

**GEL-LIKE BEHAVIOR OF BIOSOLIDS IN
CONDITIONING AND DEWATERING PROCESSES**

by

Derya Dursun

A dissertation submitted to the Faculty of the University of Delaware in
partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil
Engineering

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ABSTRACT

The key question of why biosolids retain water so tenaciously has not been answered precisely yet. Even with the addition of different chemicals, the application of high pressures and high speeds in dewatering devices, and a combination of different technologies, around 70% of biosolids still remains water at the end of treatment operations. Improved dewatering is desirable to both reduce the costs and increase the options for ultimate biosolids disposal. A major barrier to developing improved dewatering through chemical conditioning is the poor understanding of the mechanisms through which chemicals improve dewaterability. Selection of chemicals and optimum doses is usually done by trial and error, and the range of chemicals available and chemical combinations may prevent thorough examination of all dewatering options. Since chemical conditioning and dewatering are expensive processes, they are crucial steps in the disposal of biosolids in an economically and environmentally appropriate manner.

Within the last several years, a significantly different paradigm has been shown to be fruitful in describing some aspects of conditioning and dewatering of biosolids. Where biosolids have traditionally been described as concentrated suspensions of rigid particles, recent reports suggest the description of biosolids as gels. The behavior of gel systems has been investigated in many other fields such as polymer chemistry, food

science and pharmaceuticals. Therefore, fundamental approaches to gel systems are already available. These approaches typically do not apply directly to the conditioning and dewatering context of biosolid processing; however, the basics of these approaches can form the foundation for future work in this area.

This thesis describes a new approach that elaborates upon the gel model for the behavior of biosolids by combining classically used methods for biosolid description (e.g., solids, filtration tests) with others that describe gel behavior (e.g., rheometry, swelling, charge density/titration) and using them on both synthetic slurries and sampled biosolids. The additions of specific conditioning additives and the application of different forces allow understanding of the specific mechanisms behind chemical conditioning and suggesting an alternative description of the physical behavior of biosolids.

Consequently, this research proposes a conceptual framework to improve our understanding of the nature of biosolids and the specific reasons that they retain water so well. It starts with the chemistry of sludges, then uses new rheological approaches to examine the way chemistry becomes structural and how this varies according to the sludge composition and the sludge conditioner. The gel description, combined with an understanding of the chemistry of conditioning additives, improves the ability to “break” a gel-like biosolid structure to efficiently remove more water. Through a consideration and possible synthesis of gel vs. particulate descriptions of biosolids,

improved and quantitative descriptions of sludge flow, thickening, filtration, and even drying are likely to emerge. Ultimately, this might lead to the application of these practices in wastewater treatment facilities.

Chapter 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

The main purpose of water and wastewater treatment is to generate a product that does not damage the environment into which it is introduced. In recent years, as the water and wastewater treatment industry has developed, this primary goal has been largely achieved. However, at the same time, a new problem has been introduced: treatment plants produce a vast amount of an unwanted byproduct called “sludge.” Sludge can be defined as the solid, semi-solid or liquid residue generated during treatment processes (EPA, 1994). Throughout this thesis, the term *biosolids* is preferred to *sludge* to designate processed sludge during the treatment process or after treatment and immediately prior to disposal.

The production of biosolids has ramped up significantly since the 1970s, both in the US and throughout the rest of the world (Vesilind and Spinoso, 2001); currently, around 7.6 million tons of dry solid per year is generated in the US alone (McCann, 2006). Thus, there have been numerous studies to investigate the options for utilization

and disposal of biosolids as well as treatment methods. Now, the greater part (55%) of the biosolids produced annually is used for land application. Since rapidly growing public resistance against the use of biosolids for agricultural purposes has forced authorities to dispose of excess biosolids by various methods at considerable cost, reducing the amount of biosolid mass has become a major area of concern.

Advanced treatment processes have been a growing requirement due to strict environmental regulations initiated in most parts of the world, as classical treatment methods do not meet the stringent standards for nutrient control, microbial reduction, odor removal and more. With these latest developments in water and wastewater treatment, the characteristics and the structure of the biosolids has varied noticeably.

The common practice used for stabilization of biosolids is anaerobic digestion, which can be operated under various conditions (i.e., mesophilic, thermophilic). Anaerobic digestion is a widely accepted process for not only reducing the sludge volume but also inactivating the pathogens, reducing the odor and producing biogas. However, this process alters the structural properties of biosolids drastically, resulting in higher resistance to solid/liquid separation. Significant differences can be observed between activated and digested sludge for dewaterability characteristics, filterability, settleability and conditioner requirements.

Conditioning chemicals improve the dewaterability of biosolids, but the addition of these chemicals may also increase the complexity of the biosolids structure. Thus, the current approach to design and operation of conditioning and

dewatering processes is largely empirical. Selection of chemicals and optimum doses are usually done by trial and error. Furthermore, constant changes in the characteristics of biological sludge may alter chemical dosing requirements, and this again necessitates additional trial-and-error testing. The same situation exists with regard to biosolids produced in water treatment facilities.

An enhanced fundamental understanding of the structure of biosolids could have many practical benefits. Shorter-range benefits could include better methods for the selection of conditioning chemicals, reduction of conditioning chemical costs, improved operational practices for dewatering processes, and modifications to upstream processes that would favorably alter biosolid dewaterability. The ability to develop superior conditioning chemicals and processes, novel dewatering technologies, and biosolid structures that retain or release constituents at controlled rates are examples of longer-range benefits that may accrue.

1.2 SIGNIFICANCE OF CONDITIONING AND DEWATERING PROCESSES

The processes of conditioning and dewatering have become crucial steps in the management of biosolids, because the cost and the feasibility of subsequent disposal alternatives hinge on the solids concentration that can be consistently attained. Typically, dewatering operations account for 30-50% of the annual operating costs in a large treatment plant. The expense of chemical conditioning itself can be a significant portion of the operational costs of water and wastewater treatment. Although

reductions in chemical costs and improvement in water removal are desirable, there is a poor understanding of the mechanisms involved due to the complex structure of biosolids. Moreover, the physical and biological factors, as well as the environmental conditions, might alter the behavior of biosolids for separation purposes.

The main purpose of the conditioning process is to enhance the efficiency of solid/liquid separation by altering sludge properties in important ways (Dentel, 2001a). Varieties of chemicals, including inorganic additives and organic polymers in different chemical compositions and molecular weights, have been used widely for thickening and dewatering applications. The release of these chemicals into the environment initiates questions about environmental effects. Besides these direct concerns about the biodegradability, fate, and toxicity of the conditioners, there are additional concerns about whether they may lead to adverse effects such as the formation of undesirable byproducts. More notably, the mechanism of how conditioners work can not be elucidated clearly with the current hypotheses.

The dewatering of biosolids is a key step in the management of water and wastewater residuals. Many dewatering devices, treatment technologies, additives and process modifications have been exploited to enhance dewaterability. The cost of the equipment and conditioning chemicals, final solid content, and filtrate quality are the major factors in selection of a dewatering process, but the variability in sludge quality, exacerbated by poor understanding of the sludge composition and behavior, makes it difficult to predict the efficiency of the dewatering step. Therefore, improvements in

our understanding of the structure of biosolids and their dewatering behavior have been comparatively slow.

Development of a better understanding of biosolids will involve determination of the influence of shear and normal forces on dewaterability, characterization of the polymeric substances in biosolids, and elucidation of their relationship with dewaterability. Although there have been better mathematical descriptions for solid/liquid separation processes, there is no explicit connection between these descriptions and the improved development of dewatering equipment (Novak, 2001a). New models that can elucidate the relationship between conditioning-dewatering efficiency in practical applications and the theoretical mathematical formulations might also be critical.

1.3 OBJECTIVES AND THE SCOPE OF THE STUDY

This research takes a new approach to the description of biosolids, based on recent insights into their underlying physical-chemical characteristics. This approach departs from the common paradigm of assuming biosolids as a flocculated or fractal suspension with a rigid sphere substructure. Using the insight that biosolids may also be characterized as a “gel” (at least in part), new and fundamental research approaches are presented that are likely to yield advances into the mechanisms underlying conditioning and dewaterability.

Considering the significance of conditioning and dewatering processes, the overall objective of this research is *to improve our understanding of the nature of biosolids* through a consideration and possible synthesis of *gel (colligative)* vs. *particulate (structural)* descriptions of them.

There are several hypotheses on the subject that need to be clarified:

- o Synthetic slurry synthesized from a natural biopolymer (alginate) is used to mimic the sampled sludge in physical/chemical ways.
- o The effect of particulate (structural) and polymeric (gel) fractions in synthetic slurries on conditioning and dewatering differ.
- o The apparent ability of various cations to penetrate and uniformly collapse sludge gels is related to cation size and surface charge.
- o The effect of shear on normal forces is crucial in dewatering.
- o Altering sludge structure by targeting the polymeric substances with specific treatment methods (such as enzymatic treatment) changes the structure of biosolids.

To test these hypotheses, the following tasks were undertaken:

- o the synthesis of synthetic slurries that mimic the sampled biosolids in physical-chemical ways;
- o the separation of the effects of particulate and gel fractions in dewaterability by varying the fractions of the contents in synthetic slurry;

- the combination of shear tests with filterability and charge determinations with various cations;
- the application of dynamic filtration that combines normal and shear forces during filtration; and
- the characterization of extracellular polymeric substances (EPS) before and after enzyme pretreatment.

1.4 OUTLINE OF THE STUDY

Following the introduction, *Chapter 2* provides background information by reviewing the literature. It starts with the structure of biosolids, summarizes general properties of gels, goes on to explain the basics of conditioning and dewatering processes, and finishes with introducing the idea of biosolids as gels and the advantages and disadvantages of this approach to explain the mechanisms of conditioning and dewatering.

Chapter 3 focuses on the synthetic sludge that was prepared and used in this study to mimic the biosolids. The physical and chemical characterization of synthetic sludge, combined with rheological characterizations, was investigated for various synthetic sludge formulations that allow us to alter the gel and particulate fractions and separate the effect of these two fractions on conditioning and dewatering. The studies were extended with *shear tests* in order to understand the shearing effects and apply a

gel model to predict the response of samples to conditioning and dewatering under different shearing conditions.

Chapter 4 investigates the *shear sensitivity* of digested sludge, since the optimum amount of conditioner is closely related to the amount of shear applied. The relationship of shear resistance to cation size and surface charge was determined. These experiments were used in the application of a *gel model* to predict the conditioning efficiency of biosolids.

The effect of not only shear but also normal force is known to be crucial in the efficacy of dewatering processes. Thus, in *Chapter 5* the combined effect of *shear and normal forces* is explored. An innovative device called an *immobilization cell* was used to apply both shear and normal forces to digested sludge and synthetic slurry while filtration occurred. The change of viscosity and the final solid concentration were observed. The change of responses with the addition of various conditioners was also studied.

