may be divided into two general forms: chemical and biological. The former can include sludges from water treatment plants where there is minimal biological activity and the sludge produced comes predominantly from processes such as alum coagulation or lime softening. The latter includes sludges from predominantly biological (secondary) processes such as from waste water treatment plants. Sludges from industrial processes could conceivably fall in either category, depending upon the nature of the bulk of the sludge fractions. In general, sludges range anywhere from 0.5 to as high as 5% dry solids concentration prior to any form of dewatering. Thereafter, the solids concentration could increase up to the limit of the dewatering system used. The major component being removed is thought to be the free (or bulk) water fraction with some interstitial water removal (these terms may be reflected in a different manner depending upon the literature source).

The research effort attempted to quantify the fractions of water in sludges, as well as determine some other characteristics, including the relative specific surface (area) and densities (measuring both bulk and floc, and computing the dry particle density) of various sludges. The final matrix of sludges tested is indicated in a

following section. Since sludges contain a great deal of free water, this tends to obscure the relatively smaller fractions of water. As discussed later, techniques to reduce the amount of the free fraction, as is practiced in the field, were used to enable better resolution of the other water fraction(s). These included chemical and mechanical conditioning steps. An attempt was also made to study the effect of these steps upon the different fractions of water present.

## CHARACTERIZATION TECHNIQUES

The final matrix of instruments selected to characterize moisture distribution in sludges were the:

- (i) TGA (thermo-gravimetric analyzer),
- (ii) DSC (differential scanning calorimeter), and
- (iii) dilatometer

The TGA was selected as the instrument's capability to track moisture loss over time and temperature could be taken advantage of in using the drying curve rate technique. The latter two methods utilize the widely used assumption that the "free" water fraction freezes near 0°C, whereas the remaining moisture represents the "bound" fraction. While the DSC determines the amount of free water based on calorimetric measurements, the dilatometer measures the physical expansion of that fraction. The following chapter discusses the TGA and DSC instrument techniques as applied to sludge moisture characterization.

The sludge dry solids concentration (in %-D.S.) was determined using the *Standard Methods*<sup>1</sup> procedure of drying a predetermined mass of sludge sample overnight in a 105±2°C oven, and weighing the dry fraction remaining after constant weight loss has been achieved. This value provides the total initial moisture content



(the relationship used is described later). Other sludge characteristics /properties that were determined included the:

- (i) specific surface areas of the dry sludge particles using a method used widely in soil mineralogy called the EGME-specific surface technique,
- (ii) bulk density using a glass pycnometer, and
- (iii) isopycnic centrifugation technique to determine the floc density of the sludge particles, based on methodology developed by Knocke, *et al*<sup>7</sup> utilizing techniques well established in other disciplines.

#### **A NOTE ABOUT UNITS**

The review of the literature indicated that while some researchers express moisture in materials in percent (as in % Moisture or % Water, and sometimes as % Initial Dry Solids), others have used the expression: mass of water per unit mass of dry solid, while yet others have expressed moisture in molecules or moles of bound water per molecule or mole of the macromolecule (for samples with known chemical composition). For the sake of standardization and comparative studies, it is felt that an appropriate unit to express moisture is in *grams of water per gram of dry solids*, or *g-H<sub>2</sub>O/g-D.S.* This notation, and the abbreviated *g/g-DS*, has been used in the current study to report values of all water/moisture fractions. Dry solids content has been expressed in *percent* (as %-Dry Solids or %DS).

#### **MOISTURE DISTRIBUTION NOMENCLATURE**

From the review of the literature, it was determined that there is a general consensus that moisture in sludges can be characterized into free (or bulk or

unbound) and bound waters. The demarcation point between the two fractions have been the subject of some degree of discussion primarily due to the differences in the method and samples used. In addition, attempts have been made to identify various sub-fractions of bound water: viz. chemically bound, physically bound or absorbed, interstitial or capillary, etc. These latter finer distinctions have not been widely recognized in the literature.

In an effort to standardize the reporting of data using the different methods used in the study reported herein, the following nomenclature has been adopted to identify the various fractions (the values are reported in grams of water per unit gram of dry solids):

**Free Water:** For the drying rate curve method, this has been identified as the fraction that is in the horizontal (constant drying rate) section, prior to the first inflection point which signals the onset of removal of the bound fraction(s). For both the DSC and the dilatometric methods, this has been identified as the fraction that freezes by the time the temperature of the sample reaches  $-20^{\circ}\text{C}$  (the lowering of the freezing point is discussed later), or conversely, melts near  $0^{\circ}\text{C}$ .

**Bound Water:** For the drying rate curve method, this is taken to be after the onset of the first inflection point on the curve. Conversely, this can also be determined by subtracting the free water fraction from the total water determined by the dry solids analysis. For the DSC and dilatometric methods, this is obtained by subtracting the free water from the total water that was initially present as determined by dry solids analysis.

**Chemically Bound Water:** For the drying rate curve method, this was determined by drying the sample at a constant temperature until there was no more weight loss, then drying at  $150^{\circ}\text{C}$  or higher. The additional loss in

weight of the sample would provide the value of this operationally defined chemically bound fraction. This value could be determined by the TGA/drying rate curve, and is considered a sub-set of the bound water fractions determined by all three methods.

Various researchers have used other temperature settings (usually  $105^{\circ}\text{C}^{79,85,88}$ ) to operationally define the chemically bound water fraction of their samples. *Standard Methods*<sup>1</sup> appears to recognize that samples dried at  $105\pm 2^{\circ}\text{C}$  may retain some chemically bound water fraction (what they refer to as the mechanically occluded water and water of crystallization) which is usually removed at  $180^{\circ}\text{C}$ .

## **MATRIX OF SLUDGES**

Artificial silicon dioxide (Min-U-Sil 30) was provided by U.S. Silica and used to see if it could serve as a "reference" sludge. Properties of this material are provided in Table 4 in the previous chapter. Other possibilities included glass beads and calcium carbonate (with repeated washing and with  $\text{CO}_2$  bubbled through to remove impurities such as magnesium). However, due to the expense of glass beads, they were not considered in the final matrix of sludges.

Water and wastewater treatment sludge samples were obtained from plants close to the campus (Blacksburg, Virginia) or research facility (Nalco Chemical Company, Naperville, Illinois). These included: (i) anaerobically digested waste activated sludge from the Peppers Ferry Regional Wastewater Treatment Facility in Fairlawn, VA, (ii) alum water treatment sludge from the Zion Water Treatment Plant in Illinois, (iii) lime water treatment sludge (from the Topeka, Kansas, Water Treatment Plant), (iv) polyaluminum chloride (PACl) sludge from the Blacksburg-Christiansburg-VPI Water Treatment Plant, VA, and (v) pulp and paper mill sludges from various plants in Virginia and North Carolina.

In order to compare field water treatment plant sludges, "artificial" sludges were made in the laboratory on campus. This included calcium carbonate slurries made by adding a measured amount of  $\text{CaCO}_3(s)$  (Precipitated Chalk - laboratory grade, FW 100.09; from Fisher Scientific Co., Fair Lawn, NJ 07410; Lot # 703502) to a known volume of laboratory tap water, mixing and allowing to settle for 2 days. The supernatant was then decanted, tap water added and the mixture shaken thoroughly. The slurry was again allowed to settle and the process of decanting and resuspending repeated twice to wash out the dissolved solids.

Alum sludge was made by adding 4 grams of aluminum sulfate (Technical Ground Grade,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , FW 666.42; from Fisher Scientific; Lot # 745030) to one liter of laboratory tap water to which 2 g/L of bentonite and 2 meq/L (0.17 g/L) sodium bicarbonate ( $\text{NaHCO}_3$ , Certified ACS Grade; FW 84.01; from Fisher Scientific; Lot # 926222B) had been added. The mixture was then titrated with about 200 mL of 0.1N NaOH, in the pH range 6-8 until white precipitates of aluminum hydroxide were observed. The final mixture was allowed to settle, then decanted a number of times with fresh tap water to dilute the residual dissolved solids concentration present in the sludge.

## **CHEMICAL AND MECHANICAL DEWATERING TECHNIQUES**

### **General**

In moisture distribution studies, removing most of the free (or bulk) water allows better examination of the relatively smaller fractions of bound waters. Free water removal usually involves pretreating the sludge with flocculants/coagulants, etc. Polymers (metal or, more usually, chemical) are commonly used in the wastewater industry for this purpose. Polymer doses are usually optimized by free drainage testing and by the use of the capillary suction time (CST) device. Once this has been

determined, the sludge is chemically conditioned with the optimum dose and the flocculated sludge then undergoes mechanical dewatering.

### **Free Water Removal**

To better understand sludge water distribution for the current research, the larger fraction of bulk (or free water) was first removed. Physical, chemical, and mechanical conditioning was undertaken to progressively remove water in sludges and determine the changes in moisture distribution. The processes typically involved gravitational thickening (settling the solids and decanting off the supernatant), chemical conditioning, and mechanical dewatering by vacuum filtration, belt presses, or centrifuges. The twin belt press is commonly used as a dewatering device in the wastewater treatment field due to the benefits of reduced volume of dewatered sludge that need further treatment and disposal. Mechanical dewatering was conducted to determine what fractions of water were removed by the dewatering process. These processes appeared to remove some portion of the bound water fraction.

#### *Free Drainage Testing*

The work at Nalco involved use of the twin belt press (TBP) mechanical dewatering simulator for sludges. Free drainage testing was first conducted to identify an appropriate flocculant polymer and determine the optimum dose needed to maximize free drainage/filtrate volumes.

The test is widely used in the specialty chemical manufacturing industry for the evaluation of the conditioning performance of a variety of polymers, and aids in the selection of the appropriate polymer to use in the dewatering process. In order

to compare the amounts of polymer needed to optimize flocculation of the sludge sample, the field or laboratory testing uses equivalent values of the percent actives in the polymers (usually 0.2% equal active solution). The percent actives is a characteristic determined for each polymer (other characteristics usually compared are the mole percent charge and the rsv or reduced specific viscosity value). To make up 200 mL of a 0.2% active polymer solution known to have 30% actives for the free drainage testing, one requires  $0.2\% \times 200 \text{ mL} / 30\% = 1.333 \text{ mL}$  polymer. This amount of polymer is "inverted" in 200 mL of distilled water, i.e. 1.333 mL of the polymer is squirted into 200 mL of water that is vigorously stirred by a caged impeller device for 30 minutes to mix/invert the polymer thoroughly. The polymer is then ready to use in the chemical conditioning process.

The free drainage test is conducted by adding a known amount of the polymer (prepared above) to a known volume of sludge sample in a large plastic graduated cylinder, turning the mixture five times, and draining the flocculated (conditioned) sludge through a small piece of belt filter press material. The volume draining through in intervals at 5, 10, 15, 30, 45 and 60 seconds or so, is recorded. Also recorded are the visual (and hence subjective) observations of filtrate quality and condition of the flocculated sludge. The latter subjective evaluation involves squeezing a sample of flocculated sludge in one's fist to see whether the sludge "squishes" out easily. Flocculated sludges that resist being "squished out" indicate relatively greater shear resistance to the subsequent mechanical dewatering step and are hence preferred.

Results from the above tests are plotted as the free drainage volume on the y-axis (ordinate) versus the amount of polymer dose required on the x-axis (abscissa). The polymer dose that provides the greatest amount of free drainage (of acceptable filtrate quality) in the least time (and also conditions the sludge well) is usually selected as being close to the optimum dosage required.

### *Capillary Suction Time*

CST is another standard and useful technique to determine the rate of water release from sludges, and was used herein as a relative performance test to determine the optimum dose of a chemically conditioned sludge sample. The CST instrument measures the time required for sludge filtrate to travel on a small sheet of chromatography paper between two fixed concentric circles. A well flocculated sludge usually has a lower CST time (indicating better drainage of the "free" water) than a poorly flocculated one, and the minimum time recorded among sludge samples conditioned with varying amounts of polymer is assumed to indicate the optimum dose. The CST unit for this study was a Triton-W.R.C. Type 165 C.S.T. Apparatus model, using chromatography paper (Whatman 17) cut into the small pieces (approximately 7 x 9 cm). The method is similar to that described in Part 2710 G of *Standard Methods*<sup>1</sup>.

Limited sludge characterization tests were also conducted using the specific resistance to filtration technique, using the Buchner funnel apparatus connected to a vacuum pump, as described by Vesilind<sup>93</sup>. The test was considered to be time-consuming and not very reproducible (there were variations in the data due to differences in characteristics of the various sludges and the operation of the vacuum pump at a certain pressure setting). Thus it was decided to use only the CST device to measure dewatering rates of the various sludges.

### **Mechanical Dewatering Methods Used**

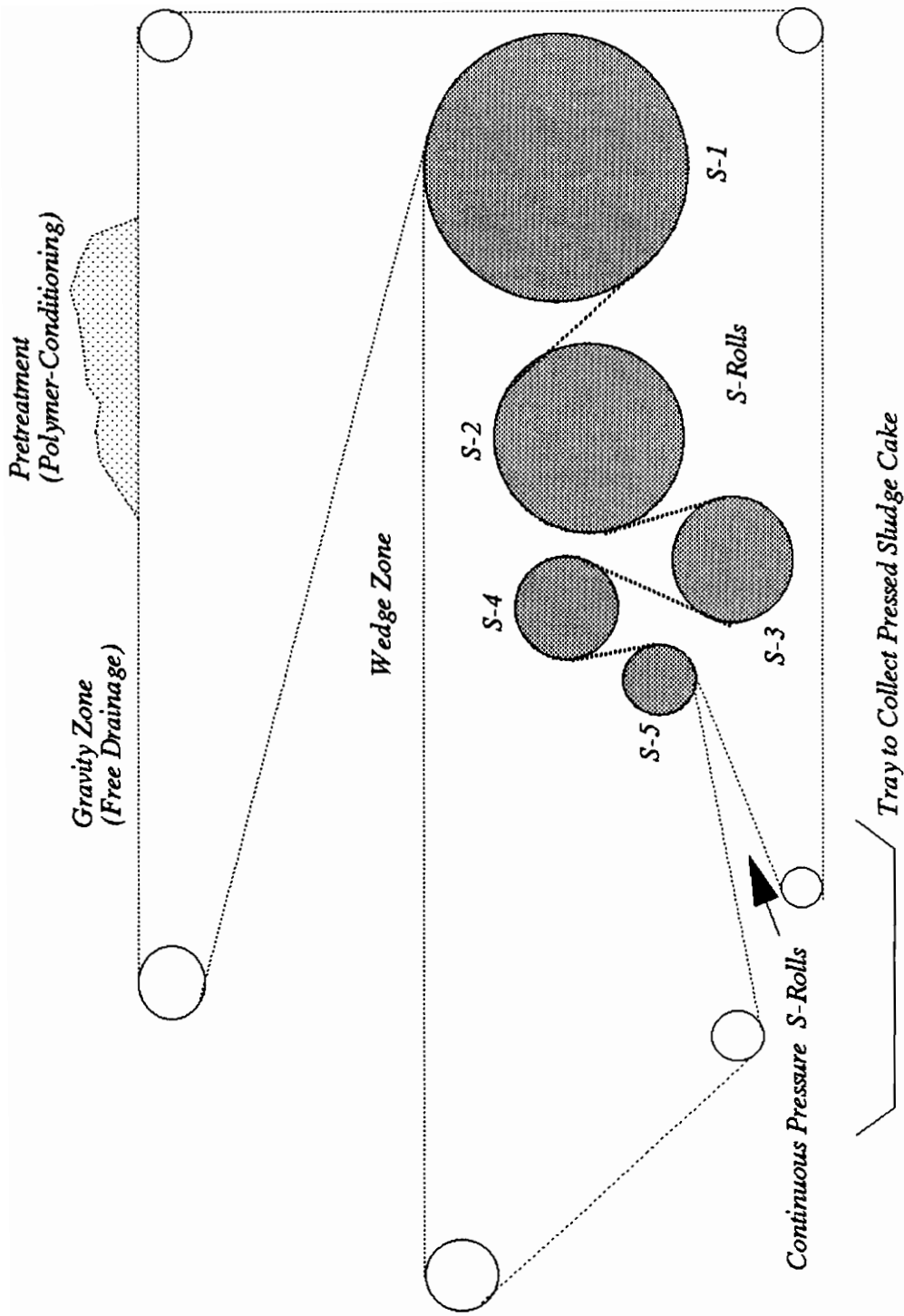
The two main methods used for the dewatering of sludges in the laboratory were the centrifuge and the TBP. For the former, sludge samples were usually centrifuged for 10 minutes at 2000 rpm in a low speed International Equipment CS swinging bucket centrifuge using 200 mL sludge samples in matched (based on weight

of samples) pairs of plastic bottles. The centrifuge was determined to be a fast, reliable, and reproducible solids/liquids separation technique. The sludge samples usually did not require prior chemical/polymer conditioning (which could have affected the moisture distribution in the sludges).

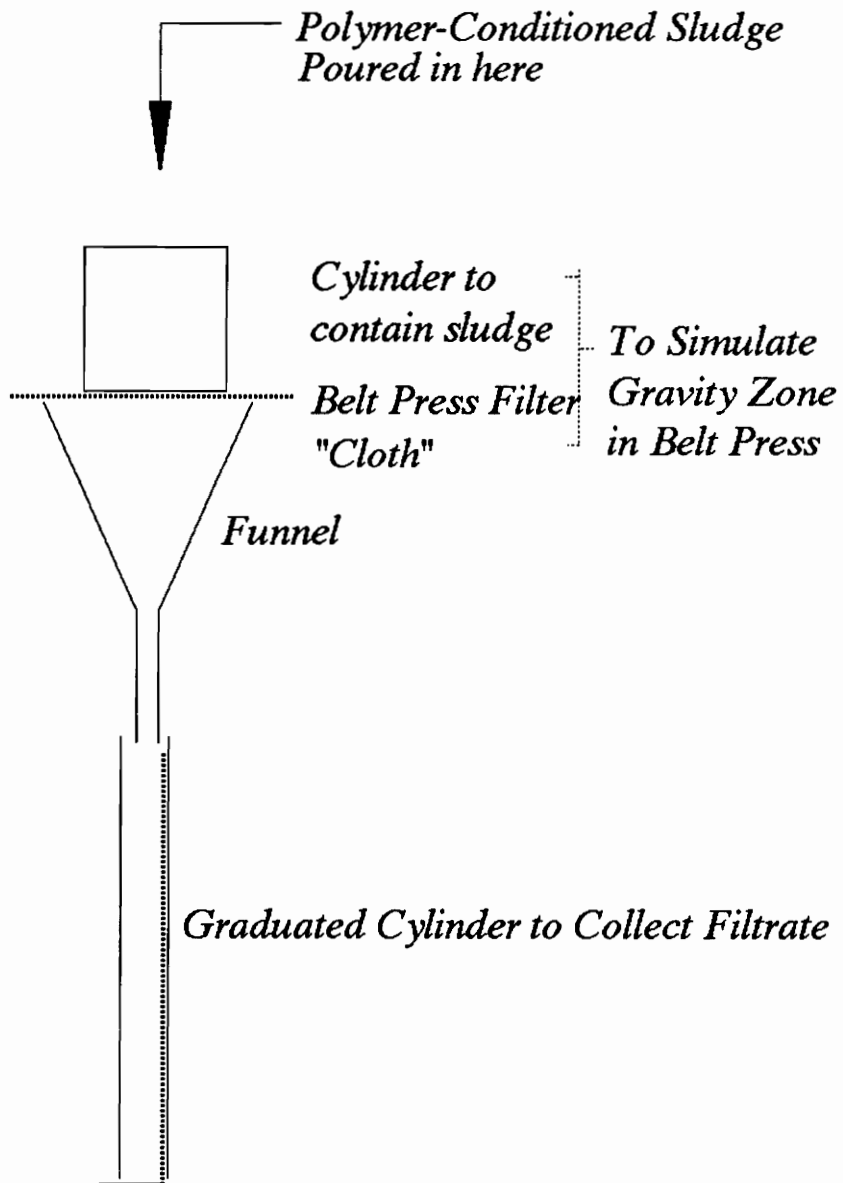
The TBP used during the experimental work at Nalco was a laboratory bench-scale simulator of a full-scale TBP typically used in the field. As indicated in the previous section, free drainage testing was first conducted to select the appropriate polymer and corresponding dosage to use with the sludge sample. Then, between 200-1,000 mL of the sludge (depending on the initial solids concentration) was polymer-conditioned and the conditioned sludge placed on top of the gravity zone tray, the wedge zone tray placed on top, and the wedge press applied. The resulting sludge cake is transferred to the continuous pressure filter press (an S-roll simulator). The belt tension and speed is varied to simulate the actual S-roll conditions in a full-scale belt press operation.

The sludge cake usually undergoes up to five passes in the TBP simulator, each subsequent pass incrementally applying greater pressure to the sludge and possibly increasing the dry solids concentration. Figures 6 presents a simplified schematic of a typical TBP while Figures 7 and 8 show the gravity and wedge zone simulators. Figure 9 is a schematic of the continuous pressure filter press (S-roll simulator).

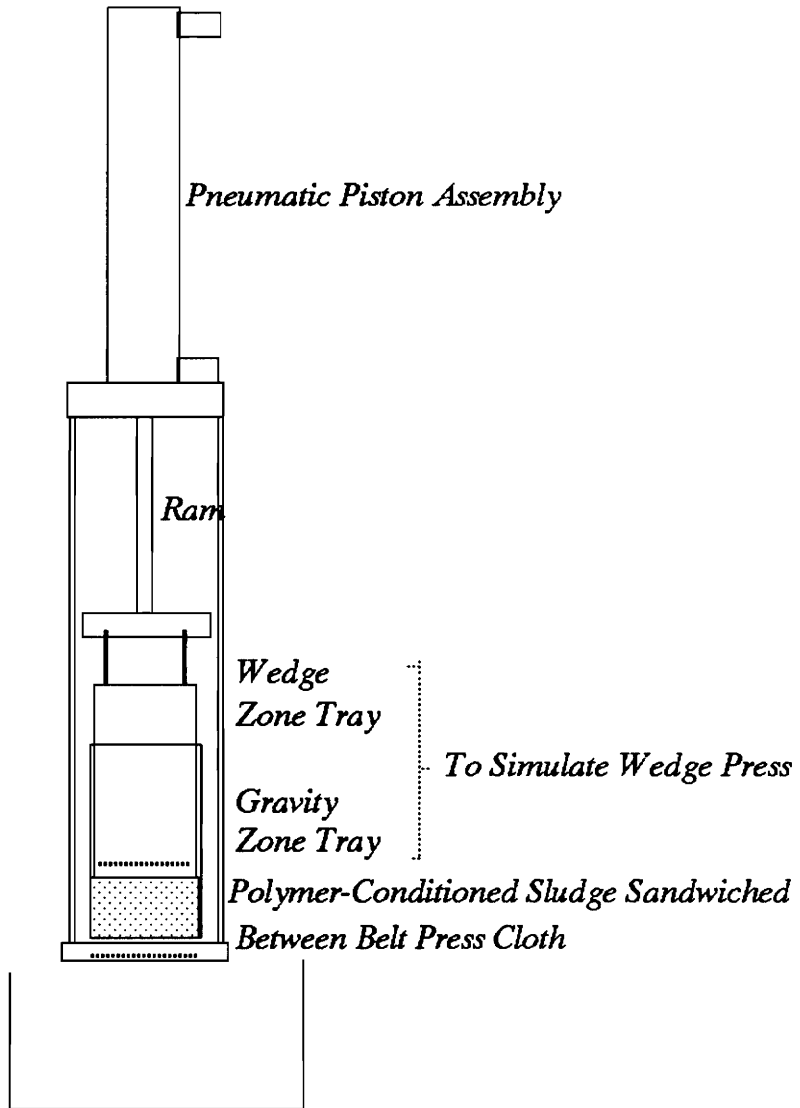




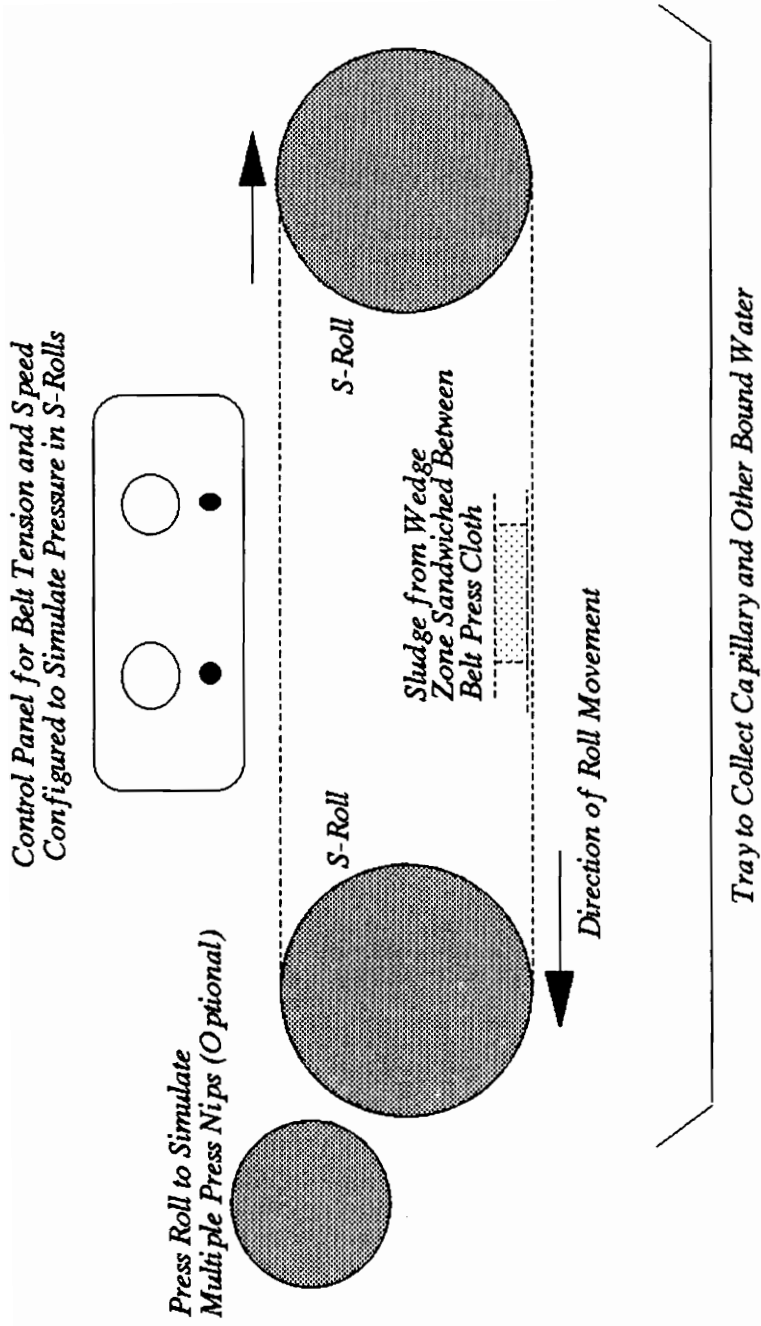
**FIGURE 6: SIMPLIFIED SCHEMATIC OF TWIN BELT PRESS MECHANICAL DEWATERING DEVICE**



**FIGURE 7: SCHEMATIC OF FREE DRAINAGE KIT USED TO SELECT POLYMER AND SIMULATE GRAVITY ZONE OF TWIN BELT PRESS**



**FIGURE 8: SCHEMATIC OF TRAY ASSEMBLY USED TO SIMULATE WEDGE ZONE OF TWIN BELT PRESS**



**FIGURE 9: SCHEMATIC OF CONTINUOUS PRESSURE FILTER PRESS (TWIN BELT PRESS S-ROLL SIMULATOR)**

## **ANALYTICAL METHODS**

### **Moisture Characterization Techniques**

#### **Thermo-Gravimetric Analyzer (TGA)**

The TGA has been used in other fields to measure bound water fractions, but has not been currently reported for evaluating sludges. The TGA has controlled temperature capabilities, can hold samples isothermally for fixed periods of time, allows purging of gases (including inert nitrogen) at different flow rates, and is able to increase temperatures at fixed rates ("ramping"). It also has a computer interface that automatically records the data (as time, temperature, and weight) at preset intervals, as well as various other functions. Due to its versatility, it appeared to be an excellent instrument to use in moisture distribution studies for sludges using the drying rate curve technique. Development of the experimental protocol to utilize this instrument for moisture characterization is presented in the following chapter.

The theory behind the drying rate technique has been described previously in Chapter 2. The hypothesis of the technique is that water can be classified into various fractions depending on the changes in the rates of drying of a sample over time in a controlled environment. Here the "free" water is supposed to be removed initially at a constant (linear) rate, then there is a reduction in the rate of change that indicates a different form of water usually some "bound" fraction that is being removed, other changes in drying rates would indicate different fractions.

The TGA instrument records the weight of sample as a function of time and/or temperature for a specific sludge sample. These data can be viewed graphically on the computer interface. However, a more useful graph (called a characteristic drying rate curve) is obtained by downloading the TGA data and using commercially available spreadsheet and graphical software (Quattro Pro or Excel) to generate the necessary information as the differential weight (moisture) loss as a function of time,

(i.e. as the drying rate) versus the moisture content (in grams of "bound" water per gram of dry solid). Inflection points of the characteristic drying curve appear to indicate the various forms of water, although these may be operator-subjective.

The TGA instrument provided for this phase of the research at the Nalco Chemical Co. during the summer 1991 period was a Du Pont Instruments (DPI) 951 Thermogravimetric Analyzer with a DPI 9900 Computer/Thermal Analyzer (computer interface).

### **Differential Scanning Calorimeter (DSC)**

The use of DSCs have been reported in various literature sources in other disciplines to characterize materials, and sometimes more specifically, moisture in the materials (for example, polyethylene glycol<sup>7</sup>, clays<sup>3</sup>, coal<sup>64,65</sup>, polymers<sup>8</sup>, frozen liquid foods<sup>50</sup>). The literature review conducted earlier into the research could only identify limited references to the use of the DSC for the characterization of moisture in bio-solids/sludges. A similar (albeit slightly less sensitive) technique called the Differential Thermal Analyzer (DTA) has been reported by Katsiris and Kouzeli-Katsiri<sup>43</sup> in their study on biological sludges. While the DTA measures the changes in temperature, the DSC measures calorimetric changes of a sample, in both cases with reference to the empty sample pan.

Since the DSC is able to record accurately the calorimetric heat changes within a sample being tested, this capability is used to measure the changes in either the observed exotherm when a sample (or portion thereof) freezes or the endotherm when the same sample melts. The data thus collected then allows for quantification of the amount of material (in this case the freezable or unbound water) within the sample. The underlying assumption of this moisture characterization technique is that the unbound water fraction freezes or melts at temperatures close to 0 °C.

Deviations from the normal phase change temperature have usually been attributed to the presence of impurities<sup>11,97</sup>.

As discussed in Chapter 2, it had been observed that water in most materials are in two fractions: free (or bulk or unbound) and bound. The bound fraction does not freeze easily and this amount is determined by subtracting the amount of freezable water (determined from measuring the calorimetric change) from the total water determined by dry solids analysis. Since the enthalpic change of interest occurs close to the freezing or melting point of water, the DSC is usually set to measure changes in a relatively short temperature range around this value. For this study, the range selected was 20 °C to -20 °C and vice versa.

The two DSCs that were available for most of the experimental work were the Perkin-Elmer (PE DSC) and the Du Pont (DP DSC). The following chapter presents the experimental protocol developed for use of the DSC as a sludge moisture characterization technique.

### **Dilatometer**

The dilatometric test apparatus was an adaptation of that used by Robinson<sup>79</sup> in his research. Sludge bulk density (or specific gravity measurements) using a glass pycnometer was first determined (see later section on "Other Sludge Characteristics" describing the technique). Dry solids concentrations of all sludge samples were determined by weighing a sample of sludge in a pre-weighed aluminum pan, drying overnight at 105±2 °C, allowing to cool, and reweighing. Percent solids could then be calculated. Sludge cake solids were correlated to bound water content, and sludge bulk density correlated to cake solids to determine the relationship between bound water content and dewatering performance.

Similar to the methodology reported by Robinson<sup>79</sup> and Robinson and Knocke<sup>80</sup>, dilatometric test units were fabricated by the Glass Shop in the Virginia

Tech Chemistry Department from standard taper ground glass joints and the top units were fused to 5 mL graduated glass pipettes (Pyrex extra-strength or equivalent). The top and bottom unit halves were labelled so that matched pairs (of known volumes for subsequent testing) could be maintained. The total volume of each dilatometer was fabricated to be twice the capacity of that reported in the previous study<sup>79,80</sup> (100 mL as opposed to 50 mL previously) in an attempt to magnify the freezing and subsequent expansion of the free water in the larger sized sample. Glass hooks were fused onto each piece so that the assembled dilatometer could be held together firmly by springs. Control cells were also made by using a bottom dilatometer unit and a rubber stopper that had a thermometer and small pore glass tube to accommodate expansion and contraction.

Hydraulic oil (10W, Texaco Rando HD315) was used as it had been determined previously<sup>79</sup> that it is a suitable measuring fluid as it: (a) is immiscible with water, (b) has a specific gravity less than 1.0, hence floats on top of the sludge sample, (c) has a linear expansion/contraction over the temperature range from 20 °C to -20 °C, and (d) does not freeze at -20 °C.

Typically, 20-25 g of sample were placed in the bottom unit of the dilatometer, hydraulic oil placed on top, the dilatometer sealed with the top unit using a small amount of stopcock/vacuum grease and held in place firmly using two small springs. The entire dilatometer was then immersed in an ethanol bath (i.e. a stainless steel container with a plexiglass platform inside to hold the dilatometers and ethanol poured into it until just covering the bottom unit of the dilatometer) placed in a styrofoam container to reduce temperature losses and moisture condensation. Using dry ice (solid CO<sub>2</sub>) chips added to the ethanol bath, the temperature of the sludge sample was reduced to 20 °C. The system was equilibrated at this temperature for a few minutes and the level of hydraulic oil in the top unit (within the graduated pipette section) of the dilatometer at this temperature noted. The temperature of the sample was then decreased by approximately -1 °C/minute to -20 °C using dry ice



added to the ethanol bath (which essentially acted as a heat sink). Triplicates of the same sludge sample were tested at the same time.

Standard cooling curves were developed for the hydraulic oil alone and distilled water so that the unit amount of expansion and contraction for each fluid could be quantified. The results were then used to calculate the average volume expansion associated with the freezing of unbound water.

The standard curve was developed by filling one dilatometer (unit #4) completely with the measuring fluid (hydraulic oil), another dilatometer (unit #3) with 25 mL distilled water and then hydraulic oil, and a control unit with 25 mL distilled water and hydraulic oil. A fourth dilatometer (unit #II) was also filled with 10 mL distilled water and hydraulic oil to compare the unit expansion/ contraction behaviors of the two sample sizes. The unit contraction of the hydraulic oil could be determined from unit #4, whereas the expansion of the distilled water determined from unit #3.

The following calculations have been used to determine the contraction per unit volume of oil and the expansion per unit volume of water:

The total volume of unit #4 was 94.57 mL. It was filled with oil, which contracted 3.02 mL over the 40°C temperature drop, or  $3.02 / 94.57 = 0.03193$  (3.19%). The total volume of unit #3 was 93.7 mL. It was filled with 25 mL of distilled water and 68.7 mL of oil (= 93.7 - 25.0). The oil in unit #3 should have contracted 2.194 mL (=  $68.7 \times 0.03193$ ) over the same 40°C temperature range. The expansion of the 25 mL of water in unit 3 was equal to the expansion of the oil-water mixture plus the contraction of the oil in the same unit. The expansion of the oil-water mixture was 0.45 mL (=  $2.15 - 1.7$ ). Thus, 25 mL of water expanded a total of 2.644 mL (=  $0.45 + 2.194$ ), or  $2.644 / 25 = 0.106$  mL per mL. Similar calculations were conducted for the unit #II and it was determined that the 10 mL water had a similar (value

was within 3%) expansion behavior, i.e. expanding 0.109 mL per mL. The expansion value was similar to Robinson<sup>79</sup> (reported as 0.11 mL per mL).

These standard curve determinations were conducted periodically to determine if there were any change in the unit expansion-contraction behavior. It was determined that the response was fairly reproducible (the expansion factor ranged from 0.106 to 0.11 mL per mL). Figure 10 is an example of one such determination. The expansion factor was determined for each series of subsequent dilatometric tests.

Based on the standard curve information, the amount of freezable or unbound water in sludge samples could be determined. The volume of sludge samples in each dilatometer was calculated by multiplying the mass of the sludge sample by the sludge bulk density. From the standard curve determinations, the volume of freezable water could then be determined. The difference between this freezable water and the total (from dry solids determinations using the  $105 \pm 2^\circ \text{C}$  oven) water was defined as the bound water. The mass of the bound water when divided by the mass of the dry solids would provide the result expressed in g-bound water/g-dry solids.

## **Other Techniques to Determine Sludge Properties**

### **Specific Surface Determinations / EGME**

Some useful qualitative comparisons of particle surfaces are possible<sup>5</sup> by using the EGME specific surface method<sup>17</sup>, which has been well established in the soil mineralogy discipline. The procedure required drying a sample overnight in a  $110^\circ \text{C}$  oven and grinding to pass a 60-mesh sieve. Approximately 1 gram of the dry sample was then placed in preweighed aluminum pans and kept overnight in the  $110^\circ \text{C}$

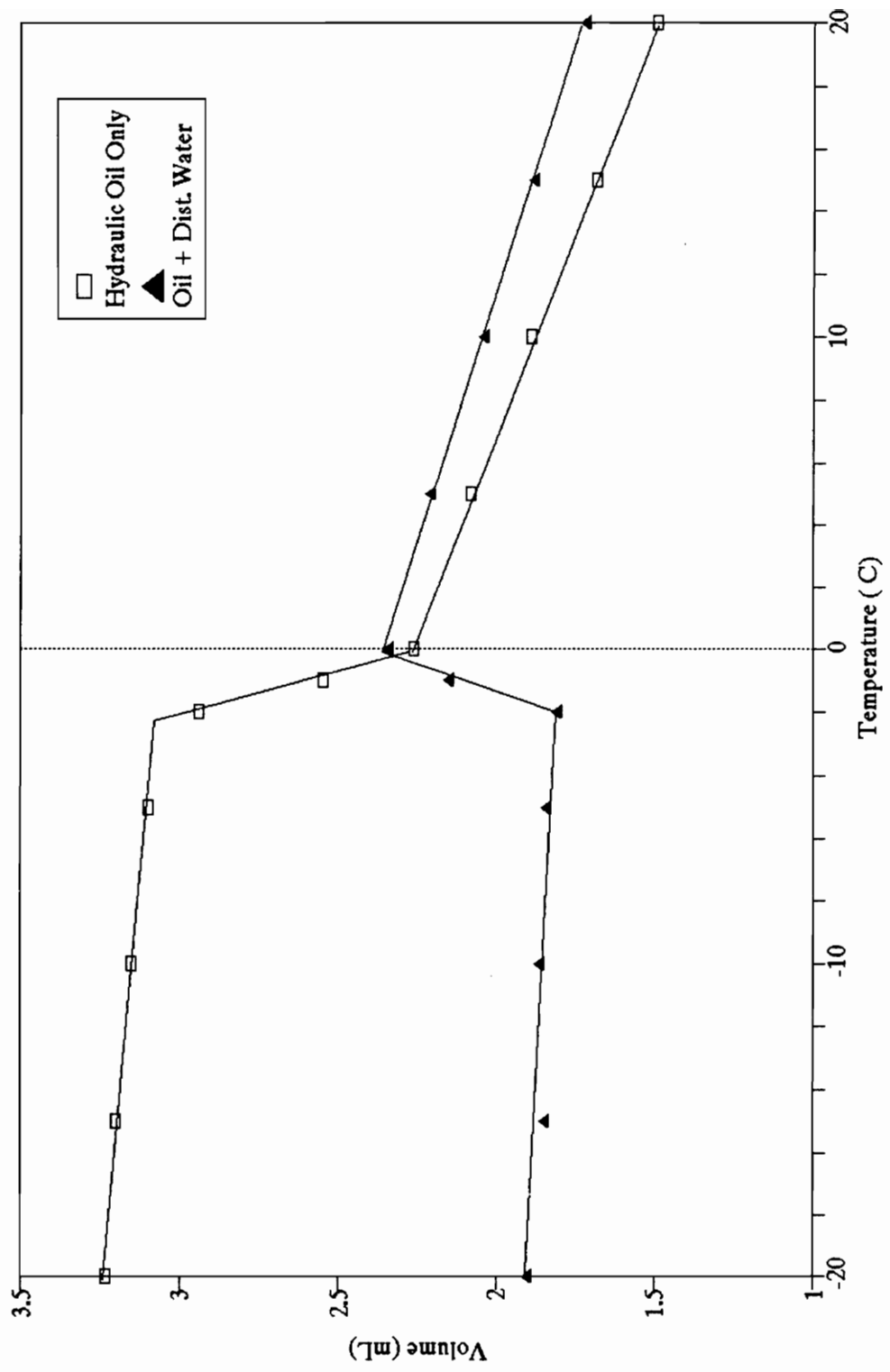


FIGURE 10: TYPICAL STANDARD CURVE FOR DILATOMETRIC TESTS

oven, after which their weights were determined using an analytical balance. Duplicates or triplicates of the same dried and ground sample were prepared.

About 3 mL of ethylene glycol monoethyl ether or 2-ethoxyethanol, C<sub>2</sub>H<sub>5</sub>-O-CH<sub>2</sub>CH<sub>2</sub>-OH (EGME) was then poured carefully on the dried sample to just saturate the sample and form a mineral/sample-adsorbate slurry. The samples were put in a desiccator (to avoid moisture adsorption onto the sample) for an equilibration period of 1 hour. Following equilibration, the pans were placed in a vacuum desiccator containing a fresh CaCl<sub>2</sub>-EGME solvate which had been prepared by mixing immediately and thoroughly 100g of previously dried (at 210 °C for 2 hours) CaCl<sub>2</sub> with 20g of EGME (the heat of the CaCl<sub>2</sub> facilitated the solvation). Fresh solvate was prepared prior to the start of a series of surface area determinations to reduce atmospheric moisture adsorption.

The desiccator was then evacuated for 45 minutes at a vacuum of 0.25 mm Hg and allowed to stand for 2 hours. Air passing through a Drierite column to remove atmospheric moisture was then allowed to enter the desiccator. The samples pans were weighed and the pans placed back into the vacuum desiccator to evacuate for 45 minutes, equilibrate for 2 hours and reweigh again. These vacuum desiccations, equilibration, and reweighing steps were repeated until there was negligible weight change. A plot of weight loss as a function of time was made to determine if monolayer coverage was being approached. Typically five to eight such weight determinations were made per set of samples.

Using the relationship<sup>17</sup> that 231.7 mg of EGME is adsorbed per 1 g of montmorillonite with a theoretical surface area of 810 m<sup>2</sup>/g, the following equation was used to obtain the specific surface of the sample:

$$A = W_g / (W_s \times 0.000286) \quad [16]$$

where:

$$A = \text{specific surface in m}^2/\text{g}$$

$W_g$  = weight in g of EGME retained by sample after monolayer equilibration

$W_s$  = weight of dried sample in g

### **Isopycnic Centrifugation / Floc Density Determinations**

Knocke, *et al*<sup>47</sup> (see also Arundel<sup>9</sup>, Dishman<sup>23</sup>, Miller<sup>62</sup>, and Vollrath-Vaughn<sup>95</sup>), developed an isopycnic centrifugation procedure to estimate the characteristic floc density for several chemical sludges. The analytical centrifugation method (of which the density gradient or isopycnic centrifugation technique is part of) has been used successfully in biological and medical sciences for isolating and characterizing various biological particles. See Knocke, *et al*<sup>47</sup>, for additional references to the use of this method in other disciplines.

The hypothesis of the technique is that upon centrifugation, particles migrate through the varying density liquid media until their density just equals that of a specific liquid layer, defined as the isopycnic point, and indicated by markers of known density in the same media. Separation of the particles appears to be independent of particle size or settling rate and is theorized to be a function of particle density only<sup>47</sup>.

For the study reported herein, the methodology as reported by Knocke, *et al*<sup>47</sup>, and Dishman<sup>23</sup> was followed using the *Percoll*<sup>R</sup> media (supplied by Pharmacia Fine Chemicals, NJ). *Percoll* is composed of colloidal silica particles coated with polyvinylpyrrolidone, is non-toxic and ideal for use with biological materials (as indicated by the manufacturer, Pharmacia LKB Biotechnology, S-751 82 Uppsala, Sweden). The physical characteristics of *Percoll*<sup>R</sup> are presented in Table 5.

Previous research<sup>9,23,47,62</sup> has indicated that *Percoll* (which has a density of 1.13 ±0.005 g/mL, low osmolality [ $<25\text{mOs/kg H}_2\text{O}$ ], and is impermeable to biological membranes) does not significantly affect sludge floc structures and provides fairly reproducible floc density numbers.

**TABLE 5**  
**PHYSICAL CHARACTERISTICS OF PERCOLL<sup>R</sup>**

<u>Property</u>	<u>Specification</u>
Composition	Silica sol with nondialysable PVP (polyvinyl-pyrrolidone) coating
Density (g/mL)	1.130 ± 0.005
Conductivity (mS/cm)	< 1.0
Osmolality (mOs/kg H <sub>2</sub> O)	< 25
Viscosity (cP)	10 ± 5 at 20°C
pH	9.0 ± 0.5 at 20°C

Source: Based on information from manufacturer, Pharmacia LKB  
Biotechnology, S-751 82 Uppsala, Sweden<sup>100</sup>

There were two separate techniques used: (i) the continuous gradient, and (ii) the step gradient, described as follows (see Dishman<sup>23</sup> for additional details on the two techniques):

(i) *Continuous Gradient*: Used to determine the density of any floc/particle placed within the media (undialyzed Percoll has a density of 1.13 g/mL) with the aid of density marker beads. For this technique, Percoll was diluted with deionized/distilled water (to avoid high osmotic pressure effects associated with sucrose or saline as dilutants) to a density close to that determined to be representative of the sludge particles. About 10 mL of the diluted media was then placed in round-bottomed, clear polycarbonate centrifuge tubes (Nalgene Cat. No. 3117-0120, supplied by Fisher Scientific, Pittsburgh, PA) with a nominal capacity of 12 mL. A small amount (<0.3 mL) of color-coded Density Marker Beads (supplied by Pharmacia, Code No. 17-0459-01, Lot No. NM 05514), was introduced just under the surface of the Percoll media. In addition, a similar amount of the biological sludge was introduced with the tip of a glass delivery pipette just below the meniscus surface of the media. The tube was then centrifuged at 15,000 rpm for 30 minutes using a high-speed centrifuge (Beckman Model J-21C, rotor type JA-20). The different marker beads would band at their respective density locations in the gradient formed. The floc density of the sludge particles could then be determined by measuring and interpolating between the two densities indicated by the marker beads(s) at the location where most of the sludge was present after centrifugation. Table 6 presents the densities of the marker beads used in the study. Bio-solid particles with densities between 1.03 to 1.09 g/mL were evaluated using this method due to the density of these beads.

(ii) *Step Gradient*: For densities above 1.13 g/mL, the Percoll media must first be concentrated. Approximately 3 feet of dialysis membrane tubing

TABLE 6  
DENSITY OF CALIBRATED DENSITY MARKER BEADS

<u>Bead No.</u>	<u>Bead Color</u>	<u>Bead Density in Percoll Diluted With</u>		
		<u>0.15M NaCl</u>	<u>0.25M Sucrose</u>	<u>Water</u>
1	Blue	1.018	1.037	<1.030
2	Orange	1.033	1.049	---
3	Green	1.049	1.054	1.046
4	Red	1.062	1.067	1.051
5	Blue	1.075	---	1.060
6	Orange	1.087	1.096	1.077
7	Green	1.098	1.107	1.085
8	Red	1.121	1.130	1.091
9	Violet	1.142	1.138	<1.093
10	Blue	---	1.081	1.053

Information abstracted from the manufacturer regarding the beads:

These Density Marker Beads are used for the calibration of density gradients of Percoll. The beads are colored derivatives of Sephadex<sup>R</sup>, each type being a modification of the basic cross-linked dextran matrix to produce beads having a specific, reproducible buoyant density in gradients of Percoll. They are supplied freeze-dried. Prior to use the beads are reswollen by addition of distilled water or aqueous buffer, 1.0 mL of water added to each vial and allowed to swell overnight.

Source: Data for above are from the manufacturer, Pharmacia LKB Biotechnology<sup>100</sup> and from Vollrath-Vaughn<sup>95</sup>



(Spectrapor) was boiled for 10 minutes in distilled/deionized water with a small amount of sodium carbonate. The tubing was then rinsed in distilled water, approximately 150 mL of Percoll was poured into it, the two ends clipped, and the tube placed in a pan. Polyethylene glycol flakes were then placed on top of the tubing. After approximately six hours of contact, the extracted moisture in the pan was poured out. Then the exterior of the tube was rinsed with water and the concentrated media inside the tube squeezed into a tightly sealed plastic container. The concentration procedure was performed in the 20 °C constant temperature room.

The density of this concentrated media was quantified by measuring its refractive index at 20 °C using a refractometer (Reichert ABBE Mark II Digital Refractometer). A standard curve was developed for the concentrated Percoll, relating its density and refractive index. Solutions containing varying amounts of Percoll (both stock and concentrated) and distilled/deionized water were prepared and measured for (bulk) density (or specific gravity) using a glass pycnometer (described later). The refractive index of each of these solutions (or step gradients) was also determined. A standard curve plot was then prepared for observed correlations between the two (as refractive index versus media density). The curve could then be used to obtain quickly referenced floc density values. Figure 11 shows the standard calibration curve for the study reported herein.

Step gradients of different densities of the concentrated and diluted Percoll media were then placed in centrifuge tubes (Nalgene, Cat. No. 3117-0120, supplied by Fisher Scientific, Pittsburgh, PA) by layering in 1 mL stages, decreasing densities (in 0.02 g/mL increments) of the media. Up to six layers of the media were carefully placed in each tube, using a 1 mL plastic pipette, with each layer level marked on the exterior of the tube. Finally a small amount (<0.3 mL) of the sludge sample was introduced just below the meniscus surface of the top layer using a long-tipped glass delivery pipette.

