THE ROLE OF BOUND WATER CONTENT IN DEFINING SLUDGE DEWATERING CHARACTERISTICS

by

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(ABSTRACT)

Several available methods of measuring sludge bound water content in the laboratory were examined. The effect of polymer conditioning on the bound water content of biological sludge samples was measured using the dilatometric method. The effects of mechanical dewatering on the bound water content of biological sludge samples and on chemical sludge samples was measured using the same method. The controlled drying method was used to measure the effect of polymer conditioning and mechanical dewatering on the chemically bound water fraction.

The relationship between bound water content and cake solids concentration was examined, as well as the relationship between cake solids concentration and sludge bulk density. The role of apparent sludge floc density was examined.

The dilatometric method was found to be the most accurate and most convenient method for measuring the chemically bound water fraction. Polymer conditioning was found to release significant volumes of bound water. Further bound water release was produced by mechanical dewatering. The amount of bound water released increased with the degree of mechanical dewatering pressure applied. The chemically bound water fraction was not affected by polymer conditioning or mechanical dewatering.

A reduction in bound water brought about a corresponding increase in cake solids concentration. Sludge bulk density increased with cake solids concentration. Apparent sludge floc density of the unconditioned, undewatered sludge sample was predictive of ultimate dewatering performance in many cases.

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CHAPTER I

INTRODUCTION

Sludge handling and disposal is often the single greatest cost in municipal water and wastewater treatment. An increase in the volumes of water and wastewater being treated, as well as more stringent treatment requirements, has resulted in greater sludge production. This sludge is composed mostly of water.

Bound water is that fraction of water in sludge which has an energy association with the solid material. Because of this energy association, bound water is more difficult and often more costly to remove. A better understanding of the distribution of water in a sludge and of the forces which bind this water within the sludge may lead to better dewatering performance. A reduction in sludge volume results in decreased handling and disposal costs. Removal of water is especially significant in cases where the sludge must be transported great distances or is incinerated as a means of ultimate disposal.

The objectives of this research study were to:

1. further define bound water and review available methods of measuring bound water content;

2. determine the effects of conditioning (chemical and freeze-thaw) and mechanical dewatering on bound water content;
3. correlate observed cake solids concentrations to bound water content;
4. determine the effects of conditioning and dewatering on the amount of chemically bound water present in a sludge;
5. determine if sludge bound water content is a predictive parameter when considering mechanical dewatering performance; and
6. determine if there is a correlation between bound water content and apparent sludge floc density.

CHAPTER II

LITERATURE REVIEW

WATER DISTRIBUTION THEORY

Sludge is a system of hydrophilic solid particles and the water associated with them. Many models have been developed to characterize this phenomenon. While each of the models differ to some extent, they all have common categories based on the intensity of the water binding forces.

Vesilind (1) has defined four categories of water in sludges. His model is based on high speed laboratory centrifugation of activated sludge samples. Each inflection point in the centrifugation curve is represented by one of the following categories of water:

1. Free water: water which is not attached to sludge solids in any way. This fraction is removed by gravity thickening.
2. Floc water: water trapped within the floc structure; removed by high speed centrifugation.
3. Capillary water: water which is adsorbed by individual solid particles; removed by very high speed centrifugation.

4. Bound water: water that is chemically bound to individual particles; not removed by the centrifugation process.

The water distribution model proposed by Smollen (2) is also composed of four categories. Emphasis is placed on specific energy requirements for liquid-solid separation. The following categories were derived by humidity-controlled, low temperature drying of a vacuum filter cake:

1. Free moisture: water which is loosely bound to sludge solids; removed by gravity thickening.
2. Immobilized moisture: water trapped within the floc structure; removed by mechanical dewatering.
3. Bound moisture: water which is adsorbed onto individual particles; removed by thermal drying.
4. Chemically bound moisture: water which is tightly bound to the solids by chemical attraction; removed only by high temperature (105° C).

With the exception of terminology, Smollen's model closely fits that of Vesilind.

A third water distribution model has been proposed by Möller (3). The model is based on the geometry of the floc and the properties of the individual liquid and solid components. Like Smollen's model, energy requirements for overcoming the water binding forces are emphasized. The first four categories constitute water that is external to the individual particles.

1. Interspace water: water that is minimally bound to solids; removed by draining.
2. Capillary water: water that is bound by capillary pressure; removed by the application of pressure.
3. Adhesion water: water that is intermediately bound to solids.
4. Adsorption water: water that is a protective layer intensely bound by ionic double layer; removed thermally.
5. Internal water: water that is inside the individual particles; defined as floc (or particle) moisture and chemically bound water. This water must be converted to external water either thermally or biologically before it can be removed.

The final model examined was constructed by Arundel (4). It is based on a three-tiered sludge structure made of primary particles, floc particles, and aggregate particles. Each degree of binding intensity corresponds to a different tier of the sludge structure:

1. Interspace/free water: water which is outside of the aggregate structure; removed by gravity thickening.

2. Interfloc/intra-aggregate water: water which is inside of the aggregate structure and outside of the floc structure; removed by centrifugation, vacuum dewatering, and during the first stages of high-pressure dewatering.
3. Intrafloc water: water which is inside of the floc structure; removed by high-pressure dewatering.
4. Adsorbed and internal water: water which is adsorbed to the primary particles; cannot be removed by mechanical dewatering.

A comparison of the water distribution models is presented in Table 1. Similar categories of water are listed in the same row. It should be noted that Möller's category of adhesion water doesn't appear to have a parallel in the other water distribution models. Also, Vesilind's capillary water and Arundel's intrafloc water differ from Smollen's bound moisture and Möller's adsorption water in the method of removal.

MECHANICAL DEWATERING

Mechanical dewatering involves the application of pressure to facilitate the removal of water from the sludge solids, thus producing a sludge of higher dry solids concentration. Mechanical dewatering is particularly

Table 1. Comparison of Water Distribution Models.

Vesilind (1)	Smollen (2)	Möller (3)	Arundel (4)
Free Water	Free Moisture	Interspace Water	Interspace/Free Water
Floc Water	Immobilized Moisture	Capillary Water	Interfloc/ Intra-aggregate Water
(none)	(none)	Adhesion Water	(none)
Capillary Water (removed mechanically)	Bound Moisture (removed thermally)	Adsorption Water (removed thermally)	Intrafloc Water (removed mechanically)
Bound Water	Chemically Bound Moisture	Internal Water	Adsorbed & Internal Water

attractive in urban areas where the high cost of land and the close proximity of residents would prohibit open air drying. It is also useful when climatic conditions do not favor open air drying and where sludges must be hauled great distances for ultimate disposal (5).

The extent of dewatering possible is a function of the energy applied in the form of dewatering pressure and the type of sludge being dewatered (5). Figure 1 displays the different degrees of dewatering achieved for different types of equipment and different proportions of primary sludge to waste activated sludge.

The belt filter press (BP in the figure) dewaters sludge by placing it between two porous belts. The belts pass over and under rollers of various diameter in a serpentine fashion. A decrease in roller diameter produces an increase in the pressure applied to the sludge. In the high pressure zone, pressure is exerted by the relative movement of one belt to the other (5).

Centrifuges (C) employ fast rotation to separate water from the sludge solids. Centrifugal force pushes the material away from the axis of rotation (against the interior walls of a solid bowl centrifuge). The more dense sludge solids travel the farthest, thus being separated from the water.

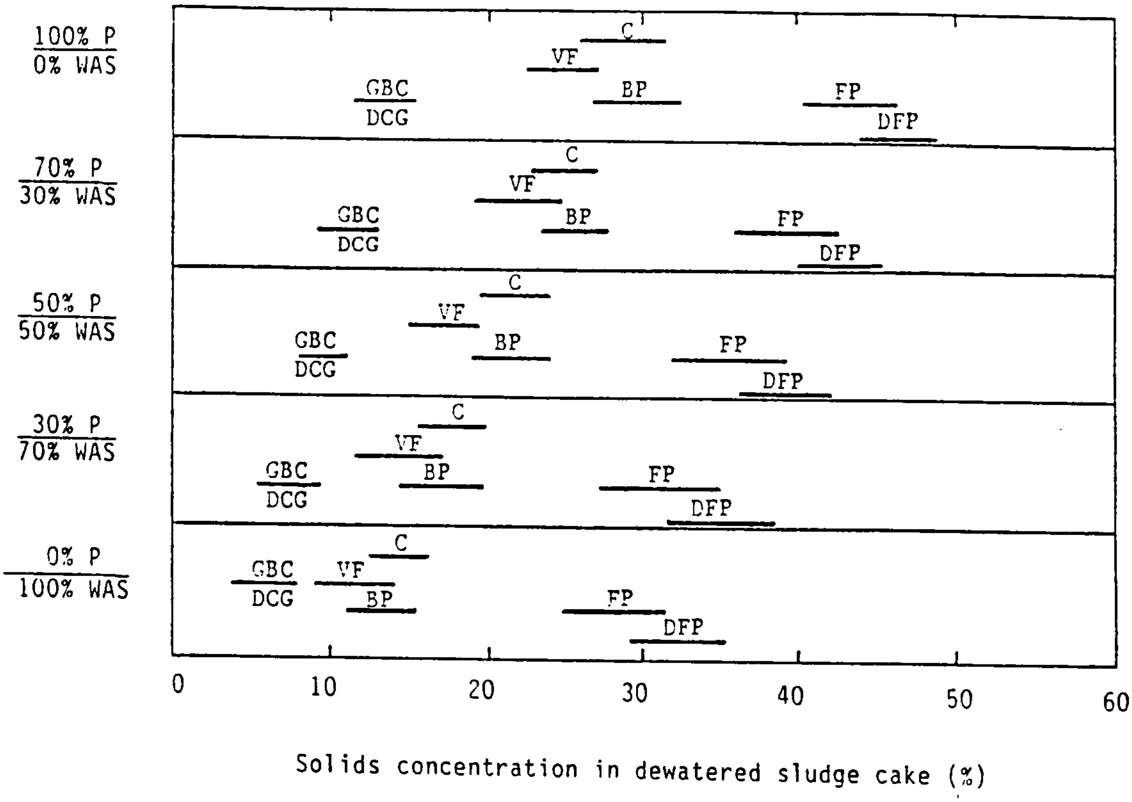


Figure 1. Degree of dewatering achieved for different types of equipment and different proportions of primary (P) sludge to waste activated sludge (WAS) (after EPA (5)).

C = Solid Bowl Centrifuge
VF = Vacuum Filter
BP = Belt Press
FP = Filter Press

DFP = Diaphragm Filter Press
GBC = Gravity Belt Concentrator
DCG = Dual Cell Gravity Unit

Higher concentrations of cake solids can be achieved using the filter press (FP), sometimes called a plate-and-frame press. Filter media are attached to the plates, which are held apart by the frames. Sludge is pumped into the void between the two plates. Liquid passes through the filter while solids are captured on it. Cake thickness can be adjusted by the thickness and number of frames separating the plates. Pressure is maintained during the filtration cycle by a fixed end and a movable end. Filter presses require a high degree of chemical conditioning as well as a great amount of operator time (5).

The vacuum filter (VF) was perhaps the most popular method of mechanical dewatering until the early 1970's, when improvements in other devices were made (5). It consists of a rotating horizontal drum covered with filter media. The bottom portion of the drum is submerged in sludge; internal vacuum pressure draws filtrate through the media. This is known as the cake-formation zone. In the cake-drying zone, the drum surface has rotated out of the sludge while the vacuum continues to remove moisture from the cake. In the cake-discharge zone, the cake is removed by a scraper blade.

Möller stated that "the removal of sludge water is above all a problem of energy" (3). For all methods of mechanical dewatering, the only water that can be removed is that which is bound to the sludge solids with a lower energy than the energy associated with the pressure applied during dewatering.

MECHANISMS OF CONDITIONING

The efficiency of sludge dewatering can be enhanced by chemical conditioning (1). Conditioners can be in the form of inorganic chemicals (i.e. metal salts) or organic chemicals (polymers).

The mechanisms by which these conditioners work are charge neutralization, interparticle bridging or a combination of the two (1). A third mechanism unique to certain inorganic conditioners is enmeshment of the particle in precipitating metal hydroxides (6).

The charge neutralization mechanism assumes an electric double layer. For example, most wastewater treatment sludge particles are negatively charged (1). Tightly surrounding each particle is a layer of positively charged ions. This is known as the Stern layer (7). The Gouy-Chapman (or diffuse) layer is a loose layer of positive and negative ions surrounding the Stern layer.

The summation of repulsive forces from like charges and attractive forces (van der Waals) equals a net repulsive force except at very short and very long particle distances (7). This net repulsive force, or energy barrier, maintains an intermediate distance between the particles.

Substitution of polyvalent cations in the Gouy-Chapman layer decreases the negative charge which in turn decreases the repulsive forces. This leads to the eventual elimination of the energy barrier, thus allowing the particles to come together (1,7).

Interparticle bridging is the mechanism where individual sludge particles attach to long-chained molecules. This creates a three dimensional floc network (1,8).

The use of inorganic conditioners decreases the compressibility of the sludge (6). A highly compressible sludge doesn't respond well to filtration. Sludge compressibility may be increased by the addition of polymers. However, polymer conditioning generally produces less additional sludge.

Polymer dose requirements increase with mixing time and intensity. By conditioning with a high molecular weight polymer and intense mixing, a floc can be produced which can withstand the shear environment within a mechanical dewatering device (9,10).

Another method of conditioning sludges is freeze/thaw conditioning. Slow freezing followed by thawing improves the response to filtration of both biological and alum sludges (1,8). As the ice crystals form, the solid particles are compacted together, forming larger flocs. The flocs, after thawing, respond well to dewatering. Also, freeze/thaw conditioning has been reported to reduce the bound water content of biological sludges by 70 percent (8).

The shear strength of the flocs produced following freeze/thaw conditioning is important because the sludge will invariably be subjected to additional pumping and piping. Freeze/thaw conditioned alum sludges showed little change in capillary suction time (CST) before and after stirring, indicating a strong floc structure. Biological sludges are not well suited for freeze/thaw conditioning because a very fragile floc structure is produced (11).

The effluent from freeze/thaw conditioned sludges is low in suspended solids. However, the effluent from freeze/thaw conditioned biological sludges has a high oxygen demand. This creates an additional burden on the treatment plant when the supernatant is recycled (6).

Finally, high energy requirements, as well as expansion/contraction fatigue of the equipment, is associated with freeze/thaw conditioning (6). Therefore, it is best utilized where climatic conditions make natural freeze/thaw conditioning possible.

METHOD OF BOUND WATER DETERMINATION

Different methods of determining the quantity of bound water in sludges have yielded different results (12).

Therefore, bound water becomes an operational parameter, the definition and value being a function of the method of determination. In general, bound water is that fraction of water which is held closely to the dry solids by some form of binding force.

Drying. One means of quantifying the distribution of water in a sludge is the drying method, developed by Smollen (14). A mechanically dewatered sludge sample is dried at a constant low temperature (35° C) and controlled humidity. The sample is weighed each hour. The hypothesis is that the rate of water removal is constant as long as immobilized water or 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 mass after drying overnight at 103° C represents the bound water fraction (2,13,14). A second characteristic is quantified by taking the mass at which no further moisture is removed at 35° C minus the mass of dry solids. This value is defined as the chemically bound water fraction (2,14).

Inorganic sludges with a definite crystal structure (such as alum) show a definite critical point. The critical point for biological sludges is not well defined (14).

Sato (13) performed the drying test on alum sludges that had been conditioned by anionic polymers and dewatered by a bench-scale, belt filter press. He found the moisture content of the dewatered cake to increase linearly with an increase in bound water.

Smollen (14) utilized the same test procedure to evaluate biological sludges that had been dewatered by vacuum filtration. She found the moisture content of the dewatered cake increased linearly with an increase in the immobilized water fraction. However, she concluded that the cake moisture was independent of the measured bound water fraction.

Differential Thermal Analysis. Differential thermal analysis (DTA) is based on the assumption that bound water does not freeze at -20° C. In this method, a sample is cooled at a low rate (2° C per min) and the temperature difference between the sample and a thermally inert material (i.e. alumina powder) is recorded. (The temperature differences seem to take place between -1° C and -4° C.) A curve is generated which depicts either the adsorption or release of heat. The area under this curve can be integrated and is proportional to the heat of reaction. From the heat of reaction, the quantity of active water can be determined. In this case, active water is synonymous with freezable water. The water which does not freeze is defined as bound water (8).

DTA has been used in clay mineralogy, biology, and medicine. With biological sludges, results from DTA were very similar to those obtained using dilatometric methods (8).

Sucrose Solution. Another method of bound water determination is the measurement of the concentration of a known amount of a soluble material added to the sample. This is based on the premise that bound water is not available to dissolve the solute. A substance which is readily soluble in water, such as sucrose, should be used. This technique has been used to a limited degree in the food industry, but it is not known to have ever been applied to sludges (12).

Cobalt Chloride. Cobalt chloride hexahydrate ($CoCl_2$ * $6H_2O$) turns from pink to blue when it loses its water and becomes pure $CoCl_2$. The bound water content of a sample can be determined by adding this substance to a sample and drying it at a low temperature similar to that used in the drying test developed by Smollen, (i.e. 35° C). When the cobalt chloride turns blue, the sample is weighed, dried at 103° C, and weighed again. The mass difference would quantify the bound water fraction (12).

One advantage of this technique over Smollen's drying test is that hourly weighing of the sample is no required. However, the sample would need to be viewed regularly in order to weigh it at the time of the color change. Another advantage is that since changes in the rate of drying are not important, the humidity does not need to be held constant. Finally, the guesswork of selecting the breakpoint on the drying curve is eliminated. The problem arises in seeing the color change because of the dark, opaque nature of many sludges.

Dilatometric/Calorimetric. The most popular method of bound water determination may be the freezing method. It has been reported to be the most reliable and reproducible (12,15,16). The basis of the freezing method is that bound water does not freeze at certain temperatures below the freezing point of water, in this case -20° C (17).