The role of EPS in biosolids structure and the physical and chemical properties of biosolids was tested by applying an enzyme pretreatment that allows degradation of the targeted components in EPS. *Chapter 6* addresses the comprehensive characterization of EPS before and after enzyme pretreatment. The effects of the EPS amount, molecular weight and various EPS compositions on the efficiency of solid/liquid separation processes were investigated.

Chapter 2

BACKGROUND

2.1 BIOSOLIDS

2.1.1 Origin of Biosolids

Sludges are generated as a result of surface water, drinking water and wastewater treatment processes; dredging activities; and decontamination of polluted sites, as well as many industrial activities. The main focus of this study is on sludge produced in wastewater treatment processes.

In conventional wastewater treatment plants, there are several processes that form sludges. Figure 2.1 shows the typical scheme of a wastewater treatment process, including sludge treatment units and origins of sludge. In order to remove coarse materials, grit and silt, preliminary treatment is required; however, the residues from this step are not considered sludge, and they are mostly disposed directly to landfill. Depending on the type of wastewater to be handled, physical-chemical treatment might be essential before biological treatment processes. This operation is common in industrial wastewater treatment plants, where hazardous and toxic materials are removed with chemical precipitation or other unit processes. The sludge originated from this step has unique characteristics depending on the type of wastewater and the

treatment option; therefore, it is generally handled separately and not entered into sludge treatment units. Almost all treatment plants have a primary treatment following the preliminary treatment where the settleable solids, grease and scum are removed with gravitational force. This step produces excess sludge, which is known as *primary sludge* and has some particularly unique characteristics. It is grayish-brown in color with an objectionable odor that makes it aesthetically unpleasing. It also contains all of the known human pathogens, since, with settlement, pathogenic organisms that are attached to solid particles are transferred from wastewater to sludge (Metcalf and Eddy, 1991).

After the removal of settleable solids, wastewater enters the biological treatment step, where organic materials are removed; this step is also called *secondary treatment*. The most common secondary treatment method is the activated sludge process in which wastewater is mixed with the active biomass to degrade the organics and reduce the oxygen demand. Although some part of the produced biomass is recycled to maintain the required amount of active biomass in the aeration tanks, the excessive part forms another important sludge source. This sludge, which is called *waste-activated sludge* (WAS), or secondary sludge, is significantly different from primary sludge. It has a brown, flocculent appearance and an earthy odor, and it is difficult to dewater.

Combined sludge then enters into sludge processing units where biosolids are formed. The sources, characteristics, and quantities of the solids to be handled must be

known for proper design of sludge processing, treatment and disposal facilities. Processes used for thickening, digesting, conditioning and dewatering are sources of biosolids (Figure 2.1). Typical characteristics of biosolids vary depending on the origin of solids and sludge, the amount of aging, and the type of processing to which they have been subjected. Trickling filter residues are brownish and relatively inoffensive, whereas aerobically digested sludge is brown to dark brown with an inoffensive musty odor, and anaerobically digested sludge is dark brown to black with an inoffensive odor and a large quantity of gas (Metcalf and Eddy, 1991). Typical chemical composition and properties of untreated sludge and digested sludge are compared in Table 2.1.

Table 2.1 Typical characteristics of untreated sludge and digested sludge

(Adapted from U.S. Environmental Protection Agency, 1979)

	Untreated primary sludge		Digested primary sludge		Activated sludge
	Range	Typical	Range	Typical	Range
Total Dry Solids (TS), %	2-8	5	6-12	10	0.83-1.16
Volatile solids (% of TS)	60-80	65	30-60	40	59-88
Grease and fats (% of TS)	6-35	-	5-20	18	5-12
Protein (% of TS)	20-30	25	15-20	18	32-41
Nitrogen (N, % of TS)	1.5-4	2.5	1.6-6.0	3	2.4-5
Phosphorus (P ₂ O ₅ , % of TS)	0.8-2.8	1.6	1.5-4.0	2.5	2.8-11
Potash (K ₂ O, % of TS)	0-1	0.4	0-3	1	0.5-0.7
Cellulose (% of TS)	8-15	10	8-15	10	-
Iron (%TS)(not as sulphide)	2-4	2.5	3-8	4	-
Silica (SiO ₂ , % of TS)	15-20	-	10-20	-	-
pH	5-8	6	6.5-7.5	7	6.5-8.0
Alkalinity (mg/l as CaCO ₃)	500-1500	600	2500-3500	3000	580-1100
Organic acids (mg/l as HAc)	200-2000	500	100-600	200	1100-1700
Energy Content (kJ/kg dry matter)	23000-29000	25500	9000-14000	11500	18500-23500

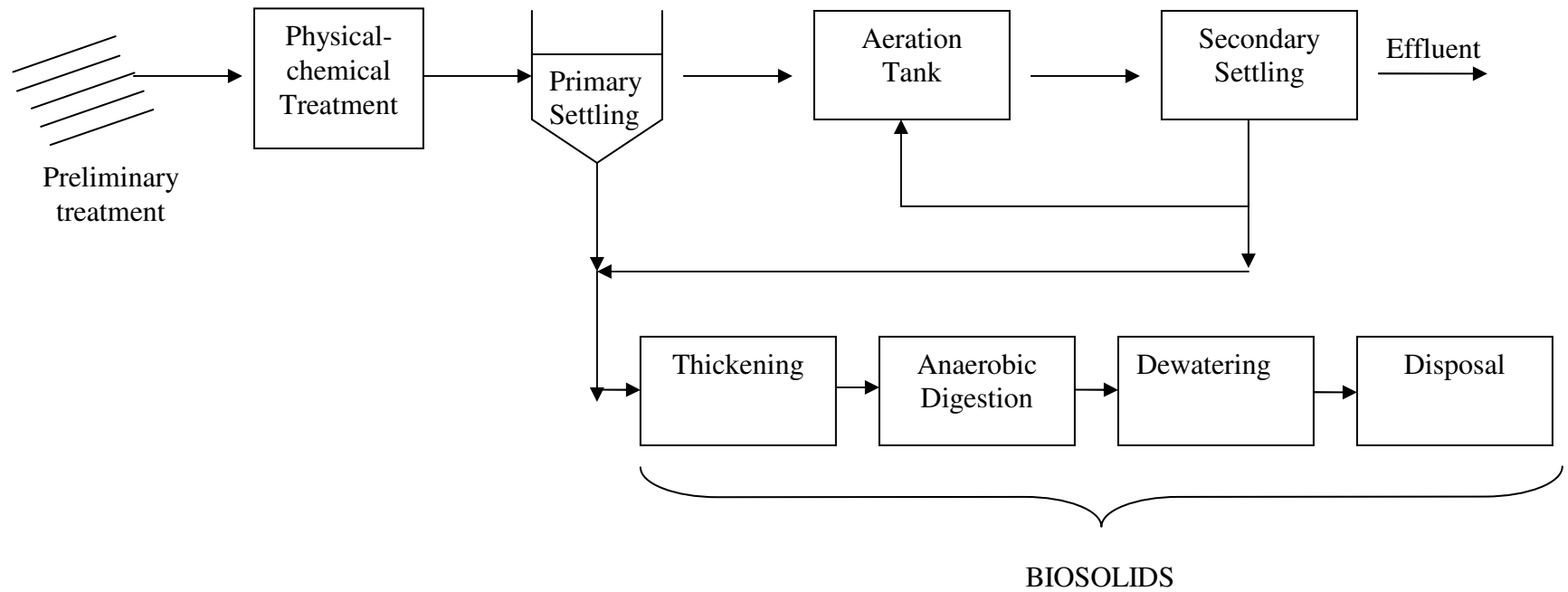


Figure 2.1 Origin of biosolids in a typical wastewater treatment plant

2.1.2 Structure of Biosolids

Biosolid structure is an essential factor in determining the performance of solid/liquid separation and thus conditioning and dewatering efficiency. The two major fractions determined in biosolid structure are flocs in gross scale and primary particles in fine scale. The particle sizes of these fractions are significantly different from each other (Jorand *et al.*, 1995; Snidaro *et al.*, 1997). Consistent with these, Mikkelsen (1999) showed that the size of primary particles varies between 0.5 μm and 5 μm , whereas the particle size of flocs ranges from 25 μm to 200 μm . Flocs are the main constituents of biosolids in terms of mass and volume; nevertheless, the smaller particles also have a substantial effect on the filterability of biosolids (Mikkelsen *et al.*, 1996).

A considerable amount of research has been done on floc structure at different stages of the treatment process using various methods, e.g., light scattering, free-settling (Wu *et al.*, 2002), and correlative microscopy (Liss *et al.*, 1996). Research indicates that biosolid flocs are complex aggregates consisting of various microorganisms, extracellular polymeric substances (EPS), inorganic particles, cations and large quantities of water (Li and Ganczarczyk, 1990). Figure 2.2 is a pictorial representation of a sludge floc. The microbial content of biosolids is also diverse, including single bacteria, filamentous organisms and bacterial colonies. A significant portion of the microbial content of biosolids is bound in a matrix structure of extracellular polymeric substances (EPS) (Li and Ganczarczyk, 1993). Filamentous

organisms are believed to have a key function in biosolid structure by sustaining a backbone for flocs (Parker *et al.*, 1971). Liss *et al.*, (1996) observed complex matrices of polymeric fibrils that were found to represent the dominant physical bridging mechanism between organic and inorganic components of the flocs. Hence, polymeric substances are considered to connect the microorganisms and particles together and provide cohesion to the floc structure. Besides EPS, the effect of cations on the integrity of flocs was investigated by various researchers (Higgins and Novak, 1997a; Keiding and Nielsen, 1997). The cations (generally multivalent) caused electrostatic interactions between negatively charged flocs and formed a stronger floc structure (Higgins and Novak, 1997b; Sanin and Vesilind, 1996).

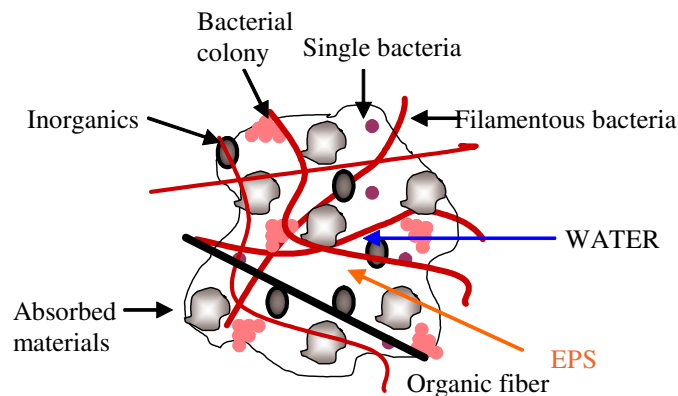


Figure 2.2 Structure of flocs in biosolids (Redrawn from Mikkelsen, 1999)

The structure of flocs is influenced by the type and operational conditions of the treatment processes from which they originate (Li and Ganczarczyk, 1990) and the

type of biosolid treatment processes following water/wastewater treatment (Barbusinski and Koscielniak, 1997). The conditioner type and dose selected are also known to change the structural properties of flocs (Wu *et al.*, 2002). Spicer and Pratsinis (1996) studied the evolution of floc structure with shear and pointed out the differences under different shear rates.