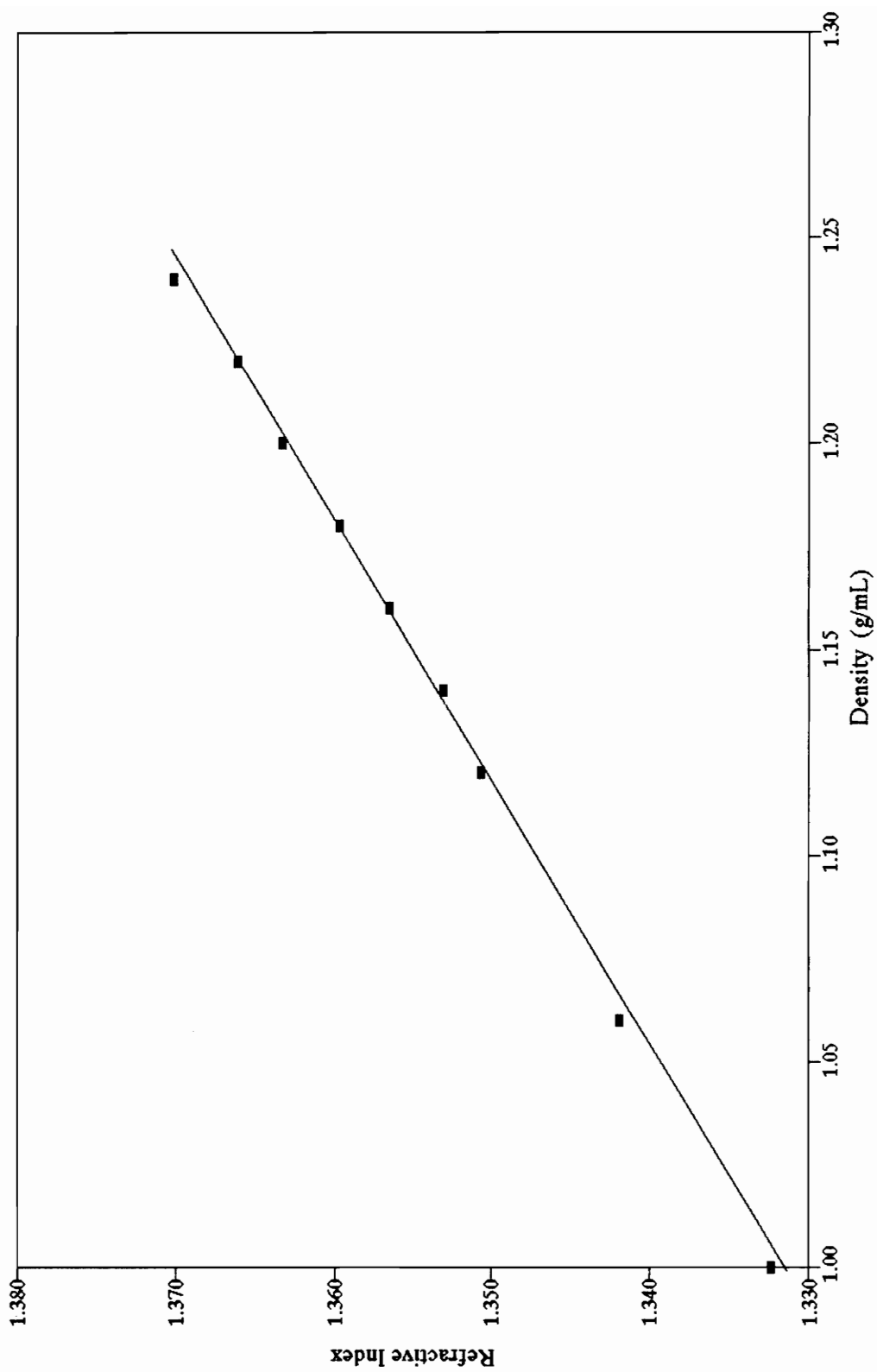


FIGURE 11: STANDARD CALIBRATION CURVE FOR PERCOLL MEDIA

The tubes were then spun in a low-speed, swinging-bucket centrifuge (International Equipment Co., CS Centrifuge) at 2000 rpm, with the level of the sludge floc being recorded every 2 minutes until the floc settled at a specific level (density gradient). Usually this occurred within 6-10 minutes.

The density of the concentrated Percoll ranged anywhere from 1.22 to as high as 1.29 g/mL, as concentrations beyond this density caused the Percoll to degenerate into granular particles. For this study, the step gradient method was used to determine the floc density of chemical or water treatment plant (lime and alum) sludges, with densities thought to be between 1.12 to 1.29 g/mL. For both techniques, the floc density values were reported as either the density of the layer in which the majority of the sludge floc particles were observed or as a range of values if the flocs banded at the interface between two or more layers after centrifugation.

The continuous gradient experiments were relatively easier and quicker to conduct, as the procedure involved diluting the Percoll media to a density close to the floc particles and using density marker beads to determine the density of the floc particles after these particles reached their isopycnic point (upon centrifugation). The step gradient tests took much longer (involved a greater degree of preparation) as the varying step densities had to be made up freshly each time and used within 30 minutes of creation (as the layers tended to diffuse together over time).

As indicated in Dishman<sup>23</sup>, prior to making the gradients, a number of different density Percoll media were prepared to cover the anticipated range of floc densities to be measured. The different densities were made by diluting the stock (at a density of 1.13 g/mL, for the continuous gradient experiments) or concentrated (usually between 1.22 - 1.29 g/mL, for the step gradient experiments) Percoll media according to the following relationship:

$$V_i = \frac{V_F (\rho_F - \rho_D)}{\rho_i - \rho_D} \quad [17]$$

where:

$V_i$  = required volume of the undiluted medium, mL

$\rho_i$  = density of the undiluted medium, g/mL

$V_F$  = desired volume of the final working solution, mL

$\rho_F$  = desired density of the final working solution, g/mL

$\rho_D$  = density of the dilutant (= 1.00 g/mL for distilled water)

### Other Sludge Characteristics

*Total (or dry) solids concentrations* (expressed as %-Dry Solids, or %DS) were determined by placing a sample onto a pre-weighed, labelled, disposable, aluminum pan, weighing, and placing into a  $105 \pm 2^\circ \text{C}$  oven overnight. The pan was then removed from the oven, allowed to cool in a desiccator, and reweighed (according to Part 2540 G in *Standard Methods*<sup>1</sup>). Percent dry solids were determined as follows:

$$\%DS = [(A - B) / (C - B)] \times 100 \quad [18]$$

where:

A = weight of dried sample and aluminum pan, mg

B = weight of aluminum pan, mg

C = weight of wet sample and aluminum pan, mg

The *bulk density* ( $\rho_b$ , or specific gravity) of sludge samples was determined using small (approximately 32 mL volume) glass pycnometers. The procedure involved taring the weight of the pycnometer, filling it with distilled water and measuring its weight. This provided the volume of the pycnometer, using the value of the density of water as 1.00 g/mL. Water was then removed and the pycnometer

dried with a paper towel, reweighed and tared. A sample of sludge was then placed in the pycnometer (again occupying the full pycnometer volume; avoiding any entrained air bubbles) and the weight taken. The bulk density was calculated as follows<sup>79</sup>:

$$\rho_b = M_{Sl} / V_{pycn} \quad [19]$$

where:

$\rho_b$  = bulk density, in g/mL

$M_{Sl}$  = mass of sludge sample, in g

$V_{pycn}$  = volume of pycnometer, in mL.

For drier sludge cakes, the method was modified by placing a sample in the pycnometer (usually occupying up to a third of the volume of the pycnometer). The weight of the sample was recorded and distilled water then added to fill the pycnometer, taking care to dislodge any air bubbles that may have been entrained in the sludge mass. The weight was again determined, and the bulk density calculated as:

$$\rho_b = M_{Sl} / [V_{pycn} - V_{wat}] \quad [20]$$

where:

$M_{Sl}$  = mass of sludge sample, in g

$V_{pycn}$  = volume of pycnometer, in mL

$V_{wat}$  = volume of water added, in mL.

The  $\rho_b$  value is reported in g/mL. The method is similar to that described in Part 2710F of *Standard Methods*<sup>1</sup>.

The *dry solid density* ( $\rho_k$ ) was calculated using the following empirical<sup>79</sup> relationship once the values of  $\rho_b$  (bulk density of sludge in g/mL),  $\rho_w$  (density of water, 1.00 g/mL), and the %DS (as indicated earlier), had been determined:

$$\rho_k = \frac{\%DS}{\frac{100}{\rho_b} - \frac{(100 - \%DS)}{\rho_w}} \quad [21]$$

### QA/QC (QUALITY ASSURANCE/QUALITY CONTROL)

Precautions were taken to ensure the reliability, reproducibility, and validity of the data. Good laboratory practice (GLP) was followed and guidelines set by the USEPA for QA/QC<sup>90</sup>, in *Standard Methods*<sup>1</sup>, and as recommended by the International Confederation for Thermal Analysis (ICTA) Standardization Committee in its Code of Practice<sup>75,97</sup>, were adhered to. These included:

- (i) the use of deionized/distilled water in the TGA/drying apparatus, the DSC, and the dilatometric tests to check and evaluate instrument performance after 20-25 sample runs,
- (ii) random selection of sludge samples when loading into the TGA and DSC to avoid any "memory" effects,
- (iii) standard warm-up periods for instruments and the running of check and calibration standards or samples at periodic intervals,
- (iv) the use of fresh hydraulic oil and ethanol to avoid degeneration of the oil due to repeated freezing/thawing in dilatometric tests and excessive contamination of the ethanol in the cooling bath,
- (v) the use of freshly prepared EGME-CaCl<sub>2</sub> solvate (as described earlier in this chapter) for each set of specific surface determinations,

- (vi) the use of gloves and tweezers to handle sample pans within the plexiglass enclosure housing the DSC cell to avoid moisture contamination,
- (vii) passing nitrogen purge gas to the TGA and DSC cells through a Drierite Gas Purifier column to remove moisture,
- (viii) for the initial testing with sample pans for the PE DSC, stainless steel pans were required to be flamed (using a Blazer Piezo Micro Torch USP 4597732) to remove any oils or moisture on the pans. Special crimpers were used to hermetically seal these pans with a rubber "O" ring, and
- (ix) other standard QA/QC procedures and precautions for GLP.

The QA/QC procedures specific to a particular method have been presented in the sections describing their methodology earlier in this chapter.

## **STATISTICAL CONSIDERATIONS**

Replicate testing was performed for all the sludge characterization studies (including dry solids concentration, bound water determination, bulk density and floc density measurements, and specific surface measurements) under similar sets of analytical conditions. When the standard deviation of a replicate series of tests exceeded 15-20%, the tests were repeated in order to determine the reason for the variability and to achieve greater reliability. The values reported in the tables and figures in the following chapters are the mean (average) values of the replicate tests (the number of samples,  $n = 3$  for most tests).

The results were tested at the 80, 90 and 95% level of significance (i.e.  $\alpha = 0.2, 0.1$  and  $0.05$ ). The mean standard error of the three different moisture characterization methods was also determined. Multiple comparisons (Duncan's multiple range test) were performed to determine whether the different methods measured statistically similar values of the sludge bound water content.

Commercially available spreadsheet/graphical/statistical software (Quattro Pro and Freelance Graphics) were used to evaluate the sludge characteristics data obtained, as well as to determine the correlations that best fit the data. The results of the least-squares linear, power, exponential, and logarithmic regressions were compared to determine that most applicable to the data. The correlation data reported in Chapter 5 was for the best-fit regression.

For the current study, the mean standard errors for the three instruments was determined to range from <5 to 20%, depending upon the sludge being tested and the experimental technique utilized (the following chapters present and discuss the data). Although no consistent relationship was identified, the mean standard error appeared to be larger when attempting to measure the relatively lower amounts of bound water in the inorganic sludges using the dilatometric and DSC techniques, as well as when samples had been polymer-conditioned and there was a greater degree of variability in removing a fairly homogeneous sample to be tested. In many cases the values were negative (below 0 g/g-DS) and the tests were repeated a second time after recalibrating the instrument(s) to reduce/remove any potential error from the instrument.

As mentioned in the above section, this was also done as a component of the overall QA/QC for the research. The results and discussion chapters provide additional details on the statistical computations and procedures used.



## **CHAPTER 4**

### **DEVELOPMENT OF ADDITIONAL MOISTURE CHARACTERIZATION METHODS**

#### **OVERVIEW**

As indicated in the previous chapter, two additional techniques were identified that appeared applicable for moisture distribution studies of sludges. These were the TGA (thermo-gravimetric analyzer) and the DSC (differential scanning calorimeter). This chapter presents the results of the effort to develop the experimental protocol for sludge moisture characterization using the two techniques. It also discusses the effects of certain properties inherent to these techniques that other researchers may need to be aware of in the use of the methods thus developed. Recommendations for the experimental protocol for sludge moisture characterization studies using these two methods are presented. The methods were applied to the matrix of sludges identified previously and the results discussed in following chapters.

#### **THERMO-GRAVIMETRIC ANALYZER (TGA)**

##### **Development of Experimental Protocol**

##### **Overview of the TGA and Drying Rate Curve Method**

The previous chapter has presented an overview of the TGA while the theory behind the drying rate technique has been described in Chapter 2. The hypothesis of the technique is that water can be classified into various fractions depending on changes in the rates of drying of a sample over time in a controlled environment.

Here the "free" or unbound water in a sample is supposed to be removed initially at a constant rate. This is followed by a reduction in the drying rate, indicated by an inflection point (or critical point), representing removal of a different form of water (usually the bound water fraction). Additional inflections in the drying rate curve is theorized to represent other bound water sub-fractions.

Since the TGA is able to measure accurately the change in mass of materials under well controlled temperature and environmental conditions, this study was conducted to determine if the instrument can collect information necessary to provide drying rate curve data to characterize sludge moisture distribution. A variety of different instrument settings were tested to determine that most appropriate for the matrix of sludges available. Results of these experiments are presented in the following section. This section presents a brief overview of the drying rate curve used for moisture characterization.

The TGA provided output graphs plotting mass of the sample over time or temperature. Figure 12 is a typical output plot from the instrument for a specific sludge sample (in this case a bio-solid) showing the change in mass of the sample as a function of both time and temperature. The instrument computer interface also has software that allows it to determine the rate of change of mass over time. This "derivative weight" is shown as a dashed line on the secondary y-axis of Figure 12. The derivative weight curve appears to show an inflection point at around 44 minutes that may indicate the beginning of removal of the bound water. The amount of free or unbound moisture present can be estimated from the graph (from the weight of the sample at this point as shown in the primary y-axis).

The data stored on the TGA computer interface can be downloaded as an ASCII file onto floppy disks for further analysis. Using commercially available spreadsheet/graphical software (Quattro Pro) to analyze the data, drying curves and characteristic drying rate curves could be generated. Figure 13 shows one such drying curve of the data presented in Figure 12 for the same sludge sample. Figure 14 is the characteristic drying rate curve of the same data, and the form of graph that

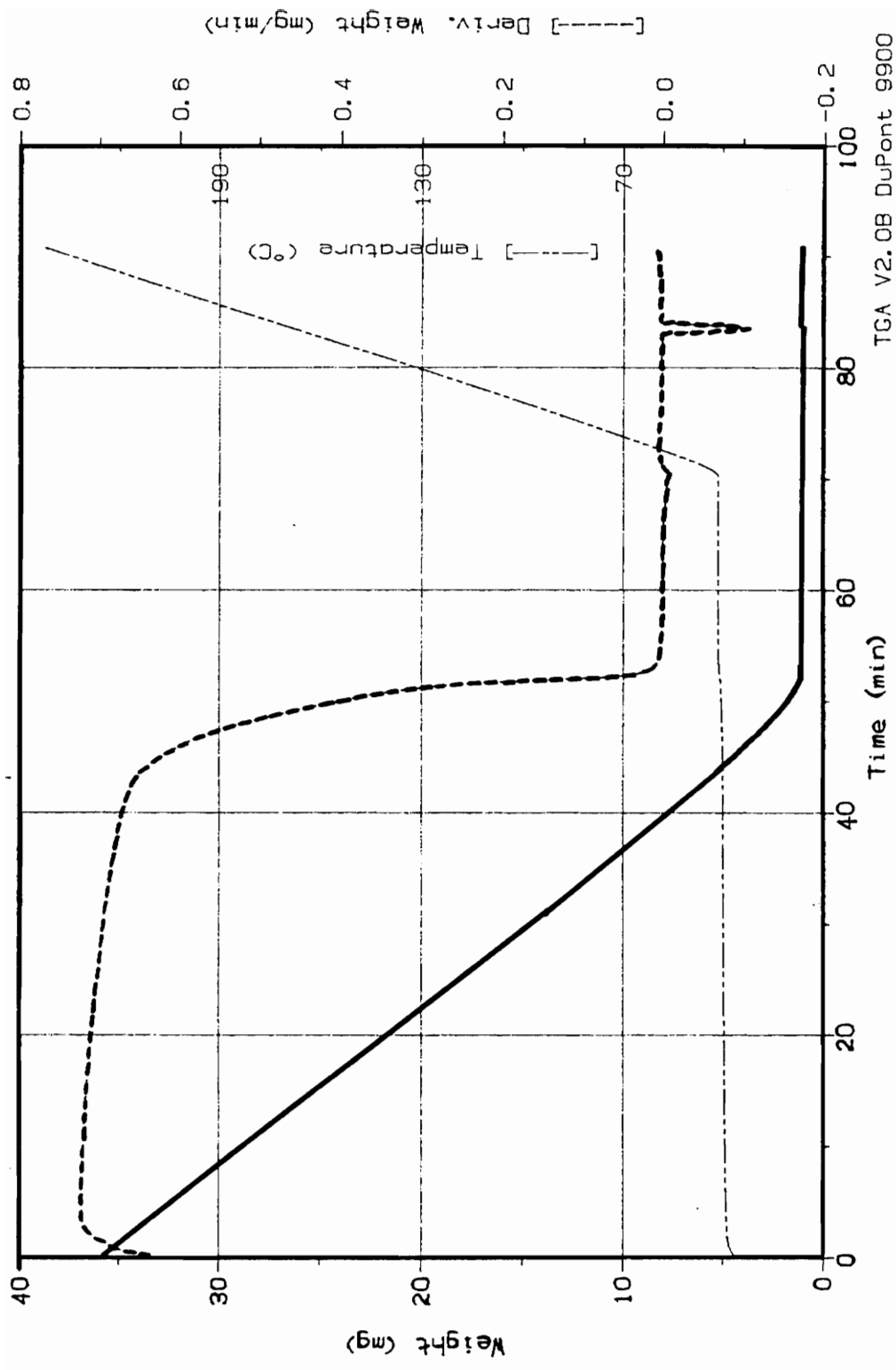


FIGURE 12: TGA (THERMO-GRAVIMETRIC ANALYZER) INSTRUMENT PLOT OF MASS VERSUS TIME FOR SAMPLE SET AT 40°C ISOTHERMAL

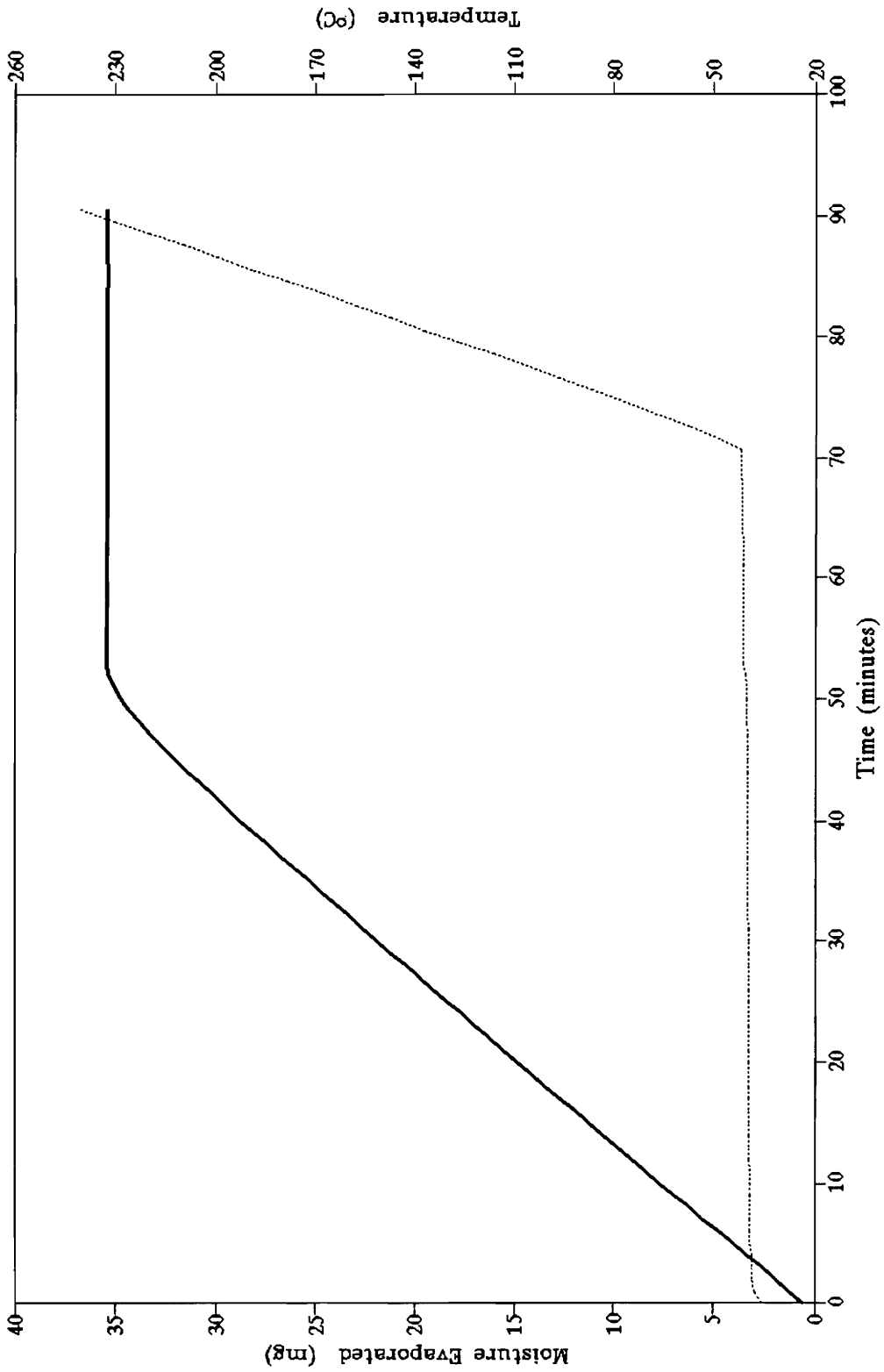


FIGURE 13: DRYING CURVE OF DATA GENERATED FROM TGA INSTRUMENT FOR SAMPLE IN FIGURE 12

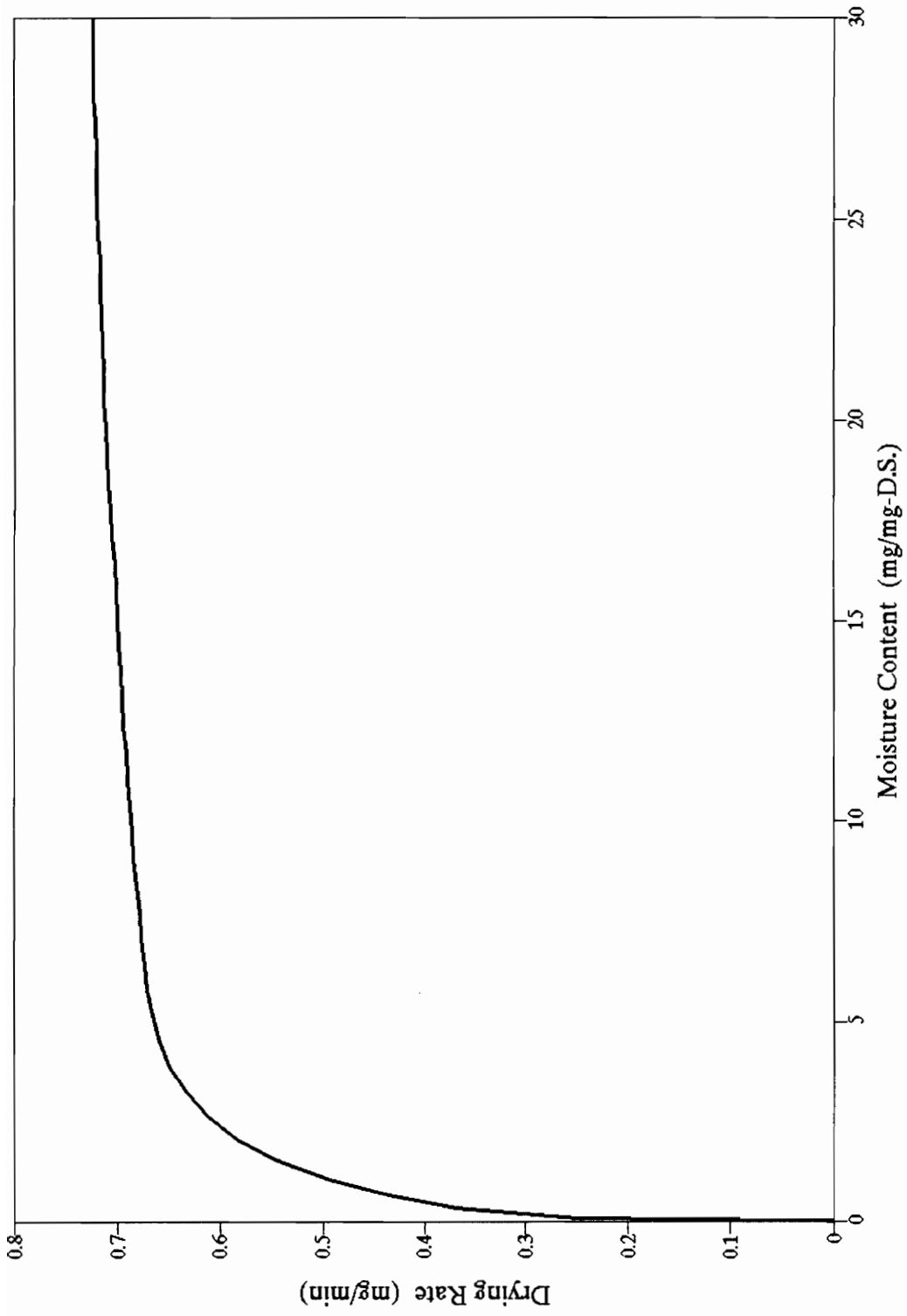


FIGURE 14: CHARACTERISTIC DRYING RATE CURVE USED TO DETERMINE MOISTURE DISTRIBUTION FOR SAMPLE IN FIGURE 12

is most useful for determining the different water/moisture fractions. The inflection or critical point on the curve denotes the onset of removal of a fraction of moisture.

These graphs indicate that the weight loss (and rate of weight loss) from the sludge sample is fairly constant in the initial phase (during the isothermal conditions, set at 40 °C for this test). According to the drying rate theory, this indicates loss of the "free" or unbound water fraction. After about 44 minutes, the rate of weight loss (see Figure 12, dashed line) changes and the bound water is being removed. At about 53 minutes (see Figure 13), there is little, if any, moisture left in the sample as it has reached a constant weight. Any additional loss in weight between this isothermal temperature setting of 40 °C and 180 °C (or higher) would indicate the removal of the chemically bound water sub-fraction.

This sub-fraction is subjective and operationally defined by previous researchers<sup>79,85,88</sup> to be the difference between their experimental isothermal setting (between 22 to 35 °C) and 105 °C. The researchers appear to agree that the inflection point between the linear (constant rate of drying) and non-linear section of the drying rate curve indicates demarcation of the unbound and bound fractions. As shown in Figure 14, this may be at 6.6 mg/mg-DS (equivalent to 6.6 g/g-DS) or between 4 to 7 mg/mg-DS) when the drying rate changes from between 0.7-0.77 mg/min and begins to decrease thereafter to a much slower rate. The small blimp in the "derivative weight" curve in Figure 12 at around 83 minutes indicates how sensitive the instrument is to knocks to the laboratory bench top holding the device.

### **Experimental Method Development**

The size (or capacity) of the aluminum sample pans specified for the TGA instrument helped define the mass of samples that could be analyzed. This was found to be between 40 to 120 mg; reproducible data for the matrix of sludges used was obtained when sample sizes of 50-60 mg were used.

Nitrogen gas (passing through a Drierite Air Purifier column to remove any moisture that could be present in the gas) was fed into the TGA at a controlled rate of 60 mL/minute to remove the water vapor leaving the sludge samples and to maintain a constant humidity above the pan. Limited tests were conducted at other flow rates but it was determined that lower N<sub>2</sub> gas purge rates were increasing the time to complete the tests, while higher rates could conceivably dry out the external surface of the sample and impede moisture movements.

Samples were analyzed at various instrument temperature settings. Since the TGA is capable of both isothermal or ramped (increasing) temperature settings or a combination of both, a variety of tests were initially conducted to determine the test conditions most appropriate and reproducible for the sludges to be tested. Six different settings chosen, these were: isothermal temperatures of 30 °C, 40 °C, and 50 °C; and ramped settings of 1 °C/minute, 5 °C/minute, and 10 °C/minute. In addition, limited tests were conducted at the isothermal settings chosen followed by ramped settings after the samples attained constant mass, to determine if additional sub-fractions of bound water could be measured.

Table 7 presents selected data on the different settings. The results of these initial sets of tests showed that the isothermal settings provided moisture distribution data that were not significantly different at the three temperatures. However, the lower isothermal setting of 30 °C took much longer than the higher temperature settings.

Statistical testing was conducted on the above data to evaluate differences between the three different isothermal settings. One-way analysis of variance (ANOVA) testing at the 95% significance level ( $\alpha = 0.05$ ) showed that the three settings provided the same values of bound water. Similarly, Duncan's multiple range test (DMRT) using unequal n values (since the number of samples per set were not the same) showed again that the isothermal settings for both the Zion WTP alum sludge and SiO<sub>2</sub>-water slurry provided values of bound water that were not

**TABLE 7**  
**SELECTED DATA FOR DRYING RATE CURVE METHOD TO**  
**DETERMINE OPTIMUM TGA INSTRUMENT TEST CONDITIONS**

<u>Experimental Settings</u>	<u>Bound Water Values *</u>				<u>Average Time (mins) **</u>
	<u>Range</u>	<u>Avg</u>	<u>S.D.</u>	<u>n</u>	
<b>Sludge: Zion WTP alum unconditioned</b>					
30 °C isothermal	0.50-0.68	0.57	0.06	5	93
40 °C isothermal	0.55-0.63	0.59	0.02	5	56
50 °C isothermal	0.57-0.65	0.61	0.03	3	40
1 °C/minute ramped	0.85	0.85	-	1	53
5 °C/minute ramped	0.68	0.68	-	1	20
10 °C/minute ramped	0.81	0.81	-	1	15
40 °C isothermal to constant mass then ramped at 5 °C/minute	0.62-0.86	0.72	0.1	3	57
<b>Sludge: SiO<sub>2</sub>-water slurry</b>					
30 °C isothermal	0.40-0.46	0.43	0.02	3	94
40 °C isothermal	0.40-0.47	0.43	0.03	3	56
50 °C isothermal	0.42-0.44	0.43	0.01	2	46
<b>Sludge: Aurora WWTP bio-solids</b>					
40 °C isothermal +	5.00-10.15	6.70	1.86	5	55
5 °C/minute ramped +	3.10-7.13	4.84	1.69	3	19
10 °C/minute ramped +	4.78-5.45	5.12	0.34	2	13
40 °C isothermal to constant mass then ramped at 10 °C/minute ++	5.00-6.60	5.58	0.72	3	53

Notes:

- \* Bound water values were determined from the first inflection point of drying rate curve. Bound water values reported are in g/g-DS
- \*\* Average time taken in minutes to complete the test at the experimental setting chosen
- + These tests were conducted on the same sample of sludge from the Aurora WWTP
- ++ This test was conducted at a later date to determine whether the experimental setting provided bound water values similar to the isothermal and ramped setting used above.

Avg = average, S.D. = standard deviation, and n = number of tests



significantly different (at the 95% level, or  $\alpha = 0.05$ ) from each other. The statistical computations for the Zion WTP alum sludge are presented in Tables 8 and 9.

Although the ramped settings appeared to have advantages of quicker testing times, there were concerns that increasing the temperature of the sample could create moisture-movement and diffusional stresses on the sample that may lead to results that are not truly representative of the initial sludge moisture distribution (especially for bio-solids). For example, Luikov<sup>56-58</sup> had indicated that the temperature gradient affects moisture transfer. In addition, the drying curve did not follow the classic horizontal drying rate followed by a sharp inflection point that indicated the onset of removal of the bound fraction.

Representative drying curves from this study have been presented in Figures 12 through 14 for the isothermal setting of 40°C (followed by an increased temperature setting to determine the relatively smaller chemically bound fraction). Figure 15 presents the drying rate curve for a sample ramped at 5°C/minute. Here the sample was subjected to increasing temperatures over time (in this case at 5°C/min). As shown, the drying rate increases to a maximum of around 5.8 mg/min as moisture leaves the sample (from an initial moisture of about 27 down to around 3 mg/mg-DS). Thereupon, the drying rate curve begins to decrease rapidly; and each inflection point in the curve could be indicative of a different form of the "bound" moisture. However, this is still quite operator-subjective and the curve does not follow the classic drying rate curve reported by other researchers. This is because the moisture release rate is a function of temperature and, in the ramped setting, the temperature was continually increasing.

**TABLE 8**  
**ONE-WAY ANALYSIS OF VARIANCE (ANOVA) TESTING OF RESULTS OF**  
**BOUND WATER DETERMINATIONS FROM TGA ISOTHERMAL SETTINGS**

Bound water values (in g/g-DS) for Zion WTP alum sludge using three isothermal settings				
Values at 30° C setting:	0.53, 0.68, 0.59, 0.50, 0.56			
Values at 40° C setting:	0.63, 0.60, 0.59, 0.55, 0.60			
Values at 50° C setting:	0.65, 0.57, 0.60			
Group	30° C	40° C	50° C	Combined
$n_i$	5	5	3	$N = 13$
$T_i$	2.86	2.97	1.82	$G = 7.65$
$Y_i$	0.572	0.594	0.607	$Y_{\bar{}} = 0.5885$
$\sum_j Y_{ij}^2$	1.655	1.7675	1.1074	$\sum_i \sum_j Y_{ij}^2 = 4.5299$
$T_i^2 / n_i$	1.63592	1.76418	1.10413	$G^2 / N = 4.50173$

$$TSS = \sum_i \sum_j Y_{ij}^2 - G^2 / N = 4.5299 - 4.50173 = 0.02817$$

$$SSB = \sum_i (T_i^2 / n_i) - G^2 / N = (1.63592 + 1.76418 + 1.10413) - 4.50173 = 2.5 \times 10^{-3}$$

$$SSW = TSS - SSB = 0.02817 - 0.0025 = 0.02567$$

**ANOVA Test at  $\alpha = 0.05$  (95% significance level)**

Null Hypothesis,  $H_0 : \alpha_i = 0$

Rejection Region, RR :  $F_{obs} > F_{(t-1, N-t), 0.95}$  or  $> F_{(2,10), 0.95} = 4.10$

<u>Source</u>	<u>df</u>	<u>SS</u>	<u>MS</u>	<u>F</u>
Between	2	0.0025	0.00125	$F_{obs} = S^2B / S^2W = MSB/MSW = 0.48695$
<u>Within</u>	<u>10</u>	<u>0.02567</u>	<u>0.002567</u>	
Total	12	0.02817		

Since  $F_{obs} < F$ , accept  $H_0$

*Thus ANOVA Test indicates that the three isothermal settings provide similar values of Bound Water. The Test is valid at the 95% significance level.*

**TABLE 9**  
**DUNCAN'S MULTIPLE RANGE TEST (DMRT) OF RESULTS OF BOUND**  
**WATER DETERMINATIONS FROM TGA ISOTHERMAL SETTINGS**

Bound water values for Zion WTP alum sludge using three isothermal settings						
	30 °C		40 °C		50 °C	
	A	A <sup>2</sup>	B	B <sup>2</sup>	C	C <sup>2</sup>
Values	0.53	0.2809	0.63	0.3969	0.65	0.4225
	0.68	0.4624	0.60	0.36	0.57	0.3249
	0.59	0.3481	0.59	0.3481	0.60	0.36
	0.50	0.25	0.55	0.3025		
	<u>0.56</u>	<u>0.3136</u>	<u>0.60</u>	<u>0.36</u>		
Sums	2.86	1.655	2.97	1.7675	1.82	1.1074
Mean	0.572	-	0.594	-	0.6067	-
(Sums) <sup>2</sup> = (∑X <sub>ij</sub> ) <sup>2</sup> =	8.1796	-	8.8209	-	3.3124	-
(Sums) <sup>2</sup> /n = (∑X <sub>ij</sub> ) <sup>2</sup> /n =	1.63592	-	1.76418	-	1.1041	-
∑ X <sub>ij</sub> <sup>2</sup>	-	1.655	-	1.7675	-	1.1074
<b>Calculate ESS (Error Sum of Squares):</b>						
a)	Find ∑ (X <sub>ij</sub> ) <sup>2</sup> = 1.655 + 1.7675 + 1.1074 = 4.5299					
b)	Find ∑ [(∑X <sub>ij</sub> ) <sup>2</sup> /n] = 1.63592 + 1.76418 + 1.1041 = 4.5042					
c)	ESS = 4.5299 - 4.5042 = 0.0257					
<b>Determine Error Standard Deviation, S:</b>						
S = ESS/(∑n - r) = 0.0257 / (13-3) = 0.0506952						
v = df = ∑n - r = 10						
<b>Find SSR (Significant Studentized Ranges) from DMRT, Table 11<sup>67</sup>:</b>						
For α = 0.05 and df = 10,						
	r = $\frac{2}{3.15}$ $\frac{3}{3.30}$ (number of ordered steps between means)					
SSR	$\frac{2}{3.15}$ $\frac{3}{3.30}$					
S(SSR)	0.1597 0.1673					
<b>Rank Means (Decreasing Order, High-to-Low):</b>						
Group	C (50 °C)		B (40 °C)		A (30 °C)	
Mean	0.6067		0.594		0.572	
Rank	1		2		3	
n	3		5		5	
<b>Duncan's Multiple Range Test Analysis:</b>						
<b>C vs A</b>						
(C -A) [2 (n <sub>C</sub> ) (n <sub>A</sub> ) / (n <sub>C</sub> + n <sub>A</sub> )] = y <sub>i</sub>						
1) If y <sub>i</sub> > SSR Table value, C is significantly different than A						
2) If y <sub>i</sub> < SSR Table value, C is not significantly different than A						
Thus, <u>none</u> of the means differ significantly at α = 0.05 level						
Here, y <sub>i</sub> = (0.6067 - 0.572) [(2x3x5)/(3+5)] = 0.0672 < 0.1597						
The three means can be linked with a bar between them, showing that they are not significantly different, as shown: <u>0.6067 0.594 0.572</u>						
<i>Thus, the mean values of bound water for the three isothermal settings are not significantly different at the 95% level</i>						

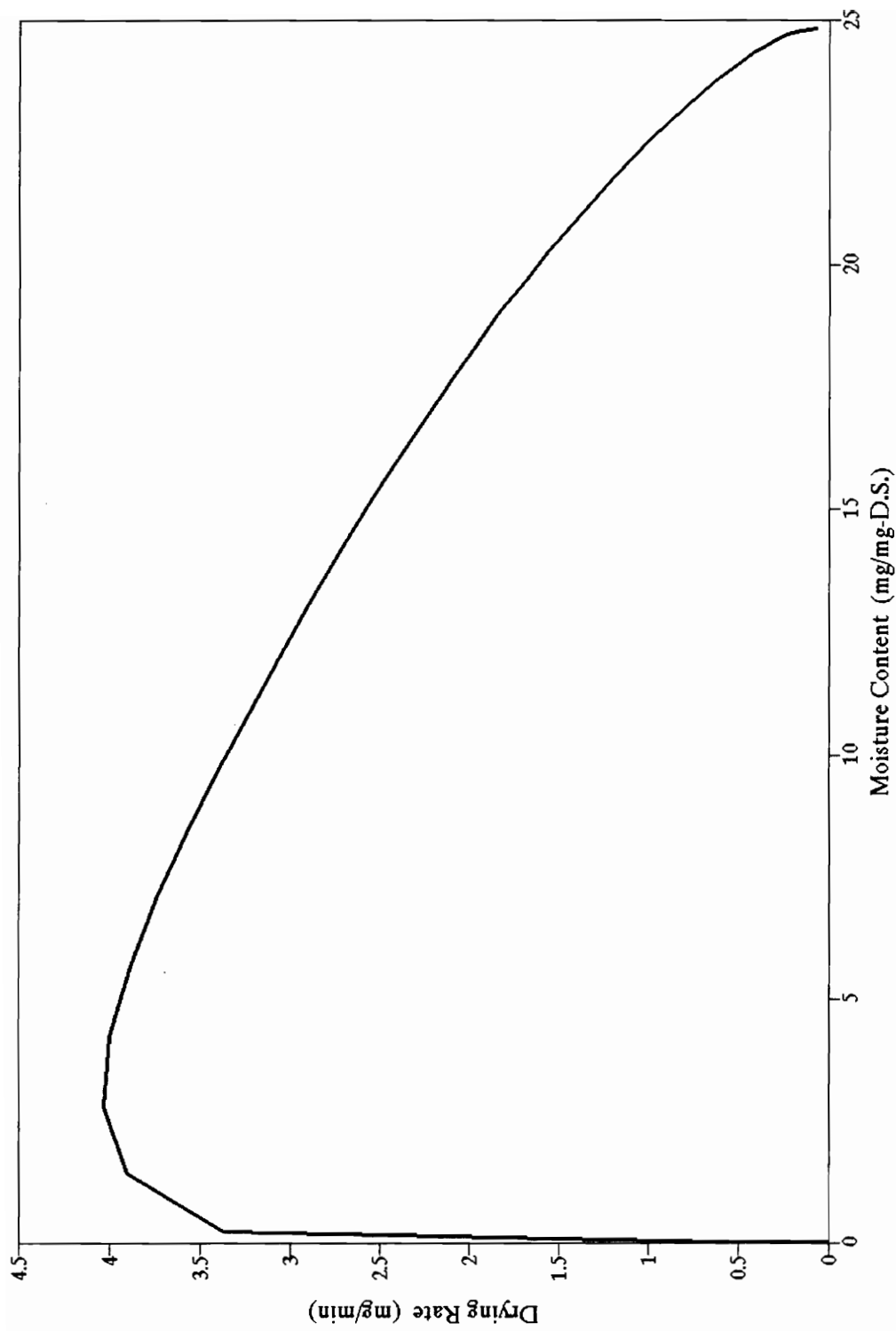


FIGURE 15: CHARACTERISTIC DRYING RATE CURVE OF SAMPLE  
AT TGA RAMPED SETTING OF 5 °C/MINUTE

## Moisture Present at Different Temperatures

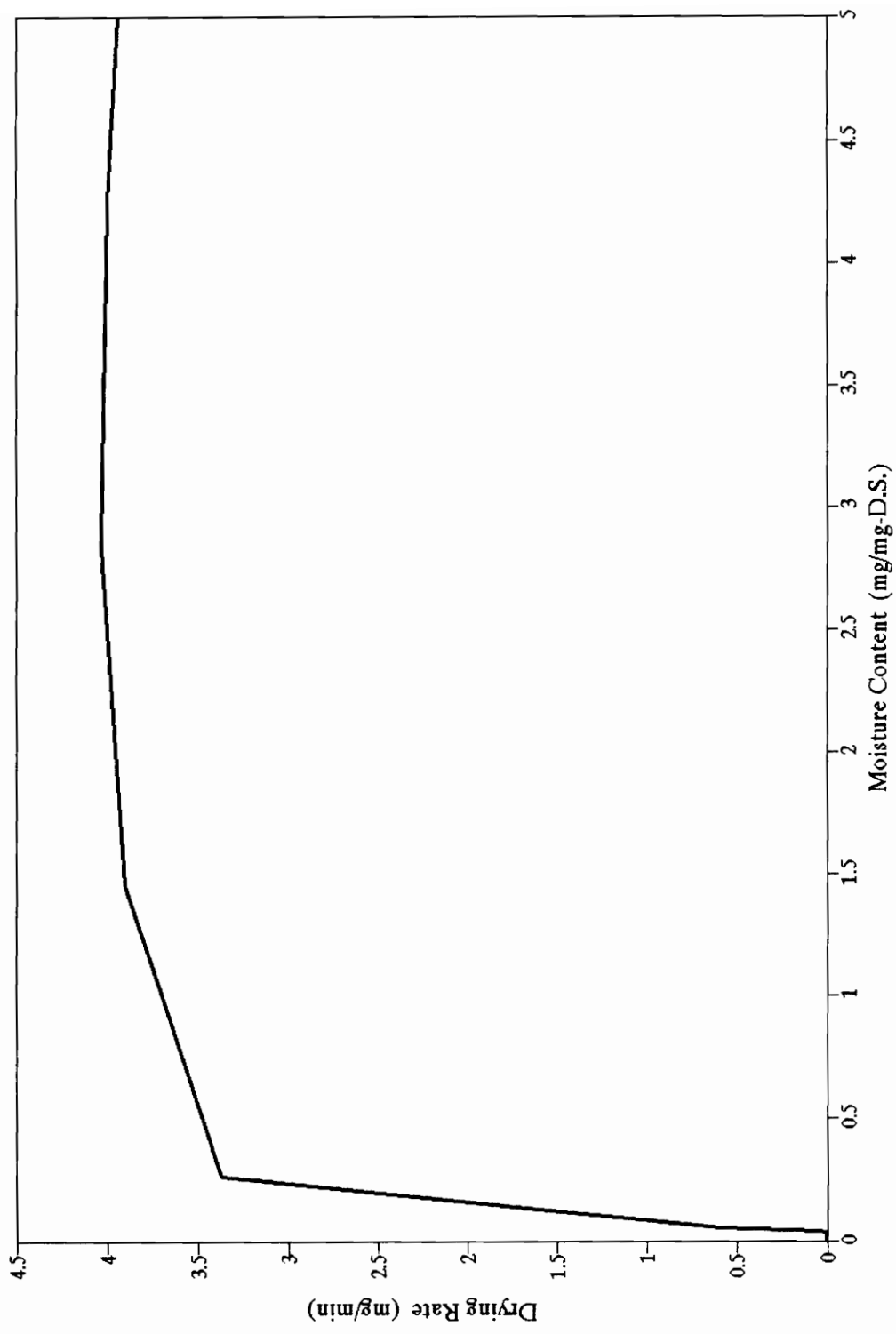
Figure 16 is a magnification of the bound water sub-fractions of the same sample in Figure 15, and it appears to show that there is very little, if any, moisture remaining in the sample. Any moisture that could remain would be considered additional chemically bound fractions (including waters of hydration), which is only removed at temperatures in excess of 250 °C.

Wunderlich<sup>97</sup> reported that samples of kaolinite release fractions of water between 700 to 1000 °K (427 to 727 °C). The author also reported that TGA analysis of iron (III) hydroxide showed loss of water taking place over the whole temperature range from 375 (102 °C) up to 1075 °K (802 °C). Samples of lithium phosphate reported moisture loss up to 475 °K (202 °C).

Studies of moisture characterization for wheat flour reported by Keey<sup>46</sup> indicated that the physically bound moisture was removed in the temperature range 20 to 130 °C, while chemical dehydration (i.e. removal of the chemically bound fraction) took place over the temperature range of 130 °C to about 400 °C. Beyond 410 °C, the organic matter was reduced to carbon, which eventually burned to leave a mineral residue (595 to 800 °C).

*Standard Methods*<sup>1</sup> indicate that drying samples at 103 to 105 °C may remove the majority of the physically bound water, but the residue may retain "not only water of crystallization but also some mechanically occluded water". Residues dried at 180 °C are supposed to lose all mechanically occluded water (or the physically bound fractions) although some water of crystallization may remain. Organic matter may be lost by volatilization, yet is not completely destroyed (the temperature has to be increased to 500 °C to ignite the sample and determine the volatile solids removed and fixed solids remaining<sup>1</sup>).

It is evident from the literature that inorganic minerals such as clays release their chemically bound waters at temperatures in excess of 400 °C, whereas organic samples tend to release this water fraction at lower temperatures. The higher



**FIGURE 16: MAGNIFIED PORTION OF DRYING RATE CURVE FROM FIGURE 15 TO DETERMINE THE CHEMICALLY BOUND SUB-FRACTION**

temperatures could also cause the volatilization of other components of the sludge particles, thereby leading to a decrease in weight/mass of the sample.

These chemically bound fractions are a subset of the total bound water. They are also generally a much smaller fraction of the total water of the materials and not currently economically feasible to remove. Data on the chemically bound fraction determined for this study are presented in a later section.

For this study (taking into account the matrix of sludges that included inorganic and organic sludges) the chemically bound fraction was defined to be the difference between the sample dried to a constant weight at 40 °C isothermal followed by ramping to 250 °C. Other researchers<sup>79,85,88</sup> have determined this fraction to be the difference in the weight of the sample after drying at a constant temperature of 30 or 35 °C to a constant weight and that determined from dry solids concentration after drying in a 103-105 °C oven. However (as indicated in *Standard Methods*<sup>1</sup>) at this temperature, there may be some fraction of the chemically bound water remaining.

### **Experimental Protocol Selected**

As indicated previously, the main focus of the research was to identify the free and bound fractions of sludge moisture. For the TGA/drying rate curve method, the demarcation point between the two fractions was defined as the first clear inflection point after the constant rate (horizontal line or regime) changed to a decreasing rate (as shown in Figure 14). Since the additional inflection points (indicating sub-sets of the bound water fractions) were not always reproducible and also operator-subjective, they were not quantified. The only sub-set of the bound water that was consistently reproducible was the much smaller chemically bound fraction (discussed in the following chapter).

Due to concerns that ramped conditions could stress the samples and because they did not provide the classic horizontal regime indicating the free water removal, it was decided to use only the isothermal settings. As indicated previously, statistical testing (ANOVA and DMRT) performed on the data for three different isothermal settings indicated that the results were not significantly different from each other. Since the 30 °C setting took about 34% longer than the 40 °C setting, the latter was selected as the operating temperature of choice.

Once the free and bound fractions were determined, the temperature was increased by setting the TGA to ramp to 250 °C (at 10 °C/minute) to obtain the dry solids concentration of the sample. This value (in %DS) was converted to g/g-DS (as mass of total water initially present per unit mass of dry solids). Total Water was considered to be equivalent to the sum of Free Water and Bound Water.