The freezing method can be performed by either calorimetric or dilatometric methods. In both cases, the sample temperature is decreased to a value well below the freezing point of water (i.e. -20° C). Calorimeters measure the amount of heat required to return the sample to ambient temperature (18). The amount of water that was frozen can thereby by determined. Dilatometers measure the expansion of a sample caused by water freezing (17). From the known expansion of a volume of distilled water freezing, the amount of frozen water can be determined. Given the total water content from drying a sample overnight at 103° C and the amount of water frozen at -20° C, the amount of water not frozen can be calculated. This unfrozen water is considered to be the bound water fraction.

When ice crystals begin to form during the freezing process, the concentration of dissolved solids in the remaining solution becomes more concentrated (12). Therefore, at temperatures just below freezing, some non-frozen water may exist not because of an association with the sludge solids but because of the concentration of dissolved solids. This free, non-frozen water fraction disappears around -20° C (18).

Newton's Law of Cooling states that the rate at which a body cools is directly proportional to the difference between the temperature of that body and the ambient temperature (19). In other words, the driving force in cooling the sample is the temperature gradient. However, it should be noted that the quantity of water frozen does not depend on the rate of freezing (20).

The dilatometric method was used by Heukelekian and Weisberg to study the relationship between bound water and bulking sludge (17). They found the bound water content of bulky sludges to be significantly higher than that of non-bulky sludges.

FLOC DENSITY

Michaels and Justin (21) hypothesized that sludge exists in a three-tiered structure: primary particles, floc particles, and aggregate particles (4). The floc structure consists of primary particles, the water closely associated with the primary particles (adsorbed and internal water), and the water between the primary particles (intrafloc water). Increases in floc density have been shown to improve thickening and dewatering characteristics (22).

Floc density can be measured using density gradient centrifugation. This method is based on the premise that a particle will move downward through a media until it reaches a density equal to its own, known as the isopycnic point (22). This downward force is provided by gravity; however, centrifugation can be used to increase the force and to overcome forces from back-diffusion.

Samples are placed on top of a density gradient, which is a column of media in a centrifuge tube with density increasing from top to bottom. The density gradient can be step or continuous. In continuous gradients, marker beads of known density are used to identify the density of the gradient at that point. The tube is centrifuged until there is no further downward travel of the sample. The density of the media at this point (known as the isopycnic point) is equal to the density of the sample (in this case, the floc density) (4,22). Fixed-angle rotor centrifugation was chosen over swinging-bucket because of a shorter gradient path length, a larger gradient cross-section (elliptical) and a shorter time of travel because of convection forces (22).

Arundel (4) made measurements of bulk density and plotted them against cake solids. The bulk densities of samples subjected to centrifugation and vacuum filtration did not exceed measured floc density. However, after high pressure dewatering, bulk densities were greater than measured floc density. This suggests that high pressure dewatering removes floc water, bringing about a corresponding increase in actual floc density.

Bulk density is the sum of the proportional fractions of floc density and the density of the interfloc water (4). Bulk density can exceed the measured density of undeformed floc, but never the actual floc density.

Knocke (23) found a direct correlation between floc density and the ultimate solids concentration of vacuum filter cake. However, he found no relationship between sludge floc density and dewatering rates.

CHAPTER III

METHODS AND MATERIALS

This section describes the experimental methods and materials used to collect data for this research study. Full-scale water and wastewater treatment facilities which served as sources for sludge used in these studies are identified. This section also discusses the dewatering techniques used for sludge characterization and describes the methods for the determination of bound water in the sludge samples.

SLUDGE SOURCES

Sludge samples were characterized from five different full-scale treatment facilities. These sources are as follows:

1. Anaerobically digested waste activated sludge: obtained from the Peppers Ferry Regional Wastewater Treatment Facility in Fairlawn, Virginia.
2. Alum water treatment sludge: obtained from the Radford Army Ammunition Plant in Montgomery County, Virginia. Raw water source is the New River.

3. Polymer water treatment sludge: obtained from the water treatment plant in Amherst, Massachusetts.
4. Lime sludge: obtained from the water softening plant in Columbia, Missouri.
5. Aerobically digested waste activated sludge: obtained from the Elliston-Lafayette Regional Wastewater Treatment Facility in Montgomery County, Virginia.

POLYMERS/CONDITIONING

Tests were performed on unconditioned sludge samples and on sludge samples conditioned by polymer addition. Polymers were supplied by Nalco Chemical Company and are listed in Table 2. Anaerobically digested biological sludge samples were conditioned by high molecular weight, high charge density cationic polymers. Aerobically digested biological sludge samples were conditioned by high molecular weight cationic polymers of both high and low charge density.

One percent by weight (10,000 mg/L) stock solutions of polymer were prepared daily. This was accomplished by transferring 400 mL of tap water to a Nalgene 1 liter, round, plastic stirring jar. A caged impeller mixing paddle was introduced into the water. The mixing paddle was

Table 2. Nalco Polymers Evaluated for Influence on Bound Water Content of Biological Sludge Samples.

Polymer	Description
52-E	strongly cationic
52-F	slightly cationic
52-G	slightly cationic
52-H	slightly cationic
52-I	strongly cationic

NOTE: All are considered high molecular weight polymers.

powered by a Cole-Parmer variable speed motor mounted on a ring stand. The mixing paddle rotated at a speed sufficient to create a vortex in the water. The emulsion flocculant was shaken for several seconds to insure product uniformity. Four 1-mL volumes of the product were injected into the vortex by a 1-mL plastic syringe. The solution was mixed strongly for 15 to 30 minutes before use (24).

Polymer stock solution was added to 0.5-L sludge samples in a calibrated bench-scale mixing device. The bottom portion of the device consisted of a 3.7-in diameter plexiglas cylinder, 8.5-in high. Four 0.5-in plexiglas baffles were located lengthwise in the cylinder at 90 degrees apart. Mounted on top of the cylinder was a Eastman Model 3 variable speed stirring motor which turned a 2-in by 0.5-in metal paddle. A 116B Powerstat Variable Auto Transformer regulated motor speed. Paddle speed was measured in revolutions per second by a Hewlett Packard Model 3734-A electronic counter. The torque on the paddle was measured by a Power Instruments Model 783 torque meter.

Mixing intensity was measured in terms of Gt, where

G = mean velocity gradient, sec^{-1}

t = mixing time, sec

Sludge samples were mixed at 10 revolutions per second, which corresponds to a G of 640 sec^{-1}.

Capillary suction time (CST) was determined using a standard CST apparatus. The device measures the time required for sludge filtrate to travel through a blotter between two concentric circles. A well dewatering sludge will have a lower CST value than a poorly dewatering sludge. Optimum polymer dosages were chosen by conditioning the samples with a series of polymer dosages at a fixed mixing intensity. The dosage corresponding to the minimum CST value was considered to be the optimum dosage for that particular sample and mixing intensity.

Sludge samples that had been freeze/thaw conditioned were also examined. 850 mL of sludge was frozen in 1-liter containers in a conventional freezer at -14° C for a minimum of 24 hours. The samples were then thawed overnight at room temperature (20-25° C). Any supernatant produced from freeze/thaw conditioning was decanted and disposed of.

SLUDGE CHARACTERISTICS

Dry solids concentrations were determined by weighing an empty aluminum pan, adding a sample of sludge to the pan, and reweighing. The sludge was dried overnight at 103° C, allowed to cool, and then reweighed. Percent solids was calculated as follows:

$$\text{\% Dry Solids} = \frac{\text{net mass of sample after drying}}{\text{net mass of sample before drying}} \times 100\% \quad [1]$$

Sludge bulk density (units of g/mL) was determined by use of a glass pycnometer. The pycnometer was initially filled with distilled water and weighed. Knowing this weight of water and the corresponding density of water, one could determine the precise volume of the pycnometer. The pycnometer was then emptied, dried, filled with a sludge sample, and weighed again. The bulk density (p_b) was calculated as follows:

$$p_b = \frac{\text{mass of sludge sample}}{\text{volume of pycnometer}} \quad [2]$$

In cases where the dewatered sample was no longer liquid, the pycnometer was filled approximately one third with the sample and weighed. Distilled water was then added until the pycnometer was filled. At this point the pycnometer was weighed again. Bulk density was then calculated by dividing the mass of the sample by the mass of the water it displaced:

$$p_b = \frac{\text{mass of sludge sample}}{\text{vol. of pycnometer - vol. of water added}} \quad [3]$$

Dry solid density (p_k) can be determined from the following equation, given bulk density and percent solids:

$$\frac{100}{p_b} = \frac{(100 - C)}{p_w} + \frac{C}{p_k} \qquad [4]$$

where C = dry solids concentration, percent by weight

p_w = density of water (1.0 g/mL)

p_b = bulk density of sludge, g/mL

The dry solids concentration (cake solids) was used in conjunction with the mass of the sludge sample to determine the mass of sludge solids in the dilatometer. Sludge bulk density was used in conjunction with the mass of sludge sample to determine the volume of the dilatometer which was occupied by the sample. Cake solids were correlated to bound water content, and sludge bulk density was correlated to cake solids to determine the relationship between bound water content and dewatering performance. Dry solid density was used to calculate apparent sludge floc density.

DEWATERING METHODS

Characteristics of the sludge samples were evaluated after gravitational thickening, and after dewatering by vacuum filtration, low speed centrifugation, high speed centrifugation, and/or pressure filtration.

Vacuum dewatering characteristics were quantified using a Buchner funnel according to methods described by Vesilind (1). Conditioned samples were poured into the funnel and a vacuum of 15 inches of mercury applied. The filtrate passed through Whatman #40 ashless filter paper into a graduated cylinder. The sludge samples were dewatered until either the cake cracked, the pressure across the cake decreased, or no further filtrate was removed from the sample. The resulting sludge cake was characterized for dry solids concentration and bound water content.

Low speed centrifugation was accomplished with an International Equipment CS swinging-bucket centrifuge. 200 mL sludge samples were placed in plastic bottles. Drops of distilled water were added to the lighter bottle of each pair until the pair was balanced. The samples were centrifuged for 10 minutes at 2000 rpm (480 g). High speed centrifugation was accomplished using a Beckman J-21C fixed-angle rotor centrifuge. Tubes containing 35 mL samples of sludge were weighed, balanced, and subsequently centrifuged for 10 minutes at 12,000 rpm (5200 g).

A bench-scale plate-and-frame press was used for pressure filtration. The press was manufactured by JWI, Inc. The space between two of the 250 mm square plates was filled with sludge and a hydraulic pressure of 6000 psi applied. The press was operated for 60 minutes at a flow pressure of 100 psi; the volume of sludge sample dewatered was approximately 10 L.

BOUND WATER DETERMINATION

Drying Method. Unconditioned, undewatered samples of each sludge were evaluated for bound water by the drying method of Smollen (14) and Sato (13). Five replicates of the sample were dried simultaneously at a low temperature (35° C) and controlled humidity. The five replicates were weighed periodically and the mass of moisture evaporated was recorded as a function of drying time. An example of the average moisture loss compared to drying time is shown in Figure 2. The point (A) at which the curve is no longer linear is considered the point at which all the free water has been driven off and only bound water remains. This critical point can be more easily determined from Figure 3, which shows drying rate as a function of moisture content. The point at which the drying rate begins to decline (Point B) is the critical point. In biological sludges, it is common for the drying rate to increase for a short time before leveling off and then declining (14).

After the drying rate reaches zero, the samples are transferred to a 103° C oven for dry solids determination.

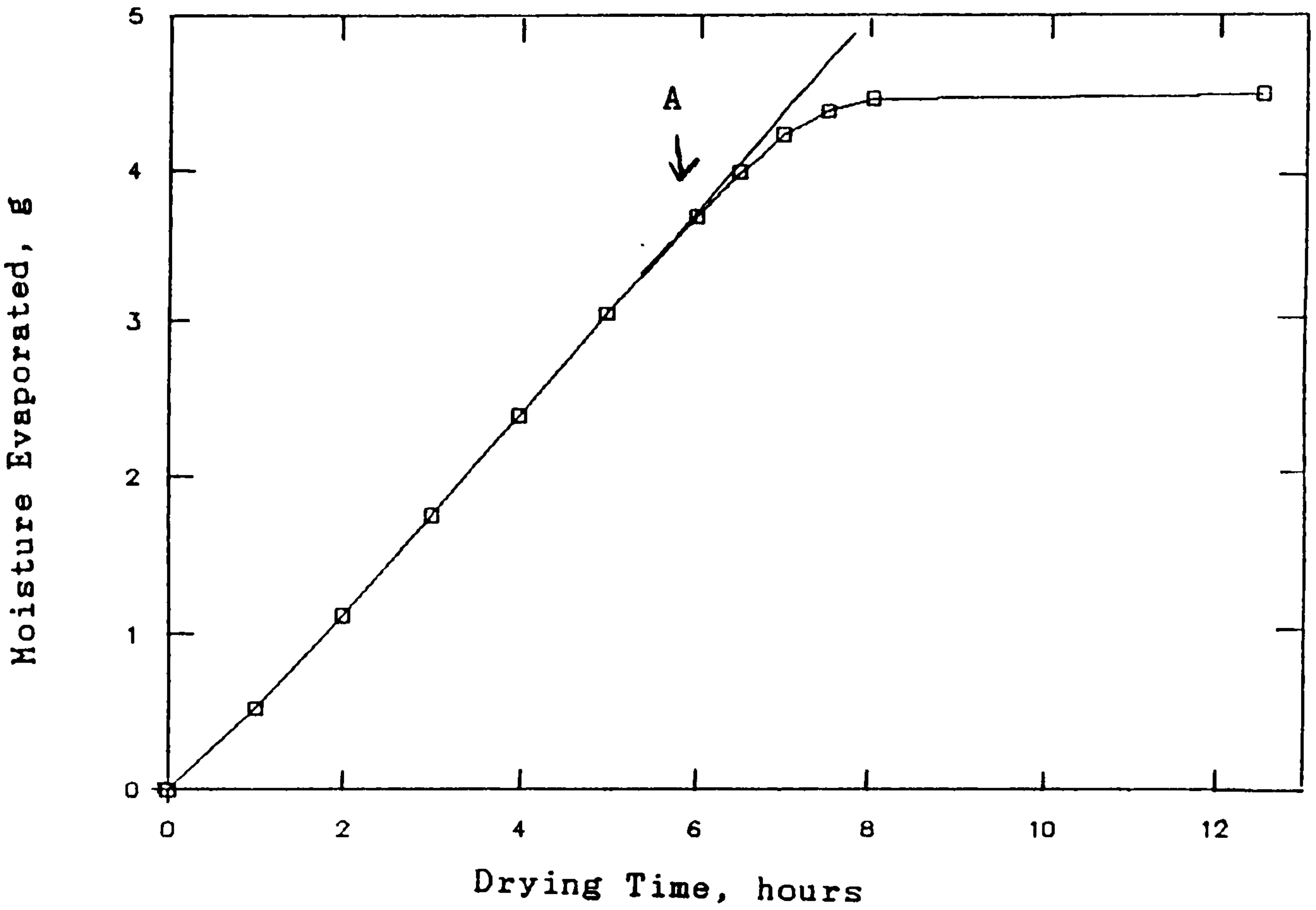


Figure 2. Moisture Loss vs. Time for an Anaerobically Digested Biological Sludge at 35° C.

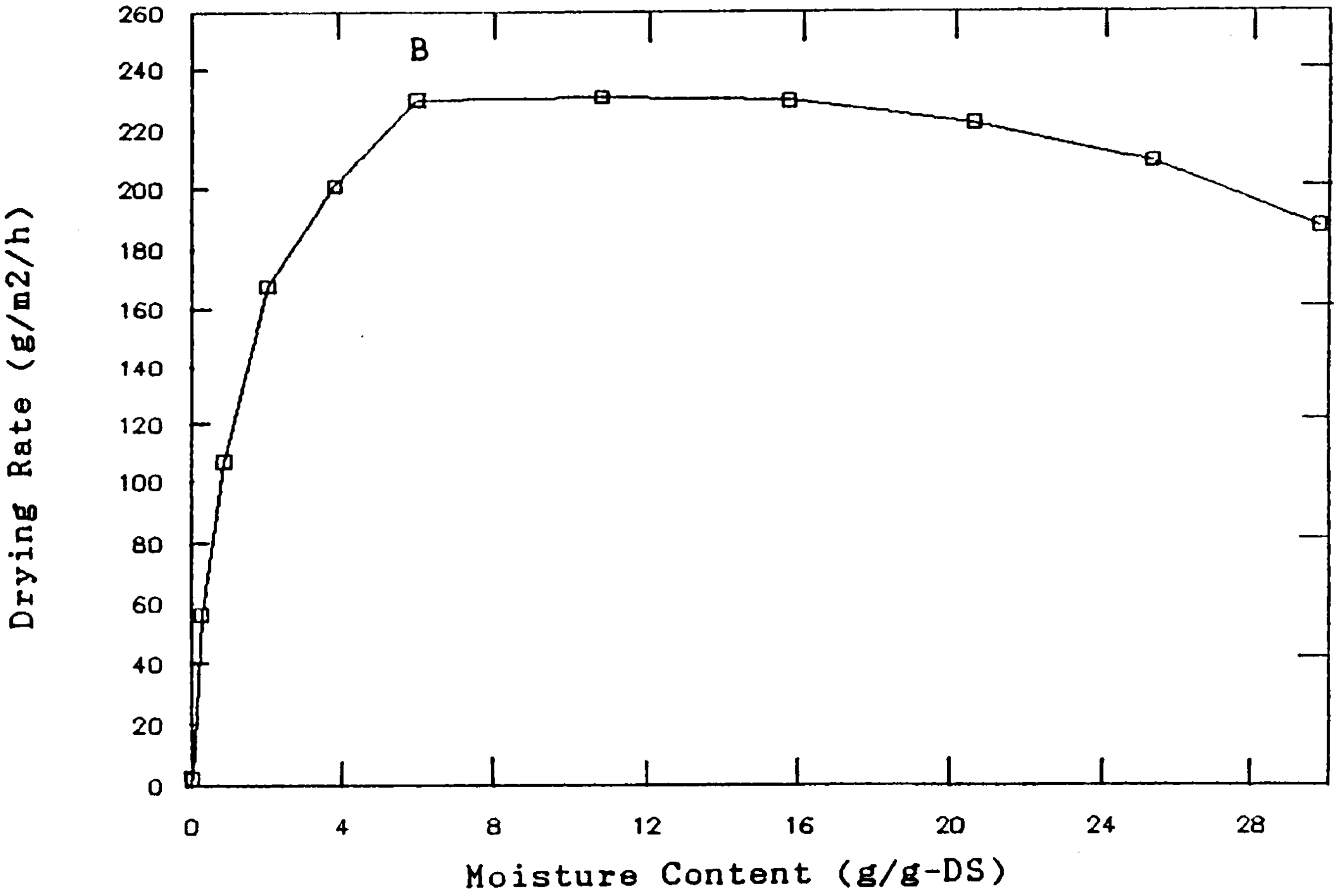


Figure 3. Drying Rate for an Anaerobically Digested Biological Sludge at 35° C.