In contrast to the complex nature of biosolids, according to the traditional biosolids model, biosolids have often been conceptualized as negatively charged rigid and uniform spheres suspended in water (CIWEM, 1999) (Figure 2.3). This approach has previously been applied to comprehend the basics of coagulation and flocculation in water treatment and chemical conditioning of biosolids. However, the structure of biosolids is more complicated than just “rigid spheres and water.” The effect of physical and structural differences on the conditioning and dewatering of biosolids has not been explained clearly with this traditional model. Consequently, some limitations are observed in this analogy.

Recently, some researchers have offered a new approach, in which biosolids are considered to be *gels* (Poxon, 1996; Legrand *et al.*, 1998). Some aspects of conditioning and dewatering are surprisingly explained with this new model, which assumes that biosolids are an entire matrix into which particles and microorganisms are embedded. Figure 2.4 illustrates the idea of this model to explain the structure of biosolids.

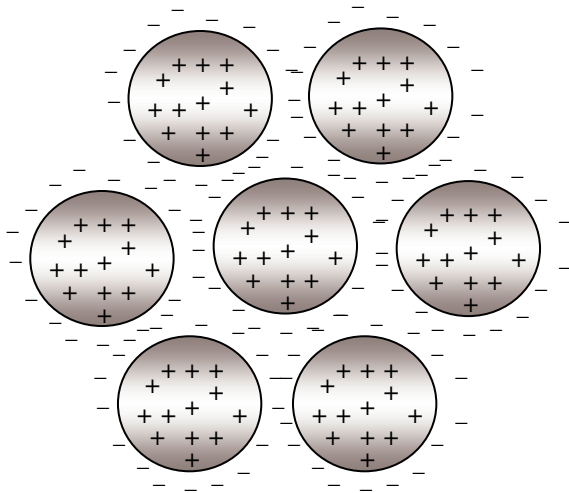


Figure 2.3 Traditional biosolids model

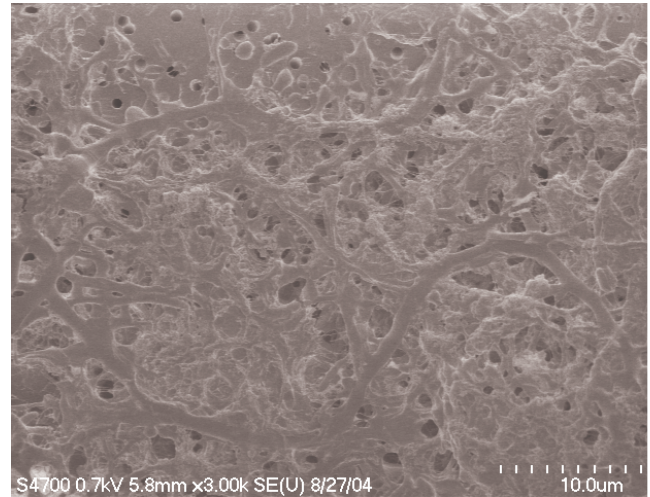


Figure 2.4 A colloidal gel model

2.1.3 Extracellular Polymeric Substances (EPS) in biosolids

Polymeric substances in biosolids structure have significant importance in the content of this thesis due to their function on the *gel-like* behavior of biosolids. EPS that are secreted by microorganisms are responsible for binding particulate materials with microbial cells (Houghton and Stephenson, 2002). They are negatively charged macromolecules that provide cohesion to, and confer gel-like behavior on, the floc structure (Wilén *et al.*, 2003a; Keiding *et al.*, 2001). In earlier studies, Legrand *et al.* (1998) also described wastewater biosolids as gels because their network structure originates from EPS. Poxon and Darby (1997) used scanning electron microscopy (SEM) to show the extensive gel-like biocolloidal structure of digested biosolids. Their work showed the importance of gel-like behavior in restricting water mobility within the biosolid and, consequently, the fairly tenacious retention of water within the

biosolid. Numerous research papers have been published in this area, some of which have convincing conclusions. A number of researchers have indicated that the extracellular organic substances present in biological biosolids are primarily responsible for their water retention and poor dewaterability (Pavoni *et al.*, 1972; Goodwin and Forster, 1985). Moreover, other research (Dignac *et al.*, 1998; Urbain *et al.*, 1993) has correlated high EPS concentrations with poor flocculation and unsatisfactory solid/liquid separation. In contrast to these results, more recent studies indicate the independence of total EPS content from settleability and filterability (Liao *et al.*, 2001). Others have elaborated upon this concept by identifying extracellular protein and polysaccharide as particular contributors (e.g., Murthy, 1998). Novak and Bivins (2000) have shown the correlation for higher molecular weight fractions of these organics. Some researchers have also pointed out that EPS exert a significant demand for flocculant polymers during the chemical conditioning process prior to dewatering (Novak *et al.*, 2003).

EPS, the major organic fraction of biosolids, are composed of different organic species (Frolund *et al.*, 1996). The composition, rather than the quantity, of EPS was found to be the governing factor in bioflocculation and settleability. There is some disagreement about which specific organic species are responsible for poor dewaterability. Poxon and Darby (1997) studied the relationship of extracellular polyanions (largely polysaccharides) to dewaterability and concluded that “colloidal polyanions are not a major contributor to the poor dewaterability of the digested

biosolid” that they studied. In recent studies, proteins, instead of carbohydrates, were found to be the predominant constituent of EPS (Wilén *et al.*, 2003a; Wilén *et al.*, 2003b; Dignac *et al.*, 1998; McSwain *et al.*, 2005). Moreover, the presence of humic compounds (Wilén *et al.*, 2003a; Wilén *et al.*, 2003b; Frolund *et al.*, 1996), uronic acids (Frolund *et al.*, 1996; Wilén *et al.*, 2003a; Wilén *et al.*, 2003b), DNA (Frolund *et al.*, 1996; Sponza, 2002; Wilén *et al.*, 2003a; Wilén *et al.*, 2003b) and lipids (Goodwin and Forster, 1985) in EPS were reported in various publications. However, information about their concentration in EPS is not consistent (Liu and Fang, 2002). This is most likely due to the different extraction methods, influent characteristics, and operational conditions.

It has not been shown that extracellular proteins and polysaccharides are the only types of organics leading to high water retention. Other components have also been suggested as responsible, including anionic surfactants (Chitikela *et al.*, 1997), natural organic matter (Novak and Bivins, 2000) and cations (Higgins and Novak, 1997a; Higgins and Novak, 1997b). Park *et al.* (2006) have relied chiefly on operational definitions (i.e., extraction methods) for determining the extracellular and/or polymeric constituents that are claimed to control dewaterability. Any correlations arrived at through this approach may be dependent on the biosolid sample involved (Poxon and Darby, 1997). Moreover, the correlation is unlikely to provide insight into how biosolids can best be destabilized. Therefore, although there is a convincing relationship between extracellular polymeric substances (EPS) and

dewaterability, it is irregular and provides mechanistic insights only in an indirect manner.

2.1.4 Water Content of Biosolids

All water within the biosolids does not behave in similar ways due to the properties of the solids, charges and polymeric materials with which they are associated (Vesilind, 1994). Different researchers suggest different approaches to explain the moisture content of biosolids.

2.1.4.1 Two categories approach

Conventionally in biosolids, two main types of water have been defined: bound water, whose properties are modified due to the presence of the solid, and bulk (free) water, which is not influenced by the solid- particle water. Bulk water can be partially or totally removed by mechanical stress, whereas bound water can be removed only by expression (Novak, 2001b). However, this simple approach is found insufficient to fully understand and envisage the mechanisms of dehydration and the treatment processes that are associated with it (coagulation, flocculation, dewaterability).

2.1.4.2 Four categories approach

Vesilind proposed to classify the water in sludge into four groups (Vesilind and Hsu, 1997; Kopp and Dichtl, 2000), with each group having specific processes for water removal:

- o *Free water* is the water that moves freely between the flocs.
- o *Interstitial water* is the part that is trapped within the flocs. Some part of it can be removed by mechanical devices such as centrifuges.
- o *Vicinal water* is associated with solid particles and can not be removed by mechanical dewatering.
- o *Hydration water* is chemically bound to the particle and can be released only by thermo-chemical destruction.

This classification system elucidates the limitations of mechanical dewatering. Hence, to increase the efficacy of dewaterability, besides removing free and interstitial water, vicinal water and, if possible, hydration water needs to be removed. This is possible only by alteration of the biosolid structure.

2.1.4.3 Continuous water approach

None of the approaches given above considers the impact of the polymeric matrix in the biosolid structure. A review done by Vaxelaire and Cezac (2004) pointed out the drawbacks of each classification. The idea of continuous water has been an important point in this work, since it fits well into the gel approach. Starting with

Legrand *et al.* (1998), some researchers state that a significant amount of water is trapped within the polymeric network (Mikkelsen and Keiding, 2002a). They introduced a term, *water-holding*, that captures both surface water and osmotic water trapped within the polymer network. Keiding *et al.* (2001) used *colligative properties* based on the same approach to explain the water/biosolid relationship. The colligative properties are defined as the lowering of the solvent (water) chemical potential as a result of introducing a solute. These result in elevation of the boiling point, depression of the freezing point, and the occurrence of osmotic pressure. Due to the high amount of charged colloids such as EPS and dissolved materials, the solute concentration in the liquid water fraction steadily increases when drying or freezing sludge samples, making it more difficult to remove this remaining water. The results of Keiding *et al.* (2001) showed that many of the moisture distribution determination experiments performed in the past could be explained by the colligative properties. Recently, the dewatering kinetics of activated sludge is modeled to some extent by the osmotic effects occurring in the dehydrating cake (Keiding and Rasmussen, 2003). However, the concept of continuous classification of water simplifies the activated sludge system, since it does not take account physical effects (barriers) such as cell walls, which separate the intracellular water from the extracellular water (Vaxelaire and Cezac, 2004).

2.1.5 Surface Properties of Biosolids

The surface properties have long been believed to be important in controlling the stability of suspensions based on DLVO (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) theory (Liao *et al.*, 2001). Microbial cells, EPS, and sludge flocs carry negative charges due to their functional groups (e.g., carboxylic and phosphate). The zeta potential or surface charge is commonly used to characterize the surface properties of biosolids. Most of the organic colloids in pH-neutral solutions are negatively charged, and the ions together with the colloids form an electric double layer, composed of a Stern layer of firmly attached positive ions around the surface of the colloid and a diffuse layer of more freely moving counter-ions (Saveyn, 2005).