The TGA instrument was allowed to cool to ambient/room temperatures upon completion of the test by passing compressed air (from laboratory taps) over the oven section. Typically, this took about an hour, whereupon the TGA cell could be opened, the sample pan (and dry residue) removed, and a fresh pan (with sample) loaded to begin the next test.

This combination of temperature settings (i.e. isothermal at 40 °C until constant mass was attained followed by ramping to 250 °C) using the TGA provided moisture distribution data in under two hours as opposed to the classic methods reported in the literature that typically took up to 10 hours.

The results (see Table 7) also showed that the ramped setting of 5 °C/minute provided comparable values of moisture distribution data for the predominantly inorganic sludges (such as the Zion WTP alum sludge). Since these tests could be conducted relatively quickly (e.g. in less than 45 minutes for ramped conditions of 5 °C/minute), they were used when a quick turnaround time was required and the tests performed on the same sludge. An example of such a case was when tests were conducted to determine the moisture distribution profile of the Zion WTP alum sludge as it was chemically and mechanically conditioned.



## Effect of Polymer Conditioning on TGA Analysis of Sludge Samples

As alluded to previously, it was observed that the drying rate curve of a polymer/chemical-conditioned sludge sample did not show the classical horizontal constant rate section (or regime). The curve appeared to begin with an initial high rate (similar to the unconditioned sludge sample) but instead of continuing to remain at this rate (thereby indicating loss of the free water fraction), the curve gradually sloped down, reflecting a decrease in the drying rate. Two such typical plots are shown in Figures 17 and 18 for polymer-conditioned bio-solids and alum sludges.

As can be seen, polymer-conditioning both sludges appeared to reduce the rate of removal of free water in the sludge sample in the initial drying period, when most samples seem to exhibit a "horizontal regime" (as shown in Figure 14, for a fairly typical drying rate curve, the constant rate denoting removal of the free water).

A review of the drying curve rate literature was undertaken to determine whether the effect had been previously reported. The observation was not directly reported in the literature for bio-solids. Halde<sup>35</sup> indicated that polymer conditioning bio-solids samples moved the first critical point of vacuum drying rate experiments but did not affect the second one, thereby leading to the author's conclusion that polymer conditioning reduced the amount of interstitial water. Vesilind<sup>94</sup> appeared to interpret this observation by stating that polymers reduce the amount of interstitial water but do not change the surface area (in turn not changing the amount of vicinal water) which could conceivably be indicated by the second critical point. The author<sup>94</sup>, however, did not present any supporting references for his interpretation of Halde's reported<sup>35</sup> observations. The authors<sup>35,94</sup> did not indicate whether the slopes of the drying rate curves from these tests were affected by polymer conditioning.

Smollen<sup>85,86</sup> had reported use of polymer conditioned bio-solid sludges using the drying rate curve method but did not indicate whether such effects were observed. The author did, however, state that polymer-conditioning appeared to decrease the immobilized bound water fraction (or the interstitial water) with a

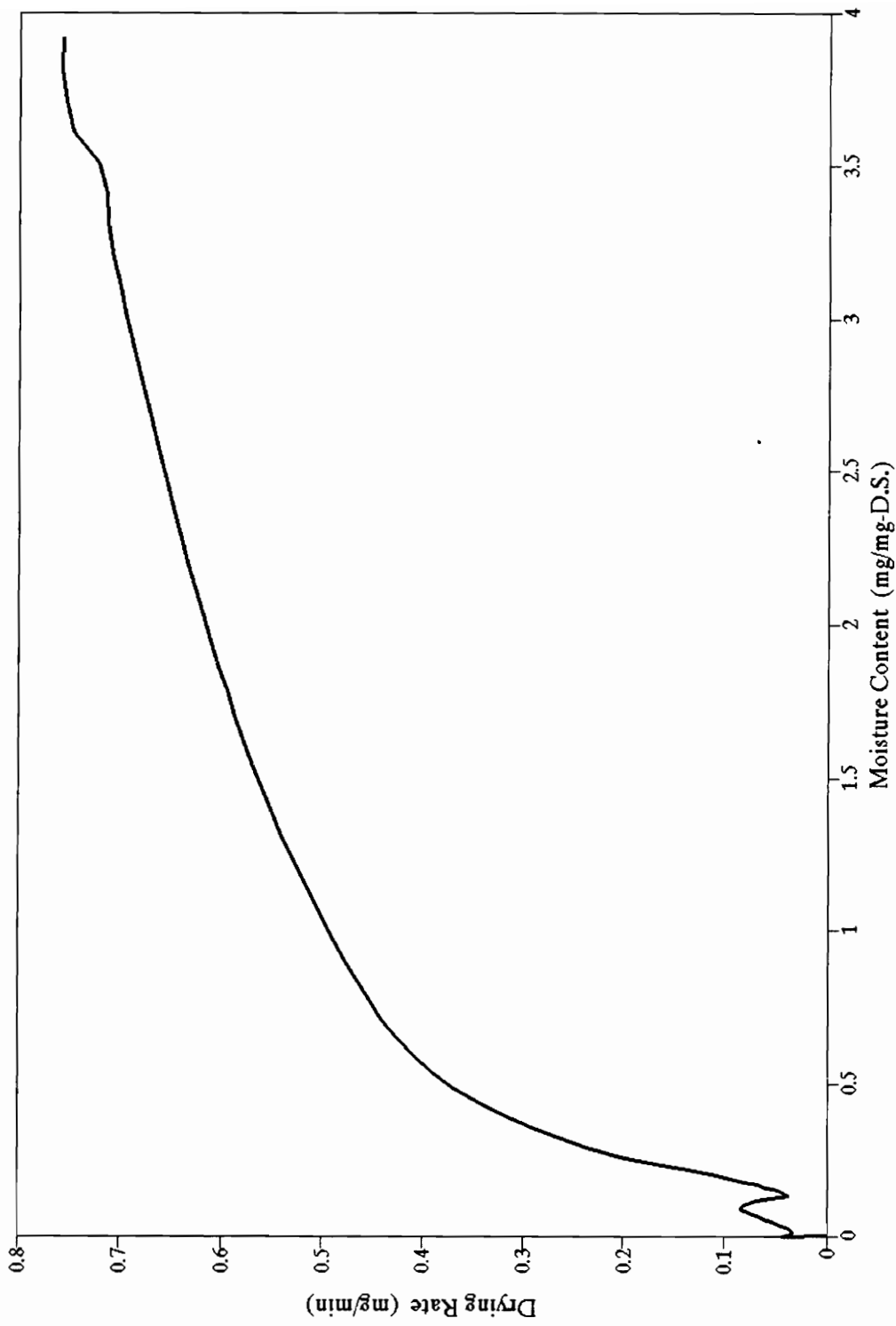


FIGURE 17: OBSERVED DECREASE IN SLOPE OF DRYING RATE CURVE  
DUE TO POLYMER CONDITIONING OF BIO-SOLIDS SAMPLE

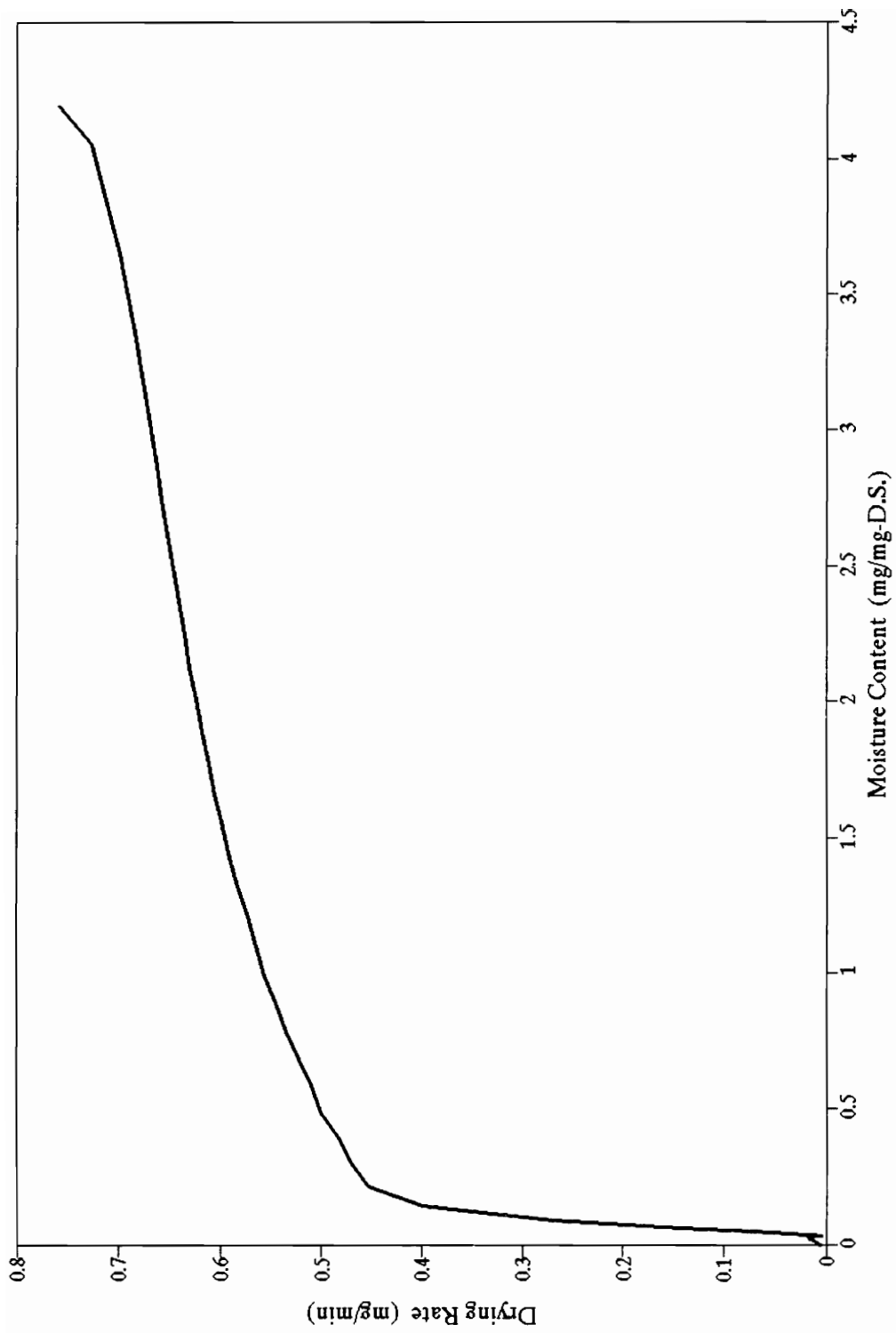


FIGURE 18: OBSERVED DECREASE IN SLOPE OF DRYING RATE CURVE  
DUE TO POLYMER CONDITIONING OF ALUM SLUDGE SAMPLE

simultaneous increase in the bound water content. In addition, the author indicated that the classic drying rate curves were of little or no use to the data obtained, as none of the curves that were generated identified clearly the critical or inflection points. The author reported<sup>86</sup> that "the constant rate of evaporation was of short duration, the rate thereafter showing a smooth fall to an ill-defined critical moisture content." Thus, the author attempted an "improvement" of the curve by plotting moisture content versus time of drying. However, even the curves generated in this fashion (only one of which was presented) did not appear to have well-defined inflection points.

Smollen<sup>86</sup> had conducted vacuum drying tests on bio-solids (based on work reported by Halde<sup>35</sup>), in an effort to optimize the author's previous low temperature drying investigations<sup>85</sup>. Free water was assumed to be absent as it was thought to have been removed by centrifugation prior to drying. Correlations were then attempted between the various moisture fractions and other sludge parameters.

A review of data for anaerobically digested sludges from nine of the twelve municipal WWTPs presented by the author for which complete moisture distribution data were reported<sup>86</sup> indicated that polymer conditioning caused increases in both the drying time and the bound water fraction as well as decreases in cake moisture (or total water) and interstitial water (what the author referred to as the immobilized water). On average, the drying time increased by slightly more than 13% (from 4.4 hours for unconditioned sludges to about 5 hours for polymer-conditioned ones).

There was, however, almost a 36% decrease in the interstitial water, a 45% decrease in the chemically bound fraction upon polymer conditioning, and an 11% decrease in the total water content (both expressed in g/g-DS). Although there appeared to be an increase of almost 14% in the amount of bound water after polymer-conditioning, when taking into account the release of the chemically bound water, the actual increase in total bound water adds up to about 2% (well within experimental error). The analysis of data abstracted from Smollen's paper<sup>86</sup> is presented in Table 10, and shows the changes in moisture distribution data before

TABLE 10  
ANALYSIS OF SELECTED DATA REPORTED BY SMOLLEN<sup>86</sup> ON  
BIO-SOLIDS USING THE DRYING RATE METHOD

Sludge Sample	Cake Moisture (%)	Total Water (g/g)	Drying Time (hrs)	Moisture Content (g/g-DS)		
				Chemically Bound	Other Bound	Immobilized or Interstitial
<b>Before Polymer-conditioning</b>						
Athlone	87.0	6.7	-	-	2.7	4.0
Athlone	84.8	5.6	3.3	0.5	3.2	2.0
Paarl	88.8	7.9	4.7	1.1	3.3	3.5
Milnerton	90.0	9.0	4.3	0.8	4.6	3.7
Kraaifontein	84.9	5.6	5.2	1.5	5.3	3.6
Cape Flats	91.1	10.2	-	-	5.2	5.0
Athlone	92.0	11.5	-	-	5.2	6.3
Mitchells Plain	90.7	9.8	-	-	4.3	3.4
<u>Athlone</u>	<u>91.2</u>	<u>10.4</u>	<u>4.3</u>	<u>1.5</u>	<u>5.3</u>	<u>3.6</u>
<i>Average</i>	88.9	8.5	4.4	1.1	4.3	3.9
<b>After Polymer-conditioning</b>						
Athlone	84.5	5.5	-	-	2.6	3.3
Athlone	80.8	4.2	4.0	0.4	3.0	0.8
Paarl	87.9	7.3	5.3	0.5	5.5	1.3
Milnerton	87.5	7.0	4.9	0.7	5.3	1.1
Kraaifontein	83.5	5.1	5.5	0.3	3.5	1.3
Cape Flats	91.4	10.6	-	-	7.6	3.0
Athlone	92.5	12.3	-	-	5.0	7.3
Mitchells Plain	88.3	7.6	-	-	5.0	2.9
<u>Athlone</u>	<u>90.4</u>	<u>9.4</u>	<u>4.8</u>	<u>0.9</u>	<u>6.8</u>	<u>1.8</u>
<i>Average</i>	87.4	7.7	4.9	0.6	4.9	2.5
<b>Comparison of Above Sludges (Before and After Polymer-Conditioning)</b>						
Athlone	2.5	1.2	-	-	0.1	0.7
Athlone	4.0	1.4	-0.7	0.1	0.2	1.2
Paarl	0.9	0.7	-0.6	0.6	-2.2	2.2
Milnerton	2.5	2.0	-0.6	0.1	-0.7	2.6
Kraaifontein	1.4	0.6	-0.3	1.2	1.8	2.3
Cape Flats	-0.3	-0.4	-	-	-2.4	2.0
Athlone	-0.5	-0.8	-	-	0.2	-1.0
Mitchells Plain	2.4	2.2	-	-	-0.7	0.5
<u>Athlone</u>	<u>0.8</u>	<u>1.0</u>	<u>-0.5</u>	<u>0.7</u>	<u>-1.5</u>	<u>1.9</u>
<i>Average</i>	1.5	0.9	-0.5	0.5	-0.6	1.4
<i>Standard Deviation</i>	1.4	0.9	0.1	0.4	1.3	1.1

**Notes:**

Numbers may not add up due to rounding. All Moisture/Water content values are in g/g-DS. Comparisons between sludges are (Before - After Conditioning). Thus negative values would indicate increases observed after conditioning while positive values denote decreases.

and after polymer-conditioning. The polymer used was Zetag-57, a cationic poly-electrolyte, applied at between 2.5 to 6.0 kg per ton of dry solids.

Although they did not specifically indicate a loss of the horizontal regime, the comments made by the author<sup>86</sup> seem to suggest similarities in the observation by this study of the loss of the horizontal regime. This non-horizontal portion of the drying curve obscures the first and subsequent additional inflection (or critical) points (i.e. fairly well-defined inflections denoting changes) in the drying rate curves that are supposed to represent the onset of removal of a different water fraction. The decline in the drying rate makes it even more difficult to characterize the categories of water in the sludge sample which are already operator-subjective.

There could be a number of reasons for the observed decline. It may be due to the entrapment of a portion of the free and interstitial water within the floc structures created from polymer-bridging or other mechanisms. However, due to the relatively small amounts of the polymer (usually less than 1% by dry weights), these adsorbed fractions should not be significantly high. The decline in drying rate could also be due to changes to the structure and surfaces (including surface tension, capillary forces, and specific area effects) of the chemically-conditioned sample that in turn affect sludge moisture-movement mechanisms, especially in the initial phase of the free water loss.

It would appear that, as the water fractions leave the sample matrix, remaining fractions come under the effect of the polymer and their movement is also hindered. As more and more water eventually leaves the sample matrix, the hindering effect gets more pronounced (the ratio of polymer to water/sludge particle increases) and the slope of the drying rate curve continues to get steeper (as observed in both Figures 17 and 18).

The seven drying theories discussed in Chapter 2 appeared to indicate that uncertainties in the pore size structure and distribution, capillary forces, and surface tension (among other sample characteristics), could alter the drying rate. It is believed that polymer-conditioning might affect some of these characteristics, thereby

leading to the observed changes. The exact reasons for the decrease in drying rate are, however, uncertain at this stage.

A review of the literature for studies in other disciplines indicated that the rate of evaporation of water can be retarded by the presence of monolayer coverage of polymers and surfactants. A fairly extensive set of investigations were reported by La Mer<sup>52</sup> in the late 1960s on spreading a monomolecular film of various materials which were usually hydrophobic in nature (including hexadecanol) over the surface of a water body. The rate of water loss was measured using a surface balance evaporimeter (which contained a desiccant that absorbed the water evaporating from the surface). According to La Mer<sup>52</sup>, "transport of a molecule of water from the liquid state, through the monolayer, to the vapor state is essentially a kinetic process involving the surmounting of a number of successive energy barriers". For the monolayer to retard evaporation, it must have a flexible but condensed structure. The "molecular architecture" of the monolayer, specifically the length of the hydrocarbon chain, nature of the polar group, branching of the chain, and degree of unsaturation in the chain determine how molecules will pack together in the monolayer<sup>52</sup>. The literature has also reported that polymers have been tested as soil amendments, both as flocculating agents for poorly draining soils and to aid in water retention of drier soils.

It is thus believed that the presence of polymers (usually polyacrylamide based, and with surface properties that would satisfy the "molecular architecture" described above) in the sludges tested using the TGA does in fact, contribute to the non-linear drying rate curve observed above. This may be due to the hindering effect or retardation of the water molecules evaporating from the polymer conditioned sludge surface.

## **Recommended Experimental Protocol for Use of TGA/Drying Curve Method**

The methodology developed for this portion of the study appears to be an improvement of the bio-solids moisture characterization technique using the drying rate method. This is due primarily to the accuracy derived from the use of the TGA which minimizes errors from three important variables: (a) handling/removal of sludge samples to record their weights, (b) collecting sufficient datapoints to better define the inflection point(s) on the drying rate curve, and (c) changes in the environmental parameters (e.g. humidity and temperature), that have traditionally been cited as drawbacks of this method.

Although more precise, the TGA is relatively expensive and other, more cost-effective, instruments (including older, refurbished TGAs) can be purchased or fabricated. These may include an analytical balance in an enclosed setting (say, a plexiglass box to control the humidity and temperature) with the data transferred to a computer interface that can monitor the results (and, for a slightly higher cost, control the balance as well as an optional temperature and humidity controller). The costs for such systems would typically be between \$5,000-\$8,000. The refurbished TGAs with relatively newer computer interfaces can be purchased for less than \$10,000.

For this study, the TGA/drying curve rate technique provided reproducible (percent standard error for replicate tests was between 9-11%) results. Of the various thermal settings, the lower temperatures took much longer (about 4 hours for 20 °C, 2.5 hours for 30 °C, 1.5 hours for 40 °C, 1 hour for 50 °C) when used in the isothermal mode. The ramped (temperature raised at a preset rate of 2-10 °C/min up to 250 °C) settings were quickest (0.75 to 1 hour for 5 °C/min, 0.5 hour for 10 °C/min). Inflection points for the different settings changed slightly with the conditions.

The recommended experimental protocol should be to first determine the range of sample sizes to use in the instrument. The TGA should then be set at 40 °C (or some other comparable temperature setting) isothermal until a constant weight



is achieved (this indicates the free and bound water fractions have been removed), then increasing the temperature to 150 °C (250 °C is recommended) to drive off all the remaining moisture (usually the chemically bound water fraction). The sample mass at this temperature (or 105 °C) would allow calculation of the dry solids concentration, and conversely the total amount of water initially present in the sample. Due to the nature of the method, only one sample can be tested at a time and the test usually takes between two to three hours.

It should be pointed out that the TGA is an accurate and sensitive device; thus there appears to be background noise due to knocks to the bench supporting the instrument. In addition, it was found that polymer conditioning the sludge sample appeared to decrease the drying rate of the sludge sample and created a non-horizontal regime in the "constant rate" section of the drying curve, thereby making it difficult to determine the inflection point demarcating the free and bound waters.

Moreover, even for unconditioned sludge samples, determining some of these inflection points is not easy and subject to operator objectiveness. The inflection point(s) do not necessarily mean that the previous water fraction has completely been removed and that the next fraction has begun to leave the sludge matrix. If one were to ignore the various inflection points after the first major drop in the drying rate (which is supposed to indicate that free water had been removed and that various sub-fractions of the bound water are beginning to come off), the method does allow for the characterization of three water fractions: free, bound, and chemically bound. The bound water fraction could conceivably include some free, interstitial, and/or capillary, waters.

## DIFFERENTIAL SCANNING CALORIMETER (DSC)

### General

The use of a DSC has been reported in various literature sources in other disciplines to characterize materials, and sometimes more specifically, moisture in the materials (for example, clays<sup>4</sup>, coal<sup>64-66</sup>, polyethylene glycol<sup>7</sup>, polymers<sup>8</sup>, frozen liquid foods<sup>50</sup>). Although the literature review conducted earlier into the research could only identify limited references to the use of the DSC for bio-solids/sludge moisture characterization, there appears to be some interest in its use recently. A similar (albeit slightly less sensitive) technique called the Differential Thermal Analyzer (DTA) has been reported by Katsiris and Kouzeli-Katsiris<sup>43</sup> in their study on biological sludges. While the DTA measures the changes in temperature, the DSC measures calorimetric changes of a sample, in both cases with reference to the empty sample pan.

Since the DSC is able to record accurately the calorimetric heat changes within a sample being tested, this capability is used to measure the changes in either the observed exotherm when a sample (or portion thereof) freezes or the endotherm when the same sample melts. The data thus collected allow for quantification of the amount of material (in this case the free or unbound water) within the sample. The underlying assumption of this moisture characterization technique is that the free water fraction freezes or melts at temperatures close to 0°C. Deviations from the normal phase change temperature have usually been attributed to the presence of impurities<sup>11,97</sup>.

As discussed in Chapter 2, it had been observed that water in most materials are in two fractions: unbound (bulk or free) and bound. The bound fraction does not freeze easily and this amount is determined by subtracting the amount of free water (determined from measuring the calorimetric change) from the total water determined by dry solids analysis. Since the enthalpic change of interest occurs close

to the freezing or melting point of water, the DSC is usually set to measure changes in a relatively short temperature range around this value. For this study, the range selected was 20 °C to -20 °C and vice versa.

The two DSCs that were available for most of the experimental work were the Perkin-Elmer (PE DSC) and the Du Pont (DP DSC). Since the experiments were conducted on the Virginia Tech campus, the matrix of sludges included sources in Virginia, as well as selected pulp & paper mill sludges from North Carolina, and WTP alum sludge from Zion, IL. The previous chapter provides the list of sources for the sludges used.

The following sections discuss the development of the experimental protocol for use of the DSC to determine bound water in the matrix of sludge samples chosen and presents the findings of these tests.

## **Test Condition Variables / Development of Experimental Protocol**

### **Overview**

Since most of the experimental work was performed on the PE DSC, the data reported reflect the results of this instrument unless otherwise indicated. The QA/QC and good laboratory practice (GLP) procedures developed and followed were generally also applicable to the other instruments. A series of tests were initially conducted to determine the overall experimental protocol to generate the most consistent and reproducible data for each specific instrument. The variables investigated included: sample size; duration, range, and rate of the test conditions (on both the cool (freeze) and the warm (thaw) settings), as well as the effect of replicate cool-warm cycles.

## **Sample Pans**

For the PE DSC, two types of sample pans were also tested: (i) volatile aluminum sample pans (Perkin-Elmer Part #: 0219-0062, sample capacity: 20 mm<sup>3</sup> or 20 mg) and (ii) large volume O-ring sealed stainless steel pans (Perkin-Elmer Part #: 0319-0218, sample capacity: 60 mm<sup>3</sup> or mg). The pans were all hermetically sealed using a volatile sample sealer accessory (Perkin-Elmer Part #: 0219-0061). While the aluminum pans could withstand an internal pressure of up to 30 psi or 2 atmospheres, the larger stainless steels pans with rubber O-rings were designed to withstand an internal pressure of 350 psi or 24 atmospheres. This was due to initial concerns that the frozen sludge samples could expand and rupture the sealed aluminum pans thereby damaging the DSC cell. In addition, it was thought that these pans could be too small to handle mechanically dewatered bio-solids with relatively small amounts of free water (and hence required larger sample sizes to provide appropriate signals that could be measured by the instrument).

It was determined after a series of tests that these more widely used hermetically sealed aluminum pans were safe (for the instrument), more cost-effective, and could handle the correct capacity (sample size). Table 11 contains a compilation of selected data for different sludges using a variety of sample sizes for the two sample pans. The tips of the peak exotherms and endotherms were cut off when larger sample sizes were used. Smaller sized samples placed in hermetically sealed aluminum pans were determined to be both safe and measurable by the PE DSC instrument in the temperature range used.

## **Sample Sizes**

Sample sizes of between 1 to 7 mg were determined to provide reproducible data, due to instrument limitations on larger sized samples. The enthalpic changes

**TABLE 11**  
**SUMMARY OF SELECTED DATA FROM TESTS ON VARIOUS SAMPLES TO**  
**DETERMINE APPROPRIATE SAMPLE SIZES AND PANS FOR PERKIN-ELMER**  
**DSC (DIFFERENTIAL SCANNING CALORIMETER)**

<u>Sample Size (mg)</u>	<u>Sample Pan Used</u>	<u>Exothermic Peak Integral (J/g)</u>	<u>Endothermic Peak Integral (J/g)</u>	<u>Descriptive Observation of Enthalpic Response</u>
<b>Zion WTP Alum Sludge</b>				
62.7	stainless steel	nc	-	exotherm cut off
62.7	stainless steel	-	nc	endotherm cut off
13.8	stainless steel	133	-	exotherm cut off
13.8	stainless steel	-	276	endotherm just cut off
42.0	stainless steel	nc	-	exotherm cut off
42.0	stainless steel	-	269	endotherm appears OK
2.6	aluminum	220	-	exotherm appears OK
2.6	aluminum	-	226	endotherm appears OK
4.6	aluminum	102	-	exotherm just cut off
4.6	aluminum	-	293	endotherm just cut off
<b>Distilled Water</b>				
11.6	stainless steel	134	-	exotherm cut off
11.6	stainless steel	-	286	endotherm just cut off
12.0	aluminum	106	-	exotherm appears OK
12.0	aluminum	-	306	endotherm appears OK
<b>Pepper's Ferry WWTP Polymer-Conditioned Bio-Solids</b>				
5.1	aluminum	277	-	exotherm just cut off
5.1	aluminum	-	297	endotherm appears OK
10.0	aluminum	290	-	exotherm appears OK
10.0	aluminum	-	297	endotherm appears OK
<b>Pepper's Ferry WWTP Belt-Pressed Cake</b>				
42.6	stainless steel	nc	-	exotherm cut off
42.6	stainless steel	-	215	endotherm appears OK
16.4	stainless steel	224	-	exotherm appears OK
16.4	stainless steel	-	231	endotherm appears OK
2.8	aluminum	232	-	exotherm appears OK
2.8	aluminum	-	234	endotherm appears OK
9.2	aluminum	205	-	exotherm appears OK
9.2	aluminum	214	-	endotherm appears OK

**Notes:**

nc = not calculated

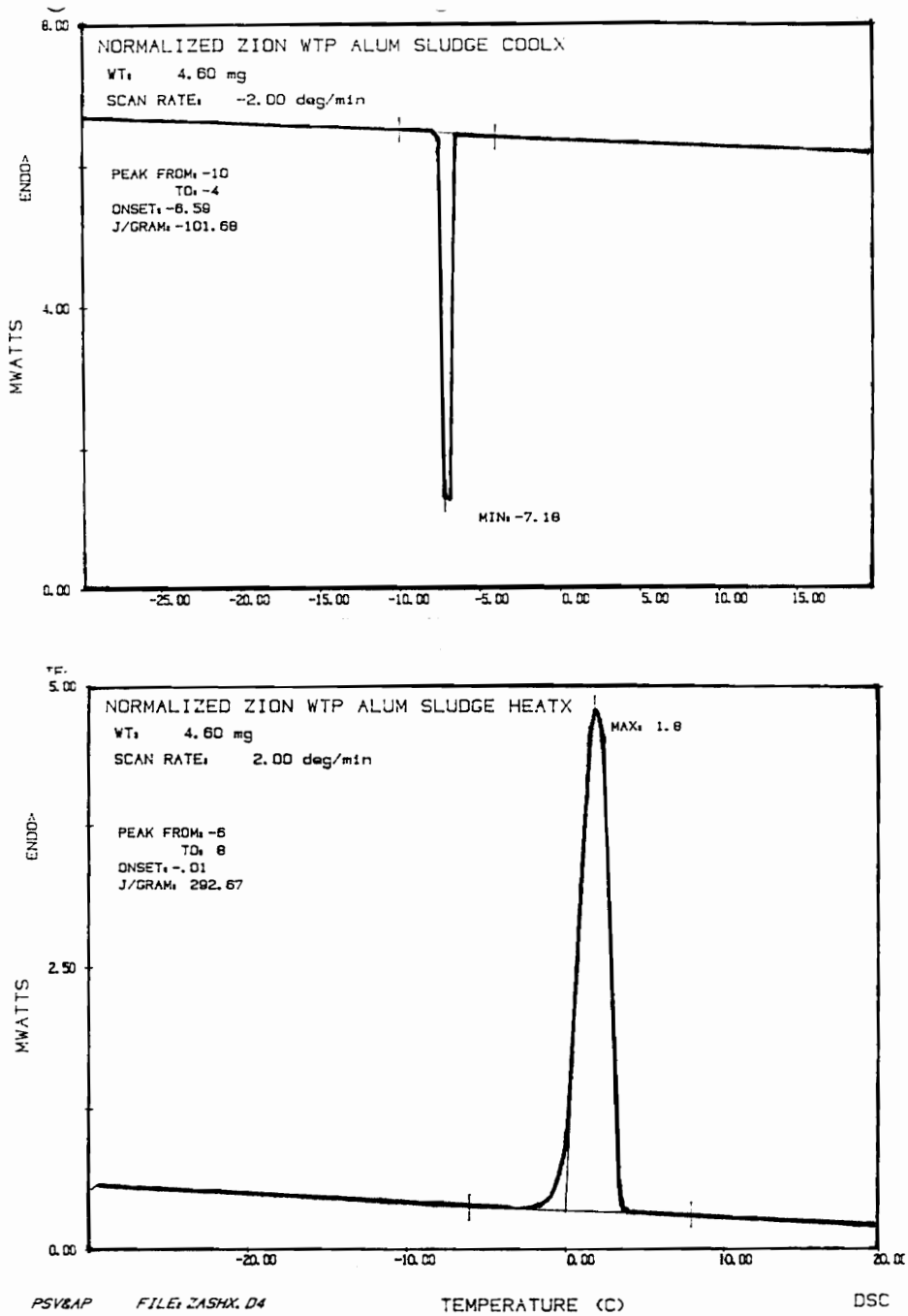
The observed exotherms all have a sharp, precipitous drop that is addressed elsewhere (on the rapid exothermic process/supercooling effect). The description "OK" refers to the completeness of tip of the peak minimum or maximum, i.e. the tip was not cut off.

that occurred during freezing or melting of the free water fraction overwhelmed the instruments' measuring capability when the sample size was too large (>4-5 mg for undewatered WTP and chemical sludges and > 12-15 mg for dewatered bio-solids). The sample size limitations were eventually determined to be due to the total amount of free water present in the sample.

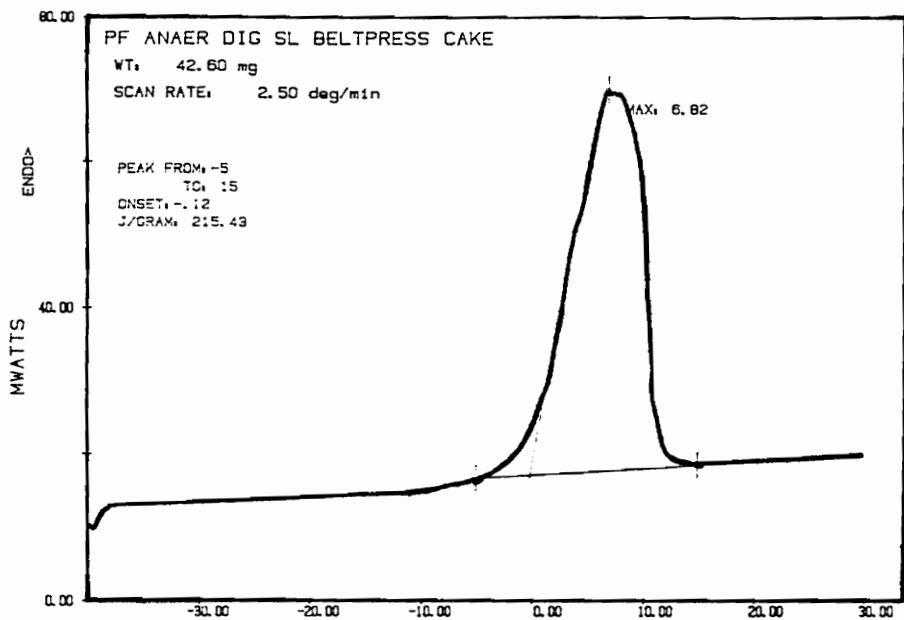
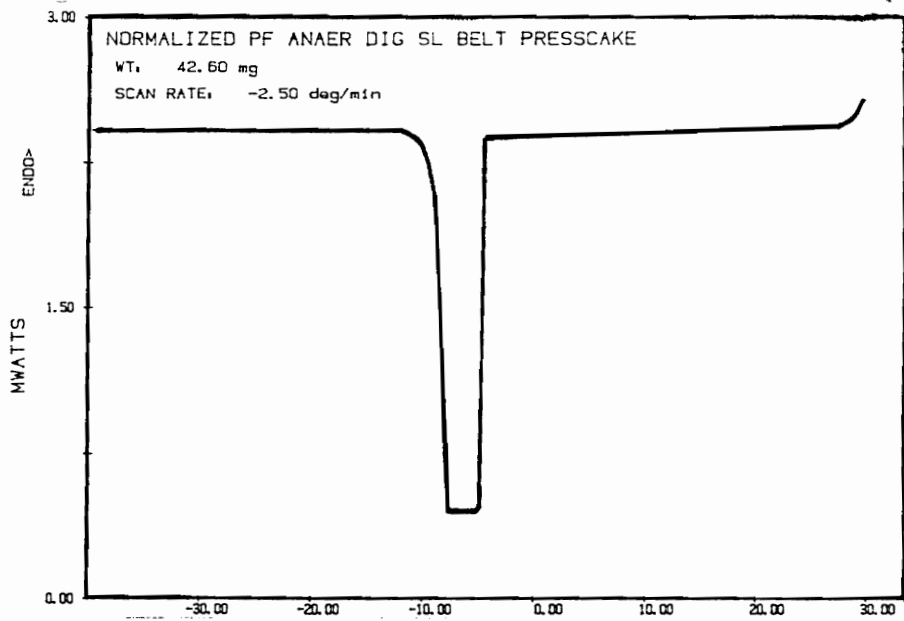
Figure 19 is an illustration of the sample size limitation for the Zion WTP alum sludge showing that the tip of the exotherm (indicating the freezing of free water) is cut off near the peak minimum at  $-7.2^{\circ}\text{C}$ . Although the sample size was quite small (only 4.6 mg, using the smaller sized aluminum pans), the calorimetric change of freezing of free water could not be measured completely. The amount of free water in this sample was relatively large (since the alum sludge has a low bound water content) and the enthalpic changes that occur when the free water undergoes a phase change tend to overwhelm the recording capability of the instrument. The effect is observed on the freeze cycle, but appears to be less pronounced on the warm cycle, indicating that the DSC instrument is able to record the melting endotherm more completely.

Another interesting observation from Figure 19 (and in other similar exothermic plots) is that the free water in the alum sludge begins to freeze below  $6.6^{\circ}\text{C}$  but melts at a temperature closer to  $0^{\circ}\text{C}$ . Furthermore, there was a sharp and precipitous drop in the exotherm for all the samples tested. The peak integral values were also different; these "super-cooling effects" were more pronounced for distilled water samples and discussed separately in a later section.

Figure 20 is a DSC instrument plot of data from a larger sized belt pressed bio-solids sample (42.6 mg) placed in the hermetically sealed stainless steel pan. The data in the figure illustrate that the instrument cannot accurately measure the enthalpic changes from large samples placed in these stainless steel pans. Here the sample size was 42.6 mg and it can be seen clearly that the exothermic peak is cut off prematurely.



**FIGURE 19: DSC (DIFFERENTIAL SCANNING CALORIMETER) PLOT OF EXOTHERM ON FREEZING AND ENDOTHERM ON MELTING OF FREE WATER IN ZION WTP ALUM SLUDGE. PLOT SHOWS LIMITATION OF SIZE DUE TO RELATIVELY LARGE AMOUNT OF FREE WATER**



PSYAL FILE: AP107.D4

TEMPERATURE (C)

DSC

**FIGURE 20: DSC PLOT OF EXOTHERM FROM FREE WATER FREEZING OF MECHANICALLY DEWATERED BIO-SOLIDS SAMPLE IN STAINLESS STEEL HERMETICALLY SEALED PAN. PLOT SHOWS LIMITATION OF SIZE DUE TO LARGE SAMPLE PAN CAPACITY**



It was determined that smaller sample sizes (1-3 mg) were more appropriate for chemical and inorganic sludge samples. For conditioned bio-solid samples that have had more of the free water removed (hence, possessing a relatively larger proportion of bound water), slightly larger sample sizes were acceptable (between 5 and 10 mg).

### **Test Conditions**

Dry solids concentrations were concurrently determined using regular aluminum pans (following *Standard Methods*<sup>1</sup>) for each set of sludge samples. For a number of tests, dilatometric tests were also conducted, which allowed for a comparison of the bound water results between the two instruments, as well as for the determination of sludge bulk density (or specific gravity). All experimental work was performed in triplicates.

After evaluating a number of different temperature settings (1, 2, 2.5, 5 °C/minute), it was determined that the ramp setting of 2 °C/minute from 20 °C to -20 °C, and vice versa, was most applicable as it allowed for good resolution of the thermal/enthalpic response in a relatively quick manner. A potential problem with faster temperature scan rates is that the sample free moisture content may not have sufficient time to freeze (which would be measured by the exotherm) on the cool cycle or melt (measured by the endotherm) completely in the relatively short temperature range (40 °C) required for the test<sup>97</sup>. Slower scan rates tend to pick up too much noise which make the baseline uneven. This is illustrated in Figure 21 for a bio-solids sample set at a warming scan rate of 1 °C/minute. Table 12 is a compilation of selected data from various test conditions indicating that the baselines were uneven (with associated scatter and bounce, or noise) at slower scan rates. Thus the 2 °C/minute scan rate was selected for the study. The 2 °C/minute has also been used by other researchers to determine bound water in various samples<sup>2,3,7,50</sup>.

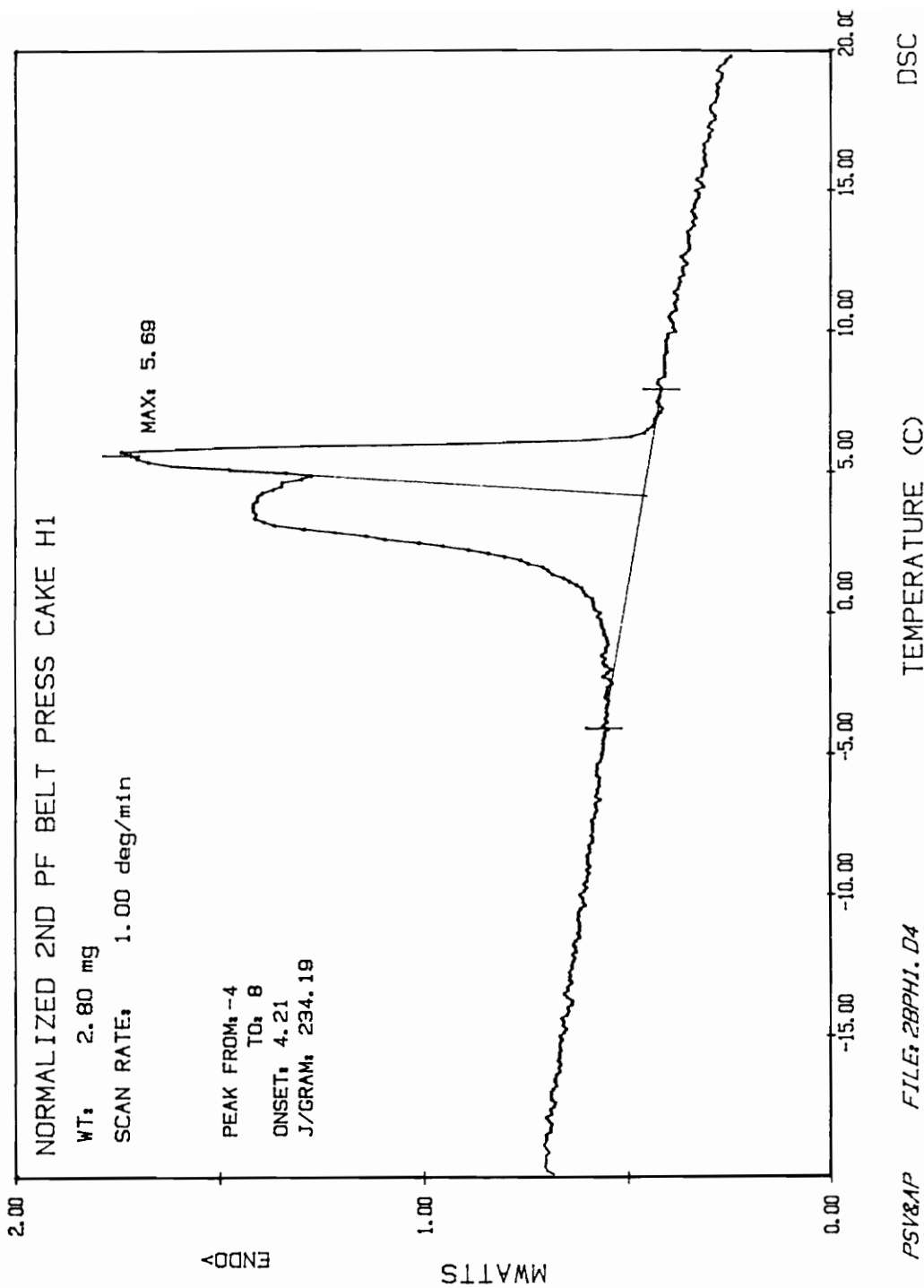


FIGURE 21: DSC PLOT SHOWING UNEVEN BASELINE DUE TO LOW WARMING RATE OF 1°C/MINUTE FOR BIO-SOLIDS SAMPLE

**TABLE 12**  
**SUMMARY OF SELECTED DATA FROM DSC TESTS AT VARIOUS SCAN RATES**

<u>Sample Used and Scanning Rate Tested</u>	<u>Onset Temperature (°C)</u>	<u>Peak Minima or Maxima (°C)</u>	<u>Peak Integral (J/g)</u>	<u>Comments on Plot of Baseline</u>
<b>Zion WTP Alum Sludge</b>				
5 °C/minute	-7.2	-7.7	-142	smooth exotherm baseline
5 °C/minute	1.8	4.2	265	smooth endotherm baseline
2.5 °C/minute	-5.1	-5.9	-133	smooth exotherm baseline
2.5 °C/minute	1.4	4.7	276	smooth endotherm baseline
2 °C/minute	-6.0	-6.3	-127	smooth exotherm baseline
2 °C/minute	1.0	2.4	238	smooth endotherm baseline
1 °C/minute	-3.0	-3.1	-220	smooth exotherm baseline
1 °C/minute	3.3	4.1	243	slightly uneven endotherm baseline
<b>Pepper's Ferry WWTP Bio-Solids Belt-Pressed Cake</b>				
2.5 °C/minute	-4.4	-4.9	-224	smooth exotherm baseline
2.5 °C/minute	1.2	7.0	231	smooth endotherm baseline
2 °C/minute	-2.0	-2.3	-216	smooth exotherm baseline
2 °C/minute	2.3	4.7	214	smooth endotherm baseline
1 °C/minute	-0.2	-0.6	-205	smooth exotherm baseline
1 °C/minute	4.1	6.3	214	slightly uneven endotherm baseline
<b>Distilled/Deionized Water</b>				
2.5 °C/minute	-6.6	-7.0	-106	smooth exotherm baseline
2.5 °C/minute	0.2	1.1	308	smooth endotherm baseline
2 °C/minute	-13.9	-14.1	-101	smooth exotherm baseline
2 °C/minute	1.2	2.9	309	smooth endotherm baseline
1 °C/minute	-20.3	-20.6	-145	smooth exotherm baseline
1 °C/minute	1.8	2.6	286	slightly uneven endotherm baseline
0.1 °C/minute	-17.6	-17.6	nc	very uneven exotherm baseline
0.1 °C/minute	2.7	3.2	217	uneven endotherm baseline

Notes:

nc = not computed as baseline was very uneven, no single clear peak integral was observed

Triplicates of a sample could be completed within three hours. Isothermal conditions of two to five minutes at the end of each temperature range were also provided to allow for equilibration of the thermal response (i.e. to allow for complete freeze or melt, if the sample had not already attained the phase change).

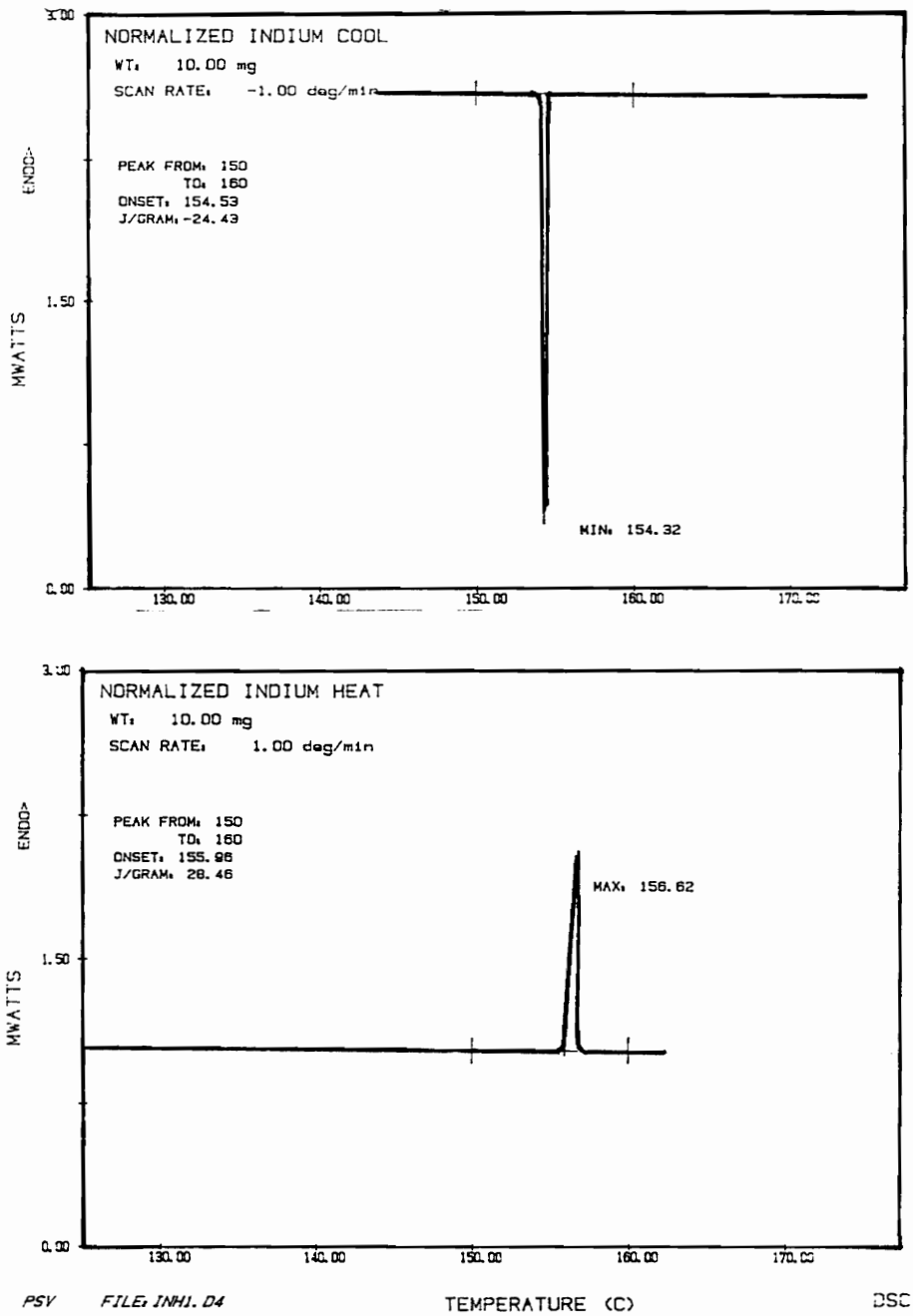
### **Calibration Standards**

A number of standards were also selected that covered the temperature range of interest, i.e. from ambient (20 °C) down to -20 °C for both the cooling and warming conditions. This was necessary to calibrate the DSC with respect to both enthalpy and temperature readings, as the instrument(s) were usually reset to different settings and experimental conditions by other users of the device.