The mass difference in the sample after drying at 35° C and after drying at 103° C is defined to be the chemically bound water fraction.

Dilatometric Method. Dilatometric units were fabricated from standard taper ground glass joints, as shown in Figure 4. A 5-mL glass pipette with its ends removed was fused into the top portion of each unit. Top and bottom halves were lettered so that matched pairs could be maintained. Hooks were fused onto each piece so that the assembled units could be held together by springs.

The bottom portion of each unit was filled with approximately 15 mL of hydraulic oil and a weighed amount of sludge sample. The top portion was lubricated with silicon and inserted into the bottom portion. The assembled units were held together by springs and filled with oil through the pipette.

A control unit was established by inserting a thermometer in a rubber stopper that had been inserted in a bottom section containing oil and sludge. A small-bore pipette was also inserted in the stopper to accommodate expansion and contraction.

A standard curve was developed by filling one unit completely with hydraulic oil (unit A), a second unit with 10 mL distilled water and hydraulic oil (unit D), and a

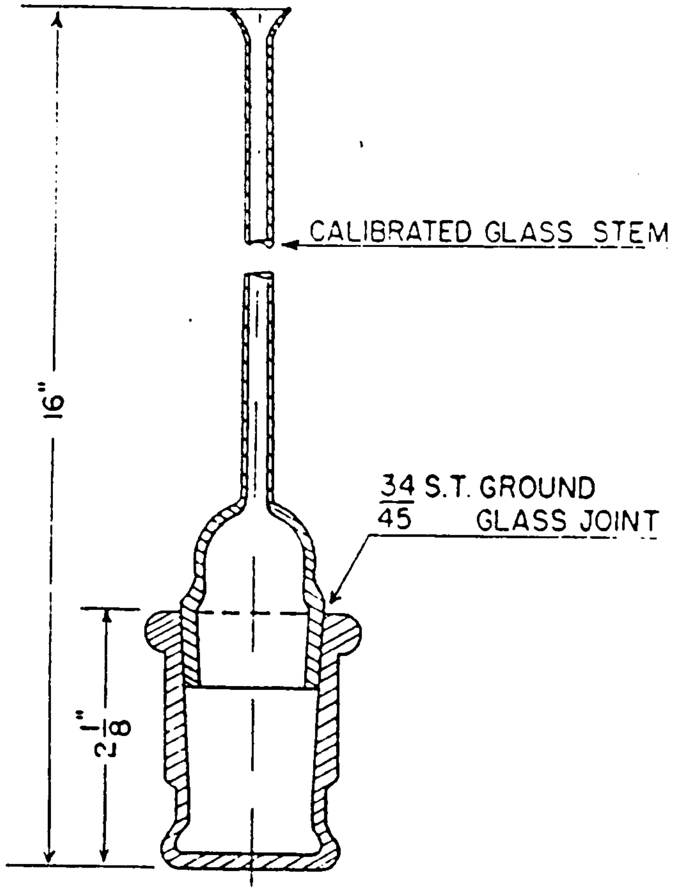


Figure 4. Dilatometer for Bound Water Determinations (after Heukelekian (17)).

control with 10 mL distilled water and hydraulic oil. The unit contraction of the hydraulic oil can be determined from unit A, and the expansion per mL of distilled water can be determined from unit D.

The three units were placed in a 20° C ethanol bath until the temperature of the control was 20° C and the level of hydraulic oil in units A and D was constant. The temperature of the bath was maintained by adding small pieces of dry ice as needed.

Once the system reached an equilibrium at 20° C, the level of oil in units A and D was recorded. (The control unit is for temperature determination alone, thus has no fluid level). The temperature of the bath was lowered to 10° C by adding more dry ice. When the system reached an equilibrium at 10° C, the oil levels in units A and D were recorded again. This procedure was repeated at 10° intervals down to -20° C. A reading was also taken just below 0° C to better define the shape of the oil and water curve.

The results of the standard curve are shown in Figure 5. The spike at 0° C in curve D is due to the expansion of freezing water. The following calculations are used to determine the contraction per unit volume of oil and the expansion per unit volume of water:

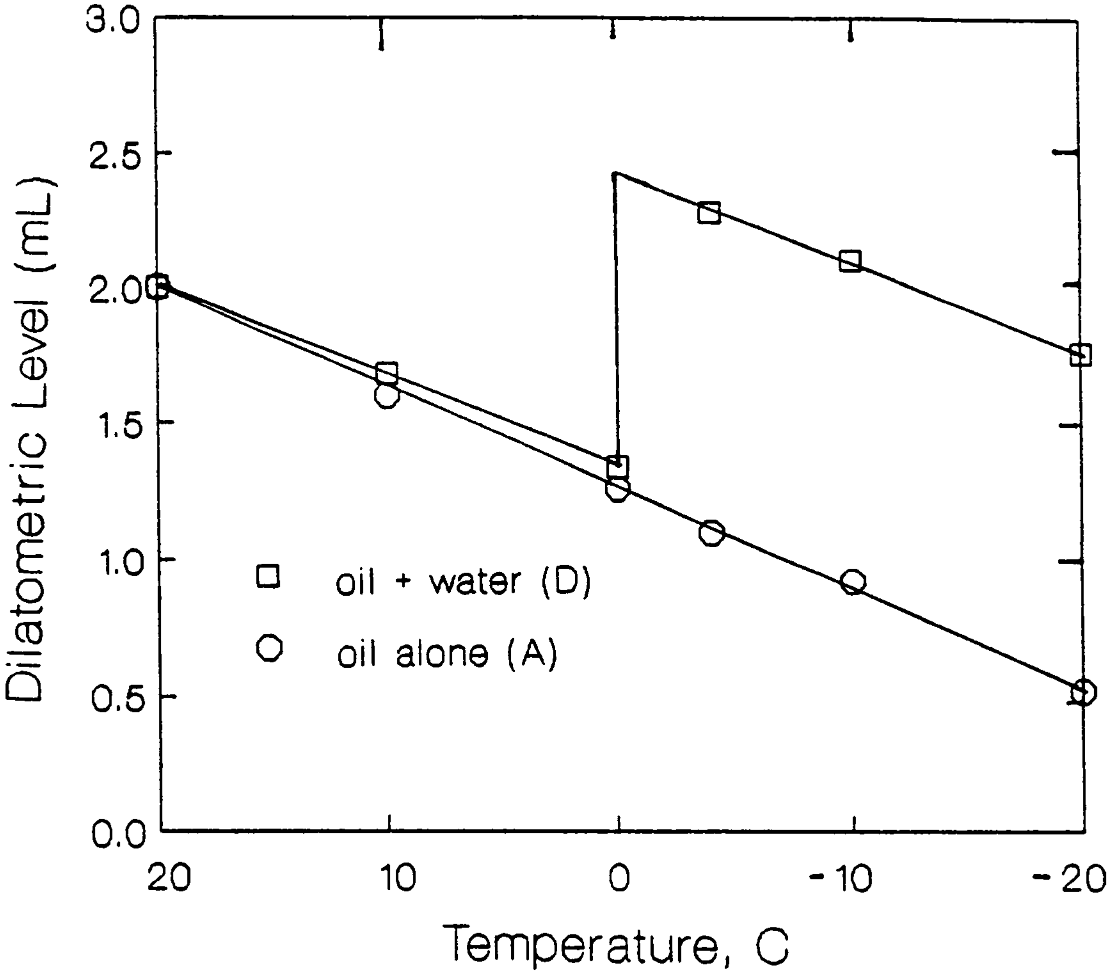


Figure 5. Standard Curve for Dilatometric Method

The total volume of unit A was 50.7 mL. It was filled with oil, which contracted 1.48 mL over the 40° C temperature drop, or 2.92 percent (1.48 / 50.7 = 0.0292).

The total volume of unit D was 52.4 mL. It was filled with 10 mL of distilled water and 42.4 mL of oil. The oil in unit D should have contracted 1.24 mL (= 42.4 x 0.0292) over the same temperature range.

The expansion of the 10 mL of water in unit D was equal to the contraction of the oil minus the contraction of the oil-water mixture in the same unit. (The contraction of the oil-water mixture was 0.24 mL.)

Thus, 10 mL of water expanded 1.00 mL (= 1.24 - 0.24), or 0.100 mL per mL.

Once the standard curve was established, replicates of three samples and one control were performed for each type of sludge and each degree of conditioning/dewatering encountered. The volume of the sludge sample in each unit was calculated by multiplying the mass of the sludge sample by the sludge bulk density.

Given the contraction per unit volume of oil and the expansion per unit volume of water over the cooling regime, the volume of freezable water could be determined from the net expansion or contraction in the dilatometric unit. The difference between this freezable (or free) water and the total water (as determined by dry solids analysis) is defined as bound water. The mass of bound water was then divided by the mass of dry solids and ultimately reported as grams bound water per gram dry solids (g/g-DS).

In selecting a measuring fluid for use in the dilatometers, the following requirements had to be met:

1. Immiscible with water. This is necessary in order to insure complete segregation between the hydrophilic sludge sample and the measuring fluid.
2. Specific gravity less than 1.0. This will keep the measuring fluid above the sample and prevent the sample from entering the calibrated stem.
3. Linear contraction over the entire temperature range. This will eliminate any irregularities in the standard curve and keep the calculations simple.
4. Does not freeze at -20° C. This will keep the measuring fluid in a liquid state so that it can move freely within the dilatometer.

The first fluid tried was conventional 10W30 motor oil. It contained detergents that formed miscelles with the water particles and was deemed unsuitable. Non-detergent 30W motor oil was examined and found to be immiscible with water. However, it was highly viscous and difficult to work with. Xylene was recommended by Forster and Lewin (15);

however, due to its volatility and flammability, it must be worked with under a hood. This was not practical in the current laboratory situation. Hydraulic oil was finally chosen because it was less viscous than motor oil and non-flammable. Hydraulic oil also satisfied the four criteria previously listed.

CHAPTER IV

EXPERIMENTAL RESULTS

This chapter begins with a comparison of bound water as measured by drying and dilatometric methods. This comparison was made using unconditioned, undewatered sludge samples. A discussion of optimum polymer conditioning doses for biological sludges follows. The effects of polymer conditioning (including underdosing and overdosing) on the bound water content of biological sludges are also considered. Freeze-thaw conditioning is also explored. Results of bound water content and cake solids of both biological sludges and chemical sludges after mechanical dewatering are presented. Values obtained from this study for alum sludge are compared to those reported by Sato (13).

The role of dry solids density and apparent floc density in predicting dewatering performance is discussed. The correlation between apparent floc density and bound water content is examined. The chemically bound water fraction of a sludge and its response to conditioning and dewatering practices is explored. Finally, the relationship between interspace water and bound water is presented.

COMPARISON OF RESULTS OBTAINED BY DILATOMETRIC AND DRYING METHODS

The bound water content of unconditioned, undewatered sludge samples was measured using both the controlled drying method and the dilatometric technique. Values for the bound water content of unconditioned, undewatered samples (measured by each method) are presented in Table 3. Depending on the type of sludge and on the method of measurement, bound water values ranged from 0.07 to 8.7 g/g-DS.

With the exception of the lime sludge, the controlled drying method reported a range of bound water values 30 percent to 220 percent higher than the dilatometric method. This suggests that some free (freezable) water remains after the drying rate of the sample begins to decline. Therefore, in the declining rate phase of drying, both free water and bound water are being driven off simultaneously.

The values reported by the drying test can vary depending on the timing and the frequency of the readings. However, the dilatometric method only requires two readings once the standard curve is developed. One reading is taken at the beginning of the test and the other reading is taken at the end of the test. Also, it can be difficult to locate the breakpoint in the drying rate curve; in comparison, the dilatometric method involves straightforward, objective

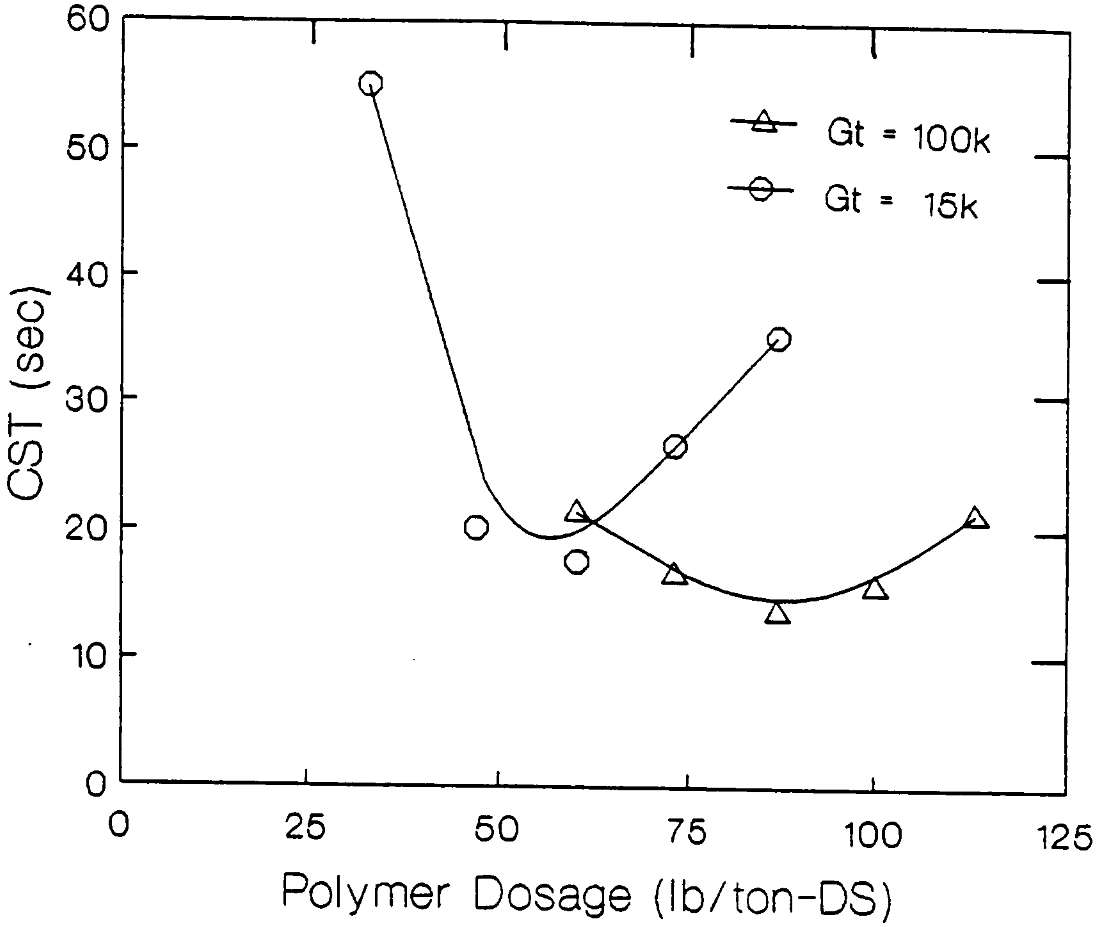
Table 3. Bound Water of Unconditioned, Undewatered Sludge Samples.

SAMPLE	35° C Drying Test (g/g-DS)	Dilatometric Method (g/g-DS)	Percent Difference
anaerobic	5.9	3.9	51
aerobic	6.8	5.2	31
alum	7.2	4.1	76
polymer water	8.7	2.7	222
lime	0.07	0.30	77

calculations. The drying test can take eight to twelve hours or longer to perform, whereas the dilatometric method can be completed in two or three hours. For these reasons, it was determined that the dilatometric test was faster, more accurate and more objective. Thus, the dilatometric method was chosen as the preferred method for characterizing the influence of conditioning and dewatering on subsequent sludge samples.

SELECTION OF OPTIMUM POLYMER DOSE FOR BIOLOGICAL SLUDGE SAMPLES

Biological sludge samples were conditioned by various Nalco polymers. The optimum dose for each polymer and sludge was determined by varying the dose to achieve a minimum CST value. An example of a characterization curve for an anaerobically digested sludge sample conditioned with a cationic polymer is shown in Figure 6. At a dose of 900 mg/L (60 lb/dry ton) 52-E1 and a low mixing regime (Gt = 15,000), the CST of the sludge was 17.6 seconds. At a higher mixing intensity (Gt = 100,000), the optimum dose of 52-E1 was 1300 mg/L (87 lb/dry ton), yielding the minimum CST value of 15.8 seconds. Table 4 summarizes the optimum polymer dose for each polymer/sludge combination. For polymers 52-E1 and 52-I, performance was evaluated at both low (Gt = 15k) and high (Gt = 100k) mixing intensities.



NOTE

The CST of the unconditioned sludge sample was greater than 400 s.

Figure 6. Characterization Curve for Anaerobically Digested Sludge Conditioned with Polymer 52-E1.

Table 4. Optimum Polymer Dosages for Biological Sludge Samples.

Polymer	Mixing (Gt)	Optimum Polymer Dose (mg/L)	Optimum Polymer Dose (lb/ton-DS)	CST (sec)
ANAEROBICALLY DIGESTED				
* 52-E1	15k	900	60	17.6
52-E1	15k	800	53	15.7
52-E1	100k	1300	87	15.8
52-I	15k	900	60	16.3
52-I	100k	1500	100	12.0
AEROBICALLY DIGESTED				
52-E1	15k	100	10	10.8
52-E1	100k	400	40	11.4
52-F	15k	140	14	12.8
52-G	15k	400	40	16.2
52-H	15k	**		**
52-I	15k	100	10	13.9
52-I	100k	400	40	12.9

* Polymer 52-E1 was evaluated on two separate batches of anaerobically digested sample.