A charged colloidal particle will move with a fixed velocity in an electric field, a phenomenon called *electrophoresis*. The zeta potential is calculated from the electrophoretic mobility of the particle, and it is related to the dielectric constant and viscosity of the suspending liquid. The zeta potential may be determined by a variety of techniques; dynamic light scattering (for dilute suspensions) and electrokinetic sonic amplitude (for concentrated suspensions) are the most common (Malvern Instruments, 2004). Figure 2.5 is a schematic representation of the zeta potential.

The surface charge is typically measured by the colloid titration method (Morgan *et al.*, 1990; Tiravanti *et al.*, 1985). This method measures the charges in the outer layer of flocs, but Mikkelsen (2003) points out the limitations of this method for charge determination of whole sludge.

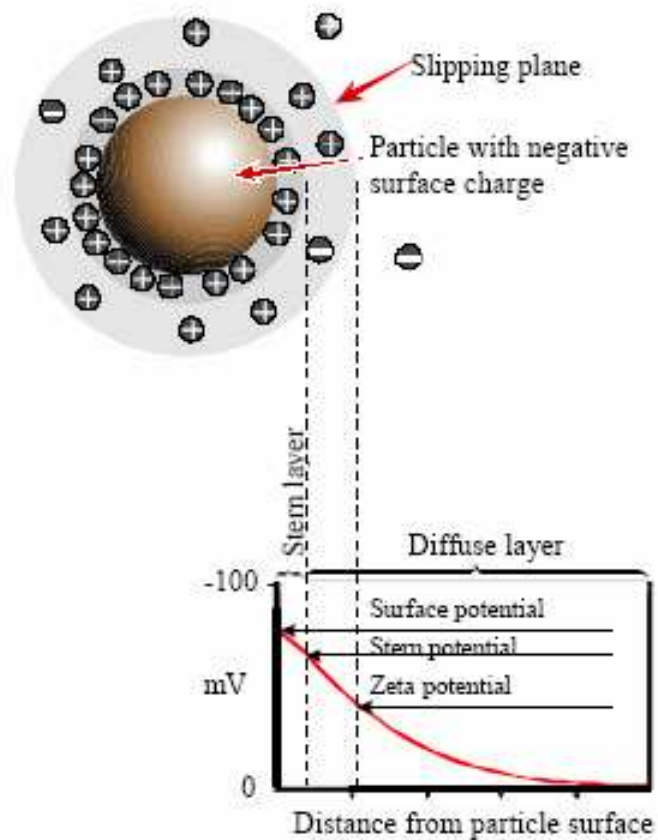


Figure 2.5 Schematic Representation of Zeta Potential (Malvern Instruments, 2004)

2.2 GELS

2.2.1 Definition of a gel

A gel is a state of matter, neither liquid nor solid, or both liquid and solid (Cohen Addad, 1996). Therefore, gels possess both the cohesive properties of solids and the diffusive properties of liquids. The unique physical properties of a gel arise from its three-dimensional crosslinked polymer network structure immersed in a solvent (Tokita and Tanaka, 1991). When a crosslinked polymer network takes up

water as a solution phase, hydrogels that are crosslinked polymers of hydrophilic monomers are formed (Borchard and Jablonski, 2003; Huther *et al.*, 2002).

2.2.2 Properties of gels

Crosslinking of hydrogels caused by physical interactions and chemical reactions leads the gels to have *viscoelastic* properties. Hydrogels are the recent focus of substantial scientific research due to their potential application in a large number of areas, including the drug delivery, cosmetics, food and chemical industries. The basis for the diverse application of hydrogels is their ability to change properties with environmental conditions such as pH, temperature, and ionic strength (Hirotsu, 1992; Ohmine and Tanaka, 1982). One type of polymeric gel, called *intelligent gels*, shrinks or expands (deswells or swells) enormously in response to changes in environmental conditions.

Gels are *osmotically* highly active. If a chemically crosslinked gel is immersed in an excess of liquid and allowed to equilibrate, the size of the sample may increase, decrease or remain constant. This effect strongly depends upon the thermodynamics of the liquid and the degree of crosslinking. Thermodynamic equilibrium for a gel is reached when the chemical potential of the solvent is equal inside and outside the gel. Accordingly, once thermodynamic equilibrium is reached, the osmotic pressure within a gel must be zero (Fernandez-Nieves *et al.*, 2000). At that time, the transfer of the solvent phase into the network structure ends and *swelling* occurs. Swelling can be

defined as the growth in volume or mass by the adsorption of moisture. If a typical gel is placed in a solvent, the volume will increase from an initial value of V_0 to V . The swelling ratio q is defined as V/V_0 . This ratio can also be defined in terms of mass.

2.2.3 Rheological characteristics of gels

Since hydrogels are defined as viscoelastic materials, rheological measurements provide valuable information about their structure. To examine the degree of crosslinking both at the molecular level and over a much longer distance, rheological techniques are applied to the study of polymer gels and networks (Kavanagh and Ross-Murphy, 1998). When a precursor liquid, composed of either small molecules or polymers, is crosslinked to form a gel, the rheological properties change from those of a viscous liquid to an elastic solid (Larson, 1999). According to Ferry (1980), a gel must show a flat mechanical spectrum in an oscillatory shear experiment. In other words, it should show a value of storage modulus (G') that exhibits a prominent plateau and loss modulus (G'') that is considerably smaller than the storage modulus in this region. The time point at the intersection of the G' and G'' curves indicates the gel point, which is a useful definition especially for industrial applications (Mezger, 2006). Fabri *et al.* (1998) pointed out the thixotropic behavior and reformation of weak gels after a standing time.

The wide knowledge of swelling and collapse behavior of gels (Ricka and Tanaka, 1984; Tanaka, 1978), e.g., their behavior in the presence of divalent cations

(Axelos *et al.*, 1994) and their rheological properties are transferred into the water retention capacity of polymeric substances to understand the complex mechanisms of natural processes. Thus, application of the gel approach to biosolids is a useful tool to comprehend the mechanisms behind the conditioning and dewatering processes.

2.3 CONDITIONING OF BIOSOLIDS

The conditioning process of the biosolid is one of the auxiliary operations in biosolid handling processes. Although there are several physical conditioning methods such as thermal drying, freeze thawing, and elution, chemical conditioning is the most common among these methods because of its cost efficiency and ease of applicability. In this method, selection of the proper conditioners, optimization of the conditioner dose, and control of the process are the most vital issues, since they affect the efficacy of the processes.

Not only for the traditional biosolid particle approach but also for the gel approach, there may be different mechanisms that affect chemical conditioning depending on the type of conditioner used. EPS is negatively charged due to the functional groups of its components; therefore, metal ions or organic polyelectrolytes are widely used for conditioning of biosolids. These conditioners lead to *charge neutralization* and effectively increase bioflocculation (Sobeck and Higgins, 2002). The addition of an appropriate amount of cationic substance reduces electrostatic repulsion, leading to coagulation and separation. However, this theory does not explain

why high molecular weight polymers work better than others. In this case, it is envisioned that the larger dimensions of the additives may allow the cationic sites to bind more than one particle, thus *bridging* the system of solid particles. A pictorial representation of these two mechanisms can be seen in Figure 2.6 (Dentel, 2001a). However, none of those mechanisms explains the *particle breakage* and its role in conditioning. The assumption of biosolids as deformable, flexible and fragile bodies can shed light on the mechanism of conditioning in particle breakage with the presence of residual flocculant in solution and reflocculation.

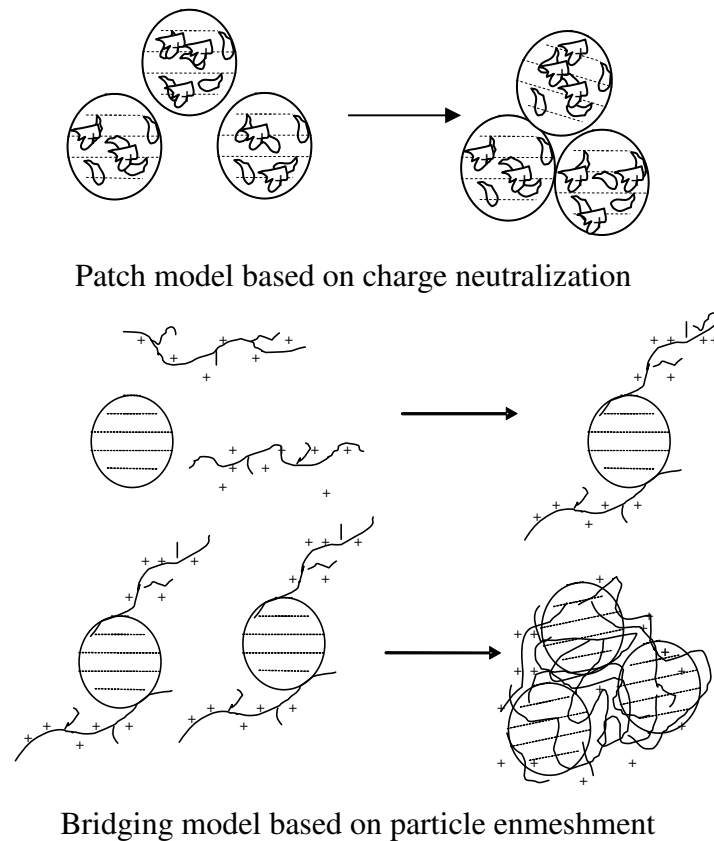


Figure 2.6 Traditional representation of flocculation mechanisms. Spheres supposedly represent “biosolid particles” (Dentel, 2001a)

2.3.1 Inorganic Conditioners

Metal ions may function to collapse the gel structure into aggregates, as suggested by Poxon's (1996) scanning electron micrographs following ferric salt addition. Results of Legrand *et al.* (1998), who conditioned a synthetic gel with an inorganic conditioner LaCl_3 , also support this collapse mechanism. The metal ions appear to diffuse uniformly throughout a gel, collapsing it into a dense and poorly filterable network.

Legrand's use of the lanthanum cation was intended to avoid complications stemming from pH-dependent hydrolysis of the more commonly used ferric salts in conditioning. The effects of OH^- ligands may be inseparable, however, from the differing ionic radii and electronegativities of the two cations. Essentially, the ability of the inorganic cations to collapse a gel may be related to both the ability to penetrate into the gel structure and the reactivity with the gel constituents. Figure 2.7 represents some results on the evaluation of the specific resistance to the filtration of biosolid particles, equilibrated in NaCl , and filtration time of the gel with LaCl_3 and PMAPTAC (cationic polyelectrolyte) additions.