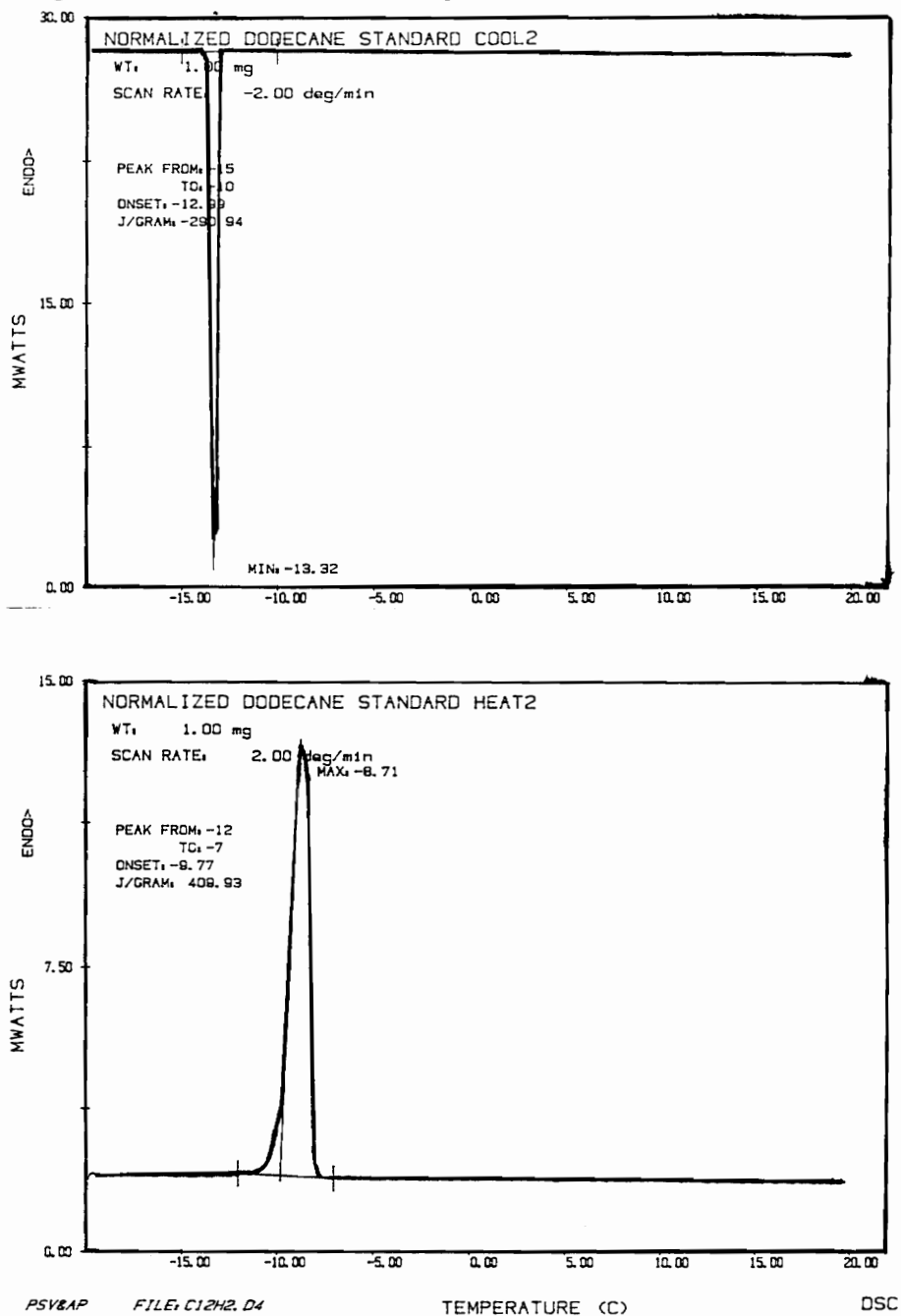
Following trials with a number of standards, three were finally selected due to their fairly well-documented enthalpy properties (melting points<sup>55</sup> and heats of fusion/melting), availability, safety and ease of handling. These were: deionized/distilled water (m.p. 0 °C), anhydrous dimethylacetamide (DMAC, m.p. -20 °C), and indium (m.p. 156 °C).

Indium has traditionally been used as a calibration standard due to its well-documented<sup>55,97</sup> melting point (430 K or 157 °C) and peak integral value (28.5 J/g). For this study, these values were reproducible to <1% and was an important standard for both the calibration and as a check standard component of the overall QA/QC for the DSC instrumental technique. This is illustrated in Figure 22 showing a peak integral value of 28.5 J/g and a melting point of 156 °C.

Dodecane, another calibration standard reported in the literature, was initially tested as a standard. This organic compound has a melting point of -9.6 °C (*CRC Handbook of Chemistry and Physics*)<sup>55</sup>. It was observed that a sample of dodecane froze at a temperature below -12 °C; although the melting point was close to -9.8 °C. This is illustrated in Figure 23. As can be observed, the melting points and peak



**FIGURE 22: DSC PLOTS FOR INDIUM USED AS A CALIBRATION STANDARD SHOWING RELATIVELY LITTLE CHANGE IN EXOTHERMIC AND ENDOTHERMIC RESPONSES**



**FIGURE 23: DSC PLOTS FOR DODECANE USED AS A CALIBRATION STANDARD SHOWING FAIRLY SIGNIFICANT DIFFERENCES IN ENTHALPIC RESPONSES**

integral values on the cooling and warming cycles were different and hence its use as a calibration standard was discontinued.

The calibration on the instrument was usually checked after about 25 samples were analyzed to check instrument response for both the exotherm produced upon freezing and the endotherm upon melting as a part of the QA/QC protocol.

### **Sub-Ambient Temperature Issues and Instrument Cooling Methods**

To perform tests in the sub-ambient (below 0°C) temperature zone, thermal analysis instruments (including the DSC) have to be connected to a heat sink. The temperature of the sink is brought down to sub-ambient temperatures by the use of coolants (such as liquid nitrogen) that may be fed to the sink at a controlled rate. Most thermal analysis equipment are capable of controlling the rate of heating while recording the thermal changes that occur. In this case, the ability of the device to supply heat in a controlled manner compensates for the uncontrolled cooling of the heat sink by applying heat to slow the cooling rate down to a preset level.

The three DSCs utilized for the study used different coolants and controlled their sub-ambient temperatures in different ways. The DP DSC employed in the initial phase of the study used dry ice that had to be added manually to a cooling can surrounding the sample cell. This metal cooling can thus acted as a heat sink for the DSC. While the instrument could not control the cooling rate, it was able to maintain an isothermal sub-ambient temperature (once the temperature of the DSC cell was lowered sufficiently) as well as ramp up at a preset warming rate. Although the DP DSC could not measure the exothermic change that occurs when free water freezes, it was able to measure the endotherm of the melting free water fraction.

However, the instrument could conceivably be measuring additional fractions of water that may not have been in the original sludge structure. These (presumably, some bound water) may have frozen due to the formation of growing ice crystals as

the temperature decreased. While these crystals would form due to the freezing of free water, its continued growth could lead to the rupture of cell flocs and the cells themselves, thereby releasing further amounts of "bound" water that would eventually thaw during the warming cycle and thus be reported as part of the free fraction. In addition, the uncontrolled cooling rate could lead to some additional pressures upon the sludge structures.

Figure 24 depicts the irregular cooling rate (in °C/minute) due to addition of dry ice to the manual cooling can of the DP DSC. The larger spikes in the curve indicate the calorimetric changes due to freezing and thawing of the frozen water fraction(s). As can be noticed, it was difficult to maintain the cooling rate in a controlled manner.

Thus, efforts were made to identify and use other DSCs which had controlled cooling capabilities. The PE and PL DSCs were found to have heat sinks connected to an external coolant source. Both instruments could modify the cooling and heating rates around their respective sample cells by supplying heat at a controlled rate to provide and maintain the rate of cooling or heating desired for the experiment. The PE DSC used freon as the coolant, whereas the PL DSC used liquid nitrogen. The type of coolant defined the lowest temperature that could be accurately maintained by the two instruments. This minimum value was -45 °C for the PE DSC using freon. In comparison, the PL DSC could be lowered to -150 °C. Both instruments were thus theoretically capable of measuring the enthalpic changes that occurred during freezing and melting of the sample free water fraction. Arrangements were then made to use the PE DSC for the major part of this study.

A recent article<sup>77</sup> indicates that DSC instrument manufacturers have begun to recognize that an increasing number of researchers are working at sub-ambient temperature ranges and have encountered problems with this indirect form of controlled cooling (which also creates moisture condensation on or around the DSC cell), and are beginning to develop more sophisticated instruments that are able to control both the cooling and heating rates separately.



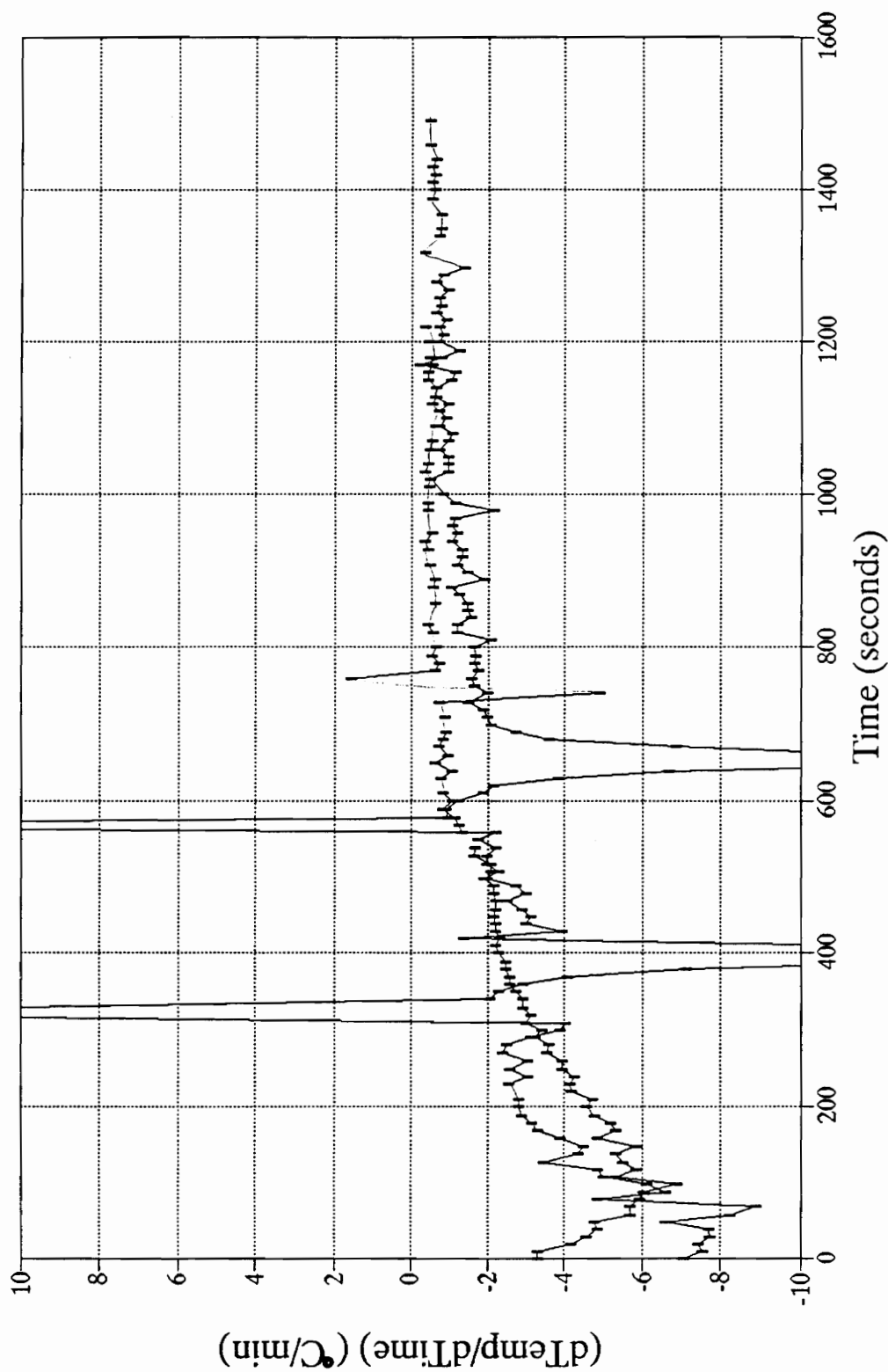


FIGURE 24: UNCONTROLLED COOLING RATE FOR DU PONT DSC FROM DRY ICE ADDITION TO MANUAL COOLING CAN

## Super-Cooling Effects

### *Freezing Point Depression*

One curious aspect to the DSC tests was that the freezing and melting points (usually indicated by the "onset" temperature of the peak, although some researchers prefer to report the peak maxima or minima values) for most of the distilled/deionized samples tested did not occur at 0 °C (the freezing point [f.p.] and melting point [m.p.] for water). Instead, for many of the samples, this transition point was frequently well below 0 °C, in most cases at between -5 to -15 °C. In addition, as mentioned earlier, this deviation from the f.p. or m.p. was also observed for the dodecane calibration standard (see Figure 23).

The observation was quite perplexing, and it was initially thought that there may have been some error in the instrument hardware or in the computer interface software. The manufacturer was contacted, and a number of tests (included various cooling rates) were conducted to fine-tune the instrument calibration and to correct any potential anomalous measurements. However, the observation was continually repeated.

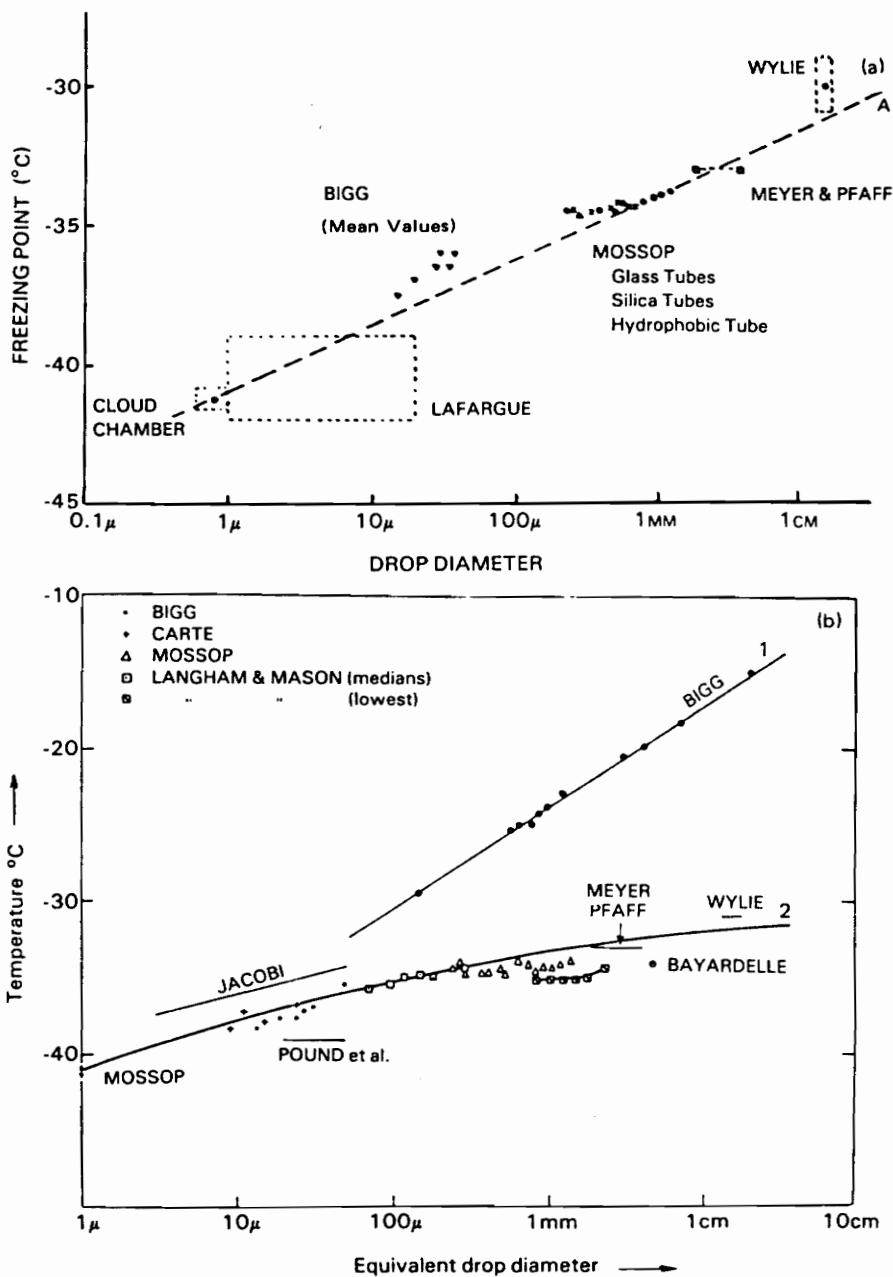
It was eventually determined that the phenomena was not an isolated quirk but had been previously reported in the literature as a "supercooling" effect due to the fairly small sample sizes used<sup>31,67,97</sup>. Angell<sup>6</sup> presented an excellent overview and discussion of the phenomena with respect to water. The onset of the water crystallization during cooling is highly unpredictable and sample-dependent. It is believed that "the crystallization of ice is not a property of water itself but rather a function of the sort of solid surfaces, particulate or otherwise, with which it is in contact"<sup>6</sup>.

The supercooling effect appears to be pronounced for very small sample sizes of water, with a probable relationship between the size of the water droplet and freezing point. There appears to be a freezing point depression with respect to droplet diameter down to -39 °C for water of 10 μm diameter (corresponding to

water in volumes of  $10^{-9}$  cm<sup>3</sup>, or approximately  $10^{-6}$  mg sample weight) determined by cloud chamber freezing experiments<sup>6</sup>. Figure 25 illustrates the probable relation between the homogeneous nucleation temperature (freezing point) and the size of the droplet of water samples from various investigations by a number of other researchers, reported by Angell<sup>6</sup>.

Table 13 summarizes the data for tests conducted under a variety of conditions and for a number of water samples in this study, including samples with various "nucleating" sites that could potentially initiate the freezing of water at a temperature closer to 0°C and may be naturally present in the matrix of sludges to be analyzed. As indicated in the table, the freezing point depression effects were more evident in samples with only water present. The effects also appeared to be slightly more pronounced with smaller samples. The use of nucleating sites such as that provided by the SiO<sub>2</sub> and present in the WTP sludges due to particulate matter decreased the super-cooling effect. These sites could conceivably slow down the freezing rate sufficiently to allow the DSC to measure more completely the rapid exothermic process when the free water freezes.

Due to the observed deviations from the f.p. for the matrix of samples tested, it was finally decided not to continue to use or report the onset or peak minimum temperature values from the DSC plots for the analysis of sample moisture characteristics. These values could not be used to determine the amount of free (and conversely, bound) water present in the sample. The peak integral values necessary to compute the free water fraction on the freezing cycle were also found to be unpredictable and consistently lower than the values on the melting cycle. This is discussed in the following section.



Source: Angell, 1982<sup>6</sup>; citing various researchers

FIGURE 25: PROBABLE RELATIONSHIP BETWEEN FREEZING POINT TEMPERATURE AND SIZE OF WATER SAMPLE

**TABLE 13**  
**OBSERVED DEPRESSION OF FREEZING POINT**  
**(SUPERCOOLING EFFECTS) FOR VARIOUS SAMPLES OF WATER**

Cooling Rate Used and Sample Tested	Sample Size (mg)	Observed Freezing Point		
		Onset Temp. (°C)	Peak Minimum (°C)	Peak Integral (J/g)
-0.1 °C/min, DI Water	3.8	did not freeze until well below -25 °C		
-1 °C/min, DI Water	12.0	-13.9	-14.3	-106
-2 °C/min, DI Water	1.3	-18.8	-19.0	-136
-2 °C/min, DI Water	3.3	-19.6	-19.9	-82.4
-2 °C/min, DI Water	4.4	-20.2	-20.5	-57.7
-2 °C/min, DI Water	7.5	-15.0	-15.5	-67.7
-2.5 °C/min, DI Water	11.6	-9.0	-9.6	-134
-2.5 °C/min, Pepper's Ferry/WWTP Effluent	10.9	-6.9	-7.8	-193
-2.5 °C/min, Topeka, KS/WTP Lime Sludge	9.7	-4.0	-4.4	-161
-2.5 °C/min, SiO <sub>2</sub> Slurry	10.0	-6.6	-7	-106
-1 °C/min, DI Water + SiO <sub>2</sub>	1.9	-13.1	-13.3	-65.4
-2 °C/min, DI Water + SiO <sub>2</sub>	1.9	-12.9	-13.1	-44.1
-2 °C/min, HPLC Water	0.5	-24.3	-24.5	-274
-2 °C/min, HPLC Water	3.7	-20.1	-20.5	-45.9

Notes:

1. HPLC Water is a high purity water supplied by Fisher Scientific for precision instrument calibration and sample dilution.
2. DI Water is deionized/distilled water.
3. Onset temperature, peak minimum, and peak integral values are for the exothermic response measured by the differential scanning calorimeter upon the freezing of the free (unbound) water.

### *Rapid Exothermic Response/Differences in Peak Integral Values*

As indicated previously, repeated tests on the PE DSC instrument showed that it was able to control the cooling rate quite well until the point that the sample free water fraction froze. Thereupon, the instrument could not adequately (completely) record the exothermic reaction due to the fairly quick freezing action. However, the instrument was able to adequately track the endothermic reaction of the melting free water fraction. The peak integral value of the freezing exotherm (heat of fusion) was usually much lower than that of the melting endotherm although they should have been similar by theoretical definition.

These observations are illustrated in Figure 19 (previously presented, on the heating cycle for the Zion WTP alum sludge) and Figures 26, 27, and 28. All four figures indicate a sudden, sharp drop below the baseline on the cooling cycle (near -7°C for the alum sludge in Figure 19, -4°C for the Topeka WTP lime sludge in Figure 26, -19°C for the distilled water sample in Figure 27, and -13°C for the sample of distilled water with SiO<sub>2</sub> added in Figure 28).

Table 14 summarizes selected data on the peak integral values for both the exotherm on freezing and the endotherm on melting of various water and sludge samples. While the differences ranged from as low as 3 to a maximum of 75%, the bulk of the tests indicated that under most of the experimental conditions studied, the difference in the two enthalpic responses was between 30-50%. While the peak integral values of the exotherm were always lower than that of the endotherm, there appeared to be no consistent relationship in the results. However, as discussed in the previous section, there may be some indication that the impurities present in the WTP and WWTP samples could slow down the rapid exothermic process in the freezing of the free water fraction to allow the DSC instrument to measure the exotherm more accurately.

A review of the literature indicates that other researchers have also reported similar problems with respect to the rapid exothermic response not being measured

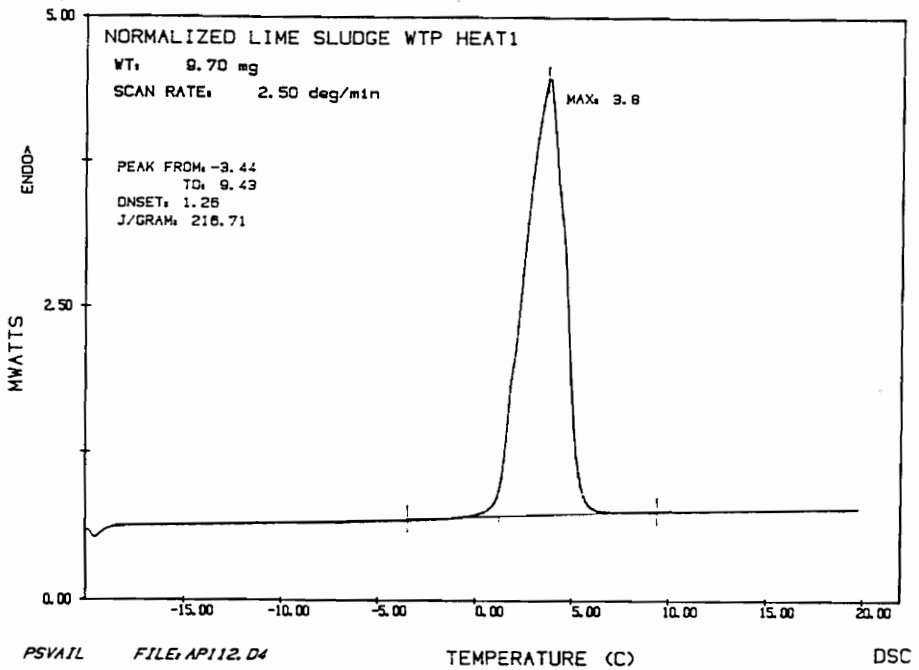
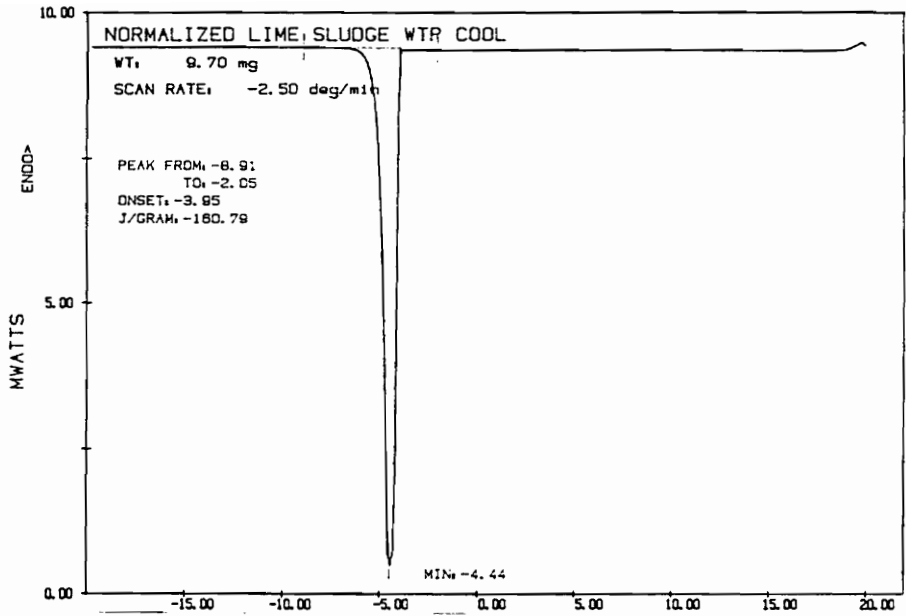


FIGURE 26: DSC PLOT OF ENTHALPIC CHANGES FOR WTP LIME SLUDGE SHOWING SUPERCOOLING EFFECT

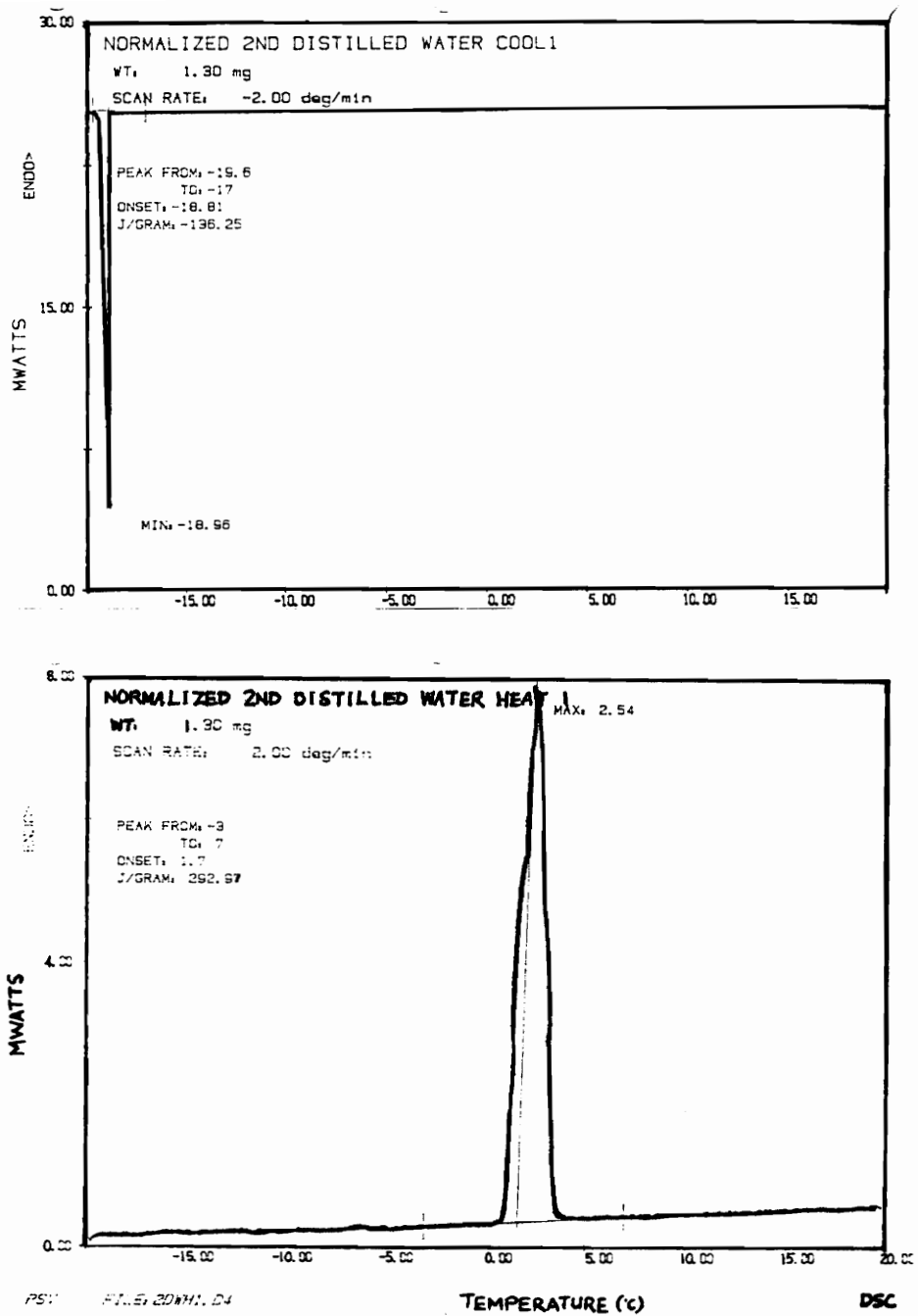


FIGURE 27: DSC PLOT OF ENTHALPIC CHANGES FOR DISTILLED WATER SHOWING SUPERCOOLING EFFECT



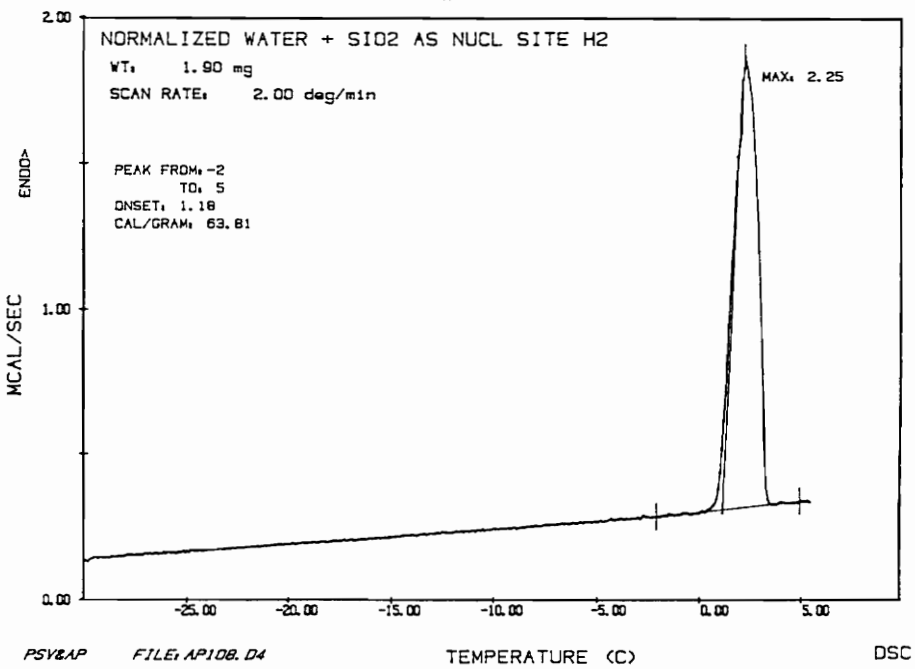
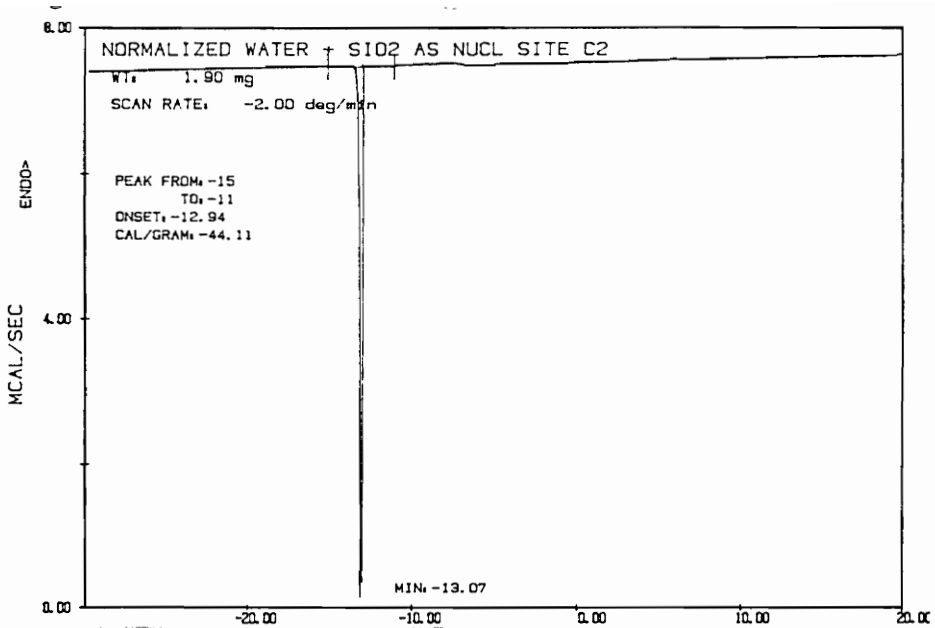


FIGURE 28: DSC PLOT OF ENTHALPIC CHANGES FOR DISTILLED WATER WITH  $\text{SiO}_2$  ADDED AS NUCLEATING SITES SHOWING SUPERCOOLING EFFECT

**TABLE 14**  
**SUMMARY OF OBSERVED ENTHALPY CHANGES UPON FREEZING**  
**AND THAWING OF VARIOUS SAMPLES**

<u>Sample</u>	<u>Cooling or Warming Rate Used (°C/min) +</u>	<u>Dry Solids Content (%)</u>	<u>Total Water Content (g/g)</u>	<u>Cool Cycle PI<sub>cool</sub></u>	<u>Warm Cycle PI<sub>warm</sub></u>	<u>Percent Difference (%) *</u>
DI Water	1.0	NA	NA	106	306	65
DI Water	2.0	NA	NA	101	309	67
DI Water	2.0	NA	NA	77.7	310	75
DI Water	2.5	NA	NA	134	286	53
WTP Alum Sludge	1.0	11.1	8.0	220	243	7
WTP Alum Sludge	2.0	11.1	8.0	127	238	47
WTP Alum Sludge	2.5	11.1	8.0	161	217	26
WWTP poly-cond. sludge	1.0	6.8	13.7	277	297	6
WWTP belt-press. sludge	1.0	16.6	5.0	205	214	4
WWTP belt-press. sludge	2.5	16.6	5.0	224	231	3
WWTP effluent water	2.5	<0.1	>1000	193	334	42
SiO <sub>2</sub> -water Slurry	2.5	22.4	3.5	106	118	11
CaCO <sub>3</sub> -water Slurry	2.0	24.5	3.1	96.3	266	64
Al(OH) <sub>3</sub> ppt. Slurry	2.0	0.4	249.0	90.3	325	72

Notes:

Total water content calculated from % dry solids

NA = not applicable

DI Water = Deionized/Distilled Water

WTP = water treatment plant

WWTP = wastewater treatment plant

PI<sub>cool</sub> = Peak Integral of the exotherm on the cooling cycle

PI<sub>warm</sub> = Peak Integral of the endotherm on the warming cycle

\* Percent Difference =  $(PI_{warm} - PI_{cool}) / PI_{warm} \times 100$

+ Rate of cooling or warming used by the instrument (PE Differential Scanning Calorimeter)

completely by the DSC instrument since it was first developed in 1964<sup>26,70,96</sup>. As indicated previously, more sophisticated instruments are being developed that may be better able to measure the exothermic process on cooling of water or other materials<sup>77</sup>.

### *Other Issues*

Tests were also conducted on a limited number of samples to observe any responses (i.e. development of exothermic or endothermic peaks) when the sample temperature was decreased all the way to -40 °C. Certain investigators<sup>3,94</sup> observed an additional peak (for clay samples) would sometimes form at between -30 to -40 °C, probably indicating the presence of some portion of the bound water fraction. The lower limit of the PE DSC instrument was close to -40 °C as the refrigerant was freon. Testing of the Zion WTP alum sludge and Pepper's Ferry WWTP belt-pressed bio-solids samples with the PE DSC did not produce evidence of any additional bound water peaks.

Tests on samples of centrifuged alum sludge formulated in the laboratory using the PL DSC down to -50 °C (see Figure 29) also did not indicate the presence of any additional peaks. This may be due the relatively low amount of bound water present, thereby making it difficult for the instrument to measure such small amounts, i.e. the values could be below the minimum detection limits of this particular instrument. However, for the sludges tested and the two DSC instruments used, no evidence of secondary, low-temperature bound water peaks could be found.

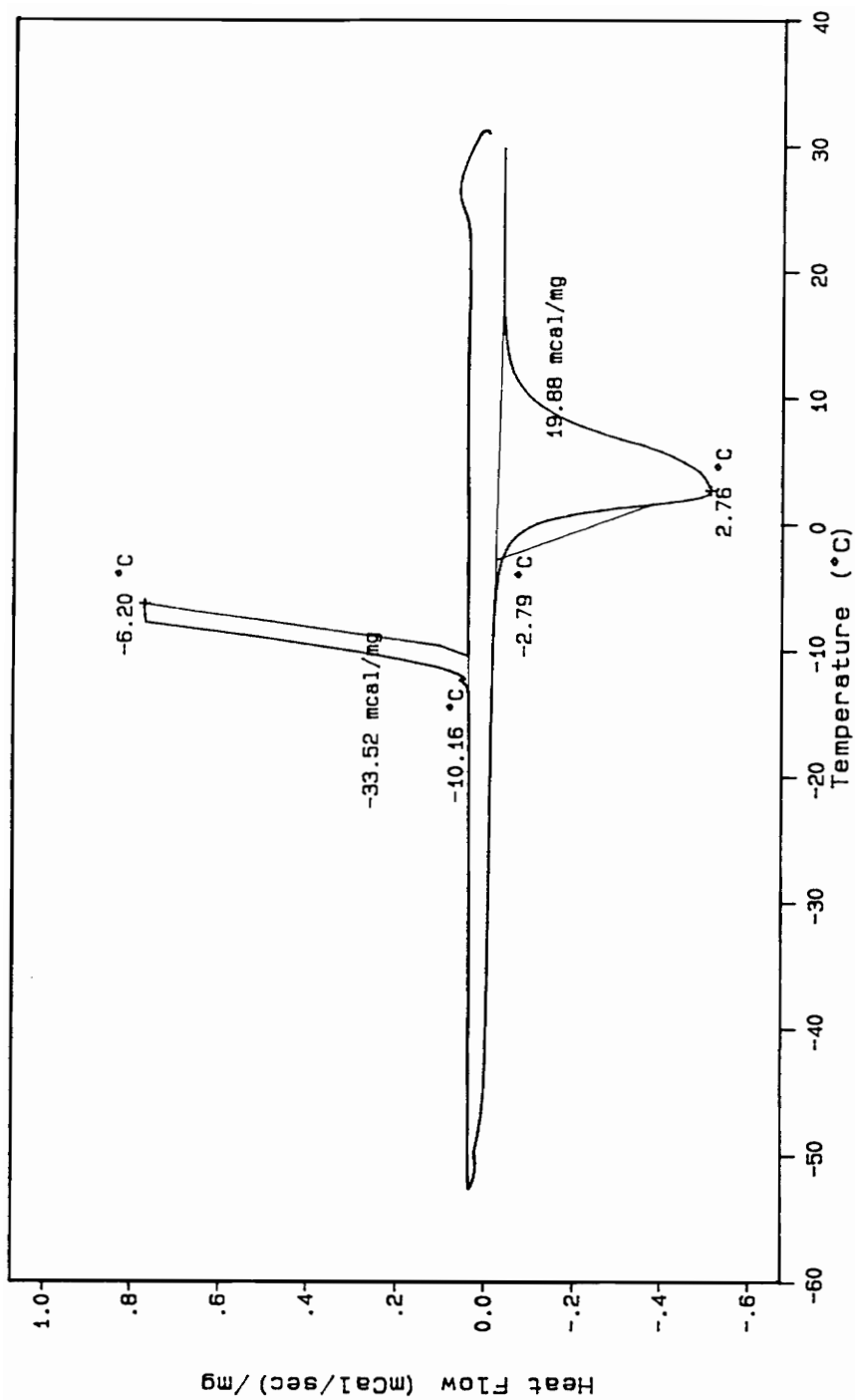


FIGURE 29: DSC PLOT FOR SAMPLE OF CENTRIFUGED LABORATORY ALUM SLUDGE IN TEMPERATURE RANGE 30 °C TO -50 °C

## **Effect of Replicate Testing**

In order to further develop the experimental protocol for use of the DSC as a moisture characterization technique, a limited number of tests were conducted to determine the effects of replicate tests on the same sample. The tests would help determine whether the average value of all the peak integrals thereby obtained could be used to determine the average bound water content for that particular sample. In addition, the tests could also be used to determine the effect of repeated cooling (freezing) and warming (thawing) cycles upon the same sludge sample due to concern that the unbound water fraction ice crystal(s) could enlarge over time to rupture and release floc or cell bound water. This could conceivably affect the sludge water distribution values as the additional frozen water fraction(s) may be incorrectly measured as a portion of the total unbound (or free) water fraction.

Table 15 is a compilation of testing undertaken specifically on one such sample, the Zion WTP alum sludge. The data show that the endothermic response on the melting of the free water fraction for the sample is fairly reproducible up to and including the fifth cycle. Values of peak integrals (as well as onset temperatures and peak maximums) were consistent, and it was only beyond these five cool-warm cycles that there were some observed changes. However, the slight decrease in the peak integral values of the endotherms upon replicate testing leads to an incremental decrease in the free water fraction, or conversely, an increase in the amount of bound water. The reason for this phenomena is difficult to explain satisfactorily, and could easily be within the experimental error of the analytical method.

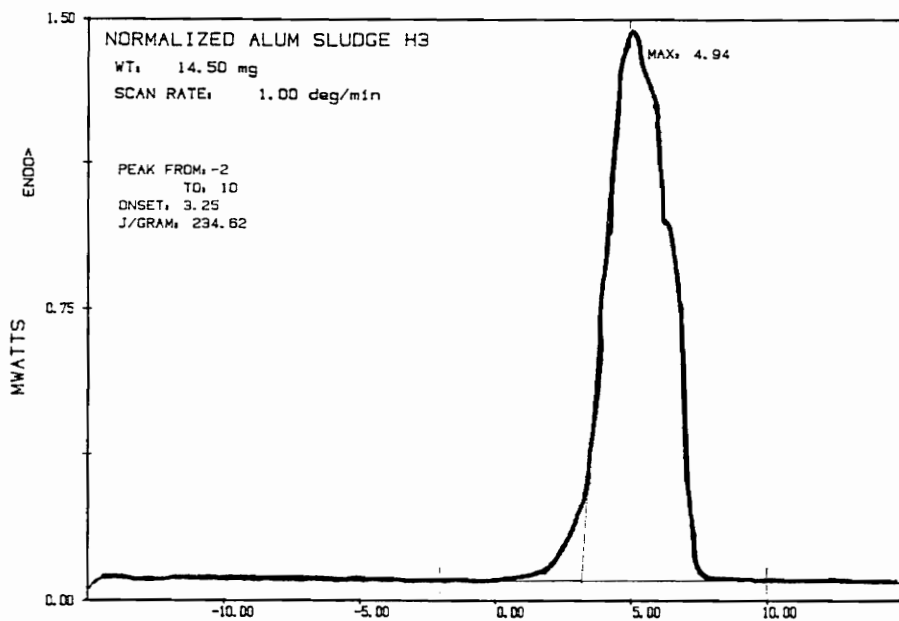
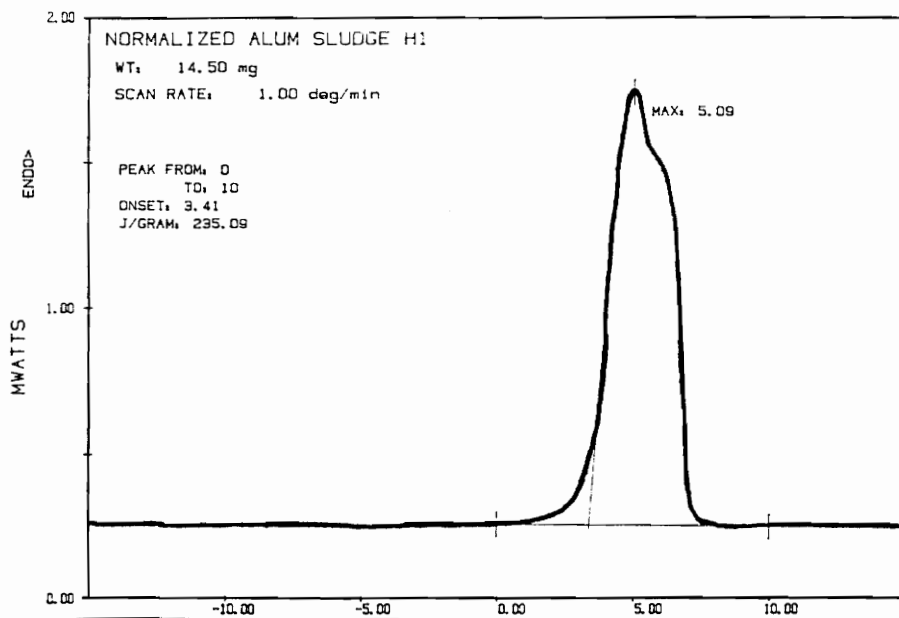
Although the peak integral values reported do not appear to be significantly different, the plots from the DSC indicated that some changes were occurring after the third replicate cycle. This is shown in Figures 30A and 30B, which compares four of the seven plots. The information from this DSC instrument was not transferable to an ASCII format that would allow it to be edited and redrawn in one graph. The plots for the first three cool-warm cycles were similar. However, the fourth cycle

**TABLE 15**  
**SUMMARY OF VALUES FROM REPLICATE DSC TESTING**  
**OF ZION WTP ALUM SLUDGE**

<u>Cycle</u>	<u>Peak Maximum (°C)</u>	<u>Onset Temperature (°C)</u>	<u>Peak Integral (J/g)</u>	<u>Calculated Bound Water (g/g-DS)</u>
First	5.1	3.4	235.1	0.6
Second	5.0	3.3	235.2	0.6
Third	4.9	3.3	234.6	0.6
Fourth	5.0	3.3	234.3	0.6
Fifth	5.0	3.3	234.2	0.6
Sixth	7.1	4.1	232.4	0.7
Seventh	7.1	4.2	231.2	0.7

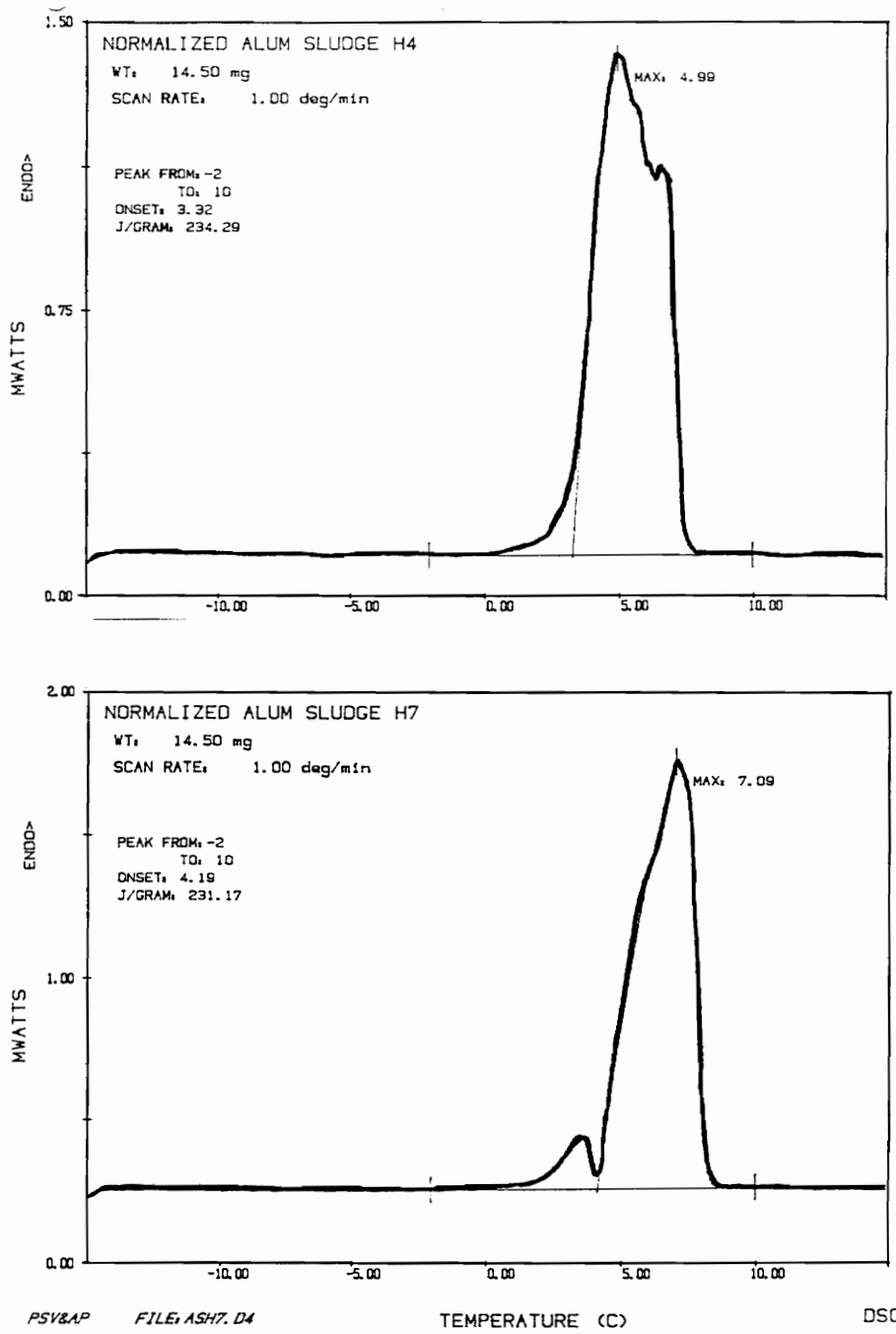
Test Conditions: Cooled and warmed at 1°C/minute  
Temperature Range: 20°C to -20°C, and vice versa  
Results reported are for the warming conditions (endotherm)  
Sample Size: 14.5 mg  
Dry Solids Content: 14.6%, thus Total Water = 5.8 g/g-DS.