** Aerobically digested sample showed no response to polymer 52-H.

Higher mixing intensity resulted in a higher optimum polymer dose. This was felt to be due to additional polymer being required to reagglomerate fractured floc particles (25).

STATISTICAL CONSIDERATION

The bound water values presented in the following sections are based upon 90 percent confidence intervals. Normally, the values were computed from triplicates having identical analytical conditions. In the event of a high standard deviation (greater than 15 percent), additional replicates were performed in order to achieve greater reliability.

The mean standard error of the dilatometric test encountered in this study was approximately 12 to 14 percent for both biological sludges and chemical sludges. No consistent relationship was seen between bound water content and percent error or between dewatering method and percent error.

The mean standard error of the drying test was approximately 15 percent for biological sludges. For chemical sludges, the mean standard error of the drying test ranged from 12 percent (alum) to 90 percent (lime).

In many cases, a "Duncan's Multiple Range" analysis was performed to see if chemical conditioning and/or mechanical dewatering had a "statistically significant" effect on sludge bound water content.

EFFECTS OF POLYMER CONDITIONING ON BOUND WATER RELEASE

Data contained in Table 5 show the effects of polymer conditioning on bound water release for an anaerobically digested sludge sample conditioned with polymers 52-E1 and 52-I. Polymer conditioning reduced the average bound water content of this sludge by about 50 percent, from slightly less than 4.0 to approximately 2.0 g/g-DS. Note that the mixing intensity had no consistent effect on bound water release.

The effects of polymer conditioning of aerobically digested sludge samples are shown in Table 6. Samples were gathered at three separate times and had an average unconditioned, undewatered bound water content ranging from 5.1 to 6.1 g/g-DS. The bound water released by polymer conditioning alone was not as great as that seen with the anaerobically digested sample, nor did the results follow a definite trend. The average bound water content of conditioned samples ranged from 3.2 to 6.3 g/g-DS. In evaluating the optimum dose for polymer 52-H, CST showed no response to conditioning so the optimum dose for polymer 52-G was used.

Table 5. Effects of Polymer Conditioning on the Bound Water Content of Anaerobically Digested Sludge.

Polymer (Dosage)	Mixing (Gt)	Average Bound Water Content (g/g-DS)
unconditioned		3.9
52-I (60 lb/ton)	15k	1.6
52-I (100 lb/ton)	100k	1.9
52-E1 (60 lb/ton)	15k	2.2
52-E1 (87 lb/ton)	100k	2.1

Table 6. Effects of Polymer Conditioning on the Bound Water Content of Aerobically Digested Sludge.

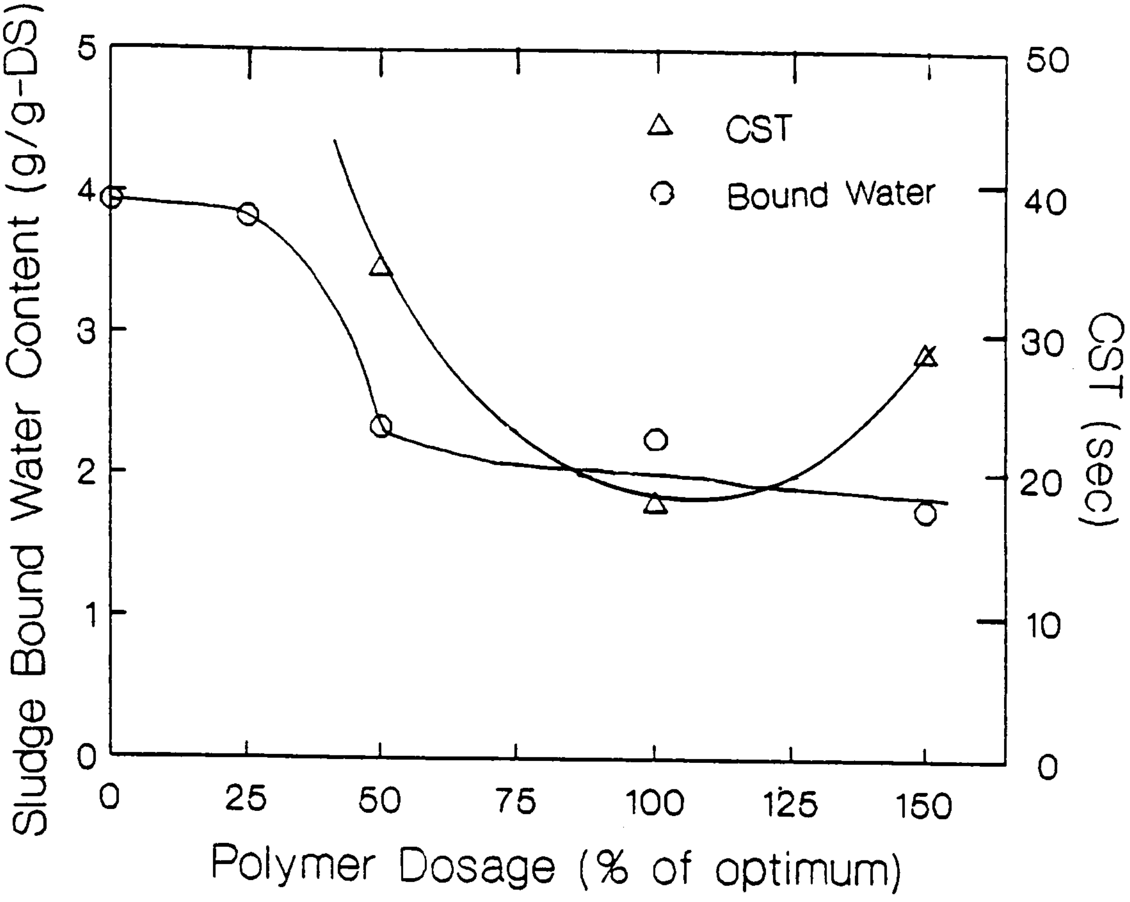
Batch	Polymer (Dosage)	Mixing (Gt)	Average Bound Water Content (g/g-DS)
#1	unconditioned	-	5.2
	52-I (10 lb/ton)	15k	4.0
	52-I (40 lb/ton)	100k	5.0
#2	unconditioned	-	5.1
	52-E1 (10 lb/ton)	15k	4.8
	52-E1 (40 lb/ton)	100k	6.0
	52-F (14 lb/ton)	15k	3.2
#3	unconditioned	-	6.1
	52-G (40 lb/ton)	15k	3.5
	52-H (40 lb/ton)	15k	6.3

EFFECTS OF UNDERDOSING AND OVERDOSING

Data presented in Figure 7 summarize the changes observed in both CST and bound water content when underdosing and overdosing an anaerobically digested sludge sample with polymer 52-E1. The addition of polymer equal to 25 percent of the optimum dosage produced results similar to an unconditioned sample (approximately 4.0 g bound water/g-DS), while a 50 percent of optimum dosage produced results similar to the optimum (approximately 2.0 g bound water/g-DS). Overdosing with polymer 52-E1 (150 percent of optimum) promoted bound water release similar to or slightly greater than the optimum dosage. (The CST at this dosage was 60 percent higher that the CST at the optimum dosage.) Thus, there would appear to be a wide band of polymer dosages which promote maximum bound water release.

EFFECTS OF FREEZE-THAW CONDITIONING

The effects of freeze-thaw conditioning on sludge characteristics are shown in Table 7. Freeze-thaw conditioning of an anaerobically digested sludge sample decreased its average bound water content by nearly 80 percent, from 3.5 to 0.8 g/g-DS. This method of conditioning likewise increased the average gravity thickened solids concentration of the sludge more than two and a one times, from 3.3 percent to 8.5 percent. The



NOTE

The CST of the unconditioned sludge sample and of the 25 percent sample was greater than 400 s.

Figure 7. Effects of Underdosing and Overdosing with Polymer 52-E1 at Low Mixing Intensity on Anaerobically DIgested Sludge.

Table 7. Effects of Freeze-Thaw Conditioning on Biological Sludge Samples.

	Anaerobically digested		Aerobically digested	
	freeze-thaw conditioned	unconditioned	freeze-thaw conditioned	unconditioned
Average Bound Water (g/g-DS)	0.8	3.5	2.1	5.1
Average Gravity Thickened Solids (%)	8.49	3.32	10.9	1.74

average bound water content of an aerobically digested sludge sample was reduced by nearly 60 percent following freeze-thaw conditioning, from 5.1 to 2.1 g/g-DS. The average gravity thickened solids concentration of this sludge correspondingly increased six-fold, from 1.7 percent to nearly 11 percent.

EFFECTS OF MECHANICAL DEWATERING ON BIOLOGICAL SLUDGE SAMPLES

The application of mechanical pressure to sludge brought about a further decrease in bound water content, both for conditioned and for unconditioned samples. This decrease is shown in Table 8 for an anaerobically digested sample. Low speed centrifugation and vacuum filtration did not promote a significantly larger bound water release than gravitational thickening, as determined by Duncan's Multiple Range. No statistically significant difference was seen in the effectiveness of polymers 52-I and 52-E1. With both high charge density cationic polymers (52-I and 52-E1) (using either high or low mixing intensity), the average bound water content was reduced from slightly less than 4.0 to approximately 2.0 g/g-DS. High speed centrifugation further reduced the average bound water of conditioned sludge samples by approximately 40 percent, to just over 1.0 g/g-DS. High speed centrifugation reduced the average bound

Table 8. Effects of Mechanical Dewatering on Bound Water Content of Anaerobically Digested Sludge.

Dewatering Method	Average Bound Water Content (g/g-DS)				
	Polymer 52-I (low Gt)	Polymer 52-I (high Gt)	Polymer 52-E1 (low Gt)	Polymer 52-E1 (high Gt)	Uncond. Sludge Sample
gravity thickening	1.6	1.9	2.2	2.1	3.9
low speed centrifugation	2.0	1.8	2.0	1.9	3.4
vacuum filtration	1.9	2.1	1.8	1.8	*
high speed centrifugation	1.1	1.0	1.1	1.3	1.2
high pressure filtration	1.5	**	**	**	**

NOTES

A multiple range analysis was performed on the gravity thickening, low speed centrifugation and vacuum filtration samples; a separate multiple range analysis was performed on high speed centrifugation samples. Values enclosed within the same set of solids lines are not significantly different.

* It was not possible to dewater the unconditioned sample by vacuum filtration.

** High pressure filtration was only applied to the sample conditioned with polymer 52-I at low mixing.

water content of the unconditioned sample by nearly 70 percent, from 3.9 to 1.2 g/g-DS. The effect of polymer conditioning prior to high speed centrifugation was not statistically significant on bound water release; in each case, the average final bound water content was just over 1.0 g/g-DS. Again, no statistically significant difference was seen in the effectiveness of polymers 52-I and 52-E1. High pressure filtration removed all except 1.5 g/g-DS bound water in the sample conditioned with polymer 52-I at low mixing intensity.

Conditioned sludge samples dewatered by the plate-and-frame press lost nearly 80 percent of their bound water content, from 3.5 to 0.8 g/g-DS for the first anaerobic sample and from 4.8 to 1.0 g/g-DS for the second anaerobic sample. These data are shown in Table 9. A decrease in bound water was accompanied by an increase in cake solids. An example of this trend is shown in Figure 8 for an anaerobically digested sludge sample.

Results of the application of mechanical pressure to conditioned and unconditioned aerobically digested samples are shown in Tables 10 through 12. The first batch of aerobic sludge samples was conditioned with polymer 52-I. Increasing amounts of bound water were removed with each increasing degree of mechanical dewatering. The average initial sludge bound water content value of 5.2 g/g-DS was

Table 9. Effects of Plate and Frame Press Dewatering on Bound Water Content of Anaerobic Sludge.

conditioning/ dewatering	Average Bound Water Content (g/g-DS)	
	Sample 1	Sample 2
unconditioned, undewatered	3.5	4.8
52-I conditioned, undewatered	2.0	2.4
52-I conditioned, plate & frame press	0.8	1.0

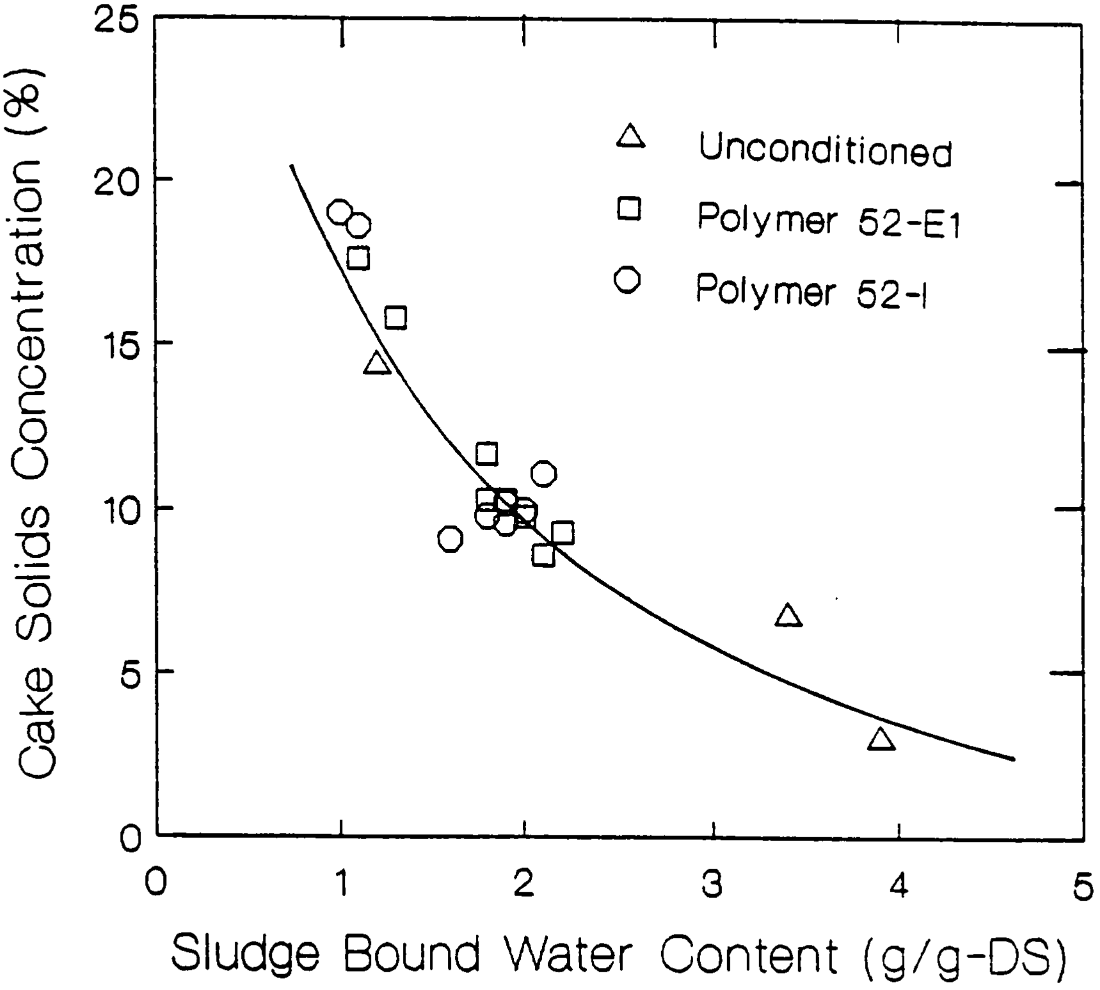


Figure 8. Cake Solids vs. Bound Water for Anaerobically Digested Sludge Conditioned with Polymer 52-E1 and Polymer 52-I.

Table 10. Effects of Mechanical Dewatering on the Bound Water Content of Aerobically Digested Sludge Conditioned with Polymer 52-I.

Dewatering Method	Average Bound Water Content (g/g-DS)		
	Polymer 52-I (low Gt)	Polymer 52-I (high Gt)	Unconditioned Sludge Sample
gravity thickening	4.0	5.0	5.2
low speed centrifugation	2.6	3.2	2.3
vacuum filtration	2.5	2.1	*
high speed centrifugation	1.9	1.9	2.4

* It was not possible to dewater the unconditioned sample by vacuum filtration.

Table 11. Effects of Mechanical Dewatering on the Bound Water Content of Aerobically Digested Sludge Conditioned with either Polymer 52-E1 or Polymer 52-F.

Dewatering Method	Average Bound Content Water (g/g-DS)			
	Polymer 52-E1 (low Gt)	Polymer 52-E1 (high Gt)	Polymer 52-F (low Gt)	Uncond. Sludge Sample
gravity thickening	4.8	6.0	3.2	5.1
low speed centrifugation	3.2	3.2	2.5	2.3
vacuum filtration	2.2	2.4	2.0	*
high speed centrifugation	2.1	1.6	1.5	2.4

NOTES

A multiple range analysis was performed on the gravity thickening samples. Values enclosed within solid lines are not significantly different.

* It was not possible to dewater the unconditioned sample by vacuum filtration.

Table 12. Effects of Mechanical Dewatering on the Bound Water Content of Aerobically Digested Sludge Conditioned with either Polymer 52-G or Polymer 52-H.

Dewatering Method	Average Bound Water Content (g/g-DS)		
	Polymer 52-G (low Gt)	Polymer 52-H (low Gt)	Unconditioned Sludge Sample
gravity thickened	3.5	6.3	6.1
low speed centrifugation	3.4	**	2.3
vacuum filtration	2.8	**	*
high speed centrifugation	2.0	**	2.4
high pressure filtration	1.8	**	*

NOTES

A multiple range analysis was performed on polymer 52-G samples. Values enclosed within the same set of solid lines are not significantly different.

* It was not possible to dewater the unconditioned sample by vacuum filtration or high pressure filtration.

** Mechanical dewatering was not applied to the sample conditioned with polymer 52-H.

reduced to 1.9 g/g-DS after conditioning and high speed centrifugation. This equals a greater than 60 percent reduction in bound water. No consistent difference in sludge bound water content was noted when comparing low mix versus high mix intensity conditions.