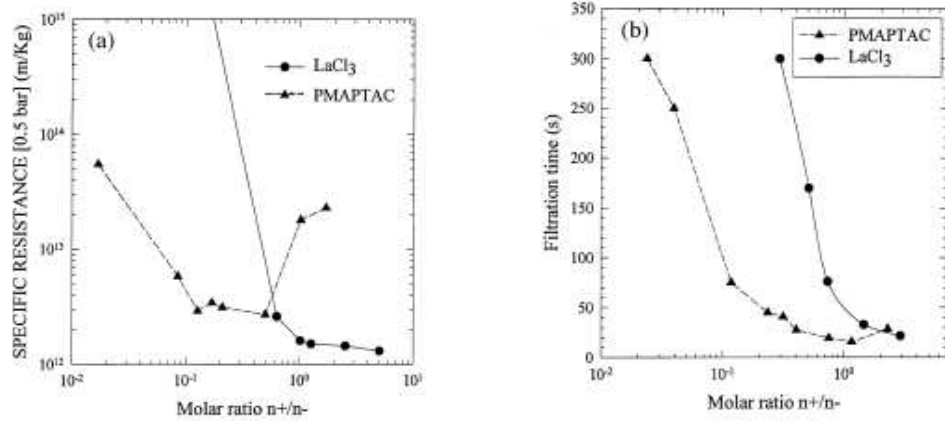


Figure 2.7 Evaluation of specific resistance to filtration of sludge and filtration time of the gel for LaCl_3 and PMAPTAC addition (adopted from Legrand *et al.*, 1998)

Even if polymeric substances are only partially responsible for the behavior of biosolids, this still suggests that the common pictorial representation of flocculation mechanisms (Figure 2.6) errs in imagining “biosolid particles” as rigid spheres. It seems unlikely that an accurate picture of biosolid conditioning could emerge from an incorrect model of the original material.

The latter supposition is consistent with Kehrer’s (1985) studies of the dewaterability effects of various metal cations. A better understanding of these interactions would facilitate the selection of inorganic conditioners, based on type, time, pH, and mode of addition for a given gel chemistry.

2.3.2 Organic Conditioners

Cationic polymers work comparably to inorganic conditioners, but only from the exterior of the sludge. They are very viscous and sticky solutions; therefore, they may affect gel collapse despite being excluded to the outer boundaries of the structure. The result is a heterogeneous collapse, with voids allowing for porous media flow. The polymer itself must provide a backbone for any rigidity in the floc structure. Legrand *et al.* (1998) showed gel swelling extent, zeta potential, and filterability behavior in model systems under these circumstances to be equivalent to those found with a variety of biosolids. Poxon's (1996) micrographs also support this type of mechanism. If the gel theory is correct, then the way to condition sludge is not so much bridging the particles together, but breaking the gel structure that retains the water. Thus, if shear is provided, it increases the interaction of polymers with the matrix structure, in which case cationic polymers might work better. Shear is therefore used not to cause particle-particle interactions, but to help the conditioners to penetrate into and collapse the gel matrix.

2.4 DEWATERING OF BIOSOLIDS

Dewatering is a key step in the management of water and wastewater residuals. A large number of dewatering devices, treatment technologies, additives, and process modifications have been exploited to enhance dewaterability. Traditional dewatering methods, such as centrifuges, belt filter presses, and recessed chamber filter presses,

can increase the solid content up to only 30%; thus, innovative methods have been sought to reduce the water content of biosolids and decrease the final mass (Abuorfi *et al.*, 2004).

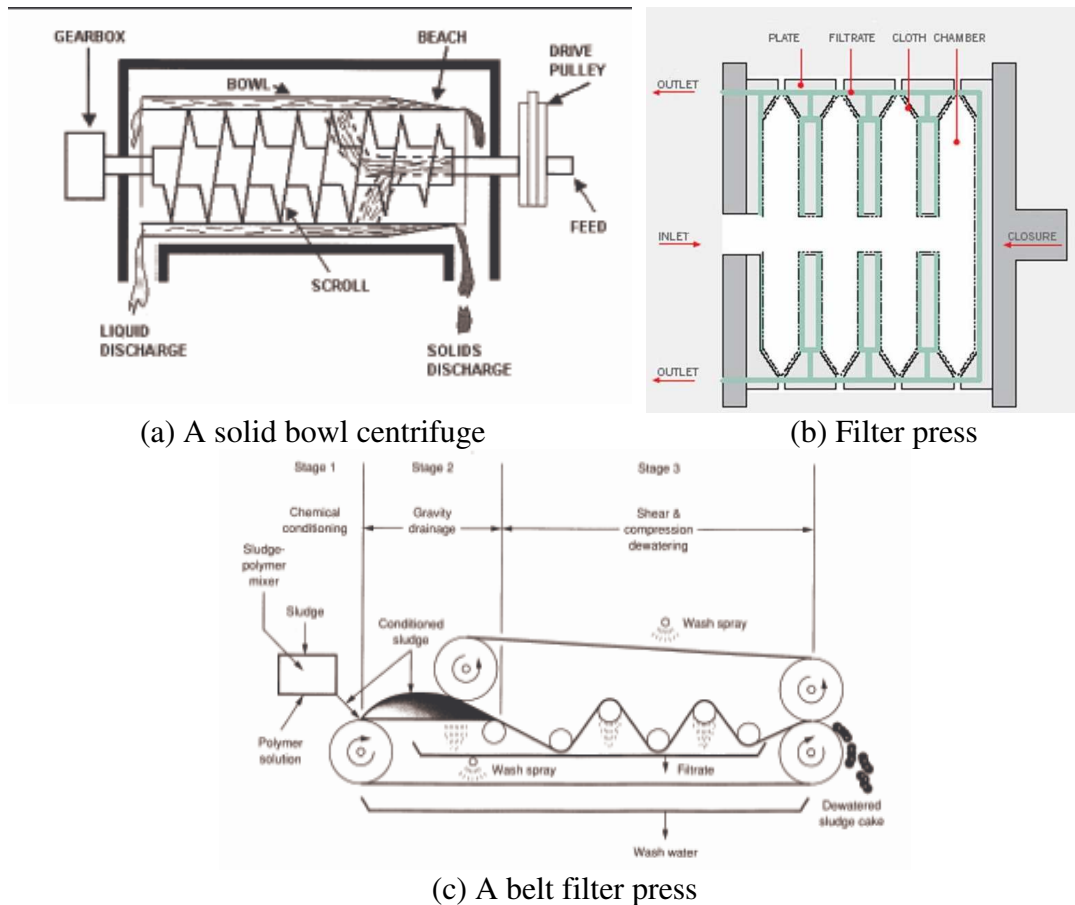


Figure 2.8 Schematic representation of most common dewatering processes

2.4.1 Dewatering processes

Many researchers have focused on improving sludge dewatering by searching for optimum conditioner type and dose; however, the role of selected dewatering equipment is also critical. Figure 2.8 shows schematics of commonly used dewatering

devices. Pan *et al.* (2003) compared the dewatering efficiency of various mechanical dewatering devices and showed the differences in efficiency even with the same sludge and conditioner type. This difference is mainly because of the applied forces in dewatering processes. The mechanism in belt filter presses is better understood and described (Severin *et al.*, 1998) than the mechanisms in centrifugal dewatering. Chu and Lee (2001) experimentally investigated the centrifugal separation of conditioned samples and concluded that new theories/correlations are essential to explain centrifugal dewatering. The fact that different forces are applied at the same time makes dewatering processes more complicated. For instance, in belt filters, both shear and normal forces are effective; in filter presses, pressure filtration is the major factor; and in centrifuges, centrifugal force is the primary force controlling dewaterability.

2.4.2 Chemical reasons of poor dewaterability

There is a debate on the reasons for poor dewaterability. In chemical aspects, the relationship between EPS and dewaterability is persuasive, although it is not consistent. Besides EPS and/or specific fractions in EPS, other organic materials have also been suggested as responsible for lower dewaterability, including anionic surfactants (Chitikela *et al.*, 1997) and natural organic matter (Novak and Bivins, 2000). The amount of cations and the ratio of monovalent to divalent cations (Vatansever *et al.*, 2005) are also found to change dewaterability. Negatively charged EPS lead to the presence of large concentrations of counter-ions. This high

concentration of ions inside the polymer network relative to the bulk water concentration forms an osmotic gradient that affects dewaterability. Mikkelsen and Keiding (2002a) have shown that EPS fractions are directly related to the quantity of negative charges of EPS and to the zeta potential of the biosolid flocs and concluded that biosolids have good dewaterability in terms of cake dry matter.

2.4.3 Physical reasons of poor dewaterability

Particle size may still be important in dewaterability. It has been shown that when small particles are added, they result in binding the cake and reducing the rate of filtration (Sorensen *et al.*, 1995).

It is also instructive to consider water treatment residuals, which may be as difficult to dewater as biological biosolids even though they are primarily inorganic. For instance, alum residuals originated from various water treatment facilities with aluminum sulphate, as the primary coagulant includes bulk water together with a floc phase. In this case, physical properties—floc size, density, and fractal dimension—might be the major factors in evaluating the dewaterability of alum residuals. However, there appears to be no direct correlation between floc size, density, or structure and the dewaterability of biosolids (Zhao, 2003).

2.4.4 Characterization of dewatering

Most research on sludge dewatering has considered the filtration rate with standardized tests in terms of capillary suction time (CST) or specific resistance to filtration (SRF). Compression cells have also been used to understand the effects of compression on dewatering rate. These tests enable assessment of the rate of filtration at the laboratory scale; however, they do not simulate the specific dewatering processes.

In order to simulate dewatering processes at the laboratory scale, a number of laboratory devices are suggested. Severin *et al.* (1998) describes a useful device called a Crown Press to simulate belt filter press dewatering. This device appears to give very accurate results compared to others. For simulating filter presses, small fixed-chamber devices are developed. The dewatering cell described by Novak *et al.* (1999) is found to be the most suitable one for this test. Due to the complexity of centrifuges, there is still no specific device that can mimic centrifugation. A standard shear test has been proposed to characterize shear in full-scale systems; however, these tests may not be successful for characterizing high-torque centrifuges.