Peak integral value of distilled water at similar test conditions was 306.2 J/g.  
Peak integral values reported above to four significant numbers to show the measured incremental changes recorded by the Perkin-Elmer Differential Scanning Calorimeter.



PSV&AP FILE: ASH3.D4 TEMPERATURE (C) DSC

FIGURE 30A: ENDOTHERMS FROM REPLICATE COOL-WARM CYCLES OF ZION ALUM SLUDGE SHOWING CHANGES IN MORPHOLOGY (1ST AND 3RD COOL-WARM CYCLES)



**FIGURE 30B: ENDOTHERMS FROM REPLICATE COOL-WARM CYCLES OF ZION ALUM SLUDGE SHOWING CHANGES IN MORPHOLOGY (4TH AND 7TH COOL-WARM CYCLES)**



began to exhibit development of additional "shoulders". The morphology of the endothermic response from this point on began to change and by the time of the seventh replicate cool-warm cycle, a second, albeit smaller, peak was visible.

It is believed that the observed changes in the peak morphology could be due to the macromolecular structures of the amorphous ice crystals that were formed due to replicate freeze-thaw cycles<sup>73</sup>. The size of a water molecule is typically 5Å; upon crystallization, the macromolecular ice structure can be tens to a hundred or more Å across. Due to replicate cycles, the sludge particle matrix could break down (as evidenced by freeze-thaw tests using the dilatometric method discussed in the following chapter) to smaller, more granular particle. These act as available nucleating sites for the onset of crystallization on the freezing cycle and create various amorphous (and oftentimes) macromolecular structures<sup>73</sup>. On the warming cycle, these crystals begin to melt and are measured as the unbound fraction. However, the crystals do not all begin to thaw at the same time, thus leading to the observed shoulders and changes in the morphology. Since the amount of bound water was small to begin with, there appeared to be very little release of the bound fraction for the Zion WTP alum sludge.

Replicate freeze-thaw tests on a dewatered (centrifuged) sludge with larger bound water fractions appeared to lend credence to the above observation. The sample used was the alum sludge synthesized in the laboratory while the calorimetric method utilized a more recent PL DSC. The instrument was able to detect changes in both the morphology and the peak integral values of this sludge. The results are shown as a plot of the four replicate freeze-thaw cycles in Figure 31A. Figure 31B presents a magnified view of the melting endotherms, since the exotherms were subject to the supercooling effect and not completely measurable. The peak integral values of the endotherms are presented in Table 16. Unlike the previous two instruments, the PL DSC was able to generate the information in one file, hence the superimposed plot as shown in Figure 31.

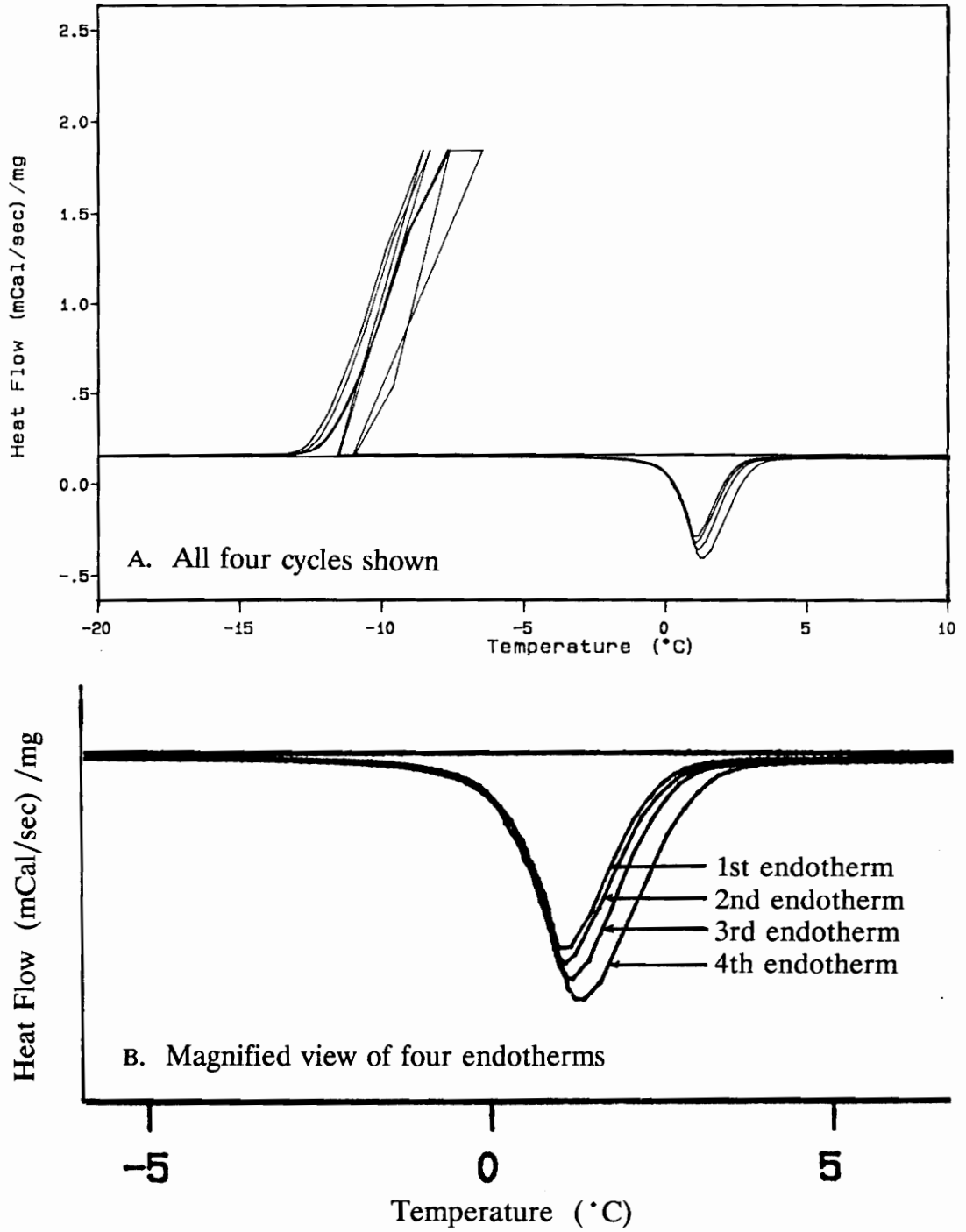


FIGURE 31: REPLICATE FREEZE-THAW CYCLES ON ALUM SLUDGE SYNTHESIZED IN LABORATORY USING POLYMER LABORATORIES DSC

**TABLE 16**  
**CHANGES IN MOISTURE DISTRIBUTION OF ALUM SLUDGE SYNTHESIZED IN**  
**LABORATORY DUE TO REPLICATE FREEZE-THAW CYCLES**  
**USING POLYMER LABORATORIES DSC**

<u>Cycle</u>	<u>Peak Integral (mcal/mg)</u>	<u>Total Water (g/g-DS)</u>	<u>Bound Water (g/g-ds)</u>	<u>Unbound Water (g/g-DS)</u>
First	19.95	4.68	3.10	1.58
Second	21.29	4.68	2.99	1.69
Third	24.88	4.68	2.71	1.97
Fourth	31.71	4.68	2.02	2.66

As can be observed, the bound water fraction progressively decreased from 3.1 to 2.0 g/g-DS, leading to a corresponding increase in the unbound water due to the replicate freeze-thaw cycles. There was little decrease in the bound water fractions from the first to the second cycles. However, the decrease was larger by the fourth cycle. The dry solids concentration of this centrifuged sludge was 17.6% while the sample size was 5.5 mg.

Replicate tests on a polymer conditioned bio-solids sample appear to exhibit similar changes in the endothermic responses up to and including the third cool-warm cycle, including a slight broadening of the base of the peak, as shown in Figure 32. However, these changes appear minor in comparison to the previous two chemical sludges.

It is believed that replicate freeze-thaw cycles on the polymer conditioned sludges were not disruptive enough to cause the changes in moisture distribution observed in the unconditioned chemical sludges discussed previously. Additional cycles could conceivably affect the sludge matrix.

Table 17 is a compilation of a series of replicate tests for both the Zion WTP alum sludge and Pepper's Ferry WWTP bio-solids to determine the percent standard deviation (error) within each set of cool-warm cycles per sample. As can be seen, the standard error was small (averaging less than 0.4% standard error for three or more replicate cool-warm tests). The average peak integral values of these experiments appeared to indicate that such tests were reproducible up to three cool-warm cycles.

Table 18 summarizes the testing to determine the variation (or percent error) in the average peak integral values of various samples tested. Here two or more sample pans were prepared from the same sludge sample and tested in the DSC under similar test conditions (e.g. scanning rates of 1 or 2 °C/minute) for only one cool-warm cycle to compare their enthalpic values. For most of the samples tested, the standard deviation was within the limits of experimental error (<5%).

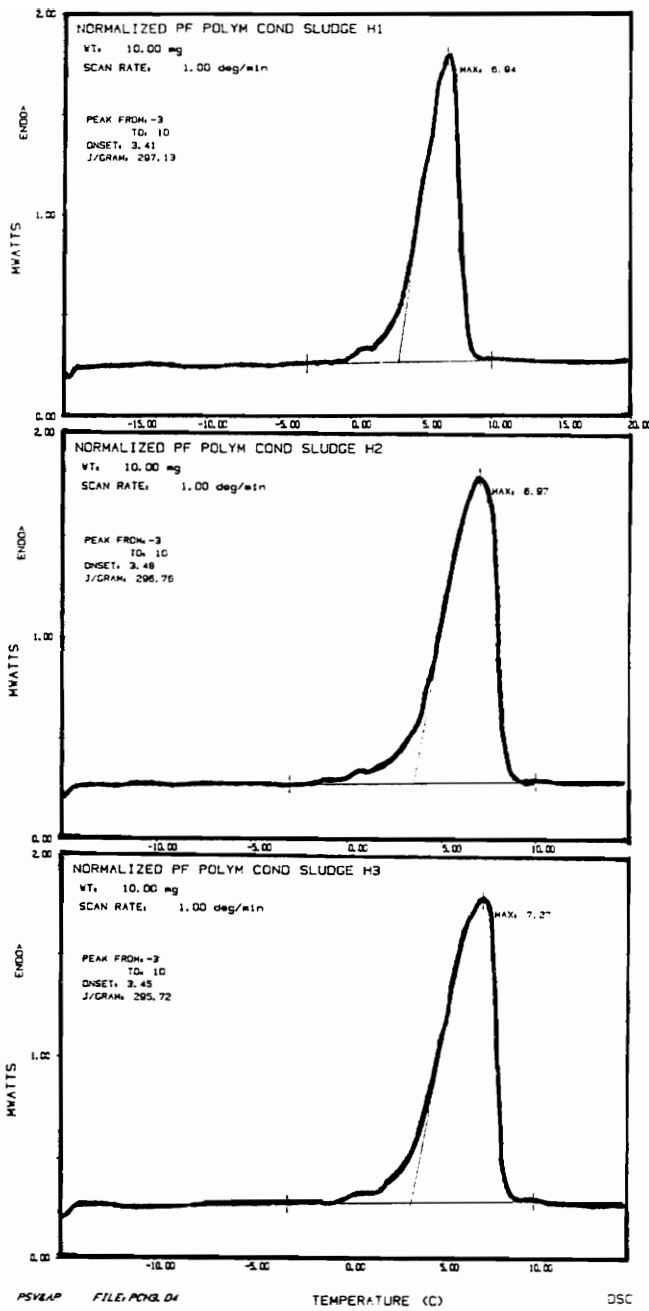


FIGURE 32: ENDOTHERMS FROM REPLICATE COOL-WARM CYCLES OF POLYMER-CONDITIONED BIO-SOLIDS SAMPLE

TABLE 17

SUMMARY OF TESTS ON TWO DIFFERENT SLUDGES USING THE DSC TO DETERMINE PERCENT ERROR WITHIN EACH SET OF REPLICATE SAMPLES

<u>Sample Used and Size (mg)</u>	<u>Peak Integral (J/g)</u>	<u>No. of Cool-Warm Cycles</u>	<u>Average (J/g)</u>	<u>Standard Deviation</u>	<u>Percent Error</u>
<b>Zion WTP Alum Sludge</b>					
3.6	315.4				
<u>3.6</u>	<u>313.8</u>	<u>2</u>	<u>314.6</u>	<u>0.8</u>	<u>0.3</u>
2.4	258.4				
2.4	256.4				
<u>2.4</u>	<u>256.5</u>	<u>3</u>	<u>257.1</u>	<u>0.9</u>	<u>0.4</u>
4.6	292.7				
4.6	293.1				
<u>4.6</u>	<u>292.4</u>	<u>3</u>	<u>292.7</u>	<u>0.3</u>	<u>0.1</u>
3.9	315.2				
3.9	313.7				
<u>3.9</u>	<u>312.8</u>	<u>3</u>	<u>313.9</u>	<u>1.0</u>	<u>0.3</u>
14.5	235.1				
14.5	235.2				
14.5	234.6				
14.5	234.3				
14.5	234.2				
14.5	232.4				
<u>14.5</u>	<u>231.2</u>	<u>7</u>	<u>233.8</u>	<u>1.4</u>	<u>0.6</u>
2.6	243.3				
2.6	243.7				
<u>2.6</u>	<u>240.2</u>	<u>3</u>	<u>242.4</u>	<u>1.6</u>	<u>0.7</u>
<b>Pepper's Ferry WWTP Sludge</b>					
<i>Polymer-Conditioned</i>					
5.1	296.5				
<u>5.1</u>	<u>295.5</u>	<u>2</u>	<u>296.0</u>	<u>0.5</u>	<u>0.2</u>
10.0	297.1				
10.0	296.8				
<u>10.0</u>	<u>295.7</u>	<u>3</u>	<u>296.5</u>	<u>0.6</u>	<u>0.2</u>
<i>Belt-Pressed Cake</i>					
5.2	213.5				
<u>5.2</u>	<u>215</u>	<u>2</u>	<u>214.3</u>	<u>0.7</u>	<u>0.3</u>
2.8	234.2				
2.8	229.4				
<u>2.8</u>	<u>228.2</u>	<u>3</u>	<u>230.6</u>	<u>2.6</u>	<u>1.1</u>
9.2	213.9				
9.2	213.3				
<u>9.2</u>	<u>214.0</u>	<u>3</u>	<u>213.7</u>	<u>0.3</u>	<u>0.1</u>

**TABLE 18**  
**SUMMARY OF TESTS USING THE DSC TO DETERMINE PERCENT ERROR**  
**WITHIN EACH SET OF SAMPLES**

<u>Sample Used and Size (mg)</u>	<u>Peak Integral (J/g)</u>	<u>No. of Samples</u>	<u>Average (J/g)</u>	<u>Standard Deviation</u>	<u>Percent Error</u>
<b>Zion WTP Alum Sludge</b>					
2.4	258.4				
2.5	237.7				
14.5	235.1				
2.6	243.3	4	243.6	9.0	3.7
<b>Pepper's Ferry WWTP Bio-Solids</b>					
<i>Polymer-Conditioned</i>					
5.1	296.5				
10.0	297.1	2	296.8	0.3	0.1
<i>Belt-Pressed Cake</i>					
5.2	213.5				
2.8	234.2				
9.2	213.9	3	220.5	9.7	4.4
<b>CaCO<sub>3(s)</sub>-Water Slurry</b>					
2.6	283.6				
2.2	265.5	2	274.5	9.1	3.3
<b>Lab Al(OH)<sub>3 (ppt)</sub> Slurry</b>					
2.4	347.6				
4.7	324.7				
4.0	317.9				
2.2	311.1	4	325.3	13.8	4.2

From the above sets of tests, the experimental protocol developed included only one sample cycle (i.e. cooled to -20 °C then warmed to 20 °C, at 2 °C/minute) to avoid any potential degeneration of the thermal response (with respect to the morphology of the enthalpic response) and corresponding error in determining the amount of bound water that may be initially present. Three samples (i.e. triplicates) of each sludge were tested under the same test conditions, to yield three bound water values. The average value of bound water could then be determined.

## **Experimental Protocol Developed**

### **Overview**

The following sections present the methodology developed for each of the three different instruments used in the study on the basis of the various tests conducted and described above. This is followed by a description of the relationship used to determine the amount of bound water in the samples tested, using the peak integral value obtained from the endotherm of the sample. Results of moisture characterization studies using the DSCs based on the experimental protocol developed are presented in the following chapter.

### **Specific Protocol for DSC Instruments Used**

As indicated previously, the two differential scanning calorimeters used for a major portion of this study were: (i) a Du Pont/TA Instruments 2910 unit with the Thermal Analyst 2000 (DP DSC) and (ii) a Perkin-Elmer DSC 4 with the System 4 Thermal Analysis Controller (PE DSC).



In addition, a limited number of tests were conducted on a third (and more recent) instrument, the Polymer Laboratories DSC PLus V (or PL DSC). For all instruments, nitrogen was used as the purge gas. A variety of test conditions were used to determine that most applicable to each specific instrument. Since the devices differed in their instrumentation, configuration, and method of use, separate methodologies had to be developed for each instrument. The final experimental protocol for each instrument is presented on the following pages.

### *Du Pont Differential Scanning Calorimeter*

For the DP DSC, the sample size was between 20 to 30 mg. After various iterations and experimentation, the typical methodology adopted was as follows:

The sample was placed in an aluminum pan, weighed, covered, and placed in the DSC cell. A manual cooling can filled with dry ice (solid CO<sub>2</sub> from the Chemistry Stockroom in Hahn Hall) was placed on top of the unit, and the cell was allowed to cool to -20 °C (or lower as required for the specific test condition). The can was then removed, the DSC cover unit and bell jar were then placed on top of the cell, and the DSC set to the test conditions. For most of the experiments the test conditions were: 1 minute isothermal at -20 °C, controlled heating at 1 (or 2) °C/minute to 20 °C, isothermal for 1 minute at 20 °C, then ramped at 5-10 °C/minute to 150 °C to drive off all the moisture, finally isothermal for 1 minute at 150 °C. The data were then saved onto the instrument computer interface/central processing unit (CPU) hard drive, and the unit cooled to room temperature by removing the bell jar and the DSC cover unit, and placing the manual cooling can filled with cold water on top of the DSC cell. The sample pan was removed and weighed upon

cooling. Percent dry solids and total water initially present could then be computed for the sample.

#### *Perkin-Elmer Differential Scanning Calorimeter*

For the PE DSC, the methodology was simpler as this unit had a controlled cooling capability. The methodology used was as follows:

The sample size was 2-10 mg. A sample was placed in an aluminum pan, weighed and hermetically sealed. The pan was placed in the DSC unit, allowed to stay isothermal at 20°C for 1 minute, then cooled at 1 (or 2) °C/minute to -20°C (or lower). The data were then saved onto the instrument CPU. After 5 minutes, the DSC was set to warm at 1 (or 2) °C/minute to 20°C, and the data again saved. Concurrent with the DSC tests, dry solids content (following the *Standard Methods*<sup>1</sup> procedure of drying in a 105±2°C oven) of samples from the same set of sludges being analyzed, were determined.

#### *Polymer Laboratories Differential Scanning Calorimeter*

A third DSC, manufactured by Polymer Laboratories (PL-DSC PLus V model), was used in the final stage of the research in an effort to determine if some of the results observed using the previous two DSCs could be duplicated on a different and much more recent machine, especially that of the depression of the freezing point of water ("super-cooling" effect, as discussed previously) and the effect of replicate cooling/warming cycles. For this instrument:

The sample size could be as large as 20 mg (for the dewatered bio-solids samples, with lower amounts of free water). A sample was placed in an aluminum pan, weighed and hermetically sealed. The pan was then placed in the DSC cell, and the tests conditions desired were keyed into the computer controller interface connected to the instrument. A total of 14 different instructions could be stored on the interface which would collect and store the data automatically. The instrument was usually set at 30 °C isothermal for 1 minute, cooled at 2 °C/minute to -30 °C/minute (or lower). This was followed by an isothermal setting of -30 °C for 1 minute and ramped at 2 °C/minute to 30 °C. The sample was finally allowed to stay for 1 minute isothermal. Dry solids content was determined separately using *Standard Methods*<sup>1</sup>.

### **Moisture Characterization Using the DSC**

As discussed previously, since all three DSC instruments tested could not accurately measure the complete exotherm of the freezing free water fraction on the cool cycle, the free water fraction in the sludge sample was determined by comparing the response of the melting endotherm on the warm cycle to that of distilled/deionized water samples.

Bound water was determined by subtracting the measured amount of free water from the total water (measured by drying overnight a similar sludge sample in a 105±2 °C oven, *Standard Methods*<sup>1</sup>) in the sludge sample. Dividing by the mass of dry solids present in the sludge would provide the amount of bound water in g/g-DS. The relationship presented on the following page was used to calculate the amount of bound water in the sludge:

$$BW = \frac{[T_{\text{sludge}} - (T_{\text{sludge}} \times \%DS/100)] - [T_{\text{sludge}} \times PI_{\text{sludge}} / PI_{\text{water}}]}{DS} \quad [22]$$

where:

BW = Bound Water, in g/g-DS

$T_{\text{sludge}}$  = Total Sludge, i.e. sample of sludge used, in g

%DS = Percent dry solids (of the sludge, determined separately)

$PI_{\text{water}}$  = peak integral value for a sample of deionized/distilled water under the same set of experimental conditions,

$PI_{\text{sludge}}$  = peak integral value for the sludge sample used, and

DS = dry solids of the sludge sample used, in g

$$= T_{\text{sludge}} \times \%DS / 100$$

The average value of  $PI_{\text{water}}$  (or heat of fusion or melting of water) from a number of different sets of tests of the warming cycle from -20 °C to 20 °C at 2 °C/minute was determined to be 307.6 J/g (with a standard deviation of 16.6, or percent error of 5.4%). This value is similar to that obtained and used by Antonsen and Hoffman<sup>7</sup> recently for their work on determining bound water in polyethylene glycol, i.e.  $H_{\text{water}} = 307$  J/g using a Seiko DSC 100 model instrument. The value reported for the heat of fusion (melting) of water in the *CRC Handbook*<sup>55</sup> is 334 J/g. While this served as a reference value, the bound water determinations for each set of sludges were based on the measured  $PI_{\text{water}}$ .

### Recommendations for Use of the Differential Scanning Calorimeter Technique

The DSC and the TGA share one common drawback: these two instruments can only analyze small sample sizes that may not truly represent the non-homogeneous sludge sample. However, both instruments do allow data to be

collected efficiently in a well-controlled environment, and collect sufficient data for more accurate analysis of these results. These advantages nevertheless do come at a greater price, as these instruments typically cost from \$25,000 to more than \$50,000.

For moisture characterization, the capability of the DSC to measure enthalpy changes from the freezing or melting of the free water fraction is utilized. In this study, it was found that all the three DSCs evaluated could not accurately measure the rapid exothermic reaction when the free water present in a sample froze. The instruments were, however, able to measure the melting endotherm in a reproducible manner.

In addition, it was found that in all three instruments, the freezing point of the free water was well below 0 °C. This initially perplexing phenomenon was eventually determined to be due to the small sample sizes, and was found to have been referred to in the literature as the *super-cooling effect*. The super-cooling effect tends to significantly lower the freezing point of the "free" water as the sample size is reduced. Cloud chamber experiments cited in the literature<sup>6</sup> using purified/distilled water have been able to show a fairly linear relationship between decreasing sample size with reduced freezing temperature up to about -38 °C. For the current study, quantitative measurements of the fractions of water present could still be made once the sample free water froze, usually by around -20 °C. Wunderlich<sup>97</sup> also indicated that supercooling effects could not be avoided and that most instruments could not accurately measure the rapid exotherm when water froze. The author also suggested that it was much more reproducible to analyze the heating curves instead of the cooling curves<sup>97</sup>.

The following experimental protocol is recommended for sludge sample moisture characterization studies:

- (a) The DSC instrument should be capable of carrying out tests at controlled sub-ambient temperatures down to -30 °C, preferably with freon or liquid nitrogen as the coolant.

- (b) Instrument baseline calibrations using appropriate standards to check/set the temperature and enthalpy readings then need to be conducted. The standards chosen should encompass the temperatures to be tested at. Suggested standards could include indium (m.p. 156 °C) and anhydrous dimethylacetamide (DMAC, m.p. -20 °C).
- (c) The appropriate sample sizes to be used have to be determined, as samples that are too large, or have greater amounts of free water, tend to overwhelm the enthalpic response of the instrument.
- (d) Depending on the nature of the purging system in the DSC cell as well as the sludge itself, sample pans should be hermetically sealed or just covered. The latter arrangement allows one to determine the actual dry solids (and thus the initial total water/moisture content) by ramping the instrument to 150 °C or more, and weighing the sample after it has cooled down. If feasible, the sample pan could be punctured and the pan dried at  $105 \pm 2$  °C in a separate oven. It can also be determined by dry solids analysis (*Standard Methods*<sup>1</sup>) of a similar sample, although both methods could introduce some degree of uncertainty due to the non-homogeneous nature of sample placed in the pan.
- (e) The instrument testing can then begin by subjecting the sample (as well as distilled water) to the test conditions. Typically these may be: cooled from 20 °C to -20 °C at 2 °C/minute, then isothermal for 1 or 2 minutes, and warmed at 2 °C/minute from -20 °C to 20 °C, then isothermal for 1-2 minutes. The peak integral of the melting endotherm then needs to be determined and the free water fraction is obtained by a relationship similar to equation 22.
- (f) The melting endotherm peak integral value is recommended for determining the unbound water fraction as it was found that the freezing exotherm values were neither appropriate, accurate, nor reproducible, due to the inability of the DSC instruments used to measure this calorimetric change. This was determined to be due to the rapid exothermic process/supercooling effect discussed previously.

Once the appropriate settings have been determined and the instrument baseline calibrations have been completed, samples can begin to be analyzed. A number of tests on distilled water are recommended at the beginning and end of each series of experiments to determine the measured enthalpy value of the melting of water (this measured value is typically between 305 - 310 J/g, while the theoretical value for the heat of fusion of water is 334 J/g). Testing can then be carried out for the matrix of sludge samples.

In addition, the instrument computer interface should allow the user to download data files for additional analyses. This provision was not available in older instruments, but due to increasing demand from the scientific community, has lately become a standard feature.

The technique is quite reproducible and accurate (percent standard error of peak integrals for replicate samples ranged from <1 to <5%, while that for the calculated bound water values ranged from 8 to 11%). However, the standard error of calculated bound water values increased to about 44% when samples with very low bound waters (e.g. WTP and inorganic sludges) were tested. Thus, while moisture distribution for most bio-solids can usually be determined, inorganic sludges with low bound waters (maybe only the chemically bound sub-fraction at  $\leq 0.2$  g/g-DS) were determined to be below the minimum detection limit of the instruments evaluated.

## **CHAPTER 5**

### **RESULTS**

#### **INTRODUCTION**

The research reported herein specifically investigated the characterization of moisture distribution in a variety of sludges, using a number of techniques that were deemed applicable to the matrix of sludges chosen. The sequence of experiments began by applying the drying rate curve technique using the TGA (thermogravimetric analyzer), and investigating the moisture distribution profiles of a specific sludge upon chemical and mechanical dewatering.

Thereupon, moisture characterization experiments were undertaken using the DSC (differential scanning calorimeter) and the Dilatometer techniques, utilizing the property that unbound and bound waters freeze at different temperature ranges. The term unbound (instead of free) may be more appropriate for sludge moisture characterization studies since it is an implied antonym of the bound water. In addition, and more importantly, the unbound water fraction appeared to include portions of the interstitial water (as well as the bulk of the free water) and other fractions that are presumably not tightly bound to the sludge particle matrix per se.

The effects of sludge conditioning methods such as polymer and freeze-thaw conditioning on moisture distribution were also investigated. Finally, other sludge characteristics including specific surface areas of the dry particles and density measurements (bulk and floc) were determined.

The previous chapter presented results of the development of the experimental protocol for the application of two moisture characterization techniques (TGA and DSC). This chapter presents results of the experimental work undertaken (in chronological sequence) using these two techniques and the dilatometric method for moisture distribution as well as additional sludge characterization studies.



The following chapters discuss these findings, attempt to interpret as well as correlate results from the various moisture distribution studies and the sludge characterization experiments performed, and draw specific conclusions from the overall study reported herein.

## **THERMO-GRAVIMETRIC ANALYZER / DRYING RATE CURVE METHOD**

### **Results of Moisture Distribution Data for Various Sludges**

Table 19 is a compilation of data from TGA/drying rate curve experiments for a variety of sludges using the experimental protocol described in the previous chapter. Each datapoint reported in this table (and similar tables that follow) is the synthesized result of at least three graphs/figures from both the TGA and data downloaded from the TGA computer interface which was then analyzed by spreadsheet/graphical software. For much of the data, the values reported represent the mean or range of values for three samples, i.e. triplicates.

As indicated in the previous chapter, dry solids concentration (or content) data are presented in % while the moisture/water distribution data are presented in g/g-DS. In addition, the total water present was determined from the dry solids concentration and the amount of unbound water was obtained by subtracting the bound water fraction from the total water. The notes at the bottom of the table are self-explanatory. The effect of chemical and mechanical conditioning on the sludges tended to obscure inflection point(s) due to loss of the horizontal regime of the constant rate curve. This phenomena has been addressed in Chapter 4.

As shown in Table 19, bio-solids have more associated bound waters compared to inorganic samples (including WTP sludges). This is due to the nature of the sludge particles and is discussed at greater length in Chapter 6.

**TABLE 19**  
**MOISTURE DISTRIBUTION DATA FOR A VARIETY OF SLUDGE**  
**SAMPLES DETERMINED BY THE TGA/DRYING RATE METHOD**

<u>Sludge</u>	<u>Dry Solids (%)</u>	<u>Total Water</u>	<u>Unbound Water</u>	<u>Bound Water</u>		
				<u>Chem. Bound</u>	<u>Other Bound</u>	<u>Total Bound</u>
<b>Zion WTP Alum</b>						
Unconditioned	11.1	8.0	7.4	0.1	0.5	0.6
Polymer-conditioned **	18.0	4.6	3.5	<0.1	1.0++	1.1++
Lab twin belt-pressed **	45.6	1.2	0.3	<0.1	0.8	0.9
<b>Aurora WWTP Bio-Solids (anaerobically digested)</b>						
Unconditioned	3.6	26.5	21.0	0.1	5.4	5.5
Belt-pressed	19.9	4.0	2.8	0.1	1.1	1.2
<b>Springbrook WWTP Bio-Solids (aerobically digested)</b>						
Unconditioned	2.8	34.7	25.9	0.3	8.5	8.8
<b>SiO<sub>2</sub>-Water Slurry</b>						
Unconditioned	24.0	3.2	2.8	0.1	0.3	0.4

Notes:

1. Dry solids concentration determined in percent dry solids (%DS)
2. Total Water (TW) expressed in g/g-DS and determined from above %DS value as  $TW = (100 - \%DS) / (\%DS)$
3. Unbound Water (UW) expressed in g/g-DS and determined from the first inflection point following the constant drying rate curve. Conversely, the Total Bound Water (BW) is the fraction remaining, or  $BW = TW - UW$ .
4. Chemically Bound Water (CBW) expressed in g/g-DS and determined by the difference in mass from constant weights at 250°C and 40°C.
5. Other Bound Water =  $TW - (UW + CBW)$ .
- \*\* Polymer-conditioned samples were also free-drained, hence removing a greater portion of the unbound water with a corresponding increase in dry solids concentration. In addition, these drying rate curves did not have the classic horizontal regime (i.e. they were sloping/curved), making the inflection point difficult to determine in a reproducible manner.
- ++ An increase in bound water may have been observed in some samples due to the polymer-water-alum sludge particle floc structure that was formed upon chemical conditioning.

Additional Data specific to the above sludges are presented separately in later tables.

## **Chemically Bound Water Fraction**

Table 19 presented the moisture distribution data for a variety of sludges including the chemically bound water (a fraction of the total bound water as defined previously). As can be seen, for all the sludges tested, the chemically bound water fraction ranged from below 0.1 to 0.3 g/g-DS. This amount was consistent and reproducible for each type of sludge, and defined for this study as that fraction (a sub-set of the total bound water) removed when the sample was dried to 250 °C.

In general, the inorganic and WTP sludges reported lower bound water (and corresponding the chemically bound fraction) than the bio-solids. The Zion WTP alum sludge had low amounts of bound water (<1.0 g/g-DS) of which the chemically bound fraction was less than 10% (<0.1 g/g-DS). For the anaerobically digested wastewater treatment sludge from the Aurora WWTP, this chemically bound fraction was determined to be 0.15 g/g-DS. Only one test was conducted on the Springbrook WWTP sludge, reporting 0.3 g/g-DS. Tests on the SiO<sub>2</sub>-water slurries reported bound water of 0.4 g/g-DS while the chemically bound fraction was between 0.1 to 0.2 g/g-DS.

The chemically bound fraction in WTP alum sludge and SiO<sub>2</sub>-water slurries represented between 15 to 50% of the total bound water (due to the low amounts of the latter), whereas this sub-fraction was much smaller for the bio-solids (as the total bound water associated with the bio-solid particles was significantly larger).

## **Moisture Distribution in Bio-Solids**

Table 20 presents the results of the TGA-drying curve method developed above for bio-solids from the Aurora WWTP. The bio-solids were dewatered in order to remove the bulk of the unbound water (except when determining the moisture distribution specifically for unconditioned samples where so reported).

**TABLE 20**  
**MOISTURE DISTRIBUTION DATA USING TGA/DRYING RATE CURVE METHOD**  
**FOR ANAEROBICALLY DIGESTED BIO-SOLIDS FROM AURORA WWTP**

<u>Condition of Sludge Sample</u>	<u>Percent Dry Solids</u>	<u>Moisture Distribution (in g/g-DS)</u>			
		<u>Unbound *</u> <u>Water</u>	<u>+</u>	<u>Bound</u> <u>Water =</u>	<u>Total</u> <u>Water</u>
Unconditioned	3.2	22.0		8.3	30.3
Belt-pressed at plant	19.9	2.8		1.2	4.0
Gravity thickened at lab	3.6	24.8		1.7	26.5
Polymer-conditioned and free drained at lab	7.0	11.2		1.7	12.9
Vacuum-dewatered at lab	11.0	6.4		1.3	7.7

Therefore, the results presented for the amount of unbound water are what remained after the supernatant or filtrate containing the additional unbound (typically considered the free or bulk water fraction in the literature) had been removed.

As can be seen, the unconditioned/undewatered sample reported 8.3 grams of bound water per gram dry solids (initial solids concentration was 3.2% for this sludge). After conditioning, the bound water fractions for the above bio-solids reduced to between 1.3 to 1.7 g/g-DS. Vacuum filtration produced the highest cake solids concentration due to the applied pressure, and thus had the lowest amount of both bound and total water. It should be noted that the majority of the water remaining after chemical conditioning and mechanical dewatering was still considered to be unbound water (including the free or interstitial water fractions typically referred to in the literature).

### **Moisture Distribution in Chemical and Water Treatment Sludges**

Most of the tests were conducted on the artificially formulated silicon dioxide slurries (made by adding distilled water to Min-U-Sil 30) and the Zion WTP alum sludge. The data for the alum sludge at three different settings/conditions are presented in Table 21. These included the 40 °C isothermal setting, and two ramped conditions, at 5 and 10 °C/minute, to evaluate whether the faster ramped settings could be used instead of the isothermal setting (discussed in the previous chapter) to determine bound water in this predominantly inorganic sludge. A quicker sample test time would allow for greater numbers of samples to be tested, an important factor for the determination of changes in moisture distribution characteristics of this type of sludge upon chemical and mechanical dewatering. The data indicated that the results were not significantly different at the three different settings. Thus subsequent tests on the alum sludge, as it was chemically conditioned and mechanically dewatered, were conducted using the ramped conditions.

**TABLE 21**  
**BOUND WATER DATA FOR ZION ALUM SLUDGE THROUGH TWIN BELT PRESS**  
**AT VARIOUS TEMPERATURE SETTINGS USING TGA/DRYING RATE METHOD**

<u>Condition of Sludge Sample</u>	<u>Sludge Bound Water Content (g/g-DS)</u>					
	<u>Isothermal at 40°C</u>		<u>Ramped at 5°C/min</u>		<u>Ramped at 10°C/min</u>	
	<u>Range</u>	<u>Avg</u>	<u>Range</u>	<u>Avg</u>	<u>Range</u>	<u>Avg</u>
Gravity Thickened	0.6 - 1.0	0.8	0.5 - 0.8	0.7	0.5 - 1.0	0.8
After Free Drainage/ Gravity Zone	0.2 - 0.5	0.4	0.2 - 0.7	0.4	0.4 - 1.0	0.6
After Wedge Zone Dewatering	0.2 - 0.3	0.3	0.2 - 0.3	0.3	0.2 - 0.4	0.3
After S-1 Roller Dewatering	0.2 - 0.3	0.2	0.2 - 0.3	0.2	0.2 - 0.3	0.2

For the Zion WTP alum sludge, various chemical conditioning experiments were first performed to determine the floc structure that would best resist shear from the TBP (twin belt press) simulator (Chapter 3 presented details on the TBP) and prevent passage through the belt/cloth. The screening tests (using 0.2% equal active polymer solutions in free drainage tests) appeared to indicate that lower mole charge anionic polymers were more effective than the more widely used cationic polymers. The latter appeared to require twice the dose of corresponding anionic polymers, although they did appear to increase slightly the free drainage volume. After determining the optimum chemical conditioning requirements, the conditioned sludge was placed on the free drainage (gravity zone) tray, the wedge zone tray placed on top and the wedge press applied. The sludge was then sent through the S-1 roller of the continuous pressure filter press. The "profile" of the bound water was then determined as the sludge passed through these components of the TBP.

Table 22 presents results of additional experiments on the Zion WTP alum sludge after chemical conditioning and mechanical dewatering using the TBP. As can be seen, there was some release of the bound water due to chemical conditioning followed by mechanical dewatering up to and including the S-2 roller. Additional passes through the S-rollers did not seem to release much more water, and the corresponding percent solids concentration remained fairly constant at around 49%.

Some of the minor variances (within 3%) in the data reported may have been due to errors introduced while removing and analyzing these samples. Moreover, one needs to be reminded that the data presented herein is specific to the sludge being tested and the dewatering sequence undertaken for the particular sludge. The observed increase in unbound (and total) water as well as the decreased solids concentration after polymer conditioning was due to the addition of dilution water.

The data from the previous two tables indicate that most of the water removal for the Zion WTP alum sludge was in the polymer-conditioning/gravity/wedge-zone press regions (the dry solids concentration increased from 14% to about 41%). There was also some significant water loss after the second S-roll, increasing the dry

**TABLE 22**  
**MOISTURE DISTRIBUTION PROFILE OF ZION ALUM SLUDGE USING**  
**TGA/DRYING RATE METHOD UPON CHEMICAL CONDITIONING**  
**AND MECHANICAL DEWATERING THROUGH TWIN BELT PRESS**

<u>Condition of Sludge Sample</u>	<u>Dry Solids Content (%)</u>	<u>Moisture Content (g/g-DS)</u>		
		<u>Unbound Water</u>	<u>Bound Water</u>	<u>Total Water</u>
Gravity Thickened	14.2	5.2	0.8	6.0
After Polymer Conditioning *	7.3 *	12.0 *	0.7	12.7 *
After Free Drainage	22.9	3.1	0.3	3.4
After Wedge Zone Tray	38.0	1.3	0.3	1.6
After S-1 Roller	41.1	1.2	0.3	1.5
After S-2 Roller	48.0	0.8	0.3	1.1
After S-3 Roller	48.4	0.9	0.3	1.2
After S-4 Roller	49.8	0.8	0.3	1.1
After S-5 Roller	49.2	0.9	0.2	1.1

**Notes:**

- \* denotes that dilution water had been added to optimize conditioning. Thus the amount of unbound and total water increased with a corresponding decrease in the dry solids concentration.

Moisture distribution data determined by setting TGA to ramp at 5° C/minute.



solids to about 48%. Subsequent S-rolls did not seem to remove much of the remaining bound water as the final cake solids was near 49%.

The data are also presented in Figure 33 as a drying rate curve profile (with the TGA set to ramp at 5 °C/minute) of the sludge as it was chemically-conditioned and mechanically dewatered through the TBP. Data in Figure 34 also show the water distribution/release profile of a similarly conditioned sludge using the TGA set to ramp at 10 °C/minute. The profiles are very similar, though the drying rates are obviously higher at the higher ramped settings. The 5 °C/minute ramped setting seemed to provide slightly better resolution of the drying rate curve profiles. In addition, the two figures indicate that the water removed was predominantly the unbound water (which includes the free and interstitial water fractions as discussed in the beginning of this chapter). While the measured unbound and some bound water fractions appear slightly different due to the increased heating rates, the trends in both cases are similar. The relative changes in water distribution in the alum sludge show that the smaller bound water fraction is not much affected by passage through the S-rollers.

## **DIFFERENTIAL SCANNING CALORIMETER**

### **Results of Moisture Characterization Studies Using DSC**

#### **Bio-Solids**

A limited number of tests were conducted on the Pepper's Ferry WWTP bio-solids using both the DP (Du Pont) and PE (Perkin-Elmer) DSCs (following the experimental protocol developed in the previous chapter) and comparing concurrently with the dilatometric method. These are summarized in Tables 23 and 24. As can be seen, both DSCs provided bound waters lower than measured by the

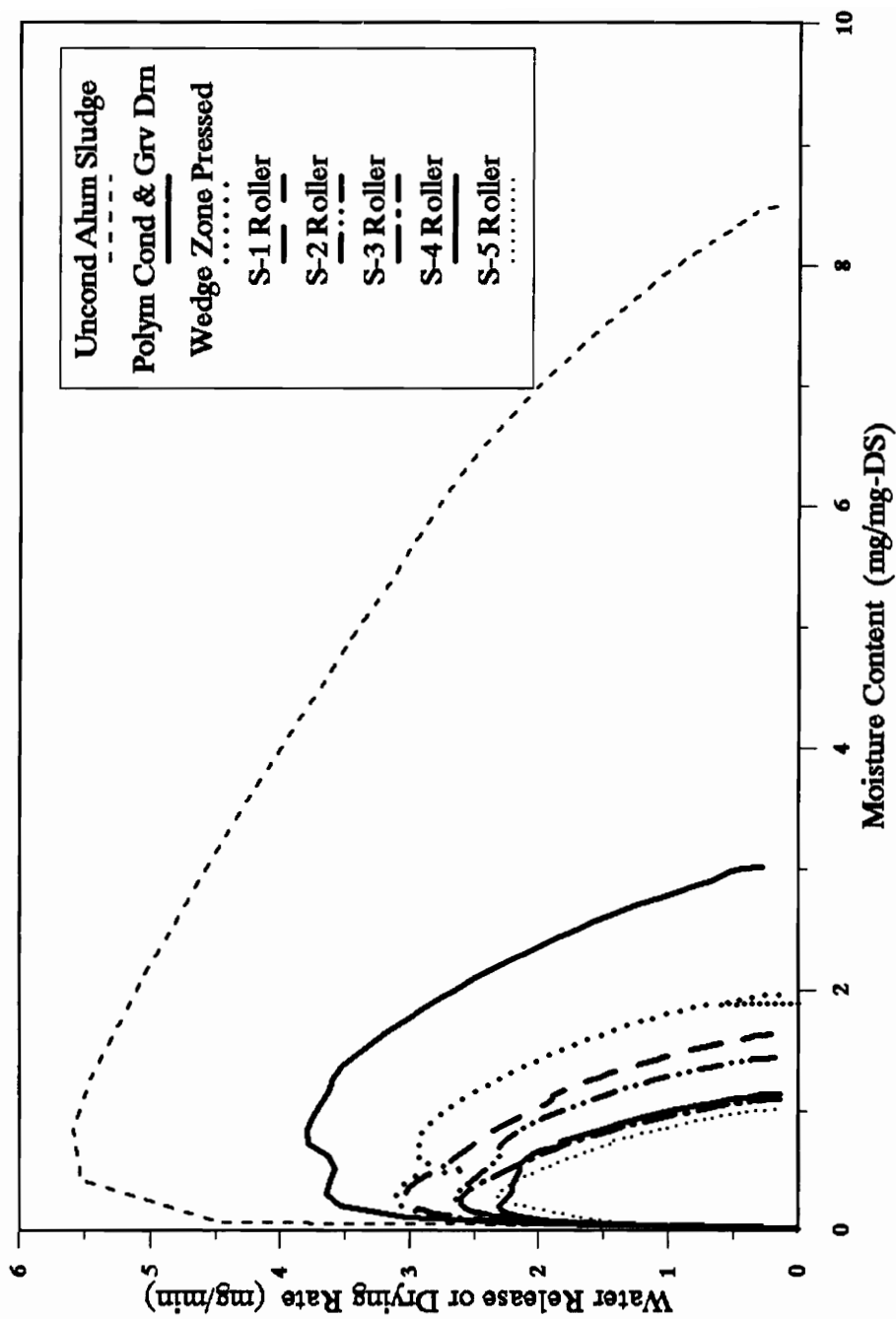


FIGURE 33: MOISTURE DISTRIBUTION PROFILE OF CONDITIONED ALUM SLUDGE USING TGA/DRYING RATE CURVE METHOD AT 5 °C/MINUTE RAMPED SETTING

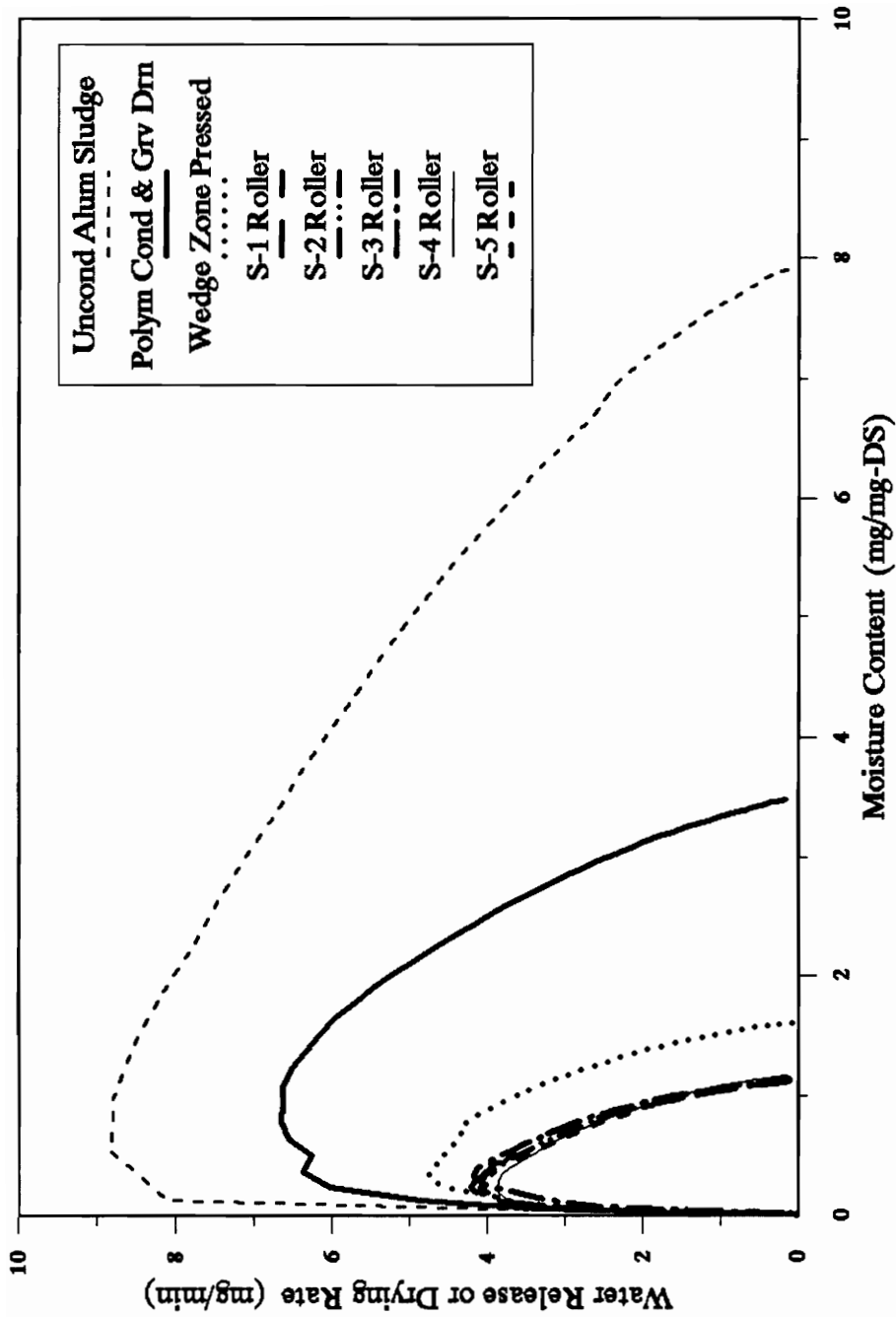


FIGURE 34: MOISTURE DISTRIBUTION PROFILE OF CONDITIONED ALUM SLUDGE USING TGA/DRYING RATE CURVE METHOD AT 10 °C/MINUTE RAMPED SETTING

**TABLE 23**  
**COMPARISON OF SELECTED MOISTURE CHARACTERIZATION STUDIES OF BIO-SOLIDS USING DSCs (DIFFERENTIAL SCANNING CALORIMETERS) AND DILATOMETER**

<u>Sample</u>	<u>Dry Solids (%)</u>	<u>Bound Water (g/g-DS)</u>		
		<u>Avg</u>	<u>Std Dev</u>	<u>n</u>
<i>a. Perkin-Elmer DSC set at 2 °C/minute from -20 °C to 20 °C</i>				
Unconditioned	2.5	2.7	0.4	3
Polymer-cond.	1.8	0.8	0.1	5
P-C & Belt-pressed	13.4	1.3	0.1	3
<i>Comparison with Dilatometer</i>				
Unconditioned	2.5	12.3	0.9	3
Polymer-cond.	1.8	4.3	0.6	3
P-C & Belt-pressed	13.4	1.6	0.2	3
<i>b. Du Pont DSC set at 2 °C/minute from -20 °C to 20 °C</i>				
Polymer-cond.	8.2	1.6	0.1	3
P-C & Belt-pressed	16.5	1.8	0.4	5
<i>Comparison with Dilatometer</i>				
Unconditioned	2.8	16.2	0.4	3
Polymer-cond.	8.2	4.5	0.2	3
P-C & Belt-pressed	16.5	2.4	0.2	3
<i>c. Polymer Laboratories DSC set at 2 °C/minute from -25 °C to 25 °C</i>				
P-C & Belt-pressed	12.6	1.0	0.2	2
<i>Comparison with Dilatometer</i>				
P-C & Belt-pressed	12.6	1.5	0.3	3

Sample Used: Pepper's Ferry wastewater treatment plant anaerobically digested sludge samples.