The second batch of aerobic sludge samples was conditioned with polymer 52-E1 at low and high mixing intensities, and with polymer 52-F at low mixing intensity (Table 11). Polymer 52-E1 had no statistically significant effect on the bound water reduction of the sample following gravity thickening. The effect of polymer 52-F was significant. However, the optimum dosage for 52-F was 140 mg/L (14 lb/dry ton) as opposed to 100 mg/L (10 lb/dry ton) for 52-E1 (Table 4). The best results were realized after high speed centrifugation of the conditioned samples. Polymer conditioning and subsequent dewatering reduced the average bound water content of the sludge from 5.1 g/g-DS to approximately 2.0 g/g-DS. As with polymer 52-I, no consistent difference was seen between low mixing and high mixing conditions for polymer 52-E1.

The sludge sample conditioned with polymer 52-G was subjected to high pressure filtration as well as to the other dewatering methods (Table 12). The response to low speed centrifugation was not significantly different from the response to gravity thickening; the response to high pressure filtration was not significantly different from the response to high speed filtration. The relative effectiveness of polymer 52-G is uncertain because it was evaluated on a different batch of sludge than the other polymers; however, the results obtained follow the general trend of decreased bound water with increasing degrees of dewatering pressure. Samples conditioned with polymer 52-H showed no response to capillary suction time or to bound water release after gravitational thickening. Therefore, 52-H was not evaluated for its effect on bound water release during mechanical dewatering.

The relationship between cake solids and bound water of aerobically digested samples is shown in Figures 9 through 11 for various polymer conditioners. As with the anaerobically digested samples, a reduction of sludge bound water content accompanied an increase in cake solids concentration following mechanical dewatering. The data from all three aerobically digested sludge samples are combined in Figure 12. It can be seen that the increase in cake solids concentration corresponding to sludge bound water reduction is consistent, regardless of the type of polymer employed.

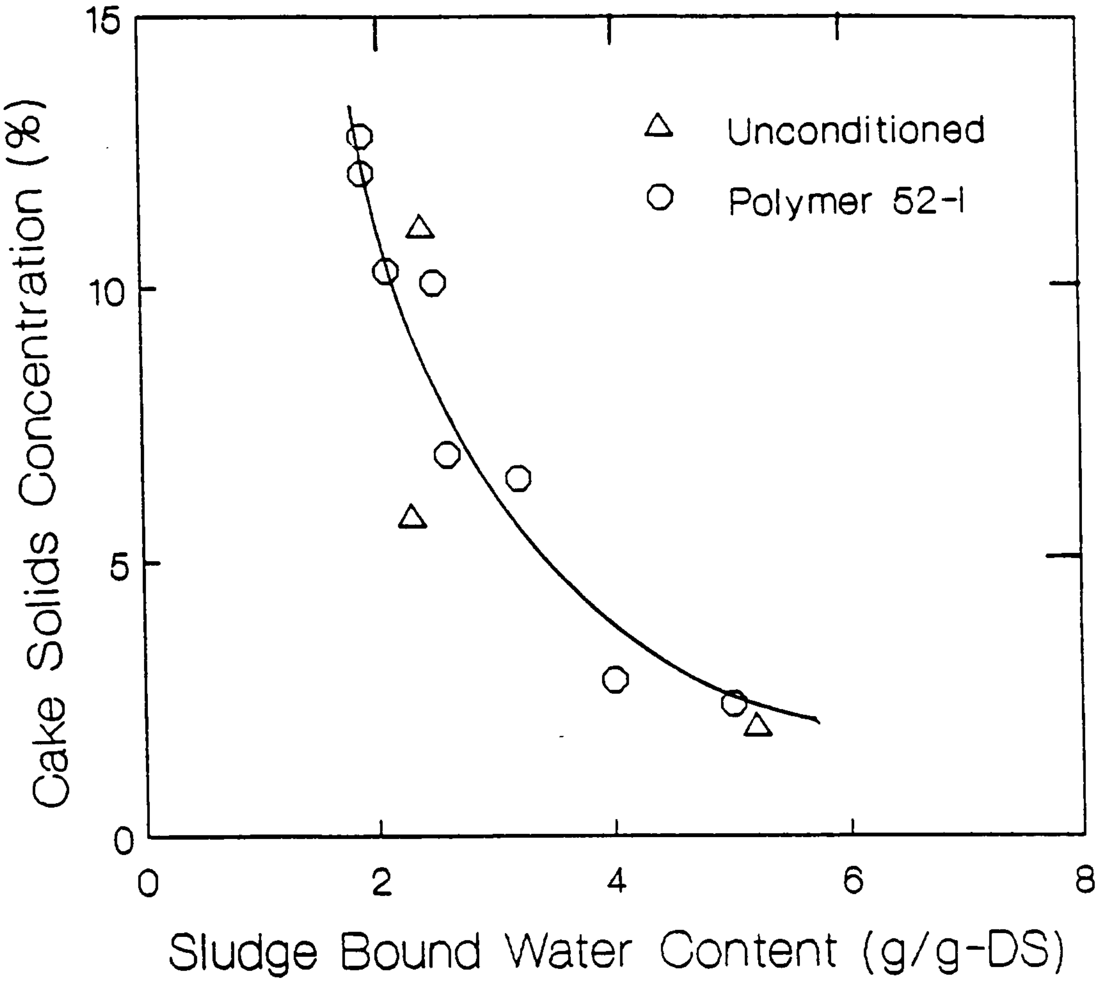


Figure 9. Cake Solids vs. Bound Water for Aerobically Digested Sludge Conditioned with Polymer 52-I.

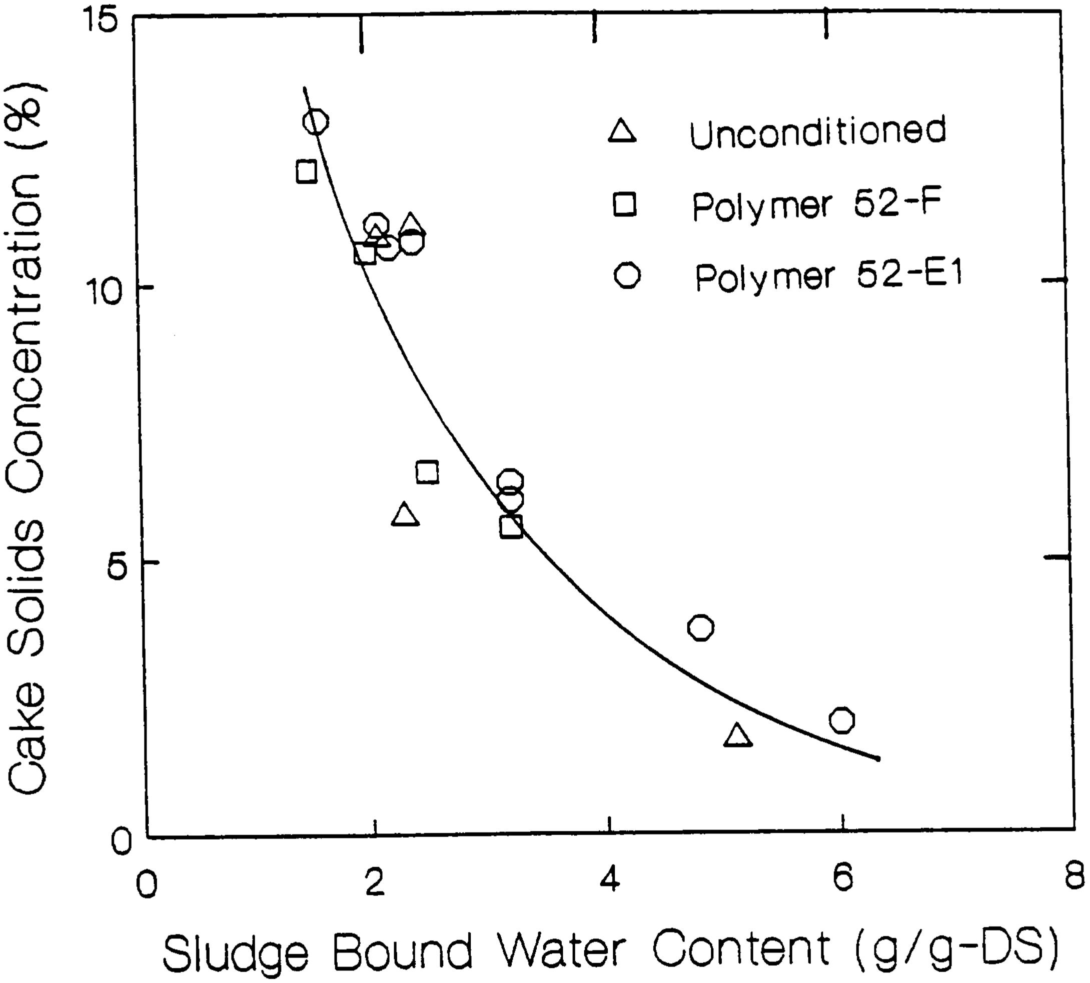


Figure 10. Cake Solids vs. Bound Water for Aerobically Digested Sludge Conditioned with Polymer 52-E1 and Polymer 52-F.

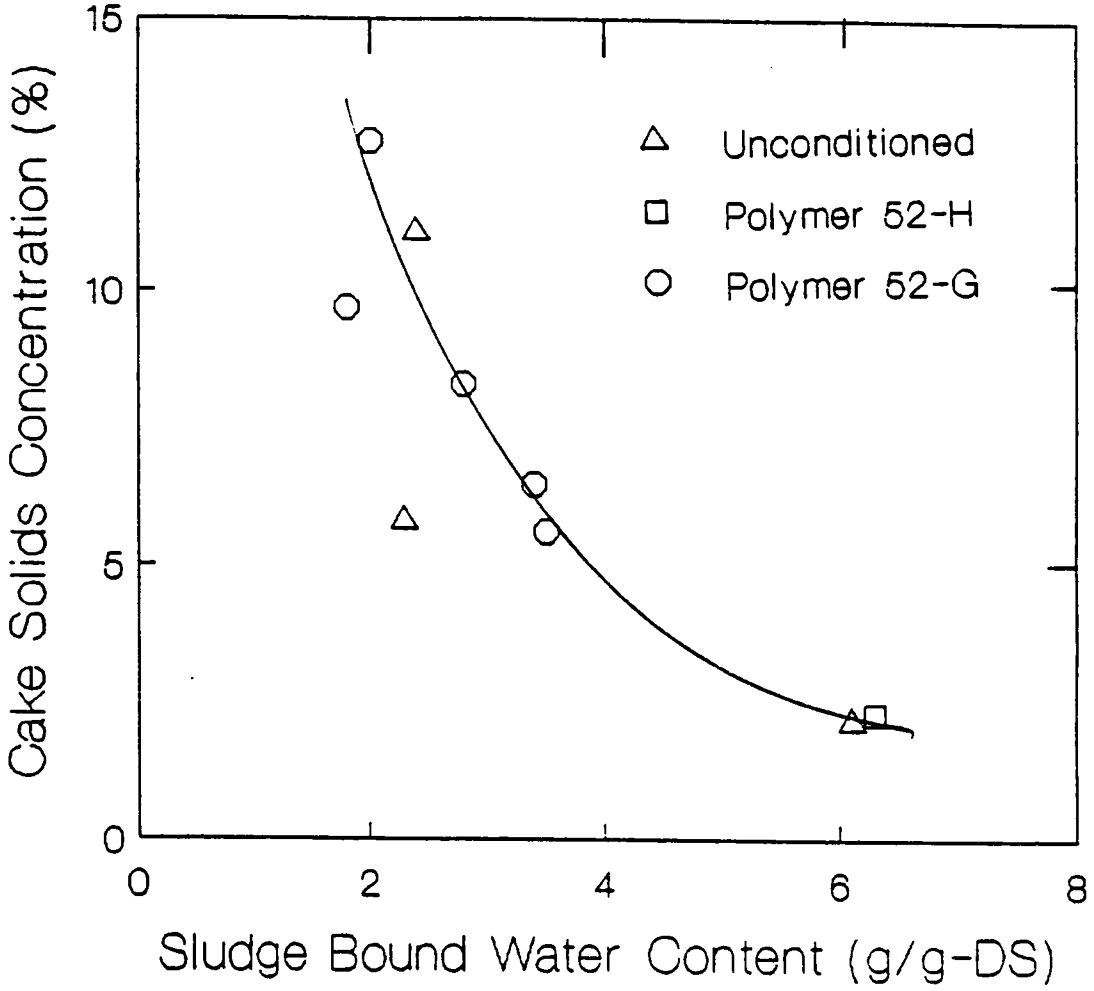


Figure 11. Cake Solids vs. Bound Water for Aerobically Digested Sludge Conditioned with Polymer 52-G and Polymer 52-H.

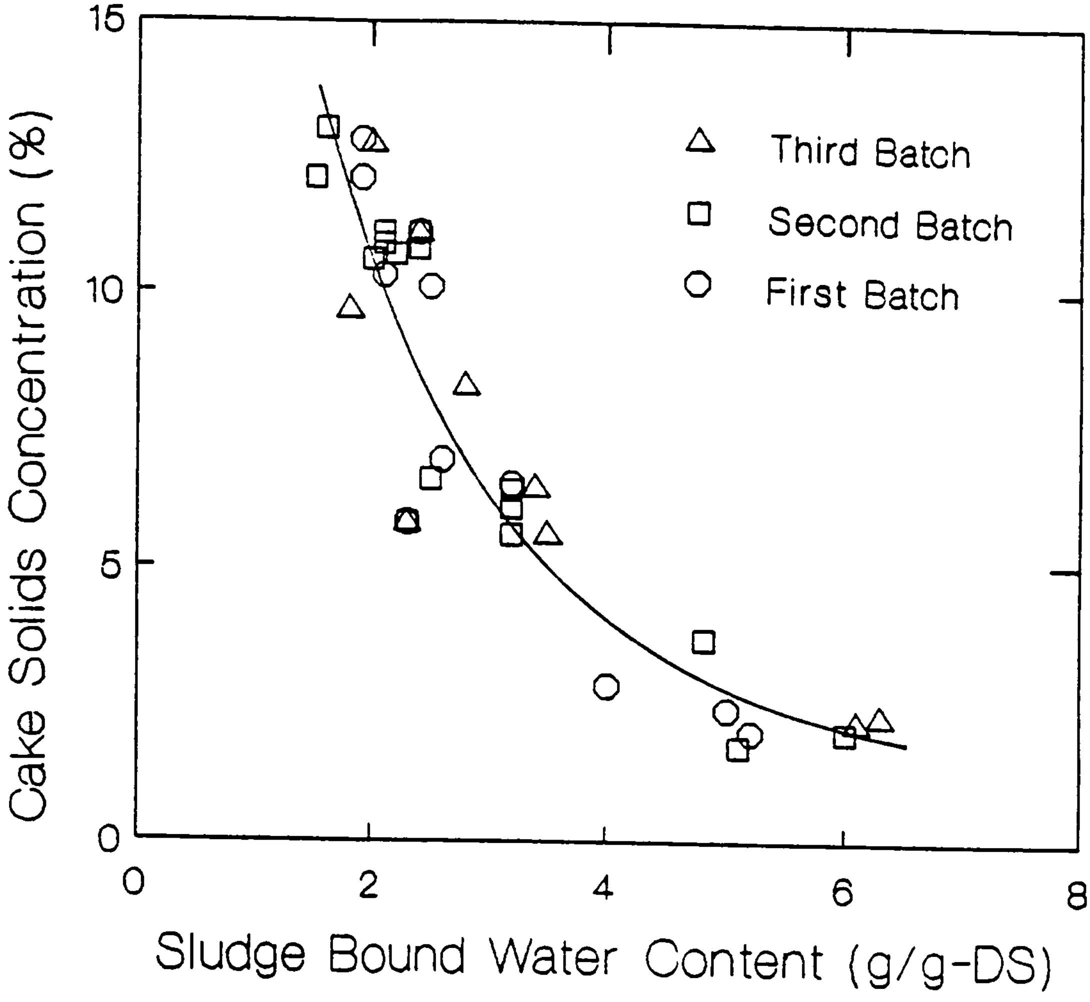


Figure 12. Cake Solids vs. Bound Water Content of all Aerobically Digested Sludge Samples.

EFFECTS OF MECHANICAL DEWATERING ON CHEMICAL SLUDGE SAMPLES

Samples of chemical sludges (lime, alum, and polymer water) were subjected to mechanical dewatering without polymer conditioning. The results are shown in Table 13. The lime sludge sample had an average initial bound water content of 0.30 g/g-DS. Low speed centrifugation reduced this value to 0.19 g/g-DS whereas high speed centrifugation decreased it to 0.16 g/g-DS. The greatest bound water removal was accomplished by vacuum filtration, yielding an average bound water content of 0.13 g/g-DS.

The average bound water content of unconditioned alum sludge was reduced from 4.1 g/g-DS to 2.1 g/g-DS and 1.6 g/g-DS by low speed and high speed centrifugation, respectively. It was not possible to dewater unconditioned alum sludge by vacuum filtration because the solid particles clogged the filter paper. However, the alum sludge sample responded extremely well to vacuum filtration after it had been freeze-thaw conditioned; the average bound water content of the sludge was reduced 85 percent, to 0.66 g/g-DS.

The polymer water sludge sample had an average initial bound water content of 2.7 g/g-DS. Low speed centrifugation had no significant effect on bound water release. High speed centrifugation reduced the average bound water content

Table 13. Effects of Mechanical Dewatering on the Bound Water Content of Chemical Sludge Samples.

Dewatering Method	Average Bound Water Content (g/g-DS)		
	Lime Sludge	Alum Sludge	Polymer Sludge
gravity thickening	0.30	4.1	2.7
low speed centrifugation	0.19	2.1	2.6
* vacuum filtration	0.13	0.66	1.5
high speed centrifugation	0.16	1.6	2.2

* Vacuum filtration was performed on freeze-thaw conditioned alum sludge sample.

to 2.2 g/g-DS and vacuum filtration reduced it to 1.5 g/g-DS.