2.4.5 Dewatering rates

In the traditional approach, the sludge cake is assumed to be a bed of small particles, and resistance to the flow of water is caused by the friction of the particle surfaces as the water passes. Thus, it is based on the modification of D'arcy's Law:

$$q = \frac{1}{A} \frac{dV}{dt} = \frac{P_T}{\mu(r^* L + R)} \quad (2.1)$$

in which q =filtrate velocity (m/s), V =filtrate volume (m^3), t =time (s), L =cake thickness (m), A =filtration area (m^2), P_T =applied hydraulic pressure (Pa), μ =absolute viscosity ($N.s/m^2$), R =support medium resistance (m^{-1}), and r^* =inverse of the permeability coefficient for the modified D'arcy expression (m^{-2}). Since cake thickness is difficult to measure in dynamic filtration tests, the expression $r^* L$ in Equation 2.1 can be replaced by $r\omega V/A$, where r =specific resistance to filtration (m/kg) ω =mass of cake deposited per unit volume of filtrate (kg/m^3); then

$$\frac{dV}{dt} = \frac{P_T A^2}{\mu(r\omega V + RA)} \quad (2.2)$$

The integrated form of this equation forms

$$\frac{t}{V} = \frac{\mu r \omega}{2 P_T A^2} V + \frac{\mu R}{P_T A} \quad (2.3)$$

In a laboratory filtration test, the time of filtration (t) is recorded as a function of volume (V) and by plotting t/V vs V and finding the slope of this curve, coefficient b (*slope*) can be determined. In this case, Equation 2.3 can be simplified as (Christensen and Dick, 1985)

$$SRF(m/kg) = \frac{2A^2 P_T b}{\mu \omega} \quad (2.4)$$

As the filtration proceeds, the cake builds up and forms a thin layer on the filter surface. At that time, solids push against each other, and the liquid pressure decreases,

while the solid pressure increases. Thus, for compressible solids such as biosolids, SRF is a measure not of cake porosity but of the porosity (or resistance to filtration) of the thin layer (Novak, 2001a). SRF is directly dependent on the applied pressure, and it is not an independent parameter that depends directly on particle size. Figure 2.9 shows the drop of liquid pressure in expression phases after the formation of the thin layer and consequently the decreases of the rate of filtration, resulting in longer filtration times. Although SRF is a useful index of the filtration rate, it reflects not only particle size but also compressibility. When floc structures collapse during dewatering, they do not behave as discrete particles but as a whole structure. At this point, the smallest fraction in the biosolids is vital to control the filtration (Novak, 2001a).

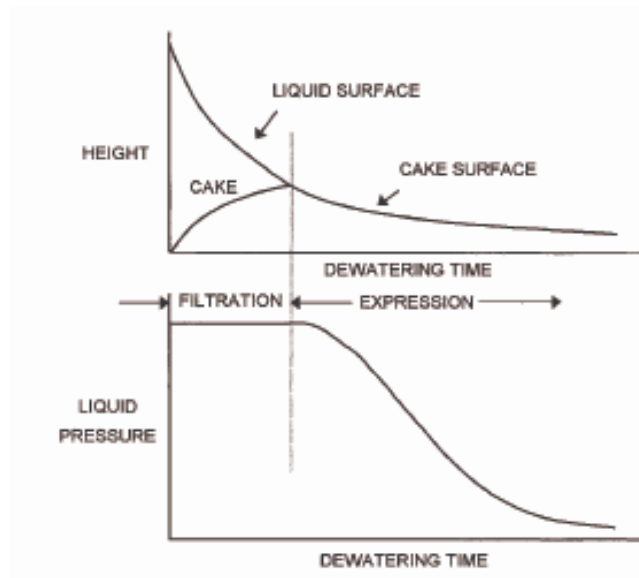


Figure 2.9 Phases of sludge dewatering (Novak *et al.*, 1999)

2.5 SHEAR SENSITIVITY OF BIOSOLIDS

It has long been known that shear and the response to shear are critical properties in mechanical dewatering (Novak and Lynch, 1990). The evolution of more successful dewatering devices—from vacuum filters to belt presses to centrifuges—has shown that the application of greater shear can lead to higher solids concentrations if the applied conditioning chemical can impart the needed resilience. Other types of mechanical equipment (particularly filter presses) apply greater normal forces and less shear but still rely on the material porosity being maintained in a stress field that includes a shear component. Furthermore, the sensitivity of biosolids to shear can also vary substantially due to the structure of biosolids (Higgins and Novak, 1997b).

2.5.1 Response of biosolids to shear

The role of shear in conditioning appears to be crucial. Novak and coworkers have quantified the effect of mixing in terms of the mean velocity gradient (G) and the time of mixing (t) (e.g., Novak *et al.*, 1988). The optimum polymer dose is shown to rise as the dimensionless product of Gt increases. This result is consistent with floc breakage and the reflocculation phenomenon, which consumes the polymer as the floc particles are strengthened (Dentel, 2001a). However, Christensen *et al.* (1995) showed that different mixing devices with the same G values yield different conditioning results. This result indicates the independence of floc breakage from the mixing period. Thus, G may be important for the growth of flocs, but the breakage depends on

the mixing intensity. Another response of shear to conditioning is the charge of particles. Increased shear leads to increased floc shear, which exposes original particle surfaces and depletes the polymer in the solution. Thus, researchers observed a positive charge with a polymer overdose, but with continuous mixing, the value became neutral and finally negative (AbuOrf and Dentel, 1997).

In dewatering itself, the response to shear is important for two reasons: First, the imposition of shear increases the response to compressive forces, enabling greater amounts of water to be forced from the solids matrix. Second, however, the shear should not lead to erosion or structural disruption that releases particulate material into the filtrate or centrate. These two factors are not usually characterized for the same material, and it is not known whether they are generally correlated. In fact, characterizations of floc or biosolids strength often do not distinguish between these two properties.

2.5.2 Assessment of shear

A standardized approach to assessing shear sensitivity is the standard stirring device suggested in CIWEM (1999). It uses a fixed mixing speed (1000 rpm) and sample volume (100 ml), a special paddle, and a 250-ml beaker. Various mixing times were defined to represent different dewatering units. Currently, it is used as a simple indicator of shear sensitivity.

Many researchers have measured particle or floc size in conditioned biosolids, using various methods such as light scattering (Spicer *et al.*, 1998) or image analysis (Wu *et al.*, 2003). With these methods, the size of particles or flocs is a relative index of floc strength in response to the amount of shear applied, i.e., the greater the applied shear, the smaller the particle size. But typically, this information is used neither to indicate the amount of free particulate material that will be released nor the physical structure of the biosolids during the dewatering processes.

Instead of dealing with particle size, Mikkelsen and Kelding (2002b) have suggested a floc strength test for activated sludge that defines the primary particle concentration in terms of turbidity. Their comprehensive work defined a shear sensitivity parameter (k_{ss}) that describes the equilibrium of primary particles under standardized conditions. Seka and Verstraete (2003) presented a corollary approach based on sludge volume measurements (SV_{30}), but concerns have been raised with the validity of their method (Dentel, 2005). Both methods assess particle release from the solids matrix, but this property has not been related to dewaterability in terms of final solids concentrations, and no such relationship was found in our own use of this approach. An important practical concern is that final cake solids to be obtained at full scale still cannot be predicted to date with simple bench-scale procedures. Consequently, it is impossible to optimize design or operation of the costly processes of conditioning, dewatering, transportation, and reuse or disposal except by full-scale trial and error.

2.6 RHEOLOGY OF BIOSOLIDS

Rheology describes flow and deformation of materials under stress. Biosolids exhibit *viscoelastic* behavior, which means that they accommodate both solid (elastic) and liquid (plastic) properties. The rheology of sludges is complicated because most sludges are *thixotropic*, which means they possess an internal structure that breaks down as a function of time and shear rate (Campbell and Crescuolo, 1982).

Many researchers, starting with Dick and Ewing (1967), used rheological measurements for characterization of activated sludge (Campbell and Crescuolo, 1982; Forster, 2002; Seyssiecq *et al.*, 2003). However, rheology is mainly connected with the pumping ability of biosolids. Since biosolids are dispersed systems having both solid and liquid phases, the shear rate is not linearly proportional to the shear stress, indicating the non-Newtonian behavior of biosolids. This behavior of biosolids has been characterized using various models, such as Bingham (Lotito *et al.*, 1997), Oswald (Moeller and Torres, 1997), and Herschel-Bulkey (Baudetz and Coussot, 2001) to understand the flow properties of sludge for the assessment of transport processes. Both the Bingham and Herschel-Bulkey models include a term called *yield stress*. The yield stress of a material stems from the solid fraction of a slurry or paste, and it can be defined as the amount of stress that must be imposed to initiate flow. There are different methods in the literature to determine the yield stress that is used as an indicator of flowability (e.g., Spinosa and Lotito, 2003). Recent research has also indicated that yield stress can be calculated from dynamic mechanical tests (oscillatory

tests), considering the elastic properties at low strains (Ayol *et al.*, 2006; Seyssiecq *et al.*, 2003).

2.6.1 Rheology and conditioning

Campbell and Crescuolo (1982) and Abu-Orf and Dentel (1999) have suggested using rheology for polymer dose assessment and control. Furthermore, Tixier *et al.* (2003) characterized the rheological properties of activated sludge for the control of bulking sludge. Although rheology is a powerful tool for monitoring the structural changes, it has not been used widely, probably due to the problems related to the non-uniform, flocculated structure and settleability of biosolids, which make the experiments harder to perform.

The application of conditioning prior to rheological tests alters the characterization of sludge, giving rise to a paste-like material (Chaari *et al.*, 2003). When flocculant polymer is added to the sludge, the common models used to characterize raw sludge fail (Ayol *et al.*, 2006). Although the rheological characterization of sludges may explain the gel-like behavior of sludge under shear, the classical rheometric methods, such as flow curves, are not sufficient for this purpose. In particular, more sophisticated dynamic rheology tests that can separate elastic and plastic portions in biosolids are needed to evaluate the gel properties of the sludge.

Considering biosolids as gels requires new definitions of physical properties such as “floc size.” Most researchers have related floc size to conditioning and dewatering; however, floc size is a relative index that is strongly associated with the amount of shear applied. More shear leads to more breakage when the physical nature is relatively weak. At this point, rheology is an important tool to determine the relationship between yield and shear without measuring floc size. It analyzes the entire sample instead of individual particles within the substance and from this point of view fits well into the gel model (Dentel, 2004).

2.6.2 Dynamic rheological tests

In traditional rheological tests, constant stress or strain is applied to a sample, and the response is monitored. It is also possible to apply step or ramp increases. Dynamic rheological tests (oscillatory tests) differ in imposing an oscillatory input to a material, such as an oscillatory strain, while observing the resulting behavior (Larson, 1999). When a stress or strain is applied, viscoelastic materials respond with a combination of fluid and solid behaviors. Thus, oscillatory testing allows these fluid and solid responses to be differentiated. For example, if stress is measured, it can be separated into an elastic stress and a viscous stress. These are described in terms of a storage modulus and a loss modulus, G' and G'' respectively, whose effects are combined in the complex modulus, G^* . When this modulus is constant, a material is in the linear viscoelastic (LVE) range, but when it starts decreasing, the yield stress is

reached (Larson, 1999). The oscillatory test provides G' and G'' , which are constant in the low-amplitude LVE range. If $G' > G''$, elastic behavior dominates over viscous behavior, which, for biosolids, provides evidence of a gel structure. If $G'' > G'$, viscous behavior predominates over elastic behavior (Larson, 1999; Mezger, 2006).