The abbreviations used above are:

- Unconditioned - sample used as is without any form of conditioning
- Polymer-cond. - polymer-conditioned at the plant, collected prior to the gravity zone of the belt-press mechanical dewatering device
- P-C & Belt-pressed - polymer-conditioned and mechanically dewatered using the belt-press at the plant

**TABLE 24**  
**BOUND WATER VALUES FOR ADDITIONAL BIO-SOLIDS**  
**DETERMINED USING DIFFERENTIAL SCANNING CALORIMETRY**  
**AND DILATOMETRIC TECHNIQUES**

<u>Sample</u>	Dry Solids <u>(%)</u>	Bound Water Content <u>(g/g-DS)</u>	
		<u>DSC</u>	<u>Dilatometer</u>
<i>Screw Press Trial Tests of Pulp and Paper Mill Sludge:</i>			
Unconditioned digested sludge	4.0	4.4	15.1
RST Solids - optimum polymer dose	8.1	1.5	11.4
Screw Press - optimum polymer dose	41.1	0.6	1.0
RST Solids - less than optimum dose	8.4	1.0	nc
Screw Press - less than optimum dose	36.6	0.5	nc
RST Solids - more than optimum dose	14.7	0.5	nc
Screw Press - more than optimum dose	38.5	1.2	nc
<i>Pepper's Ferry WWTP Anaerobically Digested Sludge</i>			
Unconditioned digested sludge	2.8	2.4	16.2
Polymer conditioned	8.2	1.6	4.3
Belt-pressed cake solids	16.5	1.8	2.4

**Notes:**

RST Solids refer to the polymer-conditioned pulp & paper mill sludge after passing through the rotary screen thickener and prior to the screw press.

Du Pont DSC used for the calorimetric technique

nc = Dilatometric test was not conducted for this sample

dilatometric method. A limited set of tests using the PL (Polymer Laboratories) DSC also showed similar differences in bound water values between this device and the dilatometer. As the sludge was conditioned and the dry solids content progressively increased, the differences in bound water values reported by the two methods began to reduce. The bound water values reported for the belt-pressed cake solids seemed to be closer.

Some of the discrepancy could be due to the non-homogeneity of the samples as well as the very small sample amounts used in the DSC (when compared to the dilatometer) sample pan. In addition, as addressed in a later section, lower values could also be due to inherent background noise in the instrument or minimum detection limit considerations. The discrepancy in the two moisture characterization techniques (both relying on the property of bound water to remain unfrozen at temperature as low as  $-20^{\circ}\text{C}$ ) is also discussed further in the following chapter.

Bio-solids in general tend to have significantly larger amounts of associated waters, due to their organic structure, constituent cell composition, water-binding mechanisms, floc characteristics, etc. The relatively larger sample sizes (10-25 g) used in the dilatometer was more representative of the nature of the sludge per se, whereas the much smaller (1-10 mg) sample sizes required for DSC analysis could have captured "snapshots" or the micro-aspects of a small portion of the sludge matrix. This was even more so for sludges that were longer and more fibrous in nature, such as that from the pulp and paper mill sludges.

The variability also increased when the sample was not homogeneous or where there could be discrete flocs separated by bulk waters that would freeze and "swamp" out the DSC instrument responses. However, the relative trends in the reduction of the bound water fractions as the sludge passed through the various conditioning operations were somewhat similar for both methods.

## Chemical and WTP Sludges

Table 25 summarizes the findings of tests using both the PE DSC and the dilatometer for selected sludges. Due to the relatively lower amounts of bound water in these inorganic sludges, both the DSC and the dilatometer have not been able to quantify accurately the amounts present. Only the Zion WTP alum sludge appeared to provide a measure of the bound water at between 0.2 to 0.6 g/g-DS using the PE DSC. However, this value could not be determined by the dilatometer. In many instances, as indicated in Table 25, the values reported appeared to be below the minimum detection limit of the two analytical techniques.

Undewatered samples of  $\text{Al}(\text{OH})_3$  (alum) slurries prepared in the laboratory appeared to have large amounts of bound water associated with the very small amount (in percent dry solids) of the precipitates present in the solution as determined by the dilatometric method. However, the PE DSC could not measure the amount of bound water present. This could have been because the total water associated with the dry solids was very high (250 g/g-DS) and there could have been a large amount of unbound water in the sample that froze fairly easily by  $-20^\circ\text{C}$ . The ice crystals thus formed could conceivably have ruptured the alum sludge floc structure, causing the "bound" water in the sludge to freeze. The DSC measurement of the endothermic response on the melting of this large fraction of water would then include the bound fraction (measured by the dilatometer on the freezing cycle) and thus the amount of bound water remaining may have fallen below the detection limit of the instrument.

Moisture distribution using dewatered (centrifuged) samples of the same slurry was determined using the PL DSC and showed that the amount of bound water measured by this device was 3.1 g/g-DS, while that by the dilatometric method was 5.6 g/g-DS. The dry solids content of this sludge was 17.6%; thus, the bound water fraction increased to 66% of the total water associated with this dewatered sludge sample, and this relatively large fraction was measurable by the PL DSC.

**TABLE 25**  
**COMPARISON OF MOISTURE CHARACTERIZATION STUDIES ON INORGANIC WATER TREATMENT PLANT AND CHEMICAL SLUDGES USING DSC AND DILATOMETER**

<u>Sample</u>	<u>Dry Solids Content (%)</u>	<u>Average Bound Water</u>		
		<u>(g/g-DS)</u>	<u>Std. Dev.</u>	<u>n</u>
<i>Values obtained using the PE DSC</i>				
Zion WTP Alum Sludge	8.2	0.2	0.01	3
Zion WTP Alum Sludge	14.6	0.6	0.02	3
Lab CaCO <sub>3</sub> Slurry	22.6	< DL	-	3
Lab SiO <sub>2</sub> Slurry	21	< DL	-	3
Lab Al(OH) <sub>3</sub> (ppt) Slurry	0.4	< DL	-	6
Lab Al(OH) <sub>3</sub> (ppt) Centrifuged +	17.6	3.1 +	<0.01 +	2
<i>Comparison with Dilatometer</i>				
Zion WTP Alum Sludge	8.2	< DL	-	3
Zion WTP Alum Sludge	14.6	< DL	-	3
Lab CaCO <sub>3</sub>	22.6	0.2	0.05	3
Lab SiO <sub>2</sub>	21	< DL	-	3
Lab Al(OH) <sub>3</sub> (ppt) Slurry	0.4	38.3	3.1	3
Lab Al(OH) <sub>3</sub> (ppt) Centrifuged	17.6	5.6	1.6	2

**Notes:**

- < DL Below the Detection Limit of the instrument. The instrument was not able to measure the amount of bound water present in the sample. It is estimated that these values could be less than 0.2 g/g-DS.
- + This value was determined using the Polymer Laboratories DSC. All other DSC bound water determinations used the Perkin Elmer DSC.



Thus, by initially removing the bulk of the unbound water from such samples, the PL DSC instrument was able to provide measurable values of the bound water fraction remaining. Values reported by the DSC and the dilatometer appeared to be closer when dewatered samples were analyzed. This observation is discussed in a later section.

## **DILATOMETRIC TESTS**

### **Overview**

The matrix of sludges and the underlying principle of the Dilatometric technique were essentially similar to that of the DSC discussed in the previous chapter. In addition, the effects of freeze-thaw conditioning and polymer/chemical conditioning on bound water using the dilatometric test characterization procedure were also investigated. Larger size (volume) dilatometers were fabricated and used in an effort to better define the relatively smaller bound water fractions that may be present in inorganic (WTP and chemical) sludges.

### **Moisture Characterization of Bio-Solids**

The data have been presented in the previous section (see Tables 23 and 24). As can be seen, the bio-solids evidently had larger amounts of bound water present. The profile of a typical bio-solid sludge appeared to indicate that the bound water fraction was reduced when the sludge was conditioned chemically and mechanically dewatered. For instance, tests on different samples of the Pepper's Ferry wastewater treatment plant anaerobically digested sludge showed that the initial unconditioned sludge usually contained between 10 to 16 g/g-DS of bound water (with dry solids

concentration of approximately 3%). Upon chemical/polymer-conditioning, this value decreased to around 4 g/g-DS with a corresponding increase in the dry solids concentration to between 2 and 8% (the larger variation in values of dry solids concentration were due to the difficulty in drawing a fairly homogenous and representative sample). Thereupon, after mechanical dewatering (belt press), the bound water decreased to between 1.5 and 2.5 g/g-DS, with an increase in cake dry solids to between 13 and 17 %.

Limited tests on the pulp and paper mill sludges (essentially organic in nature) also appeared to exhibit this general tendency, i.e. a decrease in the bound water content from 15 g/g-DS for the initial unconditioned sludge down to 1 g/g-DS for the dewatered sludge (with a corresponding increase in dry solids concentration following mechanical dewatering). In this case, the mechanical dewatering device was a much more powerful screw press (which, due to the fibrous nature of the sludge, allowed for much better dewatering performance). The higher pressure generated within the screw press could theoretically expel a greater portion of the unbound and some bound water fractions.

### **Moisture Characterization of Chemical and WTP Sludges**

The results were also presented in the previous section (Table 25). In most cases, the relatively small amounts of bound water could not be detected by the instrument, although larger capacity dilatometers were used. Most of the test results obtained indicated that the amounts present were below the detection limit of the technique used. Use of dewatered samples (e.g. as obtained after centrifuging) appeared to remove much of the unbound water and the dilatometer could begin to measure the bound water fraction remaining. The results did appear to indicate that the amounts of bound water were very low as have been observed by other investigators<sup>79,80,82,89</sup>.

Thus, the dilatometric investigations continued to focus on the characterization of moisture in bio-solids and study the effect of sludge conditioning by freeze-thaw as well as polymer-conditioning.

### **Effect of Replicate Freeze-Thaw Cycles on Moisture Distribution**

As indicated previously, the dilatometric method relied on the property of the unbound (or free) water to freeze and expand, thereby providing a measure of the amount of bound water initially present. The bound water fraction is theorized not to freeze at the operating temperatures used for the technique. An investigation was undertaken to determine if the bound water measurement could be affected by freezing and the subsequent thawing at different cooling and warming rates. The rationale was similar to that discussed in the previous chapter with regard to replicate freeze-thaw tests using the DSC. The growing ice crystals could conceivably rupture the floc and cell structures of bio-solids, thereby releasing additional amounts of bound water that would then freeze and be erroneously measured as a portion of the unbound water. In addition, a limited investigation into the effect of varying the rate of freezing of the dilatometric unit was also undertaken. It should be noted that while it was not possible to determine conclusively whether the first or initial freeze cycle is affected by the freezing of water, it was possible to determine the effects of the rate of cooling as well as replicate freeze-thaw cycles on the same sample.

As indicated in Table 26, the effect of rates of cooling/freezing by the dilatometric method and that by freezing in a commercial freezer (Whirlpool large capacity, set at  $-20^{\circ}\text{C}$ ) were investigated. In the first series of tests, the sludge was placed in the freezer and allowed to freeze overnight. It was removed from the freezer in the morning, allowed to thaw during the day on a laboratory countertop at ambient room temperature, and replaced in the freezer overnight. The procedure was repeated for a total of three such cycles and the final sludge bound water content

**TABLE 26**  
**CHANGES IN BOUND WATER VALUES DUE TO REPLICATE FREEZE-THAW**  
**CYCLES ON BIO-SOLIDS AS MEASURED BY DILATOMETRIC METHOD**

<u>Sludge Sample</u>	<u>Percent Dry Solids</u>	<u>Average Bound Water (g/g-DS)</u>	<u>CST (sec)</u>
<b><i>First Set of Tests:</i></b>			
Raw unconditioned	2.5	11.2	2580
Replicate F-T Cycles in Commercial Freezer, After three overnight cycles	--	1.75	34
Replicate F-T Cycles in Dilatometer, After three 40-minute cycles	--	4.6	310
<b><i>Second Set of Tests:</i></b>			
Raw unconditioned	2.9	6.7	3600
Replicate F-T Cycles in Commercial Freezer, After one overnight cycle	--	0.8	60
Replicate F-T Cycles in Dilatometer, After one 40-min cycle	--	2.1	281
After two 40-min cycles	--	0.5	252
Polymer-conditioned sludge (using 80 lb/ton of PM220)	--	1.3	6
Above polymer-conditioned sludge, Replicate F-T Cycles in Dilatometer,			
After one 40-min cycle	--	1.3	9
After two 40-min cycles	--	0.8	8

**Notes:**

Sample used was Pepper's Ferry Wastewater Treatment Plant anaerobically digested sludge. Freeze-thaw (F-T) cycles used the commercial freezer or dilatometer to cool samples. Thawing was carried out at ambient room temperature on laboratory countertop and typically took up to four hours.

was determined. In a similar manner, sludge was placed in glass dilatometric units, cooled in the ethanol bath at the usual rate of approximately  $-1^{\circ}\text{C}/\text{minute}$  to  $-20^{\circ}\text{C}$  (from  $20^{\circ}\text{C}$ , i.e. total of about 40 minutes freezing/cooling time). The sludge was then thawed at room temperature and cooled again in the same manner for a total of three cycles, and the bound water value was determined. It should be noted that the thawing time was approximately 4 hours for each cycle. Thus, the sludge samples were exposed to freezing conditions for at least 1-2 hours during each combined freezing and subsequent thawing cycle.

In addition, a portion of the sludge samples subject to the same freeze-thaw regime was placed into the CST (capillary suction timer) device to measure the relative dewatering rates.

As can be observed, there appeared to be a significant change in the behavior of the sludge from the replicate freeze-thaw cycles. The dewatering rate (as measured by the CST) improved markedly from about 2600 seconds for the raw unconditioned sludge down to about 35 seconds after three freeze-thaw cycles in the commercial freezer. The bound water was also reduced from 11 to 2 g/g-DS. Similar results (though not as dramatic) were observed from the freeze-thaw cycles in the dilatometer. In addition, the sludges appeared to be more distinct, granular, and flowing more freely (i.e. less viscous). These indicated marked improvements in the dewatering properties of the sludge upon exposure to freeze-thaw conditions, especially at the slower rate in the commercial freezer.

The results presented in Table 26 indicate that there are apparently effects that change the sludge floc when they have been placed through a freeze-thaw cycle. The degree to which these effects are observed (for example, the release of bound water) appear to be a direct function of the amount of time that the sludge remains in a frozen state. Longer contact times (e.g., overnight freezing in a commercial freezer, slower rates of melting promoted by thawing on the bench-top) under sub-zero conditions result in more dramatic changes in bound water content.

There appears to be insufficient conclusive data at this point to suggest that the *initial* dilatometric measurement is biased by the freezing process. The results do indicate that subsequent analysis of the same sample could lead to sources of error due to structural changes in the sludge floc brought about by freezing. Thus bound water determinations using the dilatometric technique/method should use only samples subject to the initial or first freezing cycle at a consistent and relatively quick rate of cooling (possibly not slower than 1 °C/minute).

The behavior of a polymer-conditioned sludge sample that was subject to the same replicate freeze-thaw cycles described above was also determined. The data indicated similar trends in the dewatering behavior upon polymer addition followed by freeze-thawing, even after one such cycle. The limited test on the sludge thus conditioned appeared to indicate that the polymer could have entrapped some of the bound water. The first cycle of freeze-thawing was not disruptive enough to cause release of the bound water fraction. However, the second cycle could have caused the collapse or rupture of the polymer conditioned floc structure, thereby releasing some additional bound water fraction. Bound water amounts reduced from 7 to less than 2 g/g-DS. Polymer-conditioning dramatically improved the dewatering performance and reduced the bound water present in the sludge. In addition, the two freeze-thaw cycles appeared to further reduce the bound water amounts from 1.3 to 0.8 g/g-DS. As indicated above, the slower cooling rate in the commercial freezer appeared to allow for a greater release of the bound water fraction upon subsequent thawing.

An investigation into the effect of polymer-conditioning alone was also undertaken. Three polymers of different mole percent charges were selected for their applicability to the bio-solid sludge. Measurements were made of the bound water fraction and the dewatering characteristic with respect to the CST before and after polymer conditioning. In addition, the effect after polymer-conditioning followed by mechanical dewatering using a low-speed centrifuge (set at 2000 rpm for 15 minutes) upon the bound water fractions was also investigated. As can be seen

in Table 27, the average bound water reduced from about 12 down to 4 g/g-DS before and after polymer conditioning. Polymer conditioning dramatically improved the dewatering performance of the sludge, from greater than 900 seconds down to about 10 seconds. The subsequent process of mechanical dewatering allowed for further release of the bound water fraction.

### **Comparison of Dilatometric Technique to DSC and TGA**

Of the three moisture characterization methods, the dilatometer was the only one that could handle larger sample sizes, thus reducing the variability introduced by smaller non-homogeneous samples. In addition, replicates of similar samples could be tested at the same time, thereby reducing the overall time required to obtain these moisture distribution values. The method is also fairly inexpensive, requiring fabrication of the glass dilatometric cells/units, and expendables such as hydraulic oil (as a measuring fluid), dry ice, and ethanol.

The recommended method has already been described elsewhere<sup>79,80</sup> as well as in Chapter 3. Fabrication of larger (able to hold up to 25 g of samples) did not appear to increase the minimum detection limit for low bound water inorganic sludges. They did, however, reduce the lower limit of the standard error for replicate tests (percent standard error for the larger dilatometers used for this study was between 9-12%, while that reported by Robinson and Knocke<sup>79,80</sup> using the smaller units was 12-13%). The following chapter continues the discussion comparing the three different moisture characterization methods.

**TABLE 27**  
**CHANGES IN BOUND WATER VALUES DUE TO POLYMER-CONDITIONING**  
**OF BIO-SOLIDS AS MEASURED BY DILATOMETRIC METHOD**

<u>Sludge Sample</u>	<u>% Dry Solids</u>	<u>Average Bound Water (g/g-DS)</u>	<u>CST (sec)</u>
Raw unconditioned	2.9	12	2700
Raw, diluted 1:3 with tap water	-	-	955
Raw, after centrifuging and decanting supernatant	5.4	4.4	-
<i>Polymer Conditioning Tests</i>			
10% mole charge (PL210: 140 lb/ton)			
After conditioning	0.8*	4.1	7*
After conditioning & centrifugation	9.5	1.2	-
20% mole charge (PM220: 80 lb/ton)			
After conditioning	0.8*	4.4	10*
After conditioning & centrifugation	9.5	1.5	-
30% mole charge (PM230: 80 lb/ton)			
After conditioning	0.8*	5.8	9*
After conditioning & centrifugation	8.3	3.4	-

**Notes:**

\* indicates that 1:3 dilution with tap water was used for optimum polymer conditioning. This correspondingly decreased the dry solids concentration.

Sample used was Pepper's Ferry Wastewater Treatment Plant anaerobically digested sludge. Chemical conditioning process used various mole percent charge Nalco polymers where so indicated.



## FLOC DENSITY DETERMINATIONS

The step gradient method was used to determine the floc density of water treatment plant sludges and that of the more dense chemical slurries, whereas the continuous gradient method using density marker beads was used for bio-solids. The step gradient method was limited to the highest density achieved by dialysis without compromising the Percoll media; this ranged from 1.24 to 1.28 g/mL. For some of the sludges tested, the floc density was determined to exceed the higher value, and reported likewise. The data are presented in Table 28.

The composite sludge from the unit operations at the Blacksburg WTP (using polyaluminum chloride) was determined to have a floc density of 1.23 g/mL. The mechanically dewatered sludge (upon centrifugation) had a slightly increased value of 1.24 g/mL. The Zion WTP alum sludge was determined to have a floc density of greater than 1.24 g/mL, although some fraction of the sludge floc appeared in the 1.22 g/mL band. The mechanically dewatered sludge was determined to have a value greater than 1.24 g/mL. The SiO<sub>2</sub> and the CaCO<sub>3</sub> slurries made in the laboratories had floc density values exceeding 1.24 g/mL. The laboratory alum sludge was found to have a floc density of 1.18 g/mL, while the mechanically dewatered sludge had a slightly higher density of 1.19 g/mL. Additional step density tests with more concentrated Percoll media indicated that the floc densities for the Topeka WTP lime sludge and the SiO<sub>2</sub> and CaCO<sub>3</sub> slurries may even be higher than 1.28 g/mL.

Floc density determinations using the continuous gradient technique using density marker beads showed that conditioning and subsequent mechanical dewatering the WWTP bio-solids increased the floc density from 1.05 to 1.08 g/mL.

Table 28 also showed the measured bulk densities using the pycnometer and the calculated values of the dry particle densities. As can be seen, mechanical dewatering (using the low-speed swinging-bucket centrifuge usually set at 2000 rpm for 10 minutes) tended to increase the floc density values, probably due to release

TABLE 28  
SUMMARY OF DENSITY VALUES FOR SELECTED SLUDGES

<u>Sludge Sample</u>	<u>Floc Density</u>		<u>Dry Solids (%)</u>	<u>Bulk Density</u>	<u>Dry Particle Density</u>	<u>Avg Dry Particle Density</u>
	<u>Range</u>	<u>Average</u>				
<b><i>Step Gradient Method:</i></b>						
<b><u>Zion WTP Alum Sludge</u></b>						
As Is	1.22 to >1.24	>1.23	11.1	1.077	2.81	2.9
Centrifuged	>1.24	>1.24	31.9	1.27	3.00	
<b><u>Blacksburg WTP PACl Sludge</u></b>						
As Is	1.22 to 1.24	1.23	1.5	1.01	2.94	2.7
Centrifuged	1.24	1.24	12.7	1.08	2.48	
<b><u>Topeka WTP Lime Sludge</u></b>						
As Is	>1.28	>1.28	8.1	1.06	3.28	3.4
Centrifuged	>1.28	>1.28	47.4	1.51	3.47	
<b><u>SiO<sub>2</sub> Slurry</u></b>						
As Is	>1.28	>1.28	20.8	1.18	3.73	3.9
Centrifuged	>1.28	>1.28	52.0	1.65	4.12	
<b><u>Lab Alum Sludge</u></b>						
As Is	1.16-1.20	1.18	0.4	1.006	2.04	2.2
Centrifuged	1.16-1.22	1.19	17.6	1.332	2.40	
<b><u>Lab CaCO<sub>3</sub> Slurry</u></b>						
As Is	>1.28	>1.28	22.6	1.177	2.98	3.2
Centrifuged	>1.28	>1.28	50.0	1.54	3.34	
<b><i>Continuous Gradient Method:</i></b>						
<b><u>Pepper's Ferry WWTP Anaerobically Digested Sludge</u></b>						
As Is	1.050-1.052	1.051	2.5	1.007	1.39	1.4
PPC	1.056-1.060	1.058	2.2	1.006	1.37	
PPC & Belt-pressed	1.076-1.080	1.078	16.8	1.05	1.40	

Notes:

Units for above density numbers are in g/mL.  
PPC = polymer conditioned at the plant

of some of the water fractions associated with the floc particles. These results are discussed further in the following chapter.

## **SPECIFIC SURFACE AREA DETERMINATIONS**

The EGME-specific surface area determinations indicated that the dry chemical sludge and slurry particles had lower specific surfaces in comparison to the bio-solids. As shown in Table 29, the values ranged from about 21 m<sup>2</sup>/g for the SiO<sub>2</sub> particles to 216 m<sup>2</sup>/g for the Blacksburg WTP sludge particles. The bio-solids were determined to have specific surfaces between 200 to 370 m<sup>2</sup>/g.

The effect of drying the sludges at two different temperatures (35 °C and 105 °C) was also studied. In general, drying at the lower temperature provided specific surface values that were lower than were obtained when drying at the higher temperatures. These reductions in the specific surface (anywhere from 30 to 45%) may be due to the presence of some water fractions that may not have been removed at the lower temperature. Moreover, there appears to be slightly larger variability in the data obtained for the samples dried at the lower temperature.

Limited tests on the effects of polymer-conditioning and mechanical dewatering of the bio-solids on measured surface area were undertaken. The results did not indicate a significant change in specific surface area, with only a slight decrease in the value from an unconditioned/undewatered sludge (between 4-6%). While it may represent some loss of surface area due to polymer coverage on the sludge particle surface, it could also be interpreted to be within the limits of the experimental error of this specific method.

Limited tests (one set) were initially conducted to determine the difference between the recommended method of grinding down these flakes as compared to using the dry samples without grinding. The tests indicated that while the differences between the two sample preparations were minor, there were larger standard

**TABLE 29**  
**SUMMARY OF SPECIFIC SURFACE MEASUREMENTS FOR SELECTED SLUDGES**

<u>Sludge Sample</u>	<u>Specific Surface (m<sup>2</sup>/g)</u>	
	<u>Avg.<sup>a</sup></u>	<u>S.D.<sup>a</sup></u>
<b>Dried at 105° C</b>		
<i>WTP or Inorganic Chemical Sludges</i>		
Zion WTP Alum Sludge	133	3.3
Lab Alum Sludge	76	1.7
Blacksburg WTP PACl Sludge	216	1.3
Topeka WTP Lime Sludge	90	9.6
SiO <sub>2</sub> Slurry	22	3.2
SiO <sub>2</sub> only, no water added	24	1.7
<i>Pepper's Ferry WWTP Anaerobically Digested Bio-Solids</i>		
Unconditioned sludge	358	3.5
Plant polymer-conditioned and belt-pressed	350	5
Lab polymer-conditioned	336	9
Lab polymer-conditioned and centrifuged	345	8
Unconditioned sludge, dry flakes not ground, used as is <sup>b</sup>	370	17.5
<b>Dried at 35° C</b>		
<i>WTP or Inorganic Chemical Sludges</i>		
Blacksburg WTP PACl Sludge,	155	4.4
Topeka WTP Lime Sludge	51	3.6
SiO <sub>2</sub> Slurry	33	3.9
<i>Pepper's Ferry WWTP Anaerobically Digested Bio-Solids</i>		
Unconditioned sludge	223	29
Lab polymer-conditioned	184	4

Notes:

- a. Avg (average) and S.D. (standard deviation) values are based on triplicates per sample set.
- b. In all other cases, the samples were first dried, then ground up prior to the EGME-specific surface determinations, as recommended for the method<sup>17</sup>.

deviations within the samples that were not ground. Thus, subsequent tests were conducted after grinding up the dry flakes as recommended by the method<sup>17</sup>.

## **CHAPTER 6**

### **DISCUSSION**

#### **OVERVIEW**

This chapter discusses the results presented in the previous chapters and attempts to identify some general relationships as well as draw specific conclusions from the analyzed data. It begins with a presentation of selected data using the different techniques for sludge and moisture characterization. Moisture characterization data are presented in g/g-DS instead of % initial moisture, as it is thought (by this author) to be a better unit of measurement, allowing for comparison between different types of sludges due to their various dry solids concentrations (as well as a host of other complex characteristics). Units for density measurements are in g/mL, while the specific surface area measurements have been reported in m<sup>2</sup>/g. Multiplying the specific surface of a dry sludge particle with its dry particle density (estimated from the mass balance relationship presented in equation 21, Chapter 3) should provide a relative measure of the specific surface per unit volume of the dry sludge particle. These relationships are explored in the figures presented in the following sections.

#### **SUMMARY OF SLUDGE CHARACTERIZATION STUDIES**

Table 30 is a compilation of selected data summarized from the previous chapter, showing the results of experiments to determine the various densities, specific surface, and moisture content (the latter using the dilatometric method as these moisture characterization studies included most of the sludges tested). The figures that follow are based on data from this table and from Table 31 which

TABLE 30  
SUMMARY OF SELECTED RESULTS OF SLUDGE CHARACTERIZATION EXPERIMENTS

<u>Sludge</u>	Dry Solids (%)	Bound Water (g/g-DS)	<u>Floc Density</u>		Bulk Density (g/mL)	Dry P'cle Density (g/mL)	Specific Surface (m <sup>2</sup> /g)
			Range (g/mL)	Avg (g/mL)			
<i>WTP and Chemical Sludges</i>							
<i>Zion WTP Alum</i>							
As is	11.1	<DL	1.22->1.24	>1.23	1.077	2.81	
Centrifuged	31.9	<DL	>1.24	>1.24	1.27	3.0	
Dried at 105° C							133
<i>Blacksburg WTP PACl</i>							
As is	1.5	14.3	1.22-1.24	1.23	1.01	2.94	
Centrifuged	12.7	3.1	1.24	1.24	1.08	2.48	
Dried at 105° C							216
Dried at 35° C							155
<i>Topeka WTP Lime</i>							
As is	8.1	0.2	>1.28	>1.28	1.06	3.28	
Centrifuged	47.4	0.2	>1.28	>1.28	1.51	3.47	
Dried at 105° C							90
Dried at 35° C							51
<i>Min-U-Sil 30 (SiO<sub>2</sub>) Slurry</i>							
As is	20.8	<DL	>1.28	>1.28	1.18	3.73	
Centrifuged	52	<DL	>1.28	>1.28	1.65	4.12	
Dried at 105° C							22
Dried at 35° C							33
Min-U-Sil only (no H <sub>2</sub> O) dried at 105° C							24
<i>Lab. "Alum" Slurry</i>							
As is	0.4	38.3	1.16-1.20	1.18	1.006	2.04	
Centrifuged	17.6	5.6	1.16-1.22	1.19	1.332	2.4	
Dried at 105° C							76
<i>Lab. CaCO<sub>3</sub> Slurry</i>							
As is	22.6	0.2	>1.28	>1.28	1.177	2.98	
Centrifuged	50	0.2	>1.28	>1.28	1.54	3.34	
Dried at 105° C							40

(continued)

TABLE 30 (CONTINUED)

<u>Sludge</u>	Dry Solids (%)	Bound Water (g/g-DS)	<u>Floc Density</u>		Bulk Density (g/mL)	Dry P'cle Density (g/mL)	Specific Surface (m <sup>2</sup> /g)
			Range (g/mL)	Avg (g/mL)			
<b>Bio-Solids</b>							
<i>PFWWTP Anaerobically Digested Sludge</i>							
As is	2.5	11.2	1.050-1.052	1.051	1.007	1.39	
Plant polymer-cond.	2.2	4.3	1.056-1.060	1.058	1.006	1.37	
P-C & Belt-pressed	16.8	1.6	1.076-1.080	1.078	1.05	1.40	
Dried at 105° C							358
Dried at 105° C (not powdered)							370
Dried at 35° C							223
Plant polymer-cond, belt-pressed, dried at 105° C							350
Lab polymer-cond and dried at 105° C							336
Lab polymer-cond and dried at 35° C							184
Lab polymer-cond, centrifuged, & dried at 105° C							345

**Notes:**

1. Bound water data were determined using the dilatometric method.
  2. \* indicates that a negative value was obtained. The value may be below the minimum detection limit of the instrument (MDL may be just below 0.2 g/g-DS).
  3. Floc densities for WTP (water treatment plant) sludges and slurries prepared in the laboratory were determined using the step gradient method. Those for the bio-solids were obtained by the continuous gradient method using density marker beads.
  4. Bulk densities were determined using a glass pycnometer.
  5. Specific surface area measurements were determined using the EGME-(ethylene glycol monoether) method.
  6. Dry particle density was calculated based on % dry solids and bulk density, using the mass balance relationship presented in equation 21, Chapter 3.
- <DL Below the detection limit of the dilatometric method.



**TABLE 31**  
**MOISTURE CHARACTERIZATION FOR VARIOUS SLUDGES**

Symbol Used:	[1] %DS	[2] TW	[3] BW	[4] UW	[5] $\rho_t$	[6] $\rho_b$	[7] $\rho_k$	[8] SS	[9] SS-v
Sludge Sample	Dry Solids (%)	Total Water (g/g)	Bound Water (g/g)	Unbnd Water (g/g)	Floc Density (g/mL)	Bulk Density (g/mL)	Dry Pcle Density (g/mL)	Specific Surface (m <sup>2</sup> /g)	Sp Surf per unit vol-D.S. (m <sup>2</sup> /mL)
<i>PFWWTP Bio-Solids</i>									
As Is	2.5	39	11.2	27.8	1.05	1.007	1.39	360	499
Polymer-Conditioned	2.2	44.5	4.3	40.2	1.06	1.006	1.37	345	473
P-C & Belt-pressed	16.8	5	1.6	3.4	1.08	1.05	1.40	350	488
<i>Lab Alum</i>									
As Is	0.4	249	38.3	210.7	1.18	1.006	2.04	76	155
Centrifuged	17.6	4.7	5.6	-0.9	1.19	1.332	2.4		
<i>Blacksburg WTP PACl</i>									
As Is	1.5	65.7	14.3	51.4	1.23	1.01	2.94	216	635
Centrifuged	12.7	6.9	3.1	3.8	1.24	1.08	2.48		
<i>Zion WTP Alum</i>									
As Is	11.1	8	0.15*	7.9	1.23	1.077	2.81	133	374
Centrifuged	31.9	2.1	0.1*	2	>1.24	1.27	3.0		
<i>Topeka WTP Lime</i>									
As Is	8.1	11.4	0.25	11.1	>1.28	1.06	3.28	90	295
Centrifuged	47.4	1.1	0.2	0.9	>1.28	1.51	3.47		
<i>Lab SiO<sub>2</sub></i>									
As Is	21	3.8	0.15*	3.6	>1.28	1.18	3.73	22	82
Centrifuged	52	0.9	0.1*	0.8	>1.28	1.65	4.12		
<i>Lab CaCO<sub>3</sub></i>									
As Is	22.6	3.4	0.25	3.2	>1.28	1.177	2.98	40	119
Centrifuged	50	1	0.2	0.8	>1.28	1.54	3.34		

For Notes on the above columns, please see following page

(continued)

TABLE 31 (CONTINUED)

Notes:

- [1] %DS (percent dry solids content) measured by *Standard Methods*<sup>1</sup> drying in 105 °C.
- [2] Total Water = (100 - %DS) / %DS, in g/g-DS.
- [3] Bound Water measured by dilatometer, in g/g-DS.
- [4] Unbnd = Unbound Water = Total Water - Bound Water, in g/g-DS.
- [5] Floc Density measured by isopycnic gradient technique, in g/mL.
- [6] Bulk Density measured by glass pycnometer, in g/mL.
- [7] Dry Particle Density estimated by following mass balance relationship, see also equation 21, Chapter 3:

$$\frac{100}{\rho_b} = \frac{(100 - \%DS)}{\rho_w} + \frac{\% DS}{\rho_k}$$

where  $\rho_w$  = density of water = 1.00 g/mL.

- [8] Specific Surface measured by EGME-SS technique, in m<sup>2</sup>/g.
- [9] SS-v calculated by multiplying SS with  $\rho_k$ , thus units would be m<sup>2</sup>/mL-dry solids.
- \* Estimated values of bound water. Measured values were below the detection limit of the dilatometric method.

fractionate the total water in sludges into unbound (which in turn may include the free and interstitial sub-fractions as indicated in the Introduction to Chapter 5) and bound fractions. The latter was measured by the dilatometer while the former was determined from the difference between total water (from dry solids analysis) and bound water. Table 31 also presents the sludge characterization results in other forms; for example, as various fractions of water in the sludges and as a function of the volume thought to be occupied by the dry sludge particle.

Since the relationships between the various sludge characteristics were not easily evident from the previous two tables, the following figures (Figures 35 to 42) were prepared in an effort to determine if there are any such correlations. The datapoints taken are for the various sludge samples analyzed and presented in Tables 30 and 31.

### **Relationship between Sludge Density Values and Dry Solids**

Table 28 of the previous chapter presented the bulk density (or specific gravity) and floc density measurements as well as the estimated dry particle density values. The data indicate that, in general, the bulk densities of sludge samples increase upon mechanical dewatering (centrifugation) with a corresponding increase in the dry solids concentration. This in turn implies that the total water (assuming a density of 1.0 g/mL) associated with the sludge samples has progressively been reduced or removed.

Figure 35 presents the information on measured bulk densities (or specific gravities) and their dry solids concentration as determined by *Standard Methods*<sup>1</sup>. Robinson and Knocke<sup>79,80</sup> reported that the increase in sludge cake solids concentration correlated with the bulk or cake density. This is because the sludge cake volume is occupied by the sludge solids which have densities greater than 1.0 g/mL and water (and/or various fractions thereof) with densities of 1.0 g/mL.

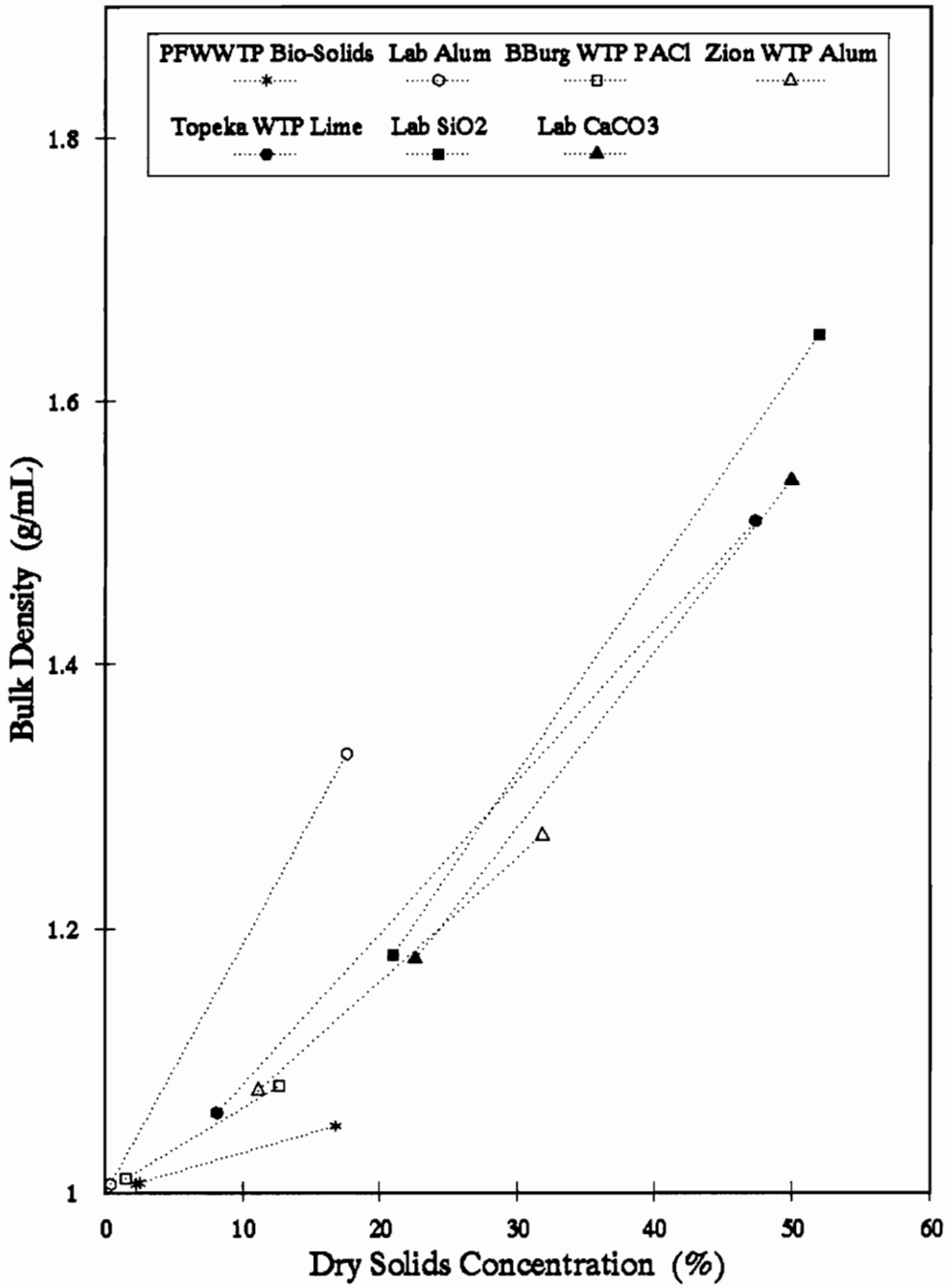


FIGURE 35: RELATIONSHIP BETWEEN BULK DENSITY AND DRY SOLIDS CONCENTRATION FOR VARIOUS UNCONDITIONED AND CENTRIFUGED SLUDGES

The application of sludge conditioning/dewatering processes, e.g. centrifugation, would cause an increase in the dry solids concentration and a corresponding increase in the bulk density of the sludge due to removal of some portion of the associated waters, some of which may have been in the floc structure.

The figure also shows the incremental increases between the unconditioned (in most cases, gravity thickened only) and centrifuged sludges for each set of sludges. The two, unconditioned and centrifuged, samples are joined by dotted lines and show the relative increases in both bulk density and dry solids concentrations for each set of sludges. As can be observed, the increases were in general more pronounced in WTP and chemical sludges due to the relatively smaller floc/bound water fractions as compared to the larger bio-solid floc particles. It should be noted that the measured bulk densities would increase as the dry solids concentration increases (i.e. as the sample is progressively dewatered) until it reaches a maximum value depending on the nature of the sludge. Different types of sludge will have different slopes that would tend toward their specific maximum cake density values.

Increases in floc densities were observed upon centrifugation with a corresponding increase in the dry solids concentrations for the sludges tested. Due to the limit on the step density of the concentrated Percoll media used in these tests, only floc densities up to and including 1.29 g/mL could be determined. In general, chemical/inorganic sludges tend to have densities that are in excess of that of bio-solids; thus some of these could not be determined in the sequence of tests undertaken. For both types of sludges, the water release was a function of the dewatering process per se.

Water release from the sludge floc structure is believed to be both from within and external to the floc structure. This is similar to results reported by Knocke, *et al*<sup>47</sup>, for observed increases in floc density (as well as a greater increase in the dry solids concentration) of a variety of gravity thickened sludges that were subject to chemical conditioning and mechanical dewatering. The bulk density values in general were lower than the floc densities, and the percent increases in both density

values upon centrifugation were greater for the bulk density, suggesting that centrifugal forces tended to remove the bulk/interstitial water (external to the floc structure). The floc water was a relatively small fraction of the total water released from the sludges after centrifugation.

### **Relationship between Bound Water and Dry Solids**

Total water in a sludge was defined as the sum of the bound and unbound water fractions. The associated amounts of total water (including the bound water fraction) would tend to decrease as a sludge sample was dewatered, thereby increasing its dry solids concentration. The data presented in Table 30 indicate that as the sludge sample undergoes conditioning and dewatering, the bound water tends to decrease. This was quite evident for the bio-solids sample. However, bound water measurements using the dilatometric method and dry solids concentration by *Standard Methods*<sup>1</sup> for unconditioned and centrifuged WTP and chemical sludge samples appeared to indicate that the relationship between these two sludge properties was not as well defined.

WTP and chemical sludges tend to have (initially) lower amounts of associated bound waters which in turn are difficult to remove by conventional mechanical dewatering methods. One of the reasons for this is that these inorganic sludge particles are smaller in both volume and surface areas (and thus may also be denser) than bio-solids. There was some degree of correlation between these physical surface characteristics and bound water and this is discussed later. The inorganic sludges also tend to have little or no floc structures (or polymeric coatings or filamentous extrusions from their surfaces) that may entrap or adsorb water.

Figure 36 shows the data for the matrix of sludges tested. As can be seen, other than the bio-solids and the WTP PACl sludge the bound waters in general are low and the relation between bound water and dry solids concentration is not easily

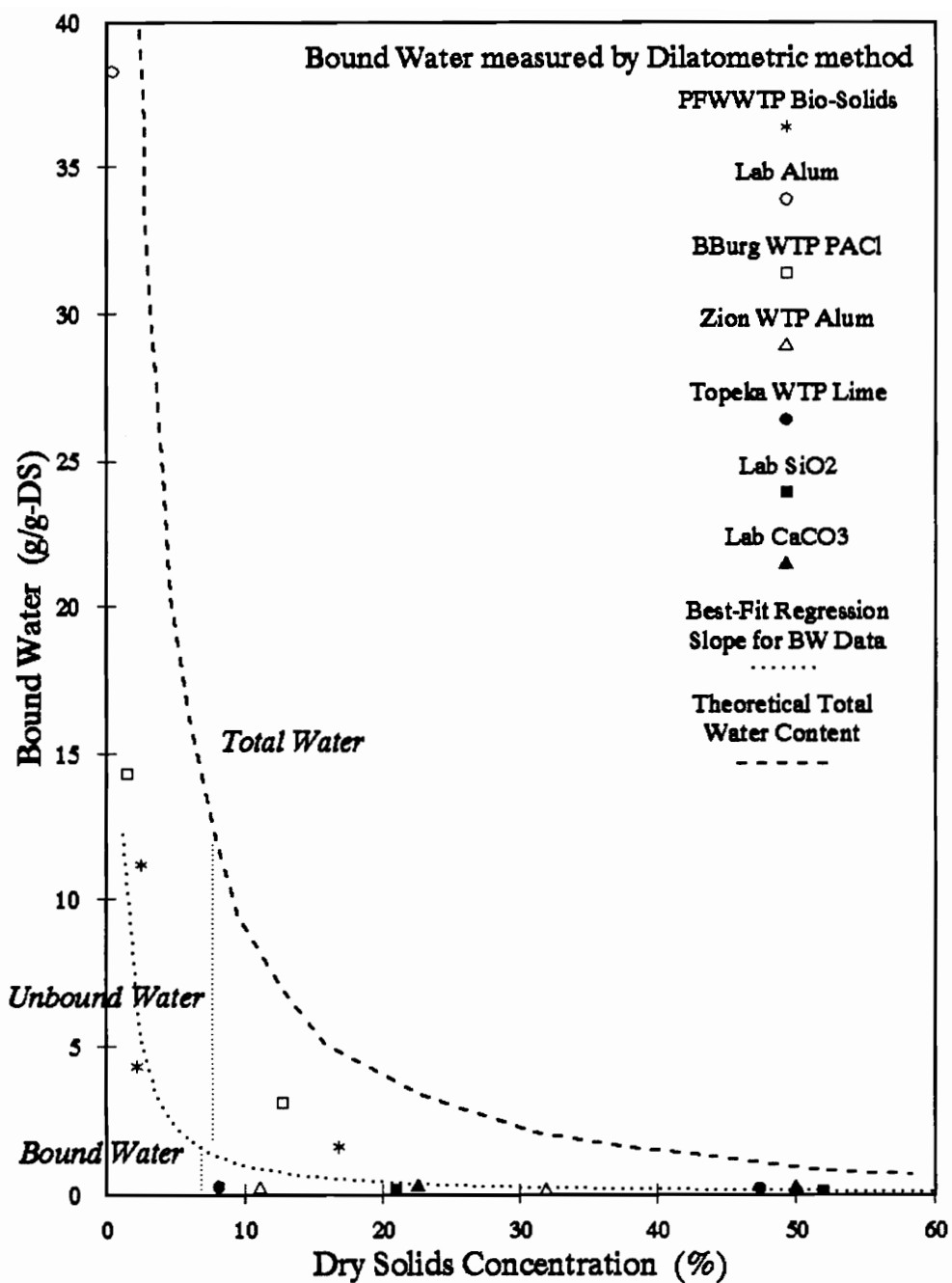


FIGURE 36: RELATIONSHIP BETWEEN MEASURED BOUND WATER AND DRY SOLIDS CONCENTRATION. TOTAL WATER CONTENT AND UNBOUND FRACTION ALSO SHOWN

evident. The figure also includes a plot of the theoretical amount of total water that may be initially present in a sample based on the dry solids concentration, and is shown by the dashed line. Since bound water is a fraction of the total water, it should fall within this curve. The dotted line below this is the best-fit power regression curve (of the form  $Y = aX^b$ ) for the bound water data and also serves as the demarcation point between the bound and unbound water fractions. The power regression had a correlation of  $r^2 = 0.7$ , and the power regression equation was of the form:

$$BW = 16 (DS)^{-1.2} \quad [23]$$

where:

BW = Bound water (in g/g-DS) measured by the dilatometric method, and  
 DS = Dry solids concentration (in %) at  $105 \pm 2^\circ \text{C}$  (*Standard Methods*<sup>1</sup>).

### **Relationship between Surface Area and Dry Solids**

As was alluded to in the previous sections, one of the possible reasons for the lower amount of bound water measured for the chemical sludges was their surface characteristics. Specific surface measurements of the gravity thickened sludge were undertaken using the EGME technique and these were correlated to various other sludge characteristics.