The observed relationship between cake solids and bound water of chemical sludges is shown in Figure 13. The highest cake solids concentrations (50 to 60 percent) were obtained for the dewatered lime sludge samples. This is believed to be due in part to the low initial bound water content of lime sludge. The alum and polymer water sludge samples had lower cake solids, corresponding to greater fractions of bound water.

The relationship between cake solids and bound water content of alum sludge is presented in Figure 14. One set of data is from this study and another set is from a similar study performed by Sato (13). The close correspondence between the results from both studies should be noted.

DRY SOLID DENSITIES

Dry solid density (p_k) is the mass per unit volume of the dry solid material present in the sludge sample. This value can be used to estimate the apparent density of the sludge flocs. The dry solid densities of the five types of sludge samples examined during this study are shown in the first column of Table 14. Note that the two biological sludges have very similar dry solid density values while the

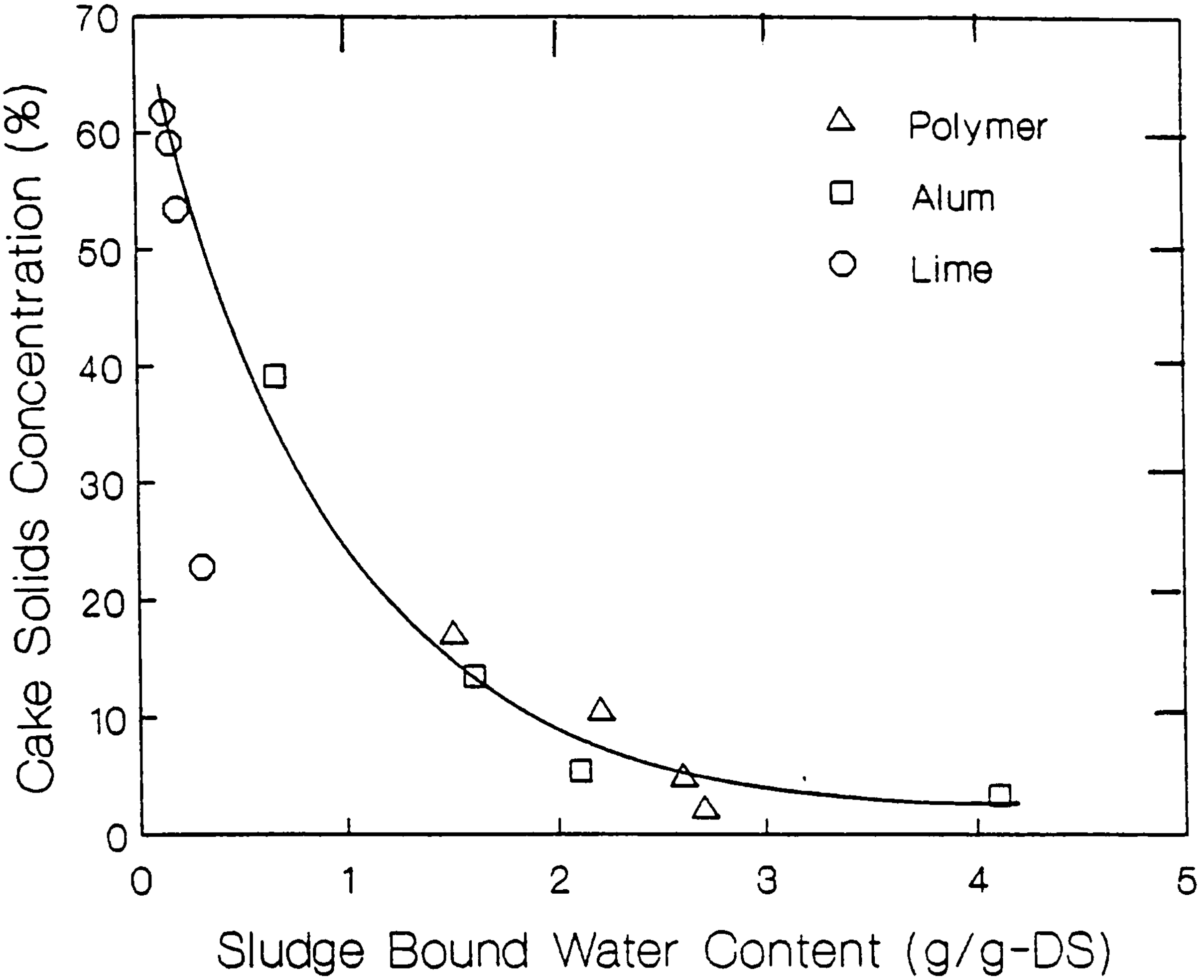


Figure 13. Cake Solids vs. Bound Water for Chemical Sludges.

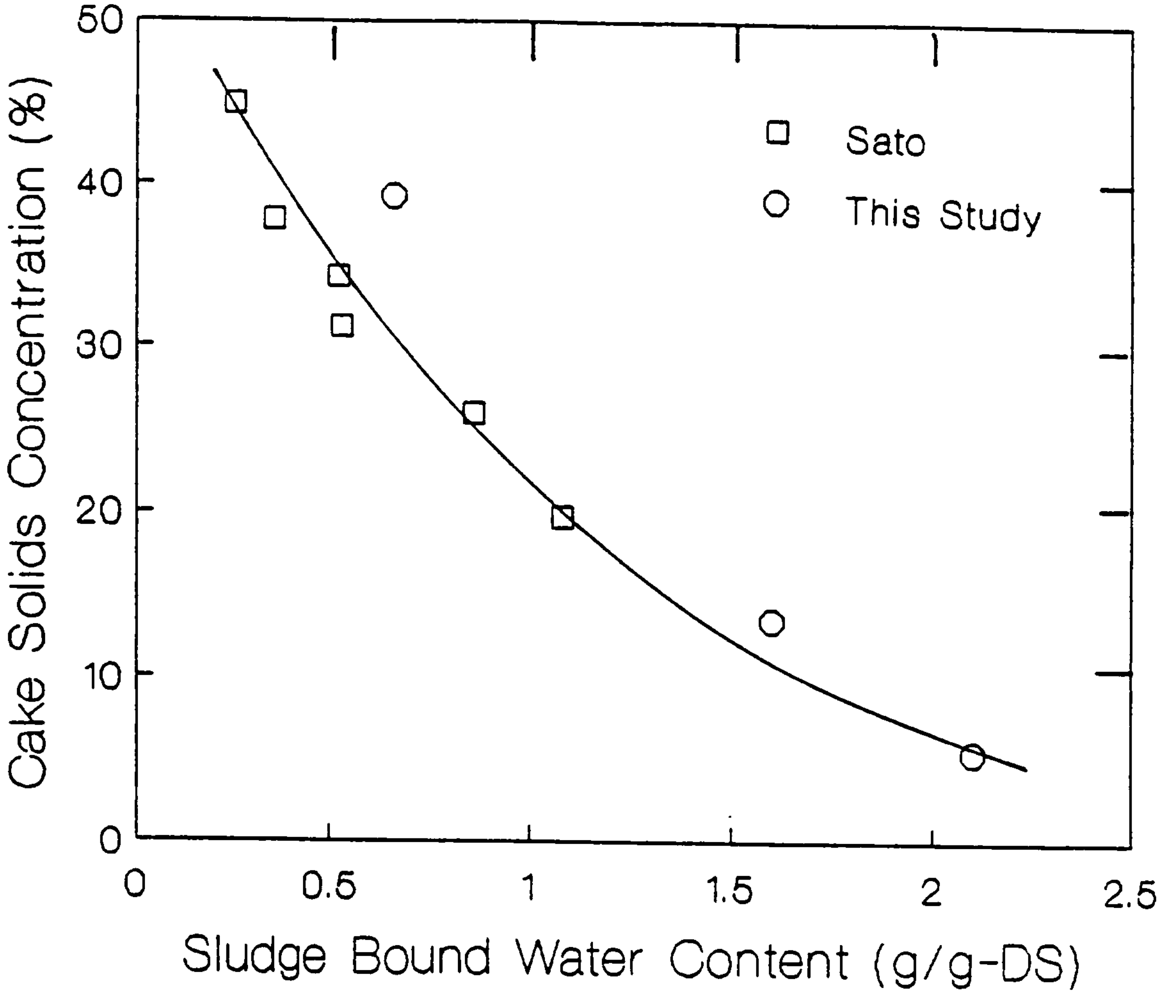


Figure 14. Cake Solids vs. Bound Water for Alum Sludge.

Table 14. Dry Solid, Apparent, and Floc Densities of Sludge Samples.

SAMPLE	p(k) (g/mL)	p(apparent) dilatometric method (g/mL)	p(floc) (g/mL)
anaerobic	1.64	1.09	1.03 - 1.035
aerobic	1.62	1.07	'unavailable'
lime	2.74	1.96	> 1.50
alum	2.50	1.13	1.13 - 1.19
polymer water	1.63	1.12	1.08

chemical sludges (with the exception of the polymer water sludge) have much higher p_k values.

ROLE OF APPARENT SLUDGE FLOC DENSITY IN PREDICTING DEWATERING PERFORMANCE

Assuming a sludge floc is composed of dry solids and the water that is bound to the dry solids, the apparent density of this component can be calculated from

$$p_{apparent} = \frac{BW + 1}{BW + 1/p_k}, \quad \frac{g}{mL} \qquad [5]$$

where BW = bound water content, g/g-DS

p_k = dry solid density, g/mL

The apparent sludge floc densities of the five sludge samples were calculated using data from dilatometric analysis procedures and are shown in the second column of Table 14.

Figure 15 shows the relationship between bulk density and cake solids for anaerobically digested sludge. The points nearest the origin represent unconditioned, undewatered samples while points to the right represent increasing degrees of sludge conditioning and/or dewatering. The point labeled "bound water" represents the calculated apparent sludge floc density corresponding to the bound

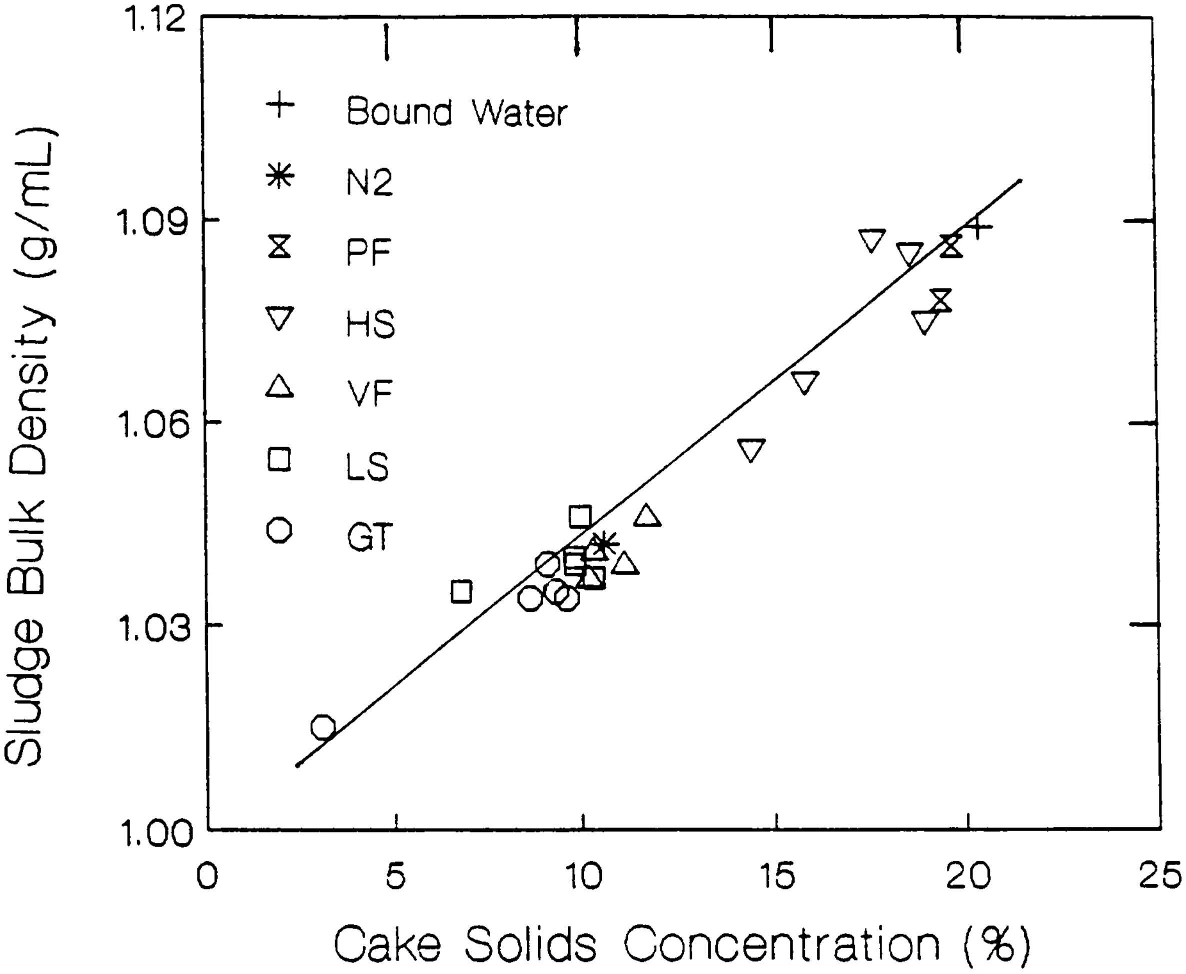


Figure 15. Bulk Density vs. Cake Solids for Anaerobically Digested Sludge.

N2 = High Pressure Filter
PF = Plate and Frame Press
HS = High Speed Centrifuge

VF = Vacuum Filter
LS = Low Speed Centrifuge
GT = Gravity Thickened

water of the unconditioned, undewatered sample (as measured by the dilatometric method). Figures 16 through 19 show the same relationship for aerobically digested, polymer water, lime and alum sludges, respectively.

The apparent sludge floc density value of the unconditioned, undewatered sample appears to be predictive of the maximum degree of dewatering that may be achieved. For example, reviewing data contained in Figure 15, the initial apparent sludge floc density of an anaerobically digested sludge sample was calculated to be 1.09 g/mL. The greatest sludge bulk density achieved by dewatering of this sludge sample was slightly less than 1.09 g/mL. This apparent relationship can also be seen for an aerobically digested sludge sample (Figure 16). The initial apparent sludge floc density value was 1.07 g/mL whereas the greatest dewatered sludge bulk density was only 1.05 g/mL.

An exception to the "dewatering limit" imposed by apparent sludge floc density was found by freeze-thaw conditioning and vacuum filtration of alum sludge. The density of the dewatered cake exceeded the apparent sludge floc density of the unconditioned, undewatered sample. This suggests that significant deterioration of the original floc structure had taken place during freeze-thaw conditioning.

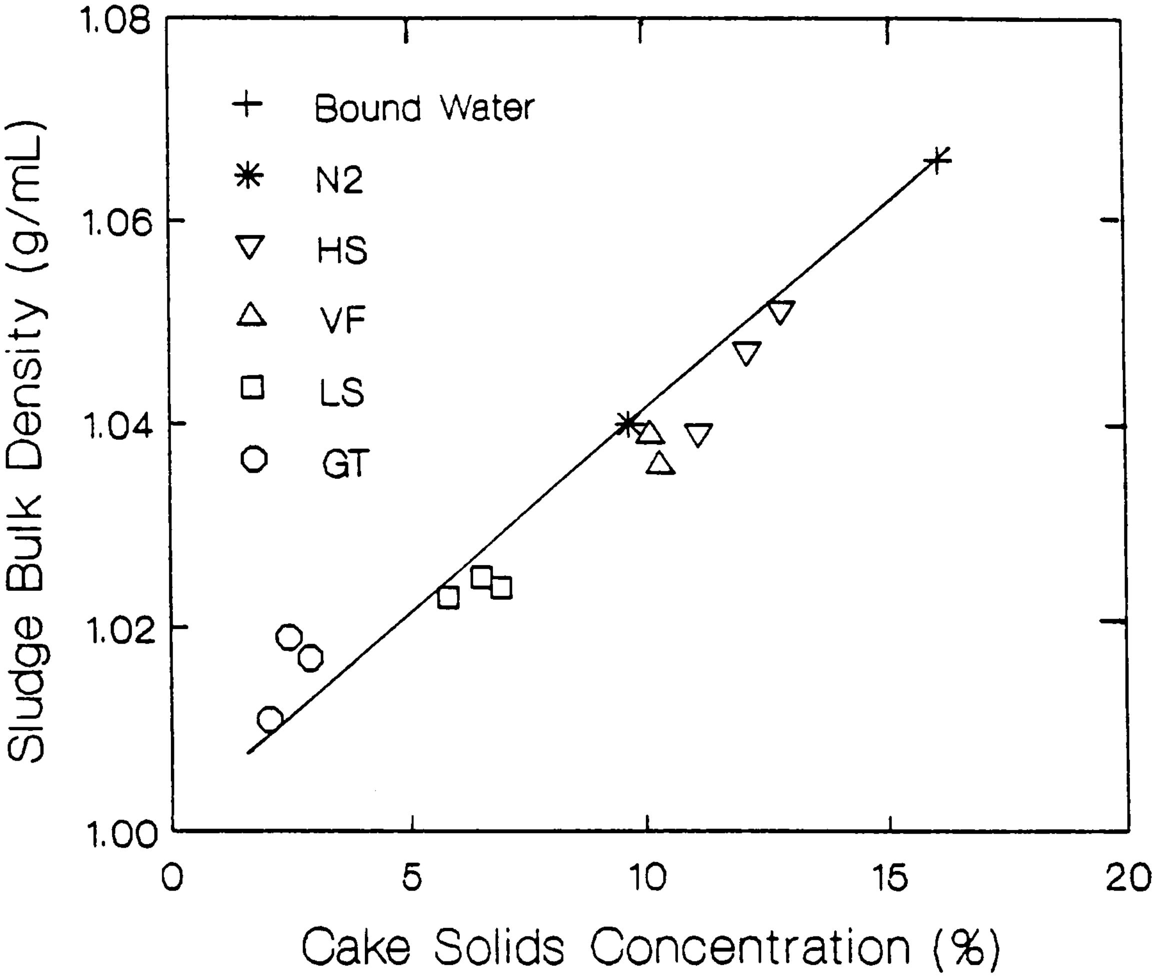


Figure 16. Bulk Density vs. Cake Solids for Aerobically Digested Sludge.