2.6.3 Rheology and Dewatering

Another important lack of information is defining the response to a combined shear and filtration process. Shearing conditions can be applied in the filtration process, which has been well characterized in the *rheometer*. This allows filtration to be characterized in a well-defined shear field. In many respects, this is what differentiates true dewaterability from filterability. There is no shear-related effect possible if dewatering is described solely by *colligative phenomena*. However, combined shear and normal stresses may be expected to alter the behavior of a flocculated particulate system.

The experimental means for this type of simulation have been reported with the performance of drilling muds using a filter cell fitted with a conical, rotating piston (Dewan and Chenevert, 2001). The conical shape allows a nearly uniform and adjustable shear field to be applied directly above the filter cake during its formation. The dynamic filtration test should be quite applicable to sludge cake formation and simulate the shear that exists in a belt filter press or centrifuge during compression. Filtrate generation during different extents of shear allows the determination of

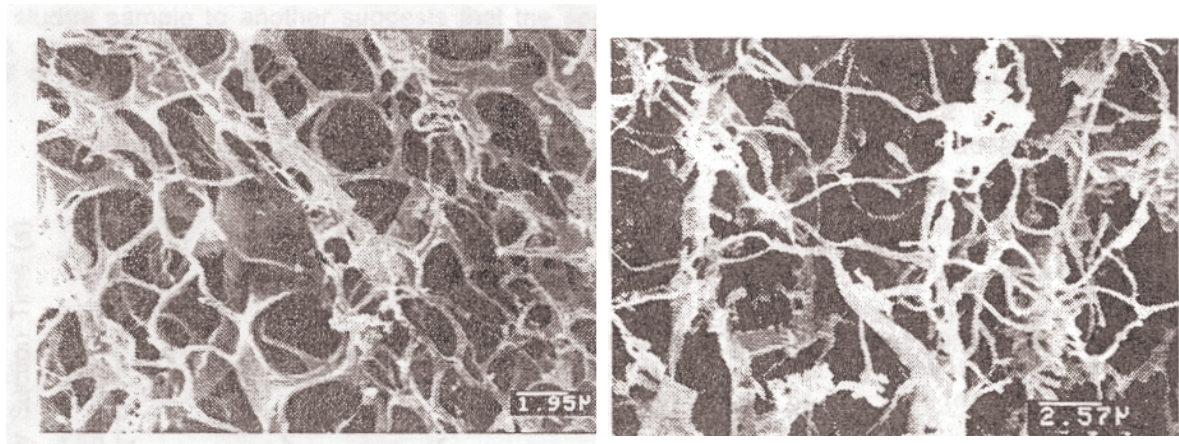
dewatering parameters such as specific resistance and filter diffusivity as a function of shear stress. Although normal and shear yield stresses have been reported for the same suspension, these measurements have been performed separately (Buscall *et al.*, 1987; Larson, 1999). Channell and Zukoski (1997) combined the shear and compressive rheology for aggregated alumina suspensions and used linear elastic models to define shear yield stress and compressive yield stress.

Accordingly, the shear that is crucial to sludge dewatering as it is actually practiced can be included in dewatering measurements. The relationship of shear to the normal yield stress is currently unknown, which has hindered application of the Landman model to dewatering processes beyond filter presses (where shear is comparatively nil). In addition, the separation of shear and normal stresses provides one more means by which *structural* and *colligative* components can be separated, since shear effects are not predicted to affect the latter. Thus, the combination of rheometry and dynamic filtration is useful in many aspects, such as differentiating the conditioning effects of metal ions from flocculant polymers, and, in general, offering a more accurate picture of dewatering processes.

2.7 BIOSOLIDS AS A GEL-LIKE MATERIAL

Consistent with an enhanced understanding of polymeric substances, biosolids were recently formulated with a description of a gel-like material (Legrand *et al.*, 1998; Poxon, 1996). The first initiative for describing biosolids as gels was the

illustration of the structural similarities between alginate (a natural biopolymer cell wall constituent of brown algae) and anaerobically digested sludge with scanning electron micrographs (Figure 2.10). Poxon (1996) claimed that the space filling structure forms a network that is gel-like in its ability to reduce the mobility, and hence the separability, of water from sludge. Larger particulate material is embedded in this matrix but is not in itself the cause of poor dewaterability. Some of the SEM images are given in Figure 2.10.



(a)

(b)

Figure 2.10 SEM images. (a) 1% solution of sodium alginate, a gelatinous polysaccharide derived from algae, (b) anaerobically digested sludge (Poxon, 1996)

The second approach to application of the gel-model to biosolid dewatering was proposed by Keiding and coworkers in the late 1990s. It may seem surprising that a “gel” model of a biosolid would successfully describe physical phenomena during filtration, freezing, or drying processes. Mikkelsen (1999) and Keiding *et al.* (2001)

have suggested that all three of these processes can be simulated by invoking the likely changes in colligative properties of the gel's solution phase as the water is removed. The osmotic effects of biosolids in dewatering were adapted to gel theory (Keiding and Rasmussen, 2003).

The simplest equation for osmotic pressure is

$$\pi = \Delta CRT \quad (2.5)$$

where π = the osmotic pressure of the solution, ΔC = concentration difference, R = gas constant, and T = the temperature.

In biosolids, the difference between the charge content of the solute phase and the solvent phase forms the osmotic pressure. Keiding and Rasmussen (2003) assumed that the counter-ions of charged polymers and surfaces determine the colligative properties. Thus, they implied that the colligative properties of biosolids can be defined by the charge density of the counter-ions.

$$\Delta C = C_{\text{counterions}} = \sigma \cdot \rho \cdot (1-\beta) / \beta \quad \text{where} \quad (2.6)$$

σ = polymeric charge per solid mass, i.e., /g solids

β = porosity of filter section

ρ = density of solids, gram/m³

They further hypothesized that the osmotic pressure can be related to the compression of the gel, since this increases the effect of locally high ion concentrations on the osmotic pressure of the gel near the filter surface. Therefore, the osmotic pressure resulting from counter-ions is calculated as follows:

$$\pi = \sigma \cdot \rho \frac{1-\beta}{\beta} RT \quad (2.7)$$

The combination of this approach with D'arcy's equation proposes the relationship between osmotic pressure and flow rate.

$$q = -\left(\frac{1}{\mu \cdot \alpha}\right) \frac{d}{dx} (P_{ext} - \pi) \quad (2.8)$$

where q = flow rate dV/dt α = filter hydraulic resistance μ = liquid phase viscosity, and as β decreases, π increases and q decreases. This approach has been used to successfully describe the resistance to filtration data (Keiding *et al.*, 2001). The Cozeny-Carman (C-C) equation proved meaningful in describing features of dewatering. Hence, the C-C equation has been used in order to describe resistance to flow as a function of porosity and specific surface area (S_0). Thus Equation 2.8 takes the following form (Keiding and Rasmussen, 2003):

$$q = -\left(\frac{\rho \cdot \beta^3}{\mu \cdot S_0^2 \cdot (1-\beta)}\right) \frac{d}{dx} (P_{ext} - \pi) \quad (2.9)$$

Another idea to support the gel-like behavior of biosolids was considered by Legrand *et al.* (1998) through their exploration of the swelling properties of gel networks and biosolids. As explained in the previous sections, swelling potential is a widely accepted parameter used to characterize gels. The swelling theory applied for synthetic gels was transferred into the swollen material, which in this case was biosolids. The charge density of colloids was related to deswelling and flocculation by the addition of conditioners selected from varying molecular weight ranges. Synthetic

anionic gels and biosolids were suggested to behave in similar ways under dewatering conditions. A remarkable study by Keiding et al. (2001) related colligative properties with biosolids. Their results showed that the swelling behavior of EPS at different pH values indicates that EPS behaves in a way similar to that of gels in biosolids.

All the above approaches support the circumstances where the traditional particulate model could not provide clarification. The behavior of complex and unstable biosolids under conditioning and dewatering conditions is elucidated by applying the basics of gel properties.

2.7.1. Advantages of a gel model

The major drawback of the traditional approach is that it has failed to describe biosolid conditioning and dewatering in some aspects. As a new approach, the gel description of biosolid conditioning runs counter to the prevailing understanding of these processes; it is also more consistent with a variety of observations.

Even if a charge attraction exists and the polymer chain length is appropriate in the conditioning process, the traditional model requires little specificity in polymer chemistry or structure for good conditioning. Dentel et al. (2000) confirmed improvements in floc strength with the use of “structured polymers” that have a high extent of crosslinking. Moreover, in laboratory studies, traditional jar test results may be explained by the specificity of polymer/biosolid (gel) interactions. These results are

not consistent with the particulate model; however, they may be explained with the collapse of a biosolid gel onto the supporting structure of the flocculant polymer.

It is widely known that charge neutralization plays an important role in conditioning but some researchers have shown that floc breakage leads in devolution of electrokinetic properties to those of the original material in the biosolids (Dentel and Abuorfi, 1995; Dentel and Wehnes, 1988). These results can be supported with the breakage of a gel structure rather than of “rigid particles” or of bridges of flocculating polymer.

Recent biosolid characterizations using dilatometric and thermogravimetric methods (Kopp and Dichtl, 2000; Vesilind and Hsu, 1997) are difficult to reconcile with a “rigid sphere” model. Kopp and Dichtl (2000) have suggested that this is primarily *interstitial* water, which exceeds intracellular water by an order of magnitude. This is true prior to conditioning, suggesting the presence of a gel structure. Removal of interstitial water was observed by these authors to correspond with shrinkage, which is consistent with the deswelling results of Legrand *et al.* (1998).

The well-known gel-like properties of concentrated aluminum hydroxide suspensions and the ability of polyacrylamide-based polymers to condition water treatment residuals (which contain a significant fraction of aluminum or ferric hydroxide) offer an additional analogy to the hypothesized gel collapse mechanism.

Conditioners that are oppositely charged to material in the biosolid may form complexes and precipitates that reduce the osmotic pressure by freeing counter-ions.

Thus, the premise of a new gel-collapse mechanism clearly warrants further investigation. It would allow important conditioning and dewatering phenomena to be understood and therefore engineered where the present models cannot.

2.7.2 Shortcomings of a gel model

The new gel model based on colligative properties, although appealing in many respects, is not likely to describe all aspects of filtration dewatering. The deficiencies can be shown in both physical and chemical interactions in the conditioning and dewatering process.

2.7.2.1 Chemical inadequacies

The main problem is associated with the surface charge of biosolids. Equation 2.7 suggests that if the biosolid has no electrical charge, the predicted resistance to filtration is zero. Although the resistance may be lower near the isoelectric point, it is not negligible. Physical resistance to flow through the sludge cake must be taken into account.