Data in Figure 37 appear to indicate a logarithmic relationship between the specific surface and dry solids concentration ( $r^2 = 0.88$ ). As can be seen, there appears to be some degree of correlation between the two sludge characteristics (surface area and dry solids). The relationship was of the form:

$$DS = 47 - 7.8 (\ln SSA) \quad [24]$$



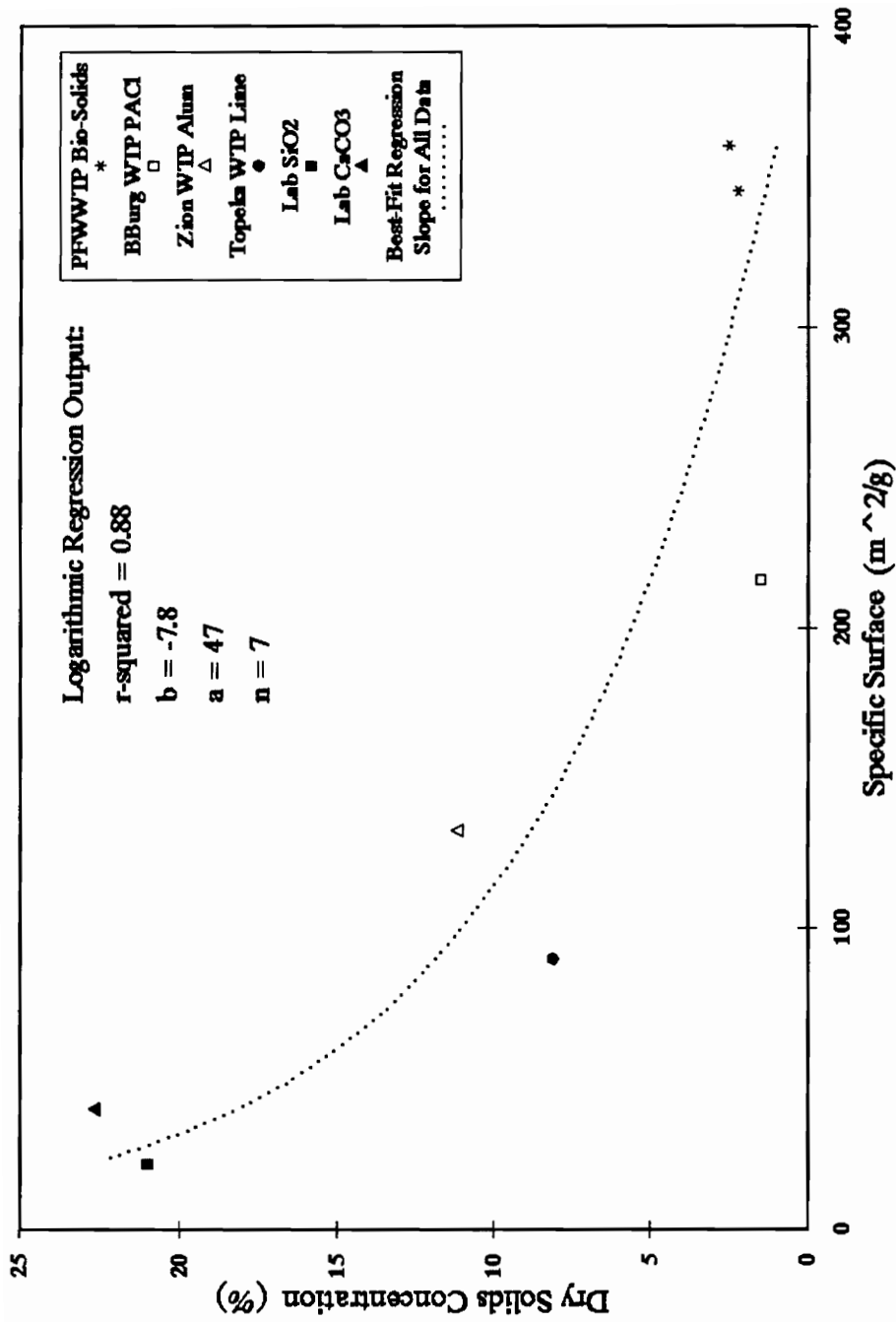


FIGURE 37: RELATIONSHIP BETWEEN DRY SOLIDS CONCENTRATION AND SPECIFIC SURFACE AREAS OF VARIOUS SLUDGES

where:

DS = Dry solids concentration (in %) at  $105 \pm 2^\circ \text{C}$  (*Standard Methods*<sup>1</sup>), and  
SSA = Specific surface area (in  $\text{m}^2/\text{g}$ ) measured by the EGME method.

In an attempt to determine if there was a better correlation between the two parameters, Figure 38 was redrawn using the information presented in column [9] of Table 31 on the specific surface per unit volume of the dry sludge particle. As can be seen, the regression improves ( $r^2 = 0.91$  for the best-fit logarithmic relationship) for the data when analyzed in this form. The equation was of the form:

$$\text{DS} = 71.8 - 11 (\ln \text{SSV}) \quad [25]$$

where:

DS = Dry solids concentration (in %) at  $105 \pm 2^\circ \text{C}$  (*Standard Methods*<sup>1</sup>), and  
SSV = Specific surface area per unit volume (in  $\text{m}^2/\text{mL-DS}$ ). The specific surface area was measured by the EGME method, then multiplied by the estimated dry particle density (in  $\text{g}/\text{mL}$ ).

An interpretation of this observation is that sludges with higher specific surface per unit volume of the dry solid particle tend to have more associated water, thereby decreasing the corresponding density of the sludge (which in turn decreases the measured dry solids concentration of the sludge). These correlations with water are explored further in the following section.

### **Correlations between Specific Surface and Other Sludge Characteristics**

The above observation appears to be substantiated in Figure 39 which shows that sludges with higher specific surface areas tend to have correspondingly lower

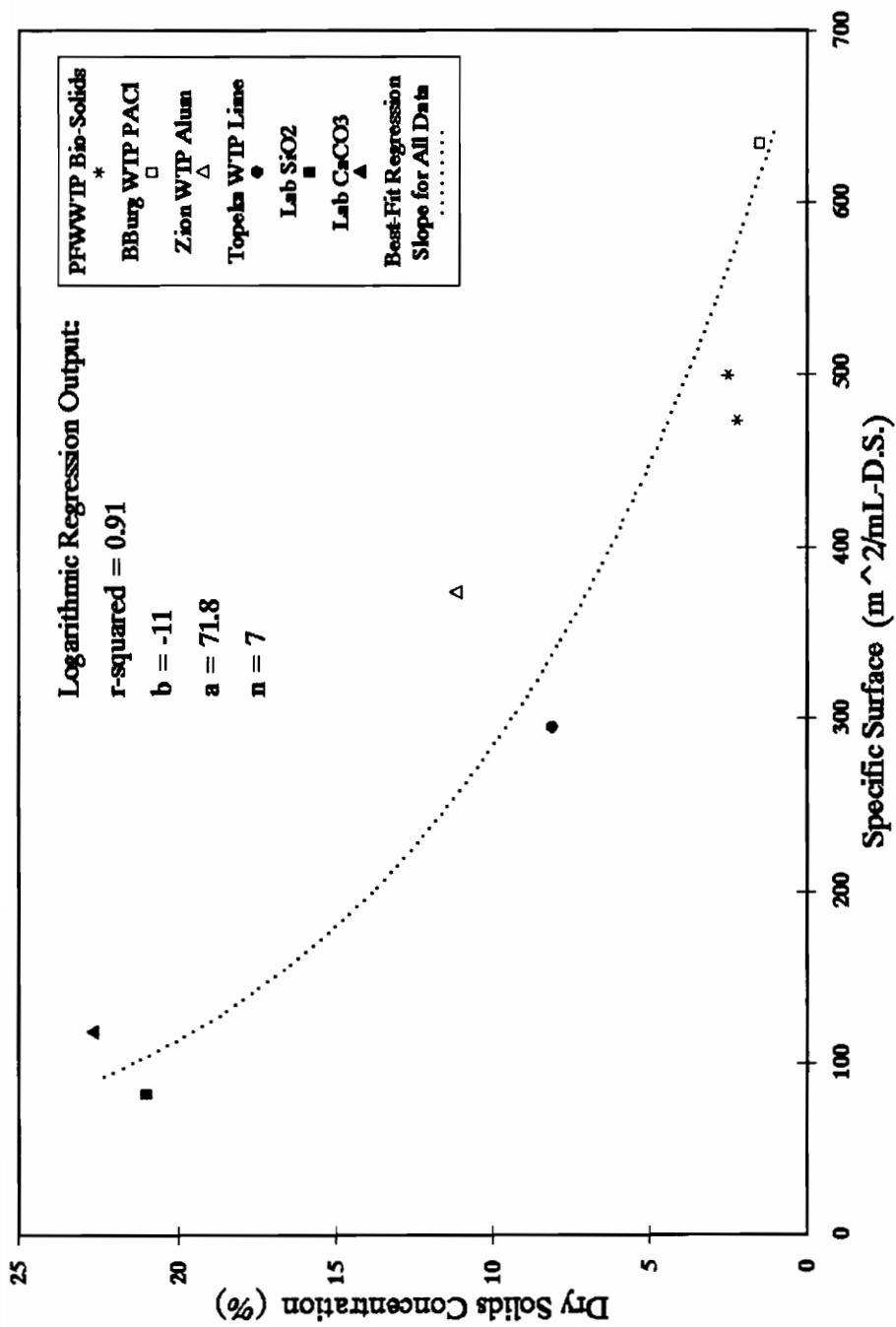


FIGURE 38: RELATIONSHIP BETWEEN DRY SOLIDS CONCENTRATION AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS

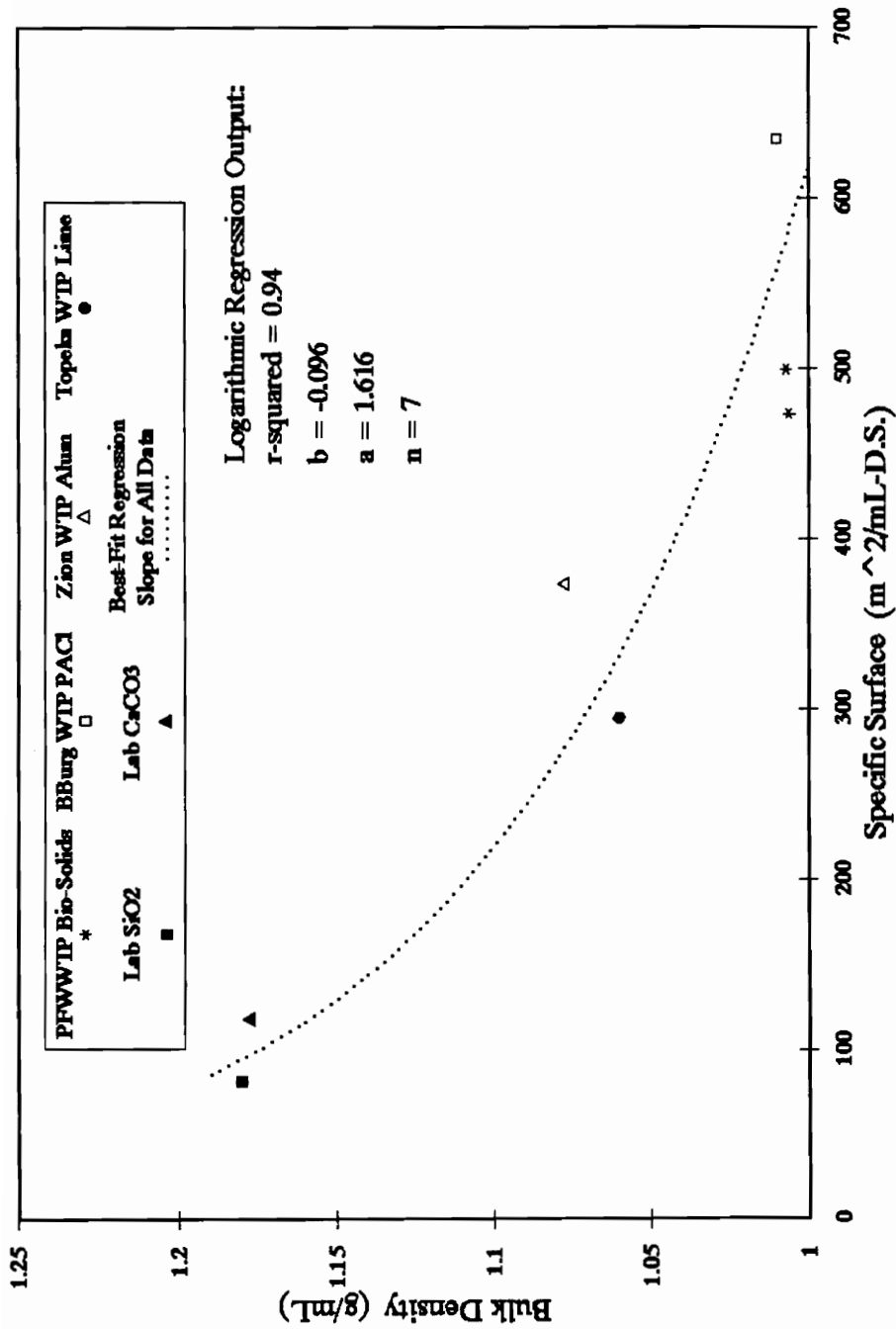


FIGURE 39: RELATIONSHIP BETWEEN BULK DENSITY AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS

bulk densities due to the associated amounts of water that may be present. In this case the best-fit logarithmic regression was found to be quite well correlated as  $r^2 = 0.94$  for the sludges tested. The equation was of the form:

$$BD = 1.62 - 0.1 (\ln SSV) \quad [26]$$

where:

BD = Bulk density (in g/mL) measured by a glass pycnometer, and  
SSV = Specific surface area per unit volume (in  $m^2/mL$ -DS).

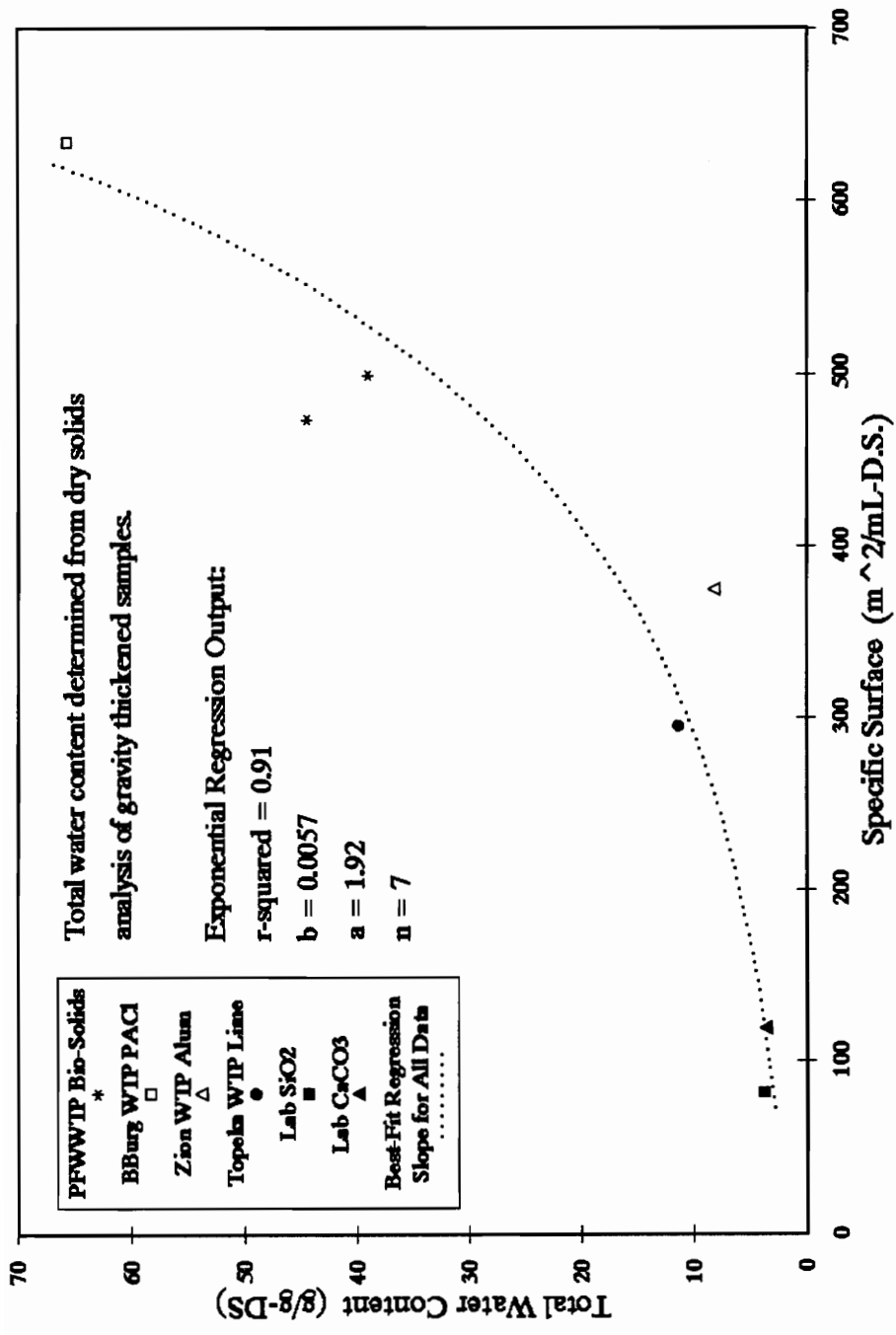
Since the bulk density value of sludges incorporates the total water associated with the sludge particles, the following figures were drawn to determine the relationship between the sludge water fractions and the specific surfaces. Figure 40 plots the data on the total water content (or initial moisture present based on the dry solids concentration) against the specific surface per unit volume dry solids. As can be observed, the relationship between the two sludge characteristics is quite pronounced. The exponential regression had a correlation of  $r^2 = 0.91$ , and the equation was of the form:

$$TW = 1.92 e^{0.006 SSV} \quad [27]$$

where:

TW = Total water content (in g/g-DS) as determined by the expression in Note [2] of Table 31, and  
SSV = Specific surface area per unit volume (in  $m^2/mL$ -DS).

The above correlation appears to lend credence to the hypothesis that as the specific surface area increases, the amount of moisture present also increases. At lower surface areas per unit volume, there are fewer water molecules that may



**FIGURE 40: RELATIONSHIP BETWEEN TOTAL WATER CONTENT AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS**

adsorb to the surface of the particle. However, as the surface area per unit volume increases, an increased number of water fractions may be associated to the particle. This observation is not unlike that by Drost-Hansen<sup>24</sup> and other researchers that show a positive correlation between surface areas and vicinal water (which includes bound water and some fraction of the unbound waters) for a variety of samples.

Figure 41 is a plot of measured bound water as a function of specific surface per unit volume dry solids. The correlation is not as high as predicted (although  $r^2 = 0.72$  for the exponential regression), probably due to inorganic nature of the bulk of the sludges tested. The equation was of the form:

$$BW = 0.045 e^{0.009 SSV} \quad [28]$$

where:

BW = Bound water (in g/g-DS) measured by the dilatometric method, and  
 SSV = Specific surface area per unit volume (in m<sup>2</sup>/mL-DS).

However, when the unbound (including free and interstitial water, as determined in column [4] of Table 31) water is plotted as in Figure 42, the relationship is much more evident ( $r^2 = 0.91$  for the exponential regression). The equation is of the form:

$$UW = 1.98 e^{0.005 SSV} \quad [29]$$

where:

UW = Unbound water content (in g/g-DS) as determined from the difference in the total and bound water content measured by the dilatometric method as indicated in Column [4] and Notes [2]-[4] of Table 31, and  
 SSV = Specific surface area per unit volume (in m<sup>2</sup>/mL-DS).

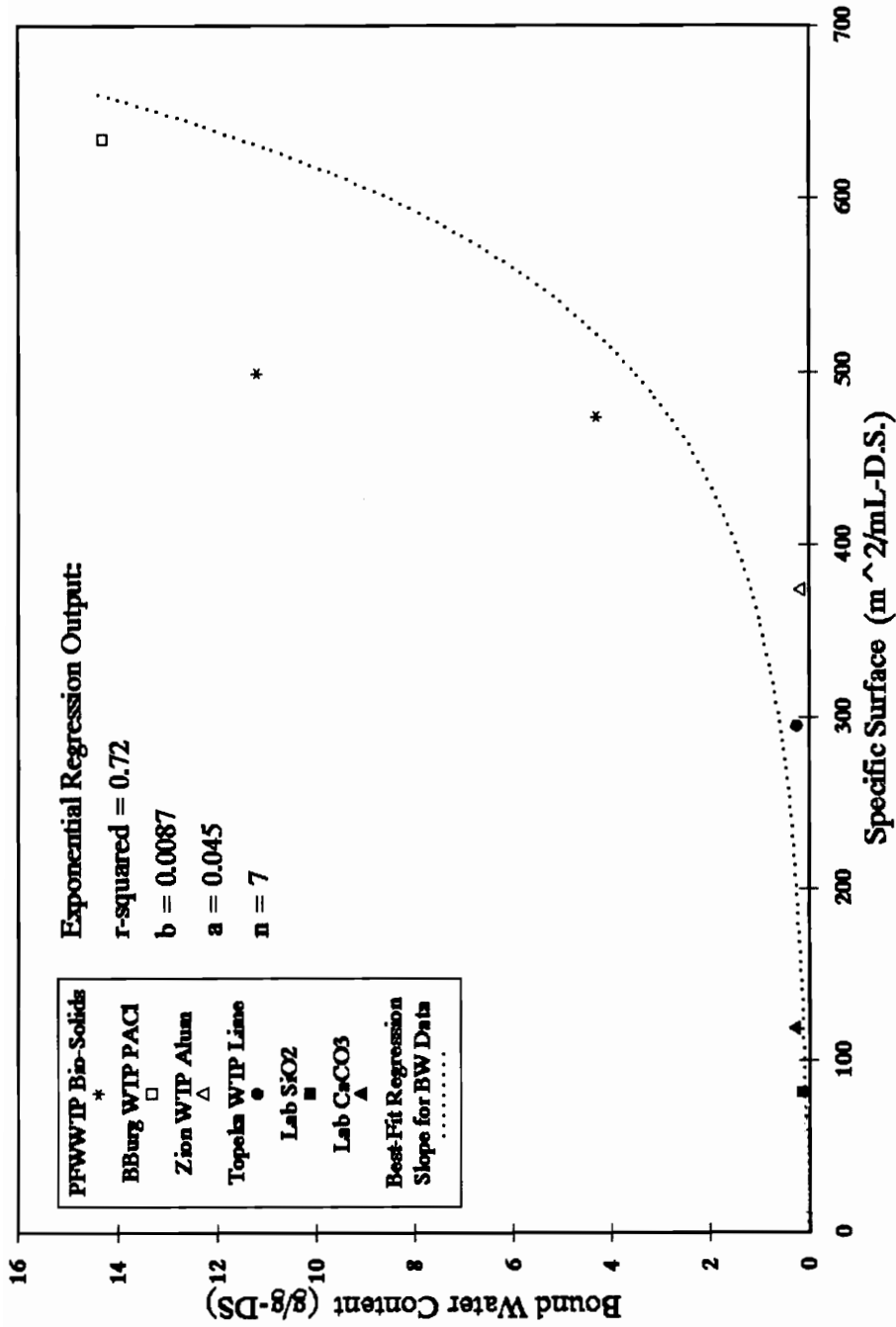


FIGURE 41: RELATIONSHIP BETWEEN BOUND WATER CONTENT AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS



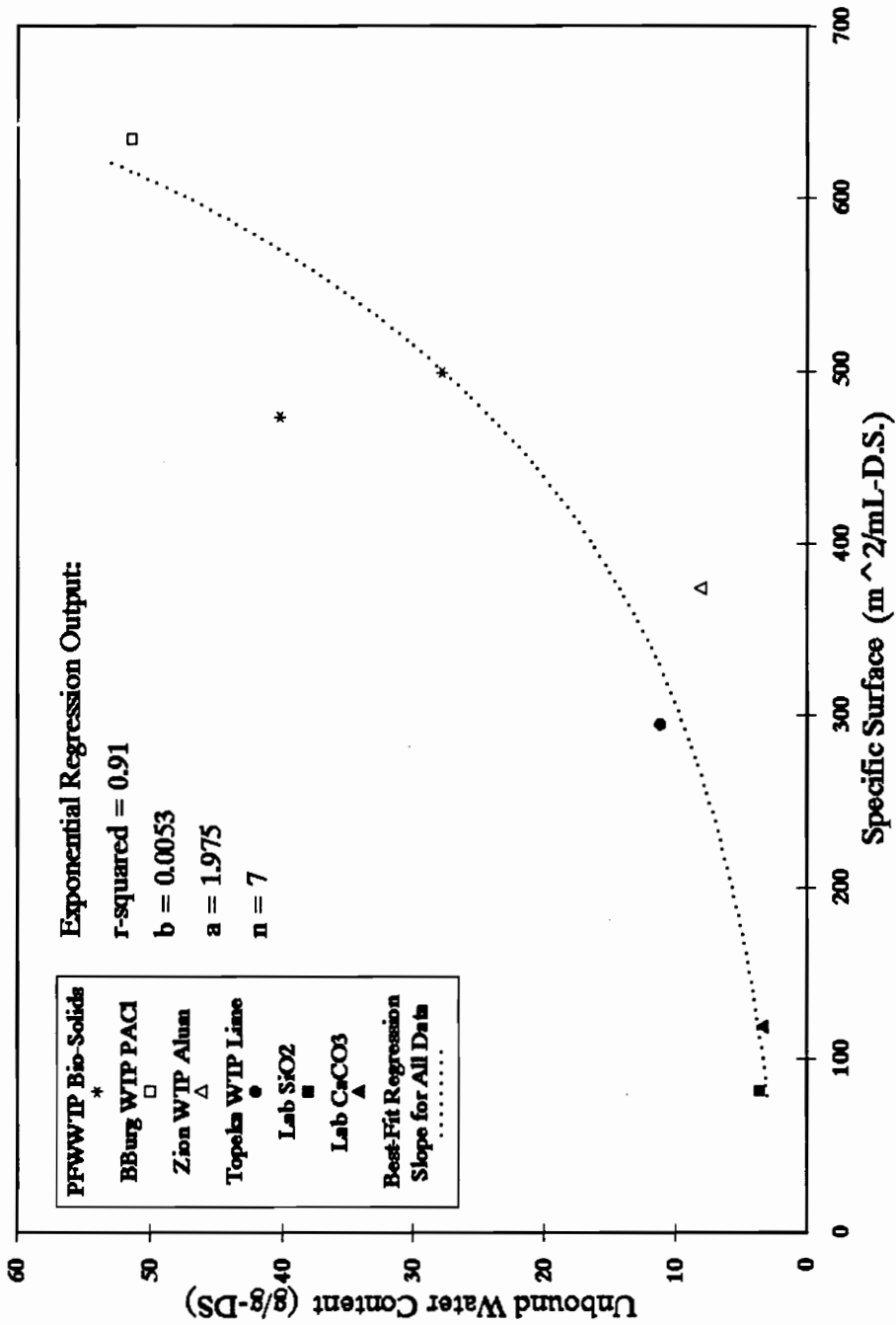


FIGURE 42: RELATIONSHIP BETWEEN UNBOUND WATER CONTENT AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS

The reason for this improved correlation (and that in Figure 41) is not entirely clear, and may be due to the original relationship of the water fractions to the initial dry solids content (Figure 40) as well as the presence of porous or void spaces between dry sludge particles that could conceivably include some unbound water.

### **Vicinal and Bound Water as a function of Specific Surface**

An attempt was made to determine if there was a direct relationship between the total possible (theoretical) vicinal water fraction to the measured specific surface of the various sludge particles. In this case, the calculations were made to determine the vicinal (or bound) water based on observations summarized by Drost-Hansen<sup>24</sup> that indicated that vicinal water had a density of 0.965 g/mL and also that the vicinal water coverage on certain samples may extend anywhere from 0.01  $\mu\text{m}$  to 0.05  $\mu\text{m}$  beyond the surface of the particle.

An example of the calculation for the Topeka WTP lime Sludge (specific surface = 90  $\text{m}^2/\text{g}$ ) assuming 0.05  $\mu\text{m}$  vicinal water coverage (i.e. the upper limit of the coverage) is presented as follows:

$$90 \text{ m}^2 \times (100^2 \text{ cm}^2/\text{m}^2) \times (0.05 \times 10^{-4} \text{ cm}) \times (0.965 \text{ g/mL}) = 4.35 \text{ g/g-DS}$$

Based on the above relationship, the upper and lower limits of the vicinal water coverage was determined (the lower limit was one-fifth that of the upper value, i.e. 0.87 g/g-DS) and plotted in Figure 43. If the density of vicinal water is taken to be equivalent to that of water free of impurities and dissolved solids (e.g. distilled/deionized water) at 1.0 g/mL, then the theoretical amounts of vicinal or bound water should increase by 3.5%. Figure 44 plots the information on theoretical vicinal water against the specific surface per unit volume of dry solids and in this case the outlying data point for the WTP PACl sludge drops down to the envelope of the theoretical vicinal water.

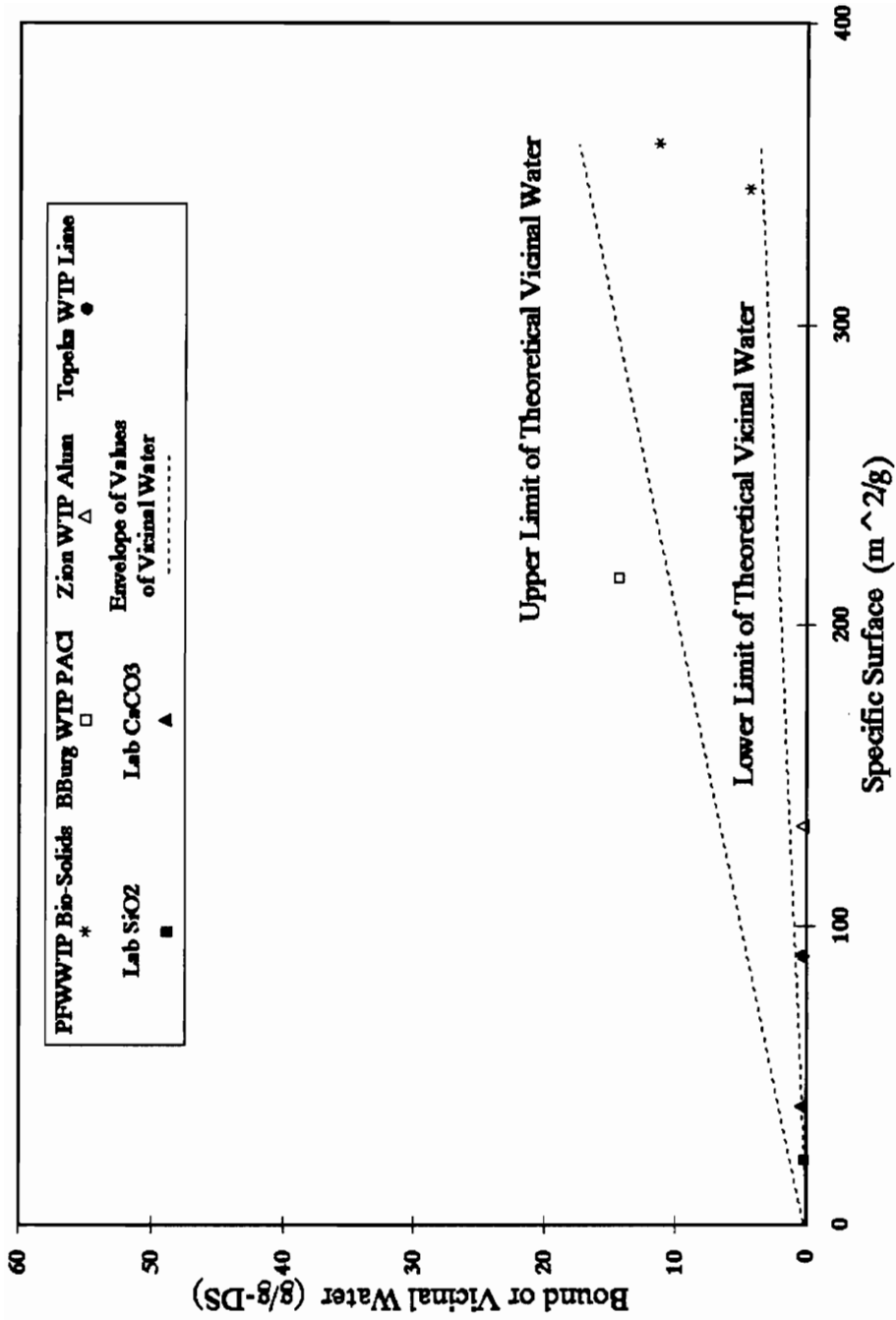


FIGURE 43: RELATIONSHIP BETWEEN BOUND OR VICINAL WATER AND SPECIFIC SURFACE

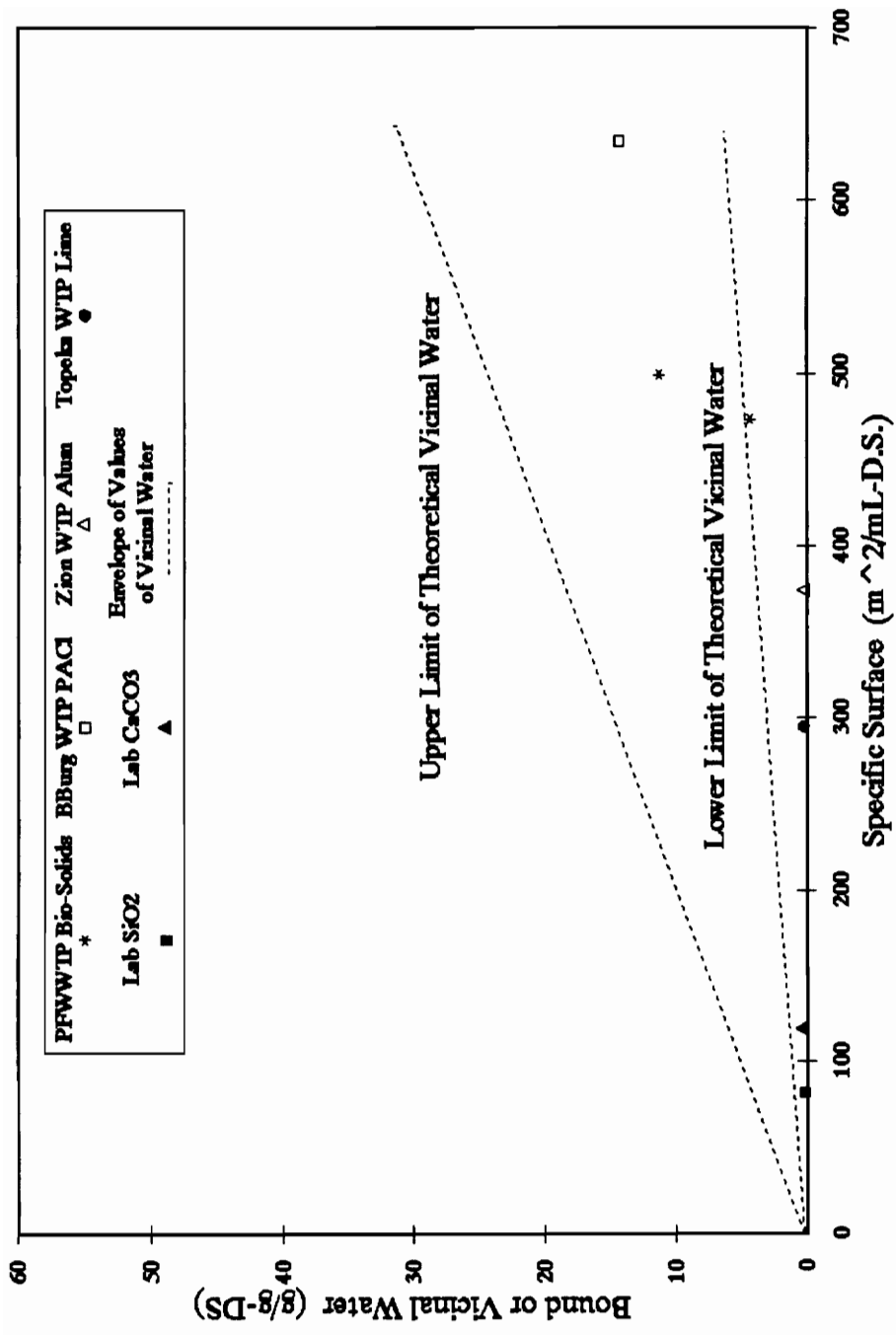


FIGURE 44: RELATIONSHIP BETWEEN BOUND OR VICINAL WATER AND SPECIFIC SURFACE PER UNIT VOLUME DRY SOLIDS

As can be seen in both the figures, the measured values of bound water for chemical and WTP sludges were close to or below the envelope of calculated values theoretically possible based on the specific surface measurements. Only the bio-solids and the WTP PACl sludge appeared to have bound water amounts that were within the range of values predicted by the vicinal water hypothesis. In general, the chemical/inorganic sludges tended to fall well below these values. While this could be a function of the characteristics of these sludges, it could also be due to the uncertainties that may be present in the specific surface and bound water measurements undertaken. In addition, the measured bound water fraction appears to be a sub-fraction of the vicinal water as hypothesized by Drost-Hansen<sup>24</sup>, as it was generally lower than the vicinal water.

Yet another factor could be the differences in the instrumentation techniques used for this research and that reported by Drost-Hansen<sup>24</sup>. As discussed in a following section, differences in the surface area measurement techniques used could be significant. The surface area of the SiO<sub>2</sub> was determined to be about 22 m<sup>2</sup>/g using the EGME method, whereas that reported<sup>21</sup> for a similar material (albeit a cleaned and acid-washed sample) using the N<sub>2</sub>-gas adsorption BET surface area was 0.32 m<sup>2</sup>/g. For this smaller surface area, the range of vicinal water values would theoretically be between 0.003 to 0.015 g/g-DS, somewhat below that measured by the TGA/drying curve method (0.4 g/g-DS, of which the chemically bound water sub-fraction was 0.1 g/g-DS). The N<sub>2</sub>-gas adsorption method collapses inner-layers of particles and thus the measured surface area is lower than that reported by other techniques. Information provided by the manufacturer of the material<sup>as cited by Ref. 88</sup> indicated that the surface area of the SiO<sub>2</sub> (called Min-U-Sil 30) was 6660 cm<sup>2</sup>/g or 0.67 m<sup>2</sup>/g (see Table 4, Chapter 2), although the specific area measurement technique was not indicated.

One should also be aware that the values presented above assume that the: (i) vicinal water theory is valid, (ii) BET or other surface area measurement techniques actually determine total surface areas of the materials tested, (iii) the

bound water determination methods are accurate, and (iii) bound and vicinal water values are comparable.

## **COMPARISONS OF MOISTURE DISTRIBUTION EXPERIMENTS**

### **TGA-DSC-Dilatometer**

While it was not possible to conduct all the moisture determination studies simultaneously in order to draw specific comparisons between the three different characterization techniques (since these instruments were not available at the same time or place), some comparisons were attempted since limited tests had been conducted on similar sets of sludge(s).

The comparative bound water measurements are presented in Table 32. For the moisture characterization studies, the sludge(s) tested that were common to all three techniques included the Zion WTP alum sludge and the SiO<sub>2</sub>-water slurry. As can be seen from the table, the results indicate that the TGA/drying curve rate was able to determine the relatively small bound water fractions in these two inorganic sludges. This may be due to limitations of the minimum detection level and noise of the other two techniques, and is discussed in a later section. Another possible explanation is that the TGA/drying curve rate set at a constant temperature of 40 °C for a period of time should be able to drive off most of the free and bound water fractions. The constant weight fraction remaining (determined by raising the temperature to beyond 100 °C, usually 150 °C) is thought to be the chemically bound fraction and usually ranged between <0.1 to 0.3 g/g-DS (see Table 19, previous chapter). This value could easily be determined by the TGA technique developed for this study, but needed to be conducted separately for the other two techniques.

It is not possible to discuss conclusively the moisture characterization data for bio-solids since the three methods were not tested using the same set of sludges

TABLE 32  
COMPARISON OF BOUND WATER MEASUREMENTS FOR  
DIFFERENT MOISTURE CHARACTERIZATION TECHNIQUES

<u>Sludge</u>	Dry Solids (%)	Total Water	Bound Water		
			TGA/ Drying Rate	DSC	Dilatometer
<i>Aurora WWTP Bio-Solids</i>					
As Is	3.63	26.5	1.7	-	-
Polymer-cond. & free-drained	7.04	13.2	1.7	-	-
P-C, & vacuum dewatered	11.0	8.1	1.3	-	-
<i>Pepper's Ferry WWTP Bio-Solids</i>					
As Is	2.8	34.7	-	2.4	16.2
Polymer-cond. & free-drained	8.2	11.2	-	1.6	4.3
P-C, & belt-pressed	16.5	5.1	-	1.8	2.3
<i>Pulp &amp; Paper Mill Sludge</i>					
As Is	4.0	24	-	4.4	15.0
Polymer-cond. & after RST	8.1	11.3	-	1.4	11.4
P-C, RST, & screw-pressed	41.1	1.43	-	0.6	1.0
<i>Zion WTP Alum Sludge</i>					
As Is	11.2	7.9	0.8	<0.2	<0.2
Polymer-cond. (w/ diln water)	7.3	12.7	0.7	<0.2	<0.2
P-C, & belt-pressed	42	1.4	0.2	-	-
<i>SiO<sub>2</sub>-Water Slurry</i>	21	3.8	0.2	<0.2	<0.2
<i>CaCO<sub>3</sub>-Water Slurry</i>	22.6	3.4	-	<0.2	0.25

Total Water, in g/g-DS determined from dry solids content (*Standard Methods*)<sup>1</sup>.  
All Bound Water results are reported in g/g-DS.

(comparative tests on similar sludges were conducted between the DSC and dilatometer and are discussed in the following section).

Knocke and Robinson<sup>79,80</sup> have conducted tests to compare the drying rate method against the dilatometric method and they reported that their controlled drying rate (at 35 °C) method yielded bound water values that were 17 to 36% higher than those reported by the dilatometric method, for three out of four sludge samples. The values of bound water using the drying rate method for one sample (lime sludge) was reported to be lower than that of the dilatometric method. Standard errors for both methods were reported to be between 12-13% for the dilatometric method and 16-20% for the drying method.

The authors<sup>79,80</sup> did state, however, that the values reported by their drying tests varied depending on the timing and frequency of the readings, and that more frequent measurements of sample weight would have aided them in better defining the inflection point(s) of the drying rate curve. The time intervals used to weigh their samples appeared to range from 30 minutes to 1 hour or longer, whereas this study used the TGA to automatically record the weight and temperature of the sample every 10 to 30 seconds or so. The instrument could also be set to record data every 6 seconds, but this was not done since the data thus generated would have been voluminous and somewhat unnecessary as tests had been conducted in the initial development stage of the TGA experiments to determine that accurate and reproducible results could be obtained at 30 second intervals.

Smollen<sup>85</sup> also indicated that better environmental controls and more frequent sample weight measurements would have assisted in better defining the inflection point(s) and reducing the error due to the subjectivity in determining the moisture distribution data. Subsequent work reported by the author<sup>86</sup> used vacuum drying and computer controlled apparatus in an effort to reduce these variabilities.

Thus, while the experimental protocol developed for the drying rate experiments using the TGA is believed to provide results that are more accurate, definitive comparisons cannot be made at this juncture due to the limited amount of



tests on all three techniques at the same time and on similar sludge samples. The three techniques did not yield identical values of bound water. This is because the TGA/drying rate curve and the DSC (as well as the dilatometer, based on the premise that bound water does not freeze by  $-20^{\circ}\text{C}$ ) are measuring different physical phenomena. The non-existence of well-defined, sharp boundaries between bound water and free water also contribute to the differences.

### **DSC-Dilatometer**

Comparisons could be made between the two techniques that rely on the difference in freezing temperatures between the free and bound water fractions, i.e. the DSC and the dilatometric tests, due to the increased number of tests on the same set of sludge samples. The results were presented in Table 32 as well as in the previous chapter (Tables 23 through 25).

They seem to indicate that the DSC consistently provides results for bound water values that were lower than that reported by the dilatometer for the matrix of bio-solids tested. The smaller values reported by the DSC were between 13 to 75% of the value reported by the dilatometer. When the amounts of bound water are relatively lower (e.g. after mechanical dewatering), the two techniques reported results that were closer to each other (between 30 to 50%).

These differences were more pronounced when the samples had greater amounts of total water (or lower dry solids concentration), and may have been due to the large differences in the sample sizes of both techniques (10-25 g for the Dilatometer and between 1-10 mg for the DSC). It could also have been due to the difficulty in drawing out a representative sample of the non-homogeneous sludges for the DSC.

As discussed previously, the differences in the bound water measurements between the two methods may have been due to the different temperature cycle

used. While the dilatometer measured the expansion of the unbound water on the initial freeze cycle from 20 °C to -20 °C, the DSC measured the melting endotherm of the unbound water of the sample which had been subject to the freezing regime and was thawed in the temperature range -20 °C to 20 °C. There does not seem to be sufficient conclusive data at this point to suggest that the initial dilatometric and DSC measurements are biased by the freezing process. The results do, however, indicate that subsequent analysis of the same sample could lead to sources of error due to structural changes in the floc brought about by freezing.

An effort was also made to determine if bound water determined by the two methods (the dilatometer and the DSC) were affected by differences in measurement of the bound water fraction as defined for each method. The dilatometer was able to record the expansion of the freezing unbound water fraction in the temperature range 20 °C to -20 °C. In contrast, the DSC measured the melting of the unbound water fraction after the sample had gone through the freezing cycle and was thawed in the temperature range -20 °C to 20 °C. Thus there could be differences in the bound water measurements between the two methods simply due to the temperature regime used. For these series of tests using the dilatometer, two sludges with relatively large (measurable) amounts of bound water were chosen to undergo up to four freeze-thaw cycles from 20 °C to -20 °C and back up again at approximately 1 °C /minute (to simulate the freeze-thaw temperature cycles in the DSC). The heat sink used for the freezing or cooling for the dilatometer was the ethanol-dry ice bath. The dilatometric units were then thawed in a warm water bath. In order to compare the data with the freeze-thaw cycle testing reported in Table 26, the experimental protocol for the data presented in Table 33 also included the approximately four hour thawing cycle at room temperature after the freezing cycle.

There appears to be insufficient conclusive data at this point to suggest that the *initial* dilatometric measurement is biased by the freezing process. The results do indicate that subsequent analysis of the same sample could lead to sources of error due to structural changes in the sludge floc brought about by freezing. This

**TABLE 33**  
**CHANGES IN MOISTURE DISTRIBUTION DUE TO REPLICATE FREEZE-THAW**  
**CYCLES OF APPROXIMATELY 1°C/MINUTE USING THE DILATOMETRIC METHOD**

Freeze-Thaw Cycle	Dry Solids Content (%)	Total Water (g/g)	Bound Water		Unbound Water (g/g)
			Avg (g/g)	Std Dev	
<b>Blacksburg WTP PACI Sludge (Gravity Thickened)</b>					
<i>40 minutes freezing and 40 minutes thawing per cycle</i>					
First	5.1	18.6	<b>8.7</b>	0.04	9.9
Second	-	18.6	<b>6.0</b>	0.11	12.6
Third	-	18.6	<b>5.7</b>	0.22	12.9
Fourth	-	18.6	<b>5.8</b>	0.31	12.8
<i>40 minutes freezing and 4 hours thawing per cycle</i>					
First	5.1	18.6	<b>8.6</b>	0.18	10.0
Second	-	18.6	<b>3.1</b>	0.24	15.5
<b>Pepper's Ferry WWTP Belt-Pressed Bio-solids</b>					
<i>40 minutes freezing and 40 minutes thawing per cycle</i>					
First	14.9	5.7	<b>3.8</b>	0.05	1.9
Second	-	5.7	<b>3.6</b>	0.16	2.1
Third	-	5.7	<b>3.5</b>	0.09	2.2
Fourth	-	5.7	<b>1.8</b>	0.11	3.9
<i>40 minutes freezing and 4 hours thawing per cycle</i>					
First	14.9	5.7	<b>4.0</b>	0.12	1.7
Second	-	5.7	<b>3.3</b>	0.07	2.4

could help explain to some extent the lower amounts of bound water as measured by the DSC of the melting endotherm after the *initial* freezing cycle.

The results presented in Tables 26 and 33 indicate that there are apparently effects that change the sludge floc when they have been placed through a freeze-thaw cycle. The degree to which these effects are observed (for example, the release of bound water) appear to be a direct function of the amount of time that the sludge remains in a frozen state. Longer contact times (e.g., overnight freezing in a commercial freezer, slower rates of melting promoted by thawing on the bench-top) under sub-zero conditions result in more dramatic changes in bound water content.

Although the increases in unbound water were evident in the dilatometer, they did not appear to be measurable (from the peak integral values of the endotherm on the thawing/melting cycle) by the PE DSC. This could be due to the relatively small sample amounts used in the latter method as well as lower overall bound and total water content of the samples tested. In addition, because of the supercooling effect, the freezing exotherms could not be accurately measured (which would have allowed for a more direct comparison of the unbound water fraction measured by the two methods).

An analysis of four replicate freeze-thaw cycles on the laboratory alum sludge (using the PL DSC) which had a relatively large initial bound water content as indicated in Figure 31 and Table 16 of Chapter 4 appear to indicate measurable changes in the water distribution for the melting endotherm. This appears to be in line with the observations of the reduction in bound water as reported in Table 33 using the dilatometric method. There are indications that DSCs are being developed with better capabilities to measure the exotherm on freezing<sup>77</sup>. More definitive correlations can then be made between the DSC and dilatometric methods on the *initial* freezing cycle once these DSCs are available.

The results for the bound water values of inorganic sludges are also not directly comparable as these may have been very small (probably less than 0.2 g/g-DS) and could have been below the detection limit of both these techniques. In

addition, as discussed in a later section, the relatively larger amounts of unbound water could be overwhelming the measurement capability of the DSC instrument. This appeared to be especially so for unconditioned/undewatered inorganic or WTP sludges.

## **SPECIFIC SURFACE MEASUREMENTS**

The results of these experiments have been presented in Table 29 of the previous chapter. The discussion that follows is specific to the EGME-specific surface technique and may be interpreted differently if other surface area measurement techniques are used, as alluded to previously. The values obtained by different methods may be different, for example, a value of  $0.32 \text{ m}^2/\text{g}$  was obtained<sup>21</sup> for the BET surface area (measured by  $\text{N}_2$  gas adsorption) of a sample of cleaned and sized fraction of  $\text{SiO}_2$  (Min-U-Sil 30), while the value obtained using the EGME-specific surface method reported in the previous chapter was  $22 \text{ m}^2/\text{g}$ . Although the  $\text{N}_2$  gas adsorption test used  $\text{SiO}_2$  samples that were treated to remove organic material, with contaminant metal oxides reported to be leached out and amorphous silica dissolved from the surface, the surface area measurements provided results that were quite different.