N2 = High Pressure Filter
HS = High Speed Centrifuge
VF = Vacuum Filtration

LS = Low Speed Centrifuge
GT = Gravity Thickened

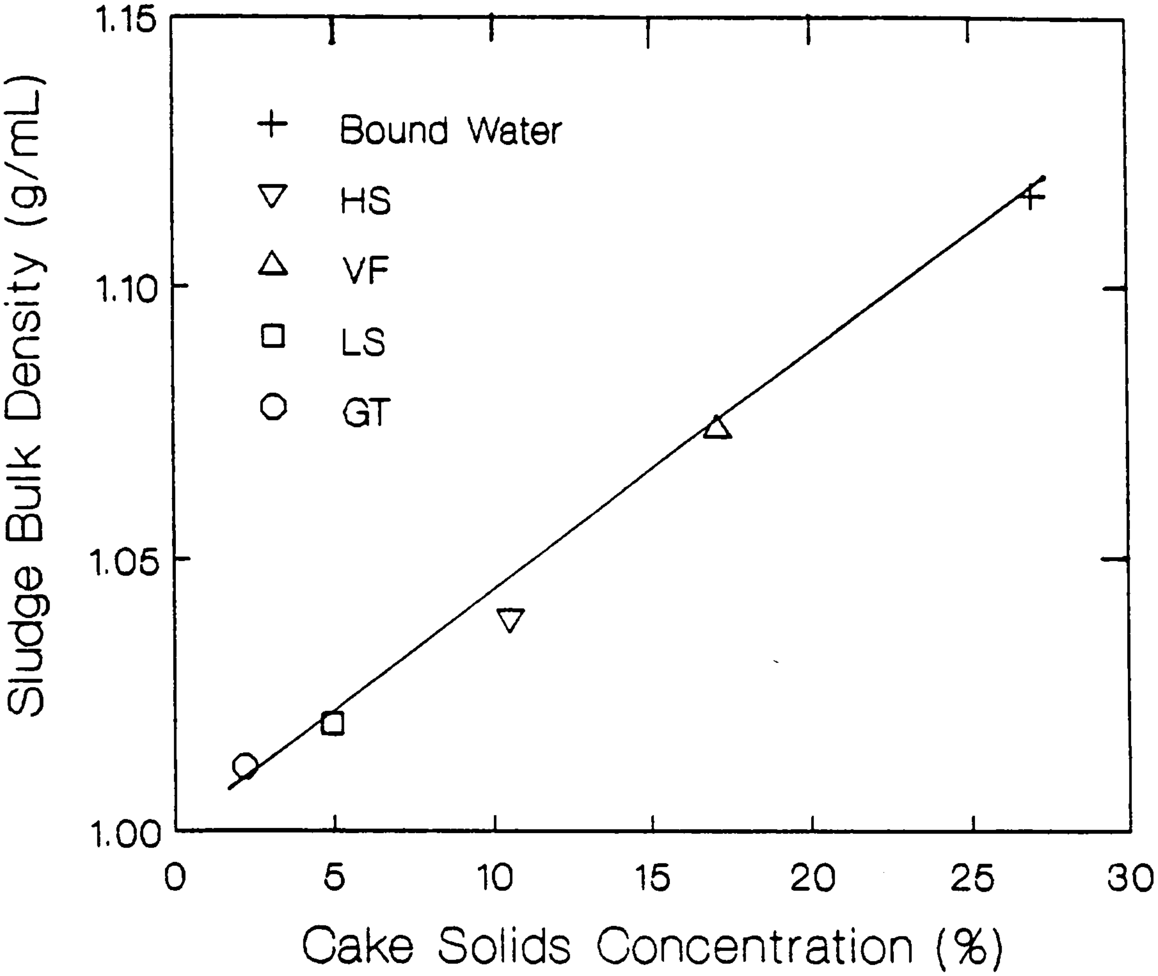


Figure 17. Bulk Density vs. Cake Solids for Polymer Sludge.

HS = High Speed Centrifuge
VF = Vacuum Filter

LS = Low Speed Centrifuge
GT = Gravity Thickened

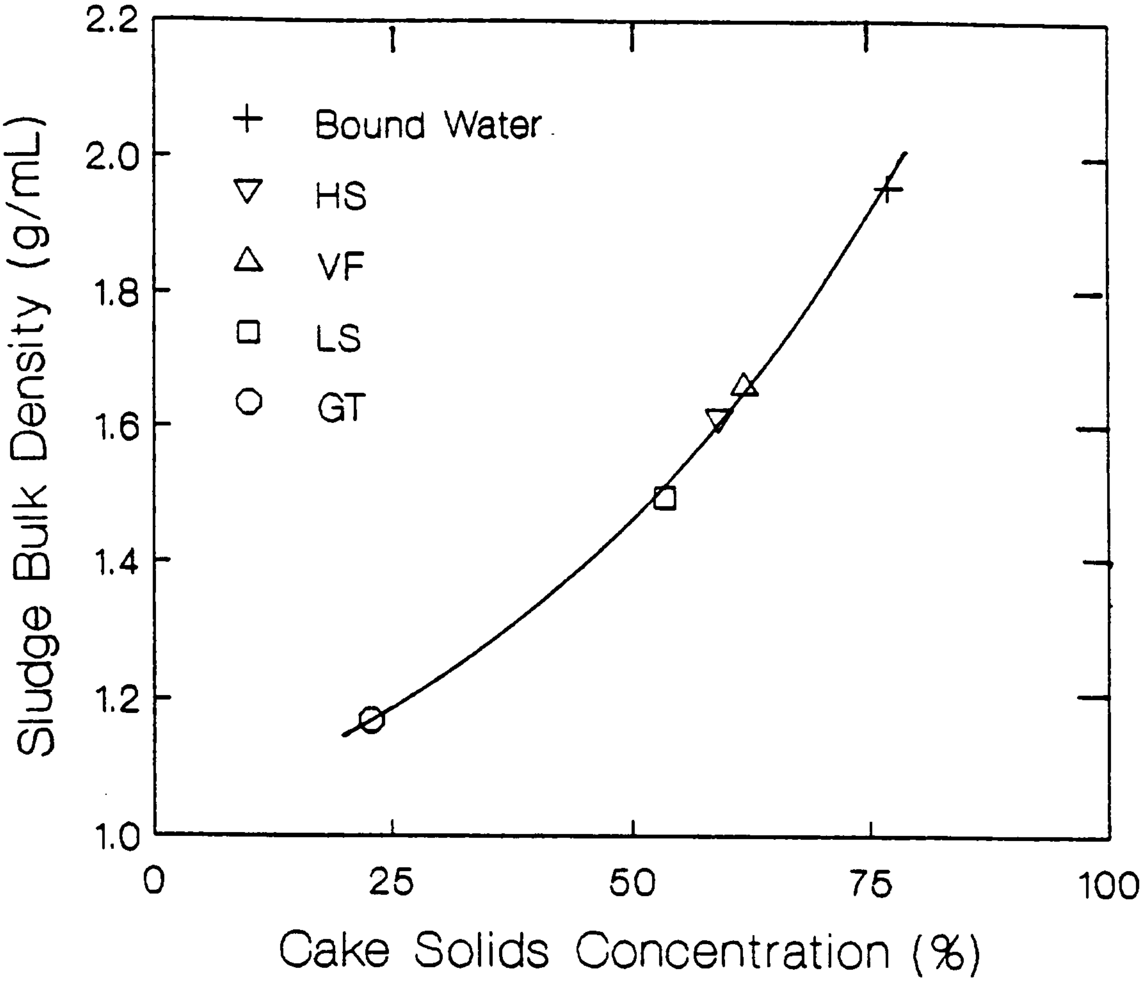


Figure 18. Bulk Density vs. Cake Solids for Lime Sludge.

HS = High Speed Centrifuge
VF = Vacuum Filter

LS = Low Speed Centrifuge
GT = Gravity Thickened

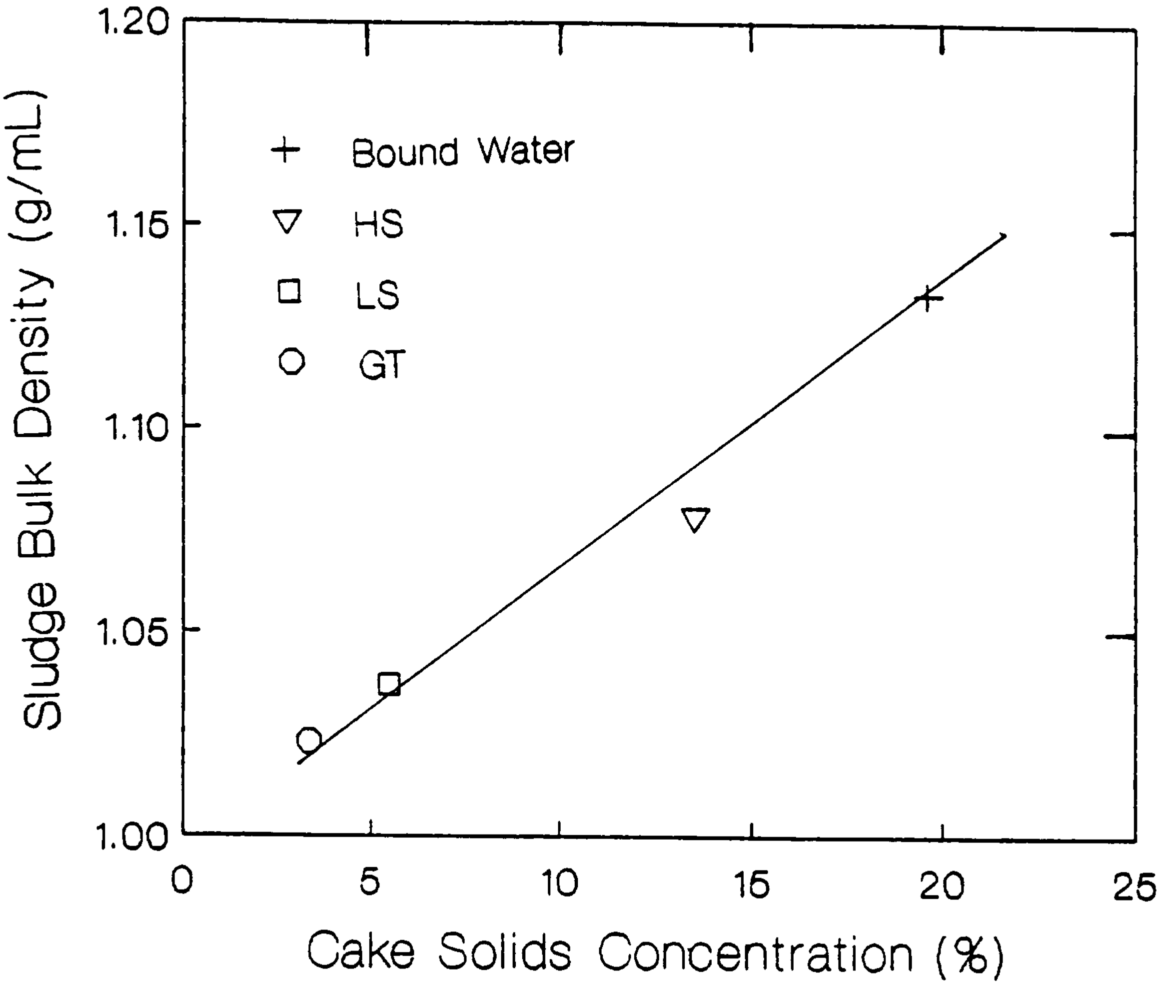


Figure 19. Bulk Density vs. Cake Solids for Alum Sludge.

HS = High Speed Centrifuge
LS = Low Speed Centrifuge
GT = Gravity Thickened

APPARENT SLUDGE FLOC DENSITY AS A FUNCTION OF DEWATERING

Table 15 shows the apparent sludge floc density of biological sludge samples following various degrees of mechanical dewatering. Each increasing degree of dewatering corresponds to a greater apparent sludge floc density. This is to be expected because of the correlation previously seen between the degree of mechanical dewatering and bound water release.

CORRELATION BETWEEN APPARENT SLUDGE FLOC DENSITY AND FLOC DENSITY

A comparison between apparent sludge floc density and the floc density as measured by isopycnic centrifugation can be seen in Table 14. The measured floc density of anaerobically digested sludge was approximately 1.03 g/mL. This was slightly less than the apparent sludge floc density calculated from the dilatometric method. The measured floc density of aerobically digested sludge was not available. The floc density of the lime sludge sample was so great that it could not be measured by isopycnic centrifugation. However, it is known to be greater than or equal to 1.50 g/mL. This value is consistent with the apparent sludge floc density value calculated from bound water data. The measured floc density of alum sludge was approximately 1.16 g/mL. This is slightly greater than the apparent sludge

Table 15. Apparent Sludge Floc Densities of Dewatered Biological Sludge Samples.

Dewatering Method	Anaerobic ρ(apparent) (g/mL)	Aerobic ρ(apparent) (g/mL)
unconditioned	1.08	1.07
gravity thickening	1.15	1.08
low speed centrifugation	1.15	1.11
vacuum filtration	1.16	1.13
high speed centrifugation	1.22	1.15
plate & frame press	1.26	*

* The aerobically digested sample was not dewatered by the plate and frame press.

NOTE

The floc density of the unconditioned, undewatered anaerobically digested sludge sample was 1.03 g/mL as measured by isopycnic centrifugation. This value was not available for the aerobically digested sludge sample.

floc density from the dilatometric bound water measurement method. The floc density of the polymer water sludge sample was measured to be 1.085 g/mL by isopycnic techniques, a value which is similar to the value of the apparent sludge floc density.

In each case where the floc density was measured, the value was similar to the apparent sludge floc density. Floc density was neither consistently higher nor consistently lower than apparent sludge floc density. This suggests that there may be some relationship in what bound water techniques and floc density techniques are measuring. However, there is no conclusive evidence that the two methods are measuring the same floc property.

EFFECT OF CONDITIONING AND DEWATERING ON CHEMICALLY BOUND WATER

The chemically bound water fraction of the five sludges examined are shown in Table 16. This value is defined as water that cannot be removed at low drying temperature (35° C). The chemically bound water fractions of both biological sludge samples and the polymer water sludge sample were approximately 0.10 g/g-DS. For comparison sake, this would correspond to a sludge cake containing 91 percent dry solids concentration. The chemically bound water fraction of the alum sludge was 0.15 g/g-DS. The lime sludge was found to

Table 16. Chemically Bound Water.

SAMPLE	chemically bound water (g/g-DS)
anaerobic	0.09
aerobic	0.10
alum	0.15
polymer water	0.10
lime	0.005

have an extremely small chemically bound water fraction, 0.005 g/g-DS.

Chemically bound water can be measured by the water content of a sample corresponding to a drying rate of zero on the drying curve or it can be measured more simply as the mass difference between drying at 35° C and drying overnight at 103° C.

The chemically bound water fraction of each sludge was not significantly affected by chemical conditioning or mechanical dewatering. However, this fraction of water is so small that its release would have an insignificant effect on increasing cake solids and reducing volume.

RELATIONSHIP BETWEEN INTERSPACE WATER AND BOUND WATER

The relationship between interspace waster and bound water is shown in Figures 20 through 23. Interspace (or capillary) water is operationally defined as the fraction of water remaining in a cake after conditioning and/or dewatering, but it not bound water.

Figure 20 shows the relationship for the biological sludge samples on a mass ratio basis; Figure 21 shows the relationship for the chemical sludge samples on the same basis. The relationship between interspace water and bound water is shown on a volume ratio basis for the same

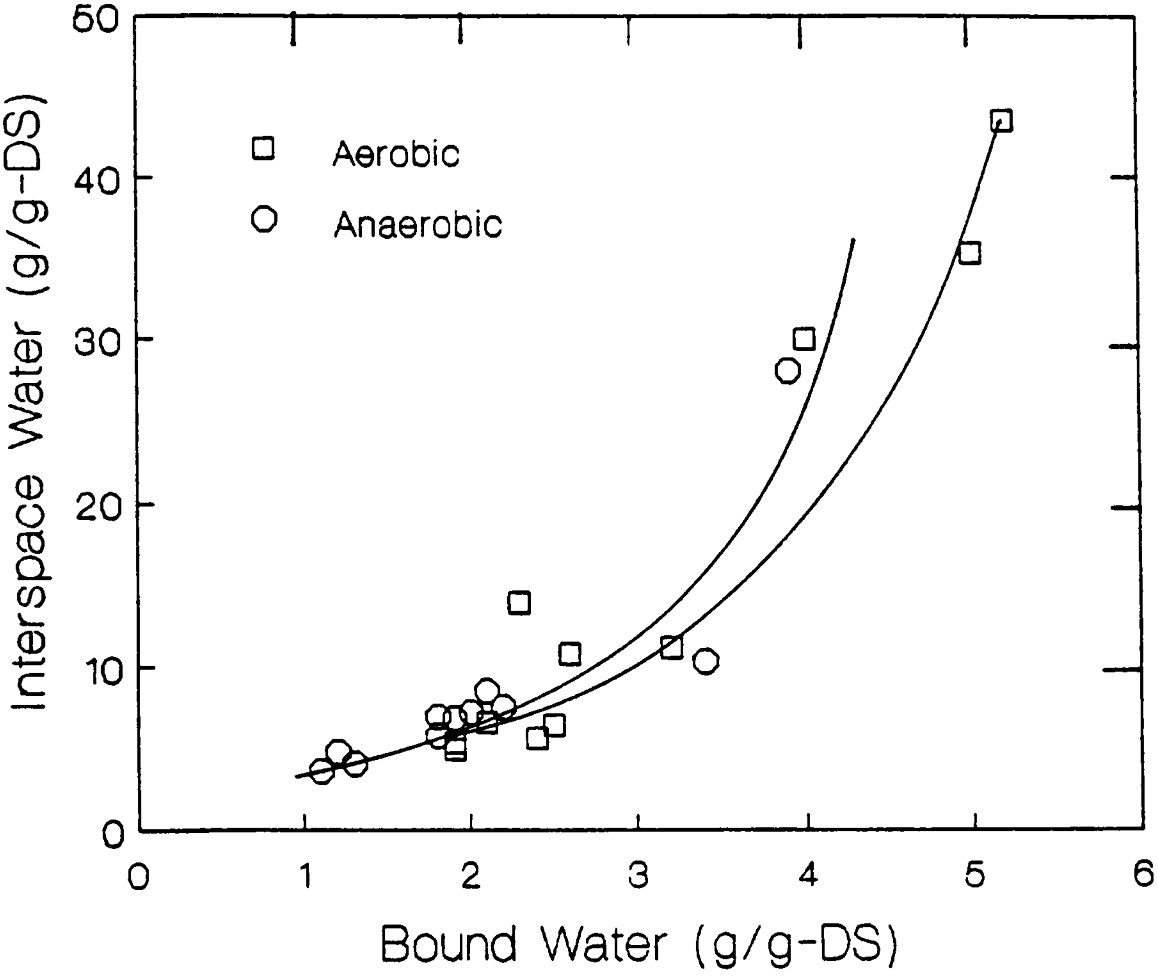


Figure 20. Interspace Water vs. Bound Water for Biological Sludges, Mass Ratio Basis.

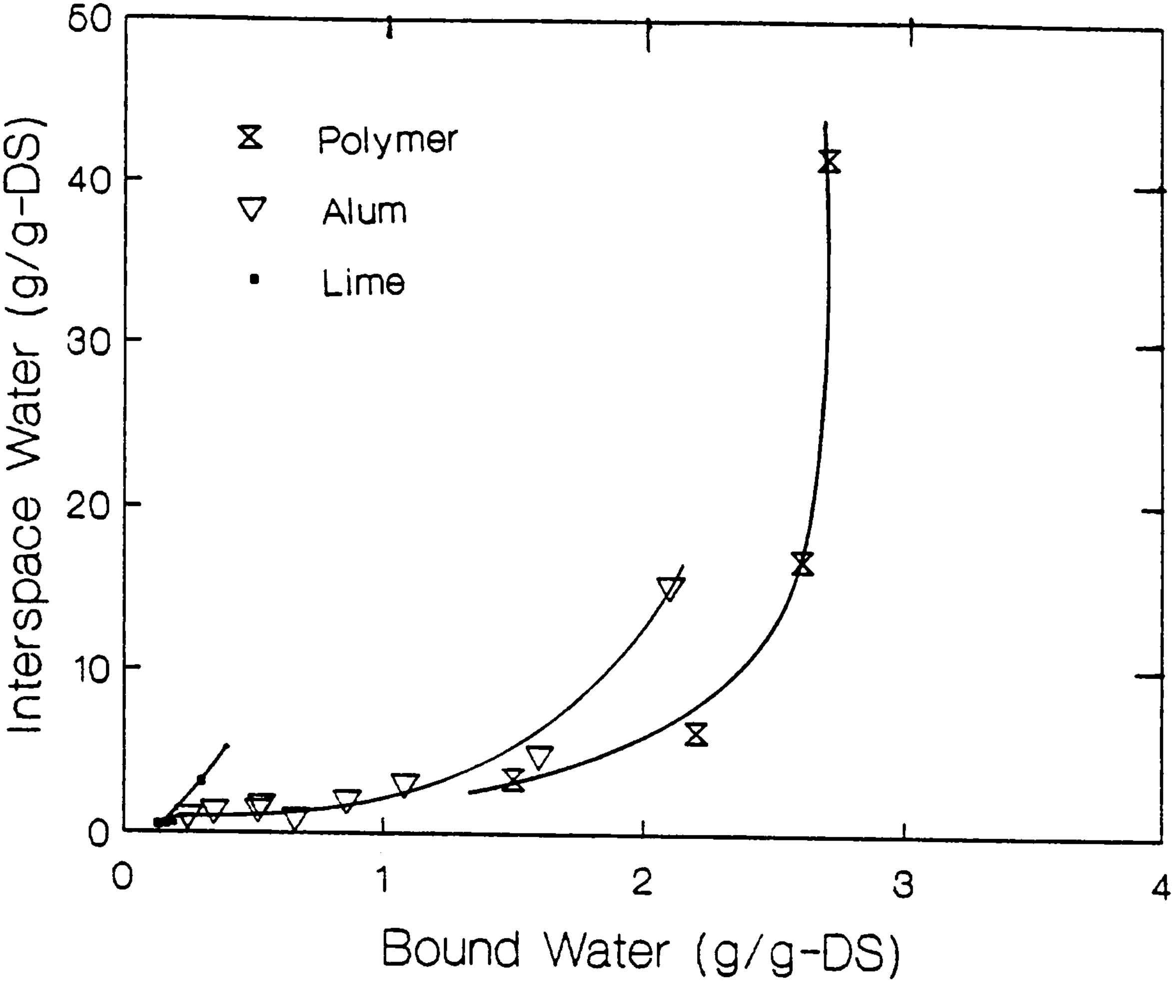


Figure 21. Interspace Water vs. Bound Water for Chemical Sludges, Mass Ratio Basis.

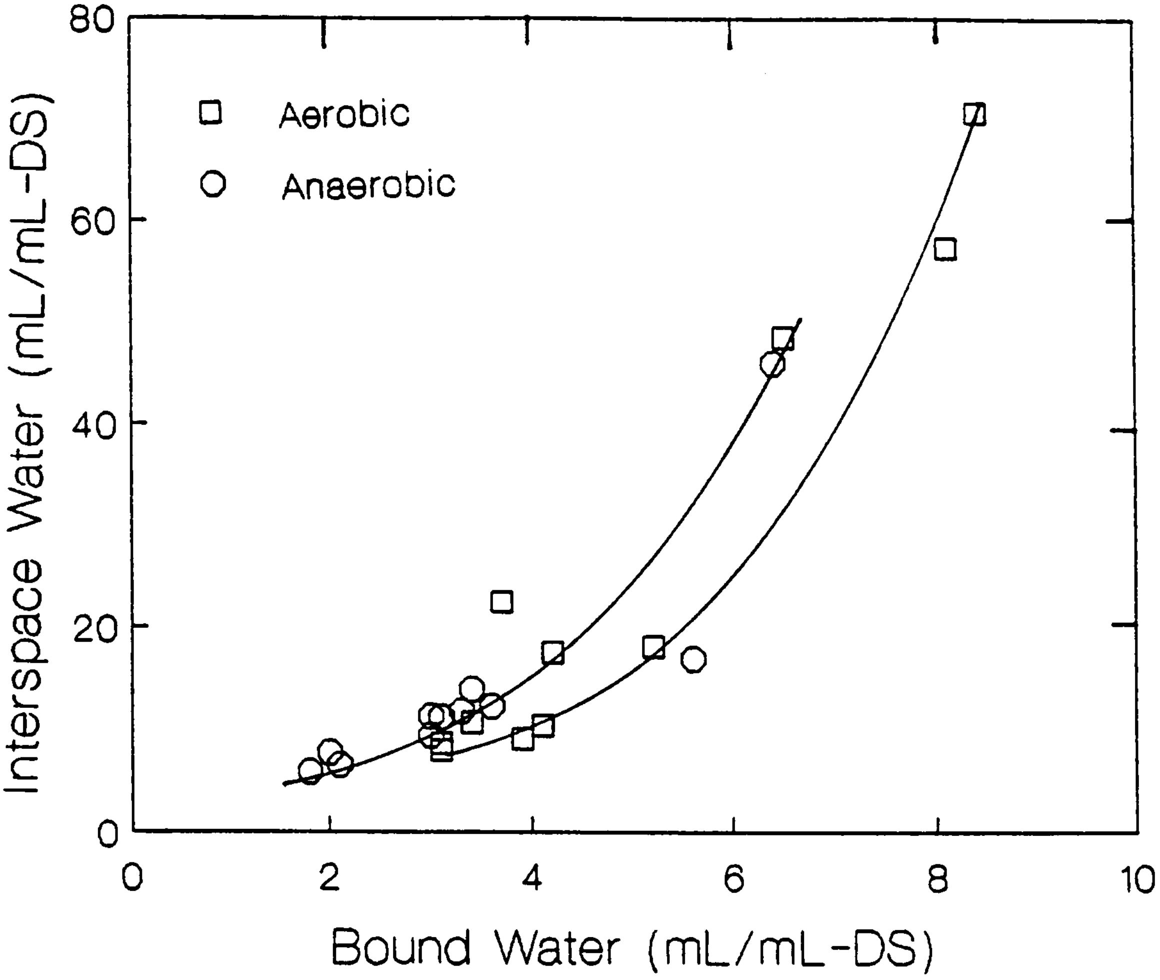


Figure 22. Interspace Water vs. Bound Water for Biological Sludges, Volume Ratio Basis.

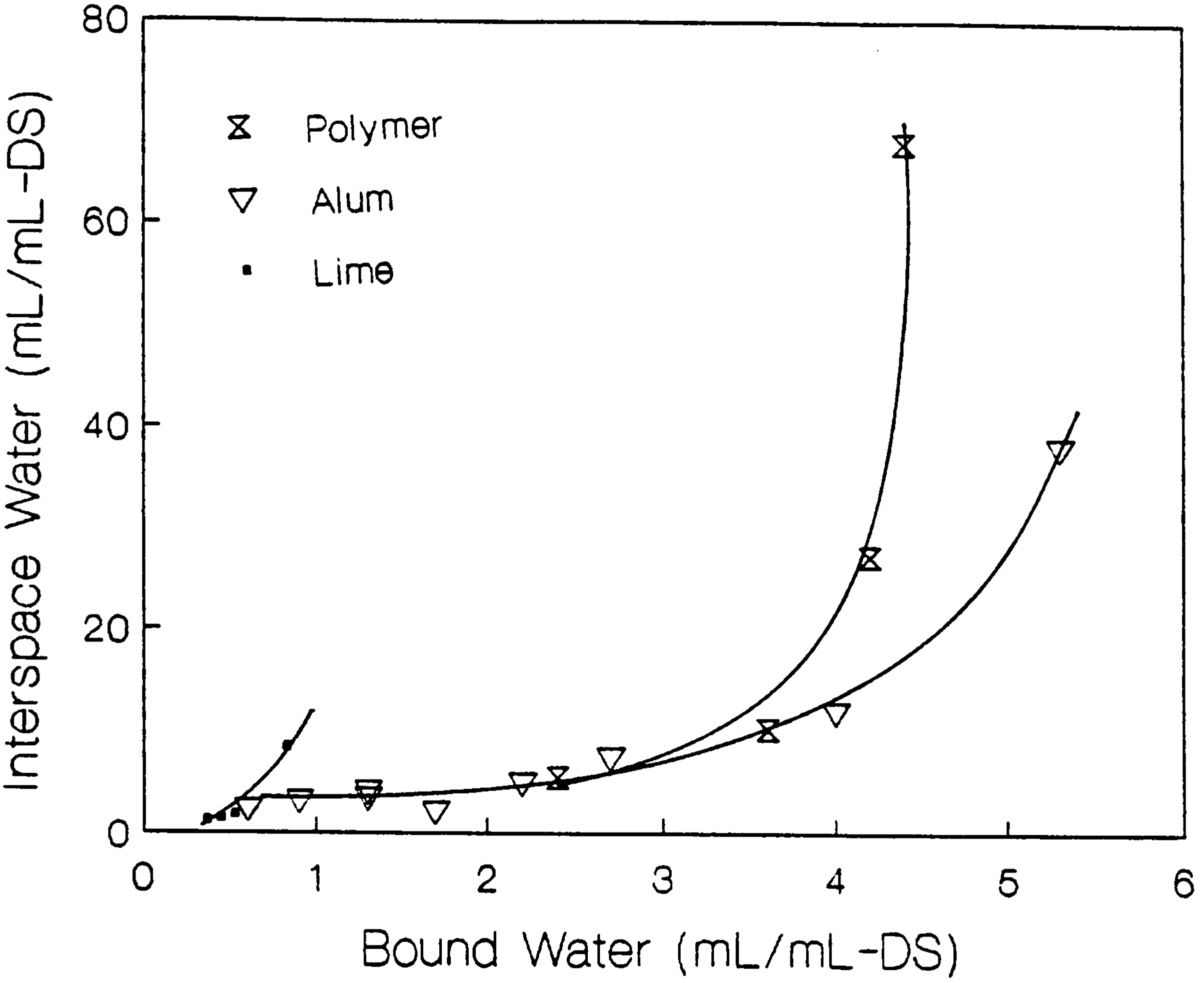


Figure 23. Interspace Water vs. Bound Water for Chemical Sludges, Volume Ratio Basis.

biological and chemical sludge samples in Figures 22 and 23, respectively.

An increase in interspace water corresponds to an increase in bound water in each sludge type. The two biological sludge samples appear to fall along nearly the same curve. Each chemical sludge sample tends to fall along a separate curve, regardless of whether it is presented on a mass ratio basis or a volume ratio basis.

CHAPTER V

DISCUSSION

This study had explored in depth two methods of measuring the fraction of bound water present in both biological and chemical sludges. Other methods were addressed in the literature review, and still others exist that were not addressed. Given the boundary of a typical eight hour workday and the necessity of objective, repeatable calculations, the dilatometric method was chosen as the preferred method. The extent to which the 35° drying method is helpful is in quantifying the chemically bound fraction of sludge water. That portion of the drying test can be performed unattended over a 24 hour period.

From results obtained by characterizing biological sludge samples with the dilatometric method, it was shown that polymer conditioning has a positive effect on bound water reduction. Several mechanisms are believed to bring about bound water release by polymer conditioning. One mechanism is an exchange of the water for the polymer on the binding sites of the dry material (8). Another mechanism is that of the polymer altering the water binding capacity of the solids particles (8). Further bound water release may be a consequence of the bound water being forced out as solid particles come together.

Freeze-thaw conditioning was also found to reduce the quantity of bound water in biological sludge samples. Freezing followed by thawing acts to destroy substances such as proteins and carbohydrates which have a high affinity towards water (8). This would tend to reduce the water binding capacity of the solid particles and account for some of the observed bound water release. Additional bound water release produced by freeze-thaw conditioning is thought to be a result of the pressure exerted as ice crystals form and expand (11).

Mechanical dewatering was found to lower bound water content with a corresponding increase in cake solids concentration noted. In order for bound water removal to occur, the pressure applied by the mechanical dewatering equipment must be great enough to overcome the forces which bind the water to the solids (3). The amount of bound water which is removed is a function of the water-binding capacity of the solids and the degree of mechanical dewatering pressure applied.

From the data acquired in this study, it can be shown that information about the bound water in a sludge can be useful in predicting its dewatering characteristics. In general terms, a sludge with a low initial (unconditioned, undewatered) bound water content can achieve high final, dewatered cake solids. An example of this trend was the lime sludge sample, which had an initial bound water content of 0.30 g/g-DS. This sludge reached an ultimate dewatered cake solids concentration of greater than 60 percent. In comparison, the anaerobically digested biological sample with an initial bound water content of approximately 4.0 g/g-DS achieved a final dewatered cake solids concentration of only 20 percent.

Secondly, and more specifically, evidence suggests that an upper limit to the dewatered cake solids can be predicted from the apparent sludge floc density of the unconditioned, undewatered sample. In other words, the density of the dewatered cake will seldom exceed the initial apparent sludge floc density. It would first appear that this indicates bound water cannot be removed by conditioning and/or mechanical dewatering. However, since it has been shown that both chemical conditioning and mechanical dewatering promote bound water release, bound and free water are being removed simultaneously. This is in agreement with the removal of water observed in the controlled drying test. An exception to this rule is encountered whenever conditions lead to significant destruction of the sludge floc structure, as seen in the vacuum filtration of freeze-thaw conditioned alum sludge.

Beyond the predictive qualities of bound water research lies perhaps the most significant benefit, that of gaining further understanding of the forces that bind water to sludge. The effect of different polymers and different dewatering methods on these forces have been shown. Using this type of information, specific protocol can be developed for the maximum water removal for each different type of sludge encountered.

CHAPTER VI

CONCLUSIONS

Several biological and chemical sludge samples were gathered and evaluated for bound water content. This evaluation was made on unconditioned, undewatered samples as well as on samples that had undergone various degrees of conditioning and/or dewatering. The controlled drying method and the dilatometric method were used. Emphasis was placed on the dilatometric method.

Other sludge properties measured were bulk density, percent cake solids, and chemically bound water. From this study, the following conclusions were made:

1. Different methods of measuring sludge bound water produce different results. In most cases, a higher value of bound water was obtained by the controlled drying method than by the dilatometric method. The dilatometric method was found to be more accurate and more convenient. The controlled drying method is necessary for measuring the chemically bound water fraction.

2. Bound water can be removed by chemical conditioning. One mechanism by which this happens is believed to be an exchange of the polymer and the water on the binding sites of the dry material. Additional bound water is believed to be released as the particles

agglomerate. Freeze-thaw conditioning is believed to release bound water due to the pressure exerted by the ice crystals as they form.

3. Mechanical dewatering promotes further bound water release. This is believed to be a result of the applied dewatering pressure overcoming the binding forces. Higher dewatering pressure removes a greater volume of bound water. A decrease in bound water content corresponds to an increase in final dewatered cake solids.

4. The chemically bound water fraction is not affected by conditioning or mechanical dewatering. However, this fraction is so small that its removal would not have a significant impact on final dewatered cake solids.

5. Apparent floc density is the sum of the proportional fractions of the dry material and the water that is bound to the dry material. Apparent floc density of the unconditioned, undewatered sample appears to define the upper boundary of mechanical dewatering. One exception to this limit was found in the vacuum filtration of freeze-thaw conditioned alum sludge.

6. The calculated apparent sludge floc density is approximately equal to the floc density as measured by isopycnic centrifugation. A relationship may exist in what bound water measurement techniques and isopycnic

centrifugation are measuring. However, it is not conclusive that the two techniques are measuring the same thing.

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