In general, it was found that the bio-solids samples had larger surface areas (anywhere from about one-third to fifteen times) than the inorganic sludges. Water treatment plant sludges may also contain some organic fractions and thus have surface areas that are larger than equivalent chemical sludges. The standard error of replicate tests using the EGME method ranged from 0.6 to 15%, although the average error was usually less than 5% for most samples. The inorganic samples ( $\text{SiO}_2$ -water slurry) with small surface areas had a higher variability (7-15%).

The variability was higher in cases where the samples were dried at  $35^\circ \text{C}$  or when the dried samples were not ground up prior to the specific surface

determinations. In fact, drying the samples at 35 °C instead of the recommended 105 or 110 °C, could conceivably allow for the continued adsorption of the chemically bound water fraction, which in turn reduces the surface sites available for adsorption of the EGME molecules. Thus the measured surface area value is usually smaller (between 28 to 45%). Some indication of the adsorption phenomena could be inferred from the slightly reduced surface area after polymer-conditioning the bio-solid sample, here there seemed to be about 6.5% reduction in the specific surface when compared to the unconditioned sample. However, such a small variability could also be due to the inherent experimental error of the technique.

Due to the greater variability in the values, it is recommended that the samples continue to be dried at 105 °C to a constant weight and then ground up prior to the EGME-specific surface determinations. Variations in the specific surface areas due to lower drying temperatures have been reported in the literature<sup>28,59,76</sup>. Rai and Franklin<sup>76</sup> reported that a more rigorous drying method (drying at 105 °C for at least 24 to 48 hours to give the lowest dry weight) removed a greater amount of water from clay samples, exposing more surface for glycol adsorption and correspondingly more retention per unit sample weight. They reported that a previous method of drying samples over P<sub>2</sub>O<sub>5</sub> in a desiccator (evacuated for 1 hour) for 4 to 6 hours to a constant weight was rarely sufficient and required considerable care to produce reproducible results. Eltantawy and Arnold<sup>28</sup> reported that it was important to dry samples adequately prior to the EGME treatment, otherwise the surface area values would be underestimated. The authors also considered that drying samples over P<sub>2</sub>O<sub>5</sub> was inadequate, and recommended drying at 110 °C for a least 24 hours.

## **SLUDGE DENSITY MEASUREMENTS**

### **Bulk Density and Dry Particle Density**

While the method is relatively quick and easy, there appears to be a greater degree of uncertainty when using the glass pycnometer, which translates into the values estimated for the dry particle density based on the mass balance relationship presented in equation 21 (Chapter 3). Figure 45 is a theoretical plot of the relationship between the two parameters for samples of different dry solids concentration (1-5% were selected for these plots). It shows that errors introduced by the inaccurate measurement of the bulk density can easily be compounded, especially at higher bulk densities and for sludges with low dry solids content. As an example, the estimated dry particle density value for a 1% dry solids sample increases from about 3.3 to 4.8 (a 45% increase) when the measured bulk density increases by less than 1% from 1.007 to 1.008 g/mL. The effect is even more magnified when the bulk density exceeds 1.008 g/mL. This variability may explain to some extent the values reported in Tables 28, 30, and 31 for various sludge samples. The standard error for determining the bulk density using the glass pycnometer ranged from 10-25%. Some degree of variability could also occur when drier sludge cake samples were tested and may have been due to some entrapped air bubbles.

Bulk density is an important sludge characteristic and some useful correlations can be made from this property. However, it may be necessary to explore additional techniques or improve the existing method to measure this characteristic in a more accurate and reproducible manner.

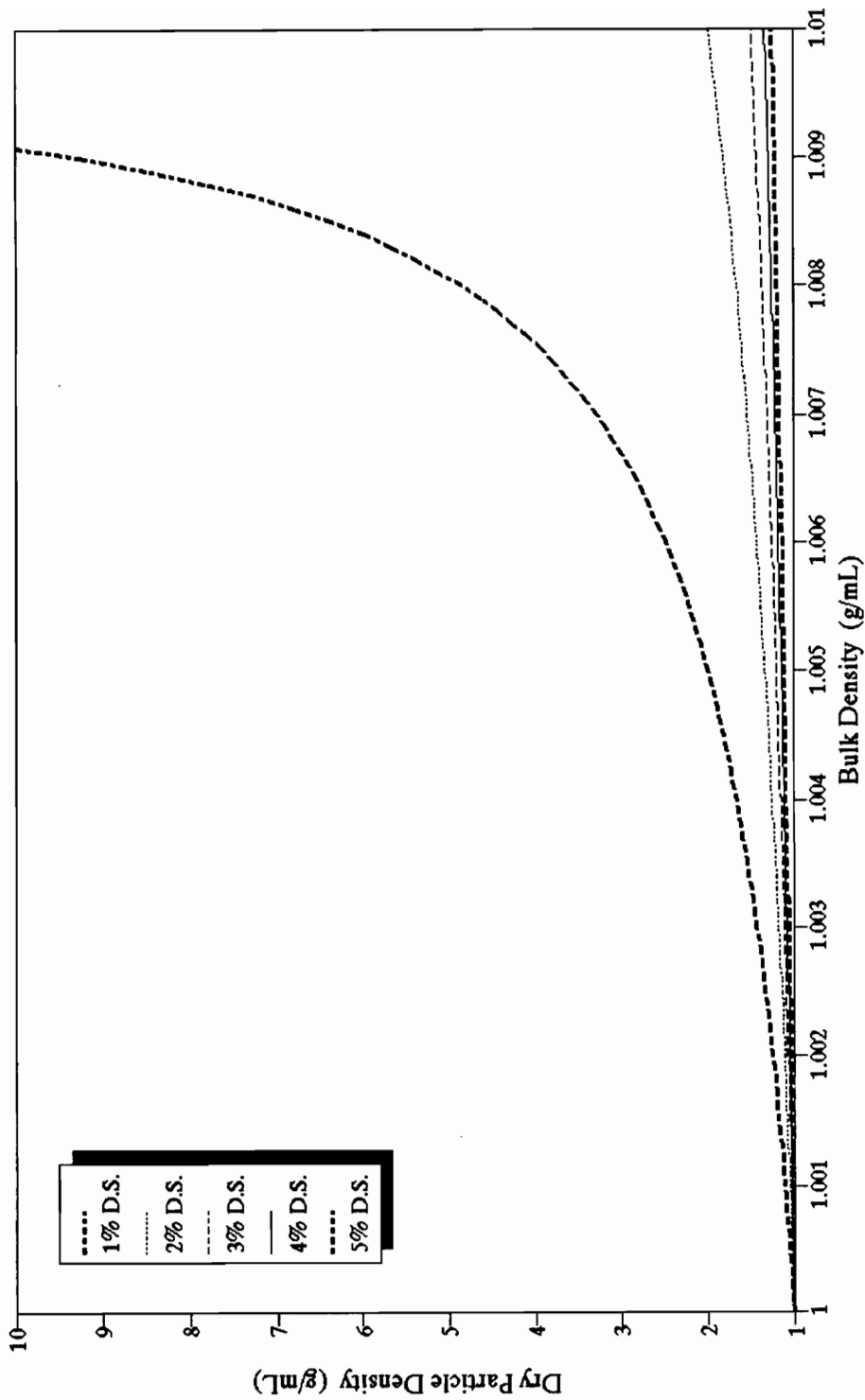


FIGURE 45: RELATIONSHIP BETWEEN BULK AND DRY PARTICLE DENSITY FOR A SLUDGE ILLUSTRATING POTENTIAL VARIABILITY DUE TO MEASUREMENT ERRORS



## Floc Density

The isopycnic centrifugation technique for the determination of floc densities has been fairly well developed and discussed by previous investigators (Knocke, *et al*<sup>7</sup>) with respect to chemical sludges and bio-solids. The results obtained are useful in estimating the relative amounts of water that may be associated with the floc structure. This can be determined from a mass balance relation similar to that used in equation 21 and is explored further in the following section.

Table 28 showed that for the sludges tested (that were within the experimental limits), the floc densities increased upon mechanical dewatering using the centrifuge. The table also summarized the density values (floc, bulk, and estimated dry particle) for the matrix of sludges tested. The increase in floc density upon polymer conditioning and mechanically dewatering the bio-solids sample was well represented by the data for the PFWWTP sludge where this was shown to increase from 1.05 g/mL for an unconditioned sludge to 1.06 g/mL upon polymer-conditioning and finally to 1.08 g/mL after belt-pressing. Each of the subsequent stages is believed to represent the release of a fraction of the bound water associated with the bio-solid floc particles. This is discussed in the following section and is believed to be from both within and external to the floc structure.

The observed increases in density values (bulk and floc) may also be interpreted in another way. Sludges can be considered to be made up of solid particles separated by water. Fractions of the water may adhere to the solid particles in a variety of binding mechanisms (these may include water as a portion of the chemical hydration structure, hydrogen bonding, and physical entrapment), while the remaining fraction is not "bound" and hence considered the unbound water (and includes the bulk or free water referred to in the literature). These waters form part of the void space between the sludge particles. Conditioning the sludge chemically and subsequently mechanically reduces the void or pore distances thereby increasing the densities of the sludges.

## Relationships Between Different Measured Sludge Parameters

It is believed that sludges can be represented by dry solid particles with associated water fractions that can be measured analytically in terms of gravimetric units (such as mass, density, and volume). An effort was made to determine whether there was a reasonable degree of correlation between the measured sludge water fractions (using the dilatometric method) and the independently measured floc density values ( $\rho_f$ , using the isopycnic centrifugation method). Other sludge parameters included the measured bulk density ( $\rho_b$ , using the glass pycnometer) and the dry (solid) particle density ( $\rho_k$ , calculated from the measured percent dry solids concentration following *Standard Methods*<sup>1</sup> and the bulk density value, as indicated in equation [21], Chapter 3).

This section presents and discusses the results of calculations undertaken to determine whether there are reasonable relationships between the above parameters. One fairly reasonable hypothesis that can be made is that the volume of a sludge floc can be represented by the sum of the volumes of the dry solid particle and bound water associated with the particle. Since density is represented by the quotient of mass over volume, the volume of a particle can be obtained by dividing the mass by its density. For the above hypothesis to be valid, there should be no difference between the volume of the sludge floc and its components (the dry solid and the associated water). The volumes were determined as follows:

$$\text{Volume}_{\text{floc}} = \text{Volume}_{\text{dry solid}} + \text{Volume}_{\text{bound water}} \quad \text{OR}$$

$$\frac{M_f}{\rho_f} = \frac{M_{ds}}{\rho_k} + \frac{M_{bw}}{\rho_w} \quad [30]$$

where:

$M_f$  = mass of sludge floc structure (solid particle and associated water), or

$M_f$  = mass of bound water determined by dilatometric method ( $M_{bw}$ , in g/g -DS) + mass of dry solid ( $M_{ds}$ , assumed to be 1.0 g),  
 $\rho_f$  = floc density of sludge floc structure (in g/mL) determined by the isopycnic centrifugation technique using Percoll media,  
 $\rho_k$  = dry particle density, in g/mL, and  
 $\rho_w$  = density of water = 1.0 g/mL.

Table 34 is a summary of the mass balance calculations that were undertaken. These results indicate that the differences between the volumes of the sludge components were close to zero for five of the six sludges tested. The percent difference between the calculated volume of the sludge floc and the sum of the volumes of dry solid and floc water averaged 10% with higher differences for the two WTP sludges. However, when the Blacksburg WTP PACl sludge was dewatered (centrifuged), the difference was close to zero (and the percent difference dropped to 6%) as predicted by the hypothesis.

In a similar fashion, the hypothesis was extended further by comparing the volumes occupied by the total sludge and its associated fractions (see Hypothesis 2 of Table 34). Here the volume of the total sludge is given by the quotient of the total water (determined from dry solids analysis) and the bulk density ( $\rho_b$ , measured by the pycnometer, in g/mL, as presented in equation [19], Chapter 3). This was compared to the sum of the volumes occupied by the floc structure (theorized to be made up of the dry particle and associated bound water) and the unbound water less the volume occupied by the dry solid particle. The relationship was of the form:

$$\begin{aligned}
 V_{\text{Total Water}} &= V_{\text{floc}} + V_{\text{Unbound Water}} - V_{\text{dry solid}} \quad \text{OR} \\
 \frac{M_{\text{TW}}}{\rho_b} &= \frac{M_f}{\rho_f} + \frac{M_{\text{UB}}}{\rho_w} - \frac{M_{\text{ds}}}{\rho_k} \quad [31]
 \end{aligned}$$

**TABLE 34**  
**MASS BALANCE RELATIONSHIPS BETWEEN MEASURED SLUDGE PARAMETERS**

Sludge Parameter	PFWWTP Bio-Solids			B'Burg	B'Burg	Zion
	As	Is	P-C	WTP PACl	WTP PACl Centr	WTP Alum
%DS (percent dry solids)	2.5	2.2	16.8	1.5	11.5	11.1
TW (Total Water)	39	44.5	5	65.7	6.9	8.0
BW (Bound Water)	11.2	4.3	1.6	14.3	3.1	0.6*
UW (Unbound Water)	27.8	40.2	3.4	51.4	3.8	7.4
$\rho_k$ (dry particle density)	1.39	1.37	1.4	2.94	2.48	2.81
$\rho_b$ (bulk density)	1.007	1.006	1.05	1.01	1.08	1.077
$\rho_f$ (floc density)	1.051	1.058	1.078	1.23	1.24	1.23

*Mass Balance Relationships:*

Hypothesis 1

Volume of Floc ( $V_f$ ) = Volume of Dry Solids ( $V_{ds}$ ) + Volume of Water in Floc ( $V_{bw}$ ), or

Calculated $V_f$ :	=	11.61	5.01	2.41	12.44	3.31	1.30
Calculated ( $V_{ds} + V_{bw}$ ):	=	11.92	5.03	2.31	14.64	3.50	0.96
Theoretical Difference: $V_f - (V_{ds} + V_{bw}) = 0$							
Calculated Difference:	=	-0.31	-0.02	0.10	-2.20	-0.20	0.34
Calculated Percent Difference:	=	2.7	0.4	4.0	17.7	5.9	26.5

Hypothesis 2

Volume of Total Water = Volume of Floc + Volume of Unbound Water - Volume of Dry Solid

Volume of Total Water, mL = (Total Water, g) / (Bulk Density, g/mL)							
	=	38.7	44.2	4.7	65	6.4	7.4
Volume of Floc (mL) + Volume of Unbound Water (mL) - Volume of Dry Solid (mL)							
	=	38.7	44.4	5.1	63.5	6.7	8.4

Thus, Percent Difference between above two volume expressions

(Theoretical percent difference = 0)

Calculated Percent Difference:	=	0.1	-0.6	-6.6	2.4	-4.7	-11
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Notes:

- \* BW value for Zion sludge determined by TGA/drying rate method as it was below the detection limit of dilatometer. All other BW values determined by dilatometric method.
- 1. P-C = polymer conditioned, B-P = belt-pressed, Centr = centrifuged.
- 2. Volume (in mL) determined by dividing the mass of water (in g; mass of dry solid particle assumed to be 1 g) by the density (in g/mL).
- 3. To calculate the volume of floc (dry particle plus associated water), the floc density value was used; for volume of total sludge water, bulk density of sludge was used; and for volume of water within the floc or bound water, density of water (1.0 g/mL) was used.

where:

$V$  = volume of the associated parameter, in mL

$M_{TW}$  = mass of total water, in g/g-DS, determined by dry solids concentration analysis ( $105 \pm 2^\circ \text{C}$ , *Standard Methods*<sup>1</sup>), see Note [2] of Table 31,

$M_f$  = mass of the sludge floc structure, in g or g/g-DS,

= mass of bound water determined by dilatometric method ( $M_{\text{water}}$ , in g/g-DS) + mass of dry solid ( $M_{\text{ds}}$ , assumed to be 1.0 g)

$M_{UB}$  = mass of unbound water, in g/g-DS, see Note [4] of Table 31,

$\rho_b$  = bulk density of sludge, in g/mL, determined by glass pycnometer,

$\rho_f$  = floc density of sludge floc structure (in g/mL) determined by the isopycnic centrifugation technique using Percoll media,

$\rho_w$  = density of unbound water = 1.0 g/mL, and

$\rho_k$  = dry particle density, in g/mL.

As can be seen, the percent differences were again close to zero as suggested by this hypothesis. Hypothesis testing by statistical methods (two-tailed t-tests and chi-squared distribution testing on variances) for the above was also conducted. The statistical tests indicated that the relationship was significantly valid at the 95% level for all but one of the sludges (the Zion WTP alum sludge). Even this sludge was significant at the 90% confidence interval.

Thus the above statistical tests show that the bound water measurements and the independent floc density measurements do yield reasonable closure.

The above relationships can conceivably be used to determine the extent to which a particular sludge may be dewatered to. The bound water fraction could include all the different operationally defined fractions suggested by various investigators. For the above mass balance relationships, the bound water fraction had been defined as that portion determined using the dilatometer that did not freeze by  $-20^\circ \text{C}$ .

Knocke, *et al*<sup>47</sup>, have recently presented mass balance calculations to determine the percent removal of water from within and external to the sludge floc structure. The equations used to determine floc water loss are presented as follows:

$$\frac{M_{ds} + M_{f-w}}{\rho_f} = \frac{M_{ds}}{\rho_k} + \frac{M_{f-w}}{\rho_w} \quad [32]$$

where:

$M_{ds}$  = mass of the dry solid particle = 1 g-DS

$M_{f-w}$  = mass of water within floc, in g

$\rho_f$  = floc density, in g/mL

$\rho_k$  = dry particle density, in g/mL

$\rho_w$  = density of water = 1.0 g/mL

Once the value of  $M_{f-w}$  (i.e. mass of water within the floc) is determined, the differences between the values for the unconditioned and conditioned/dewatered sludge samples can be calculated as follows:

$$\% \text{ Floc water removed} = \frac{(M_{f-w, \text{unconditioned}} - M_{f-w, \text{dewatered}})}{M_{f-w, \text{unconditioned}}} \times 100 \quad [33]$$

Table 35 presents the results of the above calculations, and indicate that for the Pepper's Ferry WWTP bio-solids sample, there was a 40% reduction in the floc water fraction after mechanical dewatering using the belt press. There was also a 14% removal of the floc water after polymer-conditioning. The removal was not as pronounced in the Blacksburg WTP PACl sludge, with only a 5% reduction in the floc water.

**TABLE 35**  
**CHANGES IN SLUDGE DENSITY VALUES AND CORRESPONDING WATER**  
**LOSS FOR UNCONDITIONED AND DEWATERED SAMPLES**

	<u>Sludge Type</u>	
	<u>PFWWTP</u> <u>Biosolids</u>	<u>Blacksburg</u> <u>WTP PACL</u>
<b>Density Values, in g/mL</b>		
<i>Unconditioned</i>		
Bulk	1.007	1.01
Floc	1.051	1.23
<i>After Polymer Conditioning</i>		
Bulk	1.006	-
Floc	1.058	-
<i>After Mechanical Dewatering<sup>a</sup></i>		
Bulk	1.05	1.08
Floc	1.078	1.24
Average Dry Particle	1.4	2.7
<b>Water Loss following Conditioning/Dewatering</b>		
<i>Floc Water Loss, % by weight</i>		
After Polymer Conditioning	14	-
After Mechanical Dewatering	40	5
<i>Overall Sludge Water Loss, % by weight</i>		
After Mechanical Dewatering	88	87
<i>Percent of Overall Water Loss due to</i>		
<i>Floc Water Loss</i>		
After Mechanical Dewatering	5.5	0.2

Note:

- a. Pepper's Ferry WWTP sludge was belt pressed after polymer conditioning at the plant, whereas the Blacksburg WTP PACl was centrifuged in the laboratory.

In addition, using the relationship that the mass (or volume) of the sludge could be represented by the sum of the masses (or volumes) of the dry solid particle and associated water, the following calculations were undertaken to determine the overall sludge water loss before and after dewatering:

$$V_s \times \rho_b = V_{ds} \times \rho_k + (V_s - V_{ds}) (\rho_w) \quad [34]$$

where:

$V_s$  = volume of sludge, in mL (assumed to be 1.0 mL)

$\rho_b$  = bulk density, in g/mL

$V_{ds}$  = volume of dry solid particle, in mL

$\rho_k$  = dry particle density, in g/mL

$\rho_w$  = density of water, in mL

Once the value of  $V_{ds}$  (dry solid particle volume) for the unconditioned sludge has been determined, the value of  $V_{tw}$  (i.e. volume of total water) can be determined by:

$$V_{tw} = V_s - V_{ds} = 1 - V_{ds} \quad [35]$$

Since Total Water in a sludge is assumed to be comprised of the Bound Water and Unbound Water fractions, the next step is to determine these fractions ( $V_{bw}$  = volume of the bound water fraction and  $V_{uw}$  = volume of the unbound fraction) by the following expressions:

$$(\rho_f) (V_{ds} + V_{bw}) = (V_{ds}) (\rho_k) + (V_{bw}) (\rho_w) \quad [36]$$

$$V_{uw} = V_{tw} - V_{bw} \quad [37]$$



Since the volume of the dry solid particle is assumed not to change upon dewatering, comparisons can be made between the unconditioned and dewatered sludge samples. Results of the above calculations for two sludges have been presented in Table 35. They show that dewatering leads to about 88% overall sludge water loss for both the sludges tested.

However, the reduction in the calculated internal sludge floc water content before and after mechanical dewatering to the overall sludge water loss was found to be small (<6% by weight for the bio-solid, and even lower, 0.2% for the WTP sludge). This is similar to that reported by Knocke, *et al*<sup>47</sup>, where the authors reported that the calculated contribution of internal floc water content loss to the overall sludge water loss during mechanical dewatering was <4%. This is evidently due to the nature of the two sludges as chemical and WTP sludges in general have lower floc waters as compared to bio-solids, and the conventional mechanical dewatering processes do not seem to be able to remove significant quantities of this sludge water fraction.

### **Evaluation of the Different Moisture Characterization Techniques Used**

As indicated previously, both the DSC and the dilatometer appeared to report values of bound water that were below the detection limit for some of the inorganic sludge samples. The two methods rely on the property of free water to freeze before that of bound water; the dilatometer by measuring the expansion of the frozen free water and the DSC by measuring the enthalpy change upon melting the frozen water. The operationally defined temperature demarcating the freezing point for both methods was taken to be -20 °C.

The percent standard deviation of results of the peak integral value (in J/g) reported by the DSC was less than 5% for replicate tests on the same set of inorganic sludge samples. When these peak integral values were used to determine

the bound water values in these sludges, the percent standard deviation increased to between 8 and 11%. In comparison, the standard deviation of results reported by the dilatometer ranged from 9 to 12%.

An analysis of the DSC data for both the unconditioned  $\text{CaCO}_3$ -water slurry and the laboratory  $\text{Al}(\text{OH})_3$  precipitate slurry (the two inorganic samples with the largest percent errors) indicated that in order for the instrument to report positive values of bound water (i.e. the unfreezeable fraction), the peak integral values for the free water fraction had to be at least 17% lower than reported for samples of total free water (308 J/g). Since the peak integral value represents the amount of the free water fraction, reduction of this fraction will avoid obscuring the bound water value. The large amounts of free water in the unconditioned samples used in the DSC tests "overwhelmed" the relatively low bound water fractions.

Another potential source of the error could have been the increasing size of the freezing ice crystals that may rupture the floc structure encompassing the bound water causing this fraction to freeze. While this may help to provide some indication of the variation within replicate tests of bio-solids, it is not believed to have significantly affected the inorganic sludges.

To obtain meaningful values of bound water, it is thus suggested that a major portion of the unbound water be removed, eg. by gravity thickening and decanting the supernatant or by centrifuging (mechanical dewatering may be avoided if it is believed to fundamentally change the floc structure), and a sample of this sludge analyzed. In addition, in order to be measurable (to overcome being "swamped out" or frozen over by the larger free water fraction), the amount of bound water present in a sample should exceed 0.2 g/g-DS. If, however, the bound water fractions are below 0.2 g/g-DS, negative values may be reported by the DSC as this may be within the experimental error (and/or minimum detection limits) of these instruments.

Another point that appears pertinent is the definition of the free water fraction commonly found in the literature. As indicated in the beginning of Chapter 5, this should more appropriately be called the unbound fraction as the free fraction

seems to include some interstitial/capillary waters that may freeze in varying amounts. Subtracting this amount from the total water (determined by the *Standard Methods*<sup>1</sup> recommended technique) would provide varying amounts of the bound water fraction measured by the DSC and the dilatometer. Removal of a greater portion of the unbound fraction (i.e. using dewatered samples with higher dry solids concentration) tends to provide bound water values that get closer together for both methods. It is thus proposed that the term "unbound water" be used to describe more correctly the fractions of sludge water that are not bound in subsequent moisture distribution/characterization studies.

## CHAPTER 7

### SUMMARY AND CONCLUSIONS

This chapter briefly summarizes the results and discussions of the previous chapters and presents specific conclusions based on the sludge moisture characterization studies undertaken. Recommendations for the experimental protocol for two moisture characterization studies that were developed (based on previous work using these techniques in other disciplines) have already been presented in Chapter 4.

- **Nomenclature** - It is proposed in this study that it would be more rational to classify water in sludges as either *bound* or *unbound*.

Bound water would represent water that is fairly tenaciously bound to the sludge particle matrix by a variety of chemical and physical mechanisms. These may include (and are not limited to) chemical hydration, coordination to metal ions, proximity to internal charged groups (such as  $\text{COO}^-$  and  $\text{NH}_3^+$ ), hydrogen bonding, entrapment within particles or floc structures, etc.

Unbound water would represent the remaining fraction (including sub-fractions previously referred to in the literature as free, bulk, interstitial, capillary, etc.) of the total water initially present in the sludge.

Total water can be determined from dry solids analysis of the sample at  $105 \pm 2^\circ\text{C}$  following *Standard Methods*<sup>1</sup>. This temperature setting appears to have contributed to the differences observed in the literature, as sub-fractions of the bound water are generally present even at a temperature regime of  $180^\circ\text{C}$  for bio-solids<sup>1</sup> and much higher ( $>400^\circ\text{C}$ ) for inorganic samples<sup>46,97</sup>. However, the sub-fractions of bound water that may be present above  $105^\circ\text{C}$  tend to be relatively very small and it is not economically feasible to remove these amounts.

In order to compare more easily the results of moisture characterization studies conducted by various researchers, it is also proposed that the term *g/g-DS*

be used as the measurement unit for the various sludge water fractions. In addition, data presented should also report the percent dry solids concentration and the temperature setting(s) used in the study.

● **Sludge Moisture Characterization Techniques** - For this study, the three methods used or developed based on previous work were the:

- thermo-gravimetric analyzer (TGA) using the drying rate curve technique to determine the demarcation point between the unbound and bound water fractions in a sample at the 40 °C isothermal setting,
- differential scanning calorimetric (DSC) method measuring the endotherm due to melting of the frozen unbound water in a sample in the temperature range -20 °C to 20 °C, and
- dilatometric method measuring the expansion of the freezing unbound water in the sample in the temperature range 20 ° to -20 °C.

*TGA* - This instrument was able to better define the inflection point on the drying rate curve and was also able to determine the operationally defined chemically bound water sub-fraction. It was unable to provide a clear inflection point when polymer-conditioned samples were analyzed due to loss of the constant drying rate/horizontal regime of the drying curve, and may have been because of hindered evaporation of the unbound water by the polymer.

*DSC* - The three instruments evaluated were affected by supercooling effects and hence unable to measure the rapid exothermic process that occurred on the cooling cycle when unbound water in a sample froze. Bound water was determined using the instrument's capability to measure accurately the endothermic response upon melting of the frozen unbound water fraction. There was a wider variability in the results obtained due to the small and sometimes non-homogeneous sample sizes used.

*Dilatometer* - The dilatometric method appeared to provide reproducible measurements of bound water as three relatively larger sized samples could be analyzed at the same time (the above two methods could only measure one sample at a time).

The limited sets of moisture distribution tests on the same types of sludges using the above three different characterization techniques indicated that the measured water fractions were different, due to inherent differences in the methods/techniques themselves. Observed differences in moisture measurements by the DSC and dilatometric methods may have been due to structural changes in the sludge water distribution induced upon freezing and thawing.

- **Other Sludge Characteristics**

- Limited floc density measurements using the isopycnic centrifugation method indicated that polymer conditioning and mechanical dewatering increased the sludge floc density due to release of a portion of the bound water fraction possibly within and external to the floc structure. However, mass balance calculations indicated that the vast majority of water removed during mechanical dewatering is unbound (free, interstitial) water.

- Measurements of the specific surface area of sludge samples using the EGME technique indicated that bio-solids had appreciably larger surface areas compared to inorganic/chemical sludges.

Estimates of the vicinal water fraction (based on the surface areas measured by the EGME method) as hypothesized by Drost-Hansen<sup>24</sup> indicated that the measured bound water fraction of sludges was a sub-set of the vicinal water.

Polymer conditioning was instrumental in changing the water distribution of these samples. Freeze-thaw cycling and polymer conditioning processes improved the dewaterability of the samples tested as measured by the capillary suction timer.

There was a reasonable degree of correlation between the measured sludge water fractions and the independently measured sludge density values.

## REFERENCES

1. American Public Health Association, American Water Works Association, and Water Environment Federation (APHA/AWWA/WEF), (1992). *Standard Methods for the Examination of Water and Wastewater*. 18th Ed., APHA, Washington, DC, 1100p.
2. Anderson, D.M. and Tice, A.R., "Low-Temperature Phases of Interfacial Water in Clay-Water Systems." *Soil Science Society of America Proceedings*, **35**, pp. 47-54 (1971).
3. Anderson, D.M. and Tice, A.R. (1973). The Unfrozen Interfacial Phase in Frozen Soil Water Systems. in: *Ecological Studies. Analysis and Synthesis*, **4**, Ed. A. Hadas, Springer-Verlag, Berlin.
4. Anderson, D.M. and Tice, A.R. (1985). Thawing of Frozen Clays. in: *Freezing and Thawing of Soil-Water Systems*, Technical Council on Cold Regions Engineering Monograph, ASCE, Eds. D.M. Anderson and P.J. Williams, Amer. Soc. of Civil Engrs., New York, NY, pp.1-9.
5. Anderson, D.M., Pusch, R. and Penner, E. (1978). Chapter 2: Physical and Thermal Properties of Frozen Ground. in: *Geotechnical Engineering for Cold Regions*, O.B. Andersland and D.M. Anderson, Eds., McGraw-Hill Book Co., New York, NY, pp. 37-102.
6. Angell, C.A. (1982). Chapter 1: Supercooled Water. in: *Volume 7. Water and Aqueous Solutions at Subzero Temperatures*, F. Franks, Editor, Plenum Press, New York, NY, pp. 1-82.
7. Antonsen, K.P. and Hoffman, A.S. (1992). Water Structure of PEG Solutions by Differential Scanning Calorimetry Measurements. in: *Poly(Ethylene Glycol) Chemistry: Biotechnical and Biomedical Applications*, Ed. J.M. Harris, Plenum Press, New York, pp. 15-28.
8. Apicella, A., Egiziano, L., Nicolais, L. and Tucci, V., "Environmental Degradation of the Electrical and Thermal Properties of Organic Insulating Materials." *Journal of Materials Science*, **23**(2), pp. 729-735, (1988).
9. Arundel, C.E. (1986). The Role of Flocc Density Measurements in Analyzing Sludge Dewatering Characteristics. M.S. Thesis, Department of Civil Engineering, VPI&SU, Blacksburg, Virginia.
10. Babbitt, J.D., "On the Differential Equations of Diffusion." *Can. J. Res. Sect. A*, **18**, pp. 419-474 (1950) (as cited by Fortes and Okos, 1980).
11. Bair, H.E. (1981). Chapter 9: Thermal Analysis of Additives in Polymers. in: *Thermal Characterization of Polymeric Materials*, Ed. E.A. Turi, Academic Press, Inc., New York, NY, 1981, pp. 845-909.
12. Bair, H.E., Johnson, G.E., Anderson, E.W. and Matsuoka, S., "Non Equilibrium Annealing Behavior of Poly(Vinyl Acetate)." *Polymer Engineering and Science*, **21**(14), Mid-October, pp. 930-935 (1981).
13. Barber, J.B. and Veenstra, J.N., "Evaluation of Biological Sludge Properties Influencing Volume Reduction." *Journal WPCF*, **58**(2), pp. 149-156, February (1986).



14. Berger, D. and Pei, D.C.T., "Drying of Hygroscopic Capillary Porous Solids, a Theoretical Approach." *Intl. J. Heat Mass Transfer*, **16**, pp. 293-302 (1973).
15. Briggs, D.R., "Water Relationships in Colloids. II. "Bound" Water in Colloids." *Journal of Physical Chemistry*, **36**, pp. 367-386 (1932).
16. Buckingham, E.A. (1907). Studies on the Movement of Soil Moisture. U.S. Department of Agriculture Bulletin, **38**.
17. Carter, D.L., Heilman, M.D., and Gonzalez, C.L., "Ethylene Glycol Monoethyl Ether for Determining Surface Area of Silicate Minerals." *Soil Science*, **100**, pp. 356-360 (1965).
18. Ceaglske, N.H. and Hougen, O.A., "The Drying of Granular Solids." *Transactions of the Am. Inst. of Chem. Engineers*, Vol. **33**(3), pp. 283-314 (1937).
19. Coackley, P. and Allos, R., "The Drying Characteristics of some Sewage Sludges." *Journal of the Institute of Sewage Purification*, pp. 557-564 (1962).
20. Dammel, E.E. and Schroeder, E.D., "Density of Activated Sludge Solids." *Water Research*, **25**(7), pp.841-846 (1991).
21. Davis, J.A., Fuller, C.C., Coston, J.A., Hess, K.M. and Dixon, E., "Spatial Heterogeneity of Geochemical and Hydrologic Parameters Affecting Metal Transport in Groundwater", *Environmental Research Brief*, EPA/600/S-93/006, August (1993).
22. De Groot, S.R. (1951). *Thermodynamics of Irreversible Processes*, 2nd Ed., Wiley, New York, NY.
23. Dishman, C.M. (1988). Floc Density Measurement and the Effects of Microproperty Variations on Sludge Dewatering Characteristics. M.S. Thesis, Department of Civil Engineering, VPI&SU, Blacksburg, Virginia.
24. Drost-Hansen, W.J. (1982). The Occurrence and Extent of Vicinal Water. in: *Biophysics of Water*, Eds. F. Franks and S.F. Mathias, Wiley-Interscience Publication, pp. 163-169.
25. Eagland, D. (1975). The Influence of Hydration on the Stability of Hydrophobic Colloidal Systems. (Chapter 1, Volume 5) in: *Water: A Comprehensive Treatise*, Ed. F. Franks, pp. 1-74, Plenum Press, New York, NY.
26. Eckhoff, S.R. and Bagley, E.B., "Differential Scanning Calorimetry for Rapid Exothermic Transitions." *Analytical Chemistry*, **56**, pp. 2868-2870 (1984).
27. Edlefsen, N.E. and Anderson, A.B.C., "The Thermodynamics of Soil Moisture", *Hilgardia*, **16**, pp. 31-299 (1943) (as cited by Fortes and Okos, 1980).
28. Eltantawy, I.M. and Arnold, P.W., "Reappraisal of Ethylene Glycol Mono-Ethyl Ether (EGME) Method for Surface Area Estimations of Clays." *Journal of Soil Science*, **24**(2), pp. 232-237, (1973).

29. Etzler, F.M. and Fagundus, D.M., "The Extent of Vicinal Water: Implications from the Density of Water in Silica Pores", *Journal of Colloid and Interface Science*, v 115 n 2, pp. 513-519 (1987).
30. Fortes, M. and Okos, M.R. (1980). Drying Theories: Their Bases and Limitations as Applied to Foods and Grains. in: *Advances in Drying*, Vol. 1, Ed. Arun S. Mujumdar, pp. 119-154, Hemisphere Publishing, McGraw-Hill, New York, NY.
31. Franks, F. Editor. *Water: A Comprehensive Treatise*. Volumes 1 through 7, Plenum Press, New York, NY, published from 1972 through 1982.
32. Franks, F. (1983). *Water*, The Royal Society of Chemistry, London, 96 pages.
33. Gordling, P. (1958). Physical Phenomena during the Drying of Foodstuffs. in: *Fundamental Aspects of the Dehydration of Foodstuffs*, Society of the Chemical Industry, London, U.K.
34. Gurr, C.G., Marshall, T.J. and Hutton, J.T., "Movement of Water in Soil due to a Temperature Gradient," *Soil Science*, 74, pp. 335-345 (1952).
35. Halde, R.E., "Sewage Sludge Characterization by Vacuum Drying," *Filtration and Separation*, 16, pp. 238-242, May/June (1979).
36. Harmathy, T.Z., "Simultaneous Moisture and Heat Transfer in Porous Systems with Particular Reference to Drying," *Ind. Eng. Chem. Fundam.*, 8(1), pp. 92-103 (1969).
37. Henry, P.S.H., "Diffusion in Absorbing Media," *Proc. R. Soc. London*, 171A, pp. 215-241 (1939).
38. Heukelekian, H. and Weisburg, E., "Bound Water and Activated Sludge Bulking," *Sewage and Industrial Wastes*, 28(4), pp. 558-574 (1956).
39. Hougen, O.A., et al, "Limitations of Diffusion Equations in Drying." *Transactions of the Amer. Inst. of Chem. Engineers*, 36(2), pp. 183-206 (1940) (as cited by Fortes and Okos, 1980).
40. Huang, Ju-Chrong. (1979). Sludge Characterization and Dewatering. Ph.D. Dissertation, Department of Civil Engineering, University of Missouri, Columbia, Missouri.
41. Jones, I.V. and Gortner, R.A., "Free and Bound Water in Elastic and Non-Elastic Gels." *Journal of Physical Chemistry*, 36, pp. 387-436 (1932).
42. Karr, P.R. and Keinath, T.M., "Influence of Particle Size on Sludge Dewaterability." *J. Water Pollut. Control Fed.*, 50(8), pp. 1911-1930 (1978).
43. Katsiris, N. and Kouzeli-Katsiris, A., "Bound Water Content of Biological Sludges in Relation to Filtration and Dewatering." *Water Research*, 21(11), pp. 1319-1327 (1987).
44. Kazansky, M.F., *Zh. Tekh. Fiz.*, 19, p. 743 (1949) (as reported by Luikov<sup>56</sup>).
45. Keey, R.B. (1973). *Drying: Principles and Practice*. Pergamon Press, Oxford, U.K.

46. Keey, R.B. (1992), *Drying of Loose and Particulate Materials*. Hemisphere Publishing Corp., New York, NY.
47. Knocke, W.R., Dishman, C.M. and Miller, G.F., "Measurement of Chemical Sludge Floc Density and Implications Related to Sludge Dewatering", *Water Environment Research*, **65**(6), pp. 735-743, September/October (1993).
- 48a. Knocke, W.R., "Comment on "Density of Activated Sludge Solids" by E.E. Dammel and E.D. Schroeder, *Wat. Res.* **25**, 841-846 (1991)," *Water Research*, **26**(11), pp. 1559-1561 (1992).
- 48b. Knocke, W.R., "Measurement of Chemical Sludge Floc Density and Implications Related to Sludge Dewatering." Author's Closure, to be published in *Water Environment Research*, 1994.
49. Krischer, O. (1963). *Die wissenschaftlichen Grundlagen der Trocknungstechnik*, Chap. IX, Springer, Berlin (as cited by Fortes and Okos, 1980).
50. Kumagai, H., Nakamura, K. and Fujiwara, J., "DSC Measurement of Frozen Water in Liquid Foods." *Agricultural and Biological Chemistry*, The Agricultural Chemical Society of Japan, **49**(11), pp. 3097-3101 (1985).
51. Kuzmak, J.M. and Sereda, P.J., "The Mechanism by which Water moves through a Porous Material Subjected to a Temperature Gradient: II. Salt Tracer and Streaming Potential to Detect Flow in the Liquid Phase." *Soil Science*, **84**, pp. 419-422 (1957).
52. La Mer, V.K., and Healy, T.W., "Evaporation of Water: Its Retardation by Monolayers." *Science*, **148**, pp. 36-42, 2 April (1965).
53. Lebedev, P.D., "Heat and Mass Transfer during the Drying of Moist Materials." *Intl. J. Heat Mass Transfer*, **1**, pp. 37-45 (1961).
54. Lewis, R.W., Morgan, K. and Thomas, H.R. (1983). The Nonlinear Modeling of Drying-Induced Stresses in Porous Bodies. in: *Advances in Drying*, Vol. 2, Ed. Arun S. Mujumdar, pp. 233-268, Hemisphere Publishing, McGraw-Hill, New York, NY.
55. Lide, D.R., Editor (1990). *CRC Handbook of Chemistry and Physics*, 71st Edition, CRC Press, Boca Raton, Florida.
56. Luikov, A.V. (1964). Heat and Mass Transfer in Capillary-Porous Bodies. in: *Advances in Heat Transfer*. Eds. T.F. Irvine et al., Vol. 1, Academic, New York, NY.
57. Luikov, A.V., "Application of irreversible thermodynamic methods to investigation of heat and mass transfer." *International Journal of Heat and Mass Transfer*, **9**, pp. 139-152 (1966).
58. Luikov, A.V. (1966). *Heat and Mass Transfer in Capillary-Porous Bodies*, Pergamon, Oxford, U.K.
59. McNeal, B.L., "Effect of Exchangeable Cations on Glycol Retention by Clay Minerals." *Soil Science*, **97**(2), pp. 96-102, February (1964).

60. Miller, E.E. and Miller, R.D., "Theory of Capillary Flow: I. Practical Implications." *Proc. Soil Sci. Soc. Am.*, **19**, pp. 267-271 (1955).
61. Miller, E.E. and Miller, R.D., "Theory of Capillary Flow: II. Experimental Information." *Proc. Soil Sci. Soc. Am.*, **19**, pp. 271-275 (1955).
62. Miller, G.F. (1988). The Role of Floc Density Measurement and the Centrifugal Density Gradient Technique in the Determination of Sludge Mechanical Dewatering Properties. University of Massachusetts, Amherst, Massachusetts.
63. Möller, U.K. (1983). Water Binding. in: *Sludge Characteristics and Behavior*, Eds. J.B. Carberry and A.J. Englande Jr., NATO ASI Series E: Applied Sciences-No. 66, Martinus Nijhoff.
64. Mraw, S.C. and Naas-O'Rourke, D.F., "Water in Coal Pores: Low-Temperature Heat Capacity Behavior of the Moisture in Wyodak Coal." *Science*, **205**, pp. 901-902, 31 August (1979).
65. Mraw, S.C. and O'Rourke, D.F., "Water in Coal Pores: The Enthalpy of Fusion Reflects Pore Size Distribution." *Journal of Colloid and Interface Science*, **89**(1), pp. 269-271, September (1982).
66. Mraw, S.C. and Silbernagel, B.G. (1981) Heat Capacity and NMR Studies of Water in Coal Pores. *AIP Conf. Proc. No. 70, Chemistry and Physics of Coal Utilization -1980*, Eds. B.R. Cooper and L. Petrakis, Amer. Inst. of Physics, New York, NY, pp. 332-343.
67. Neilsen, G.W. and Enderby, J.E., Eds. (1986). *Water and Aqueous Solutions*, Proceedings of the 37th Symposium of the Colston Research Society, Univ. of Bristol, April 1985, The Colston Research Society, Adam Hilger Publishers, U.K., 349 pages.
68. Novak, J.T., Beck, R. and Huang, T. (1982). The Distribution and Removal of Water from Sludge. Department of Civil Engineering, University of Missouri, Columbia, Missouri, unpublished.
69. Oliphant, J.L. (1985). A Model for Dielectric Constants of Frozen Soils. in: *Freezing and Thawing of Soil-Water Systems*, Eds. D.M. Anderson and P.J. Williams, Amer. Soc. of Civil Engrs., New York, NY, pp. 46-57.
70. O'Neill, M.J., "Differential Scanning Calorimetry for Rapid Exothermic Transitions." *Analytical Chemistry*, **57**, pp. 2005-2007 (1985).
71. Ott, R. Lyman. (1993). *An Introduction to Statistical Methods and Data Analysis*. 4th Ed., Duxbury Press, Wadsworth, Inc., Belmont, CA.
72. Personal Communication with Dr. Joseph Merola, Chemistry Department, VPI&SU, Blacksburg, November (1990).
73. Personal Communication with Dr. Thomas Ward, Chemistry Department, VPI&SU, Blacksburg (1993-1994).

74. Philip, J.R. and De Vries, D.A., "Moisture Movement in Porous Materials Under Temperature Gradients." *Transactions of the American Geophysical Union*, **38**(2), pp. 222-232, 594 (1957).
75. Pope, M.I. and Judd, M.D. (1977). *Differential Thermal Analysis. A Guide to the Technique and its Applications*. Heyden, London, U.K.
76. Rai, D. and Franklin, W.T., "Effect of Moisture Content on Ethylene Glycol Retention by Clay Minerals." *Geoderma*, **21**, pp. 75-79, Elsevier Scientific Publishing Co., Amsterdam (1978).
77. Redfern, J.P., "Precision-Controlled Cooling of a Differential Scanning Calorimeter." *American Laboratory*, p. 35, February (1994)
78. Rha, C. (1989). Advanced Centrifugation Technology for Sewage Treatment, Characterization of Sludge and Analysis of Dewatering Process: Bound Water in Municipal Wastewater Sludge. First progress report submitted to Bird Industrial Group. (as cited by Tsang, 1989)
79. Robinson, J.K. (1989). The Role of Bound Water Content in Defining Sludge Dewatering Characteristics. M.S. Thesis, Department of Civil Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA.
80. Robinson, J.K. and Knocke, W.R., "Use of Dilatometric and Drying Techniques for Assessing Sludge Dewatering Characteristics." *Water Environment Research*, **64**(1), pp. 60-68, Jan/Feb. (1992).
81. Rounsley, R.R., "Multimolecular Adsorption Equation". *American Institute of Chemical Engineers*, pp. 308-311 (1961).
82. Sato, H., Eto, S. and Suzuki, H., "Dewatering Sludges: Relationship Between Amount of Bound Water and Dewatering Characteristics of Alum Sludges." *Filtration and Separation*, **19**, pp. 492-497, November/December (1982).
83. Sherwood, T.K. and Comings, E.W., "The Mechanism of Drying of Clays." *Transactions of the American Institute of Chemical Engineers*, **27**, pp. 118-140 (1932).
84. Sherwood, T.K., "The Air Drying of Solids." *Transactions of the American Institute of Chemical Engineers*, **32**, pp. 150-168 (1936).
85. Smollen, M. (1986). Categories of Moisture Content and Dewatering Characteristics of Biological Sludges. *Proceedings of the 4th World Filtration Congress*, Ostend, Belgium, 22-25 April.
86. Smollen, M. (1990). Evaluation of Municipal Sludge Drying and Dewatering with respect to Sludge Volume Reduction. *Proceedings of the LAWPRC Specialty Conference on Sludge Management*, Los Angeles, CA.
87. Snoeyink, V.L. and Jenkins, D. (1980). *Water Chemistry*, John Wiley & Sons Inc., NY, 463p.
88. Tsang, R. Kwok-Wai (1989). Moisture Distribution in Wastewater Sludges. Ph.D. Dissertation, Department of Civil and Environmental Engineering, Duke University, Durham, N. Carolina.

89. Tsang, K.R. and Vesilind, P.A., "Moisture Distribution in Sludges." *Proceedings of the LAWPRC Speciality Conference on Sludge Management*, Los Angeles, California, January (1990).
90. United States Environmental Protection Agency (1986). *Test Methods for Evaluating Solid Waste*. Vol. IC: Laboratory Manual - Physical/Chemical Methods. Chapter 1: Quality Control. Office of Solid Waste and Emergency Response, USEPA, Washington, DC 20460, SW-846, Third Ed., November.
91. Van Arsdel, W.B., Copley, M.J. and Morgan, A.J.Jr. (1973). *Food Dehydration*. 2nd Ed., Vols. 1 and 2, AVI Publishing, Westport, Conn.
92. van Brakel, J. (1980). Mass Transfer in Convective Drying, in: *Advances in Drying*, Vol. 1, Ed. Arun S. Mujumdar, pp. 217-267.
93. Vesilind, P.A. (1979). *Treatment and Disposal of Wastewater Sludges*, revised edition, Ann Arbor Science.
94. Vesilind, P.A., "The Role of Water in Sludge Dewatering", *Water Environment Research*, **66**(1), pp. 4-11, Jan/Feb 1994.
95. Vollrath-Vaughn, J.A. (1984). Metal Sludge Thickening Characteristics: Particle Density Considerations. Department of Civil Engineering, VPI&SU, Blacksburg, Virginia.
96. Watson, E.S., O'Neill, M.J., Justin, J. and Brenner, N., "A Differential Scanning Calorimeter for Quantitative Differential Thermal Analysis." *Analytical Chemistry*, **36**, pp. 1233-1238, June (1964).
97. Wunderlich, B. (1990). *Thermal Analysis*, Academic Press, San Diego, CA, 450 pages.
98. Yakubu, P.I., Baianu, I.C. and Orr, P.H., "Unique Hydration Behavior of Potato Starch as Determined by Deuterium Nuclear Magnetic Resonance." *Journal Food Science*, Institute of Food Technology, Chicago, Illinois, **55**(2), pp. 458-461, March/April (1990).
99. Young, J.H., "Simultaneous Heat and Mass Transfer in a Porous Hygroscopic Solid." *Trans. ASAE*, **12**, pp. 720-725 (1969).
100. Pharmacia LKB Biotechnology, S-751 82 Uppsala, Sweden. Manufacturer's product information for Density Marker Beads<sup>R</sup> and Percoll<sup>R</sup> media (undated).

## VITA

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Upon graduation, Amit worked in the international consulting engineering arena in Southeast Asia for five years holding increasingly responsible positions including Assistant Managing Director of Seatec International, in Bangkok, Thailand.

In January 1989, he came to the United States to enroll in the Master of Science in Environmental Engineering at Virginia Tech, and subsequently remained to complete his graduate studies toward the Doctor of Philosophy degree in Civil (Environmental) Engineering.

He met his wife, Guneet Kumar, while at IIT and they were married in 1987. They have a one year old son, Abhik Kumar Pramanik, and presently live in Blacksburg.



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