The colligative model invoked by Keiding and Rasmussen (2003) assumes a uniform distribution of counter-ions at all distances from the ionized gel sites, which may be appropriate in an idealized gel but is unlikely to apply to complex fluids such

as biosolids. They claimed that as the solids concentration increases during filtration, the concentration of counter-ions also increases, increasing the osmotic pressure and resistance to flow (Equation 2.8). There is no detailed knowledge about the hypothesis of Keiding and Rasmussen. Therefore, conductimetry combined with classical filterability tests such as specific resistance to filtration (SRF) and capillary suction time (CST) should be beneficial in determining the extent to which this osmotic pressure is associated with filterability.

2.7.2.2 Physical inadequacies

A colligative model does not account for physical factors such as lateral shear that have any effect on dewatering efficacy. However, intensive shear is commonly imposed in filtration processes to enhance dewatering. Thus, the shear field during dewatering might be the crucial stage. Combined shear and normal stresses may be expected to alter the behavior of the flocculated particulate system. This suggests the importance of a physical structure during dewatering.

A new approach would relate applied pressure—perhaps in a shear field—with mixing to flow normal to the filter plane. The differing descriptions hinder the development of a unified approach to the two processes, although floc breakage and reformation and even consumption of conditioning polymer may continue well into the dewatering process (Dentel, 2001a). It may therefore be advantageous to identify a physical description that can describe both the conditioning and dewatering processes.

Ostensibly, this is done with the Camp velocity gradient. However, this is a crude parameter, since it indicates a mean value regardless of the spatial distribution of shear. Thus, Christensen *et al.* (1995) showed that different mixing devices give the same “G” values but yield quite different biosolid conditioning results. In any case, determination of “G” requires knowledge of the system viscosity, which itself is shear and locality dependent in typical stirred systems where conditioning takes place.

Additional evidence indicating the significance of physical structure is given in the work done by Ormeci and Vesilind (2000). They have found it necessary to include fibrous material (cellulose) in a “synthetic sludge” in order to satisfactorily duplicate the structural and dewatering behavior of biosolids.

Therefore, colligative properties may be necessary but not sufficient for a full understanding of conditioning and dewatering mechanisms.

2.7.3 Combination of a particulate and a gel model

The advantages of a gel model may be applied to the traditional particulate model in order to enhance our understanding of sludge structure in conditioning and dewatering processes. Buscall (1990) addressed the possibility of “chemical” vs. “continuum” (engineering) descriptions of hindered settling, which has strong analogies to filtration. In a parallel manner, Landman *et al.* (1995) have incorporated solid phase and fluid phase resistances in D’arcy filtration equations, although colligative properties were not considered. The Landman approach utilizes a

compressive yield stress $P_y(\phi)$ for the solids behavior. Equation 2.9 gives the filtration flow formulated as a function of solids volume fraction ϕ .

$$q = -\left(\frac{1}{\mu.\alpha}\right) \cdot \frac{dP_y}{d\phi}(\phi(x,t)) \cdot \frac{d\phi}{dx} \quad (2.10)$$

It seems clear that these expressions for q (Equations 2.8 and 2.10) can be combined when neither is predominant. In addition, a relation of $P_y(\phi)$ to shear rate, by rheological and filtration tests, might allow the Landman model to be improved.

Chapter 3

**CONCEPTION OF SYNTHETIC SLUDGE TO UNDERSTAND
THE GEL-LIKE BEHAVIOR OF BIOSOLIDS**

Abstract

Considering biosolids as gels requires a broad physical-chemical characterization and assessment in combination with a controlled gel system, in this case, a synthetic surrogate. An appropriate synthetic surrogate is prepared using alginate, cellulose, yeast, and potassium and calcium ions to simulate the physical-chemical characteristics of biosolids under conditioning and dewatering operations. Comparison of sampled biosolids with a prepared gel, or synthetic slurry, indicates the similarities in their physical-chemical characteristics and especially their behavior in conditioning. Following the development of a stable, standard gel system, rheological analyses and swelling tests are used to provide evidence for the gel-like behavior of biosolids. Frequency sweep tests show the dominating effect of the elastic part over the viscous part for both synthetic slurry and biosolids. Conditioning increases the rigidity of samples, and the response of samples to conditioning is revealed to be similar in rheological analyses. Finally, shear sensitivity measurements with variation of ingredients in a synthetic sludge is related to the structural properties and particulate

amount of biosolids. The shear sensitivity is primarily controlled by the gel fraction, with alginate and the associated cations increasing the gel-like behavior. However, the effect of particulate fraction on shear sensitivity should also be taken into account. Shear sensitivity is thus a complex parameter including two types of response: the resistance to dispersed mass concentration into centrate and the maintenance of desired strength while the solids concentration increases in the shear field.

3.1 INTRODUCTION

A significant amount of biosolid production requires efficient and economic management. Crucial to this effort is the optimization of conditioning and dewatering, so that high solids contents can be obtained in the final product. Although conditioning and dewatering are strongly interrelated, the former is primarily a chemical process and the latter a physical one. Thus, to better understand the overall outcome, the physical and chemical characteristics of biosolids must both be defined, and they must be linked. However, conducting physical-chemical tests with biosolids is difficult due to their constantly changing properties.

A synthetic surrogate that behaves as a hydrogel was prepared by combining alginate with Ca^{2+} , K^{+} and adding cellulose and yeast. The synthetic sludge was similar to those suggested by Sanin and Vesilind (1996) and Ormeci and Vesilind (2000) but improved by Muller (2003). Their results showed the resemblance of sampled biosolids to a synthetic surrogate. This revised synthetic sludge formulation

was used for purposes of comparison and reproducibility (Dursun *et al.*, 2004).

Alginate is a structural biopolymer of brown algae found in extracellular polymeric substances (EPS). It is a binary copolymer of linked β -D mannuronic acid and α -L guluronic acid that has a strong affinity for Ca^{2+} (Draget *et al.*, 1996). Alginate was used to simulate the polymeric substances in biosolids, and Ca^{2+} , K^{+} were used as a bridging mechanism to form gels. Cellulose and yeast were also added into the slurry to simulate the filamentous organisms and bacteria, respectively. Alginate and Ca^{2+} and K^{+} aims to compose a gel (polymeric) fraction, whereas cellulose and yeast aims to form a particulate (structural) fraction in synthetic slurry. The components of the slurry and the amounts were changed deliberately to observe the effect of each component on the physical-chemical characteristics. This enables creation of a synthetic slurry with desired properties for various purposes (such as a slurry with high solid content, low filterability).

The behaviors of the synthetic surrogate in conditioning were also compared with sampled biosolids to validate the use of this slurry for further investigations. The conventional measurements were combined with specific measurements to characterize gels. Hydrogels that are crosslinked polymers of hydrophilic monomers can absorb/desorb large amounts of water and hydrophilic solutes; hence, they swell/deswell in aqueous solutions (Huthner *et al.*, 2002). Swelling/deswelling behavior, which is used extensively in characterization of gels, is related to the mechanisms of conditioning and dewatering.

Since a biosolid is neither a solid nor a liquid, it exhibits viscoelastic behavior such as gels exhibit. Rheology describes flow and deformation under stress and analyzes the entire sample instead of individual particles. The structure of biosolids changes as a function of time and shear rate; thus, the rheology of sludges is complicated in itself. Furthermore, application of conditioning polymers prior to rheological tests alters the characterization of sludge, giving rise to a paste-like material (Chaari *et al.*, 2003). The rheological characterization of biosolids explains the gel-like behavior under shear; however, the classical rheometric methods are not sufficient for this purpose (Ayol *et al.*, 2006). In this work, the gel-like behavior of sludge was assessed by performing oscillatory tests. The rheological behavior of this synthetic slurry was compared with the sampled sludge to show that the sludge behaves in the same way as gels under conditioning. In particular, the yield stress and elastic properties of the sludge were considered. The relationship among surface properties, filterability, and swelling was investigated with the parameters derived from rheological analysis.

The conceptual gel model has been found essential to explain some aspects of conditioning and dewatering (Keiding and Rasmussen, 2003; Legrand *et al.*, 1998), but it has not been related to shear sensitivity. As dewatering technologies are trending towards increased shear application, it becomes crucial to understand how the biosolids will respond. It was recently shown that alteration of sludge structure via enzyme addition may result in differences in shear sensitivity (Dentel and Dursun,

2006). Mikkelsen *et al.* (2002b) also evaluated the shear sensitivity of various types of biosolids and pointed out the relationship between shear sensitivity and EPS fraction. In fact, the way that any biosolid will respond to shear might be determined by either its gel or particulate properties—or perhaps both.

3.1.1 Theory

3.1.1.1 Dynamic Rheology

The yield stress of a material stems from the solid fraction of a slurry or paste; it can be defined as the amount of stress that must be imposed to initiate flow. There are different methods in the literature to determine the yield stress that is used as an indicator of flowability. Dynamic mechanical tests (oscillatory tests) that consider the elastic properties at low strains are also used for this purpose (Mezger, 2006). This method, although somewhat approximate, does not require specification of any model, which is an important advantage of dynamic mechanical tests (Larson, 1999). Dynamic measurements apply small-amplitude oscillatory shearing. This kind of deformation can be achieved in a cone-and-plate geometry by rotating the cone with an angular velocity (ω) that oscillates sinusoidally. Then the shear rate is also a sinusoidal function of time. These measures apply a sinusoidal strain [$\gamma(t) = \gamma_A \cdot \sin \omega t$], with the strain amplitude γ_A (%) and the angular frequency ω (1/s), while observing the resulting behavior [stress $\tau(t)$]. For viscoelastic materials such as sludge, the $\tau(t)$ curve makes a phase shift(δ) with $\gamma(t)$ curve. In this case, strain is defined as

$$\gamma(t)=\gamma_A \cdot \sin (\omega t + \delta) \quad (3.1)$$

The response of the material is translated in terms of the phase angle difference between complex deformation and stress and complex modulus ($G^* = \tau^* / \gamma^*$) from which elastic (G') and viscous (G'') portions can be calculated. Performing strain (amplitude) sweep tests makes it possible to obtain the critical amplitude of deformation above which the linear domain ends. Above this deformation, the complex modulus is no longer constant and begins to decrease. The strain value before critical strain (γ_{cr}) gives the linear viscoelastic range (LVE) where stress is constant. The evaluation of stress as a function of strain is represented in Figure 3.1. The product between the complex modulus on the plateau and the critical strain (γ_{cr}) gives the yield stress (Seyssiecq *et al.*, 2003). Although strain sweep tests allow determination of the yield stress and LVE, the elastic properties of the material are also valuable in determining the gel-like properties of sludge. At this point, frequency sweep tests that apply various frequencies at a small strain value (lower than their critical strain) are used to determine the storage and loss modulus, which indicate the elastic and viscous properties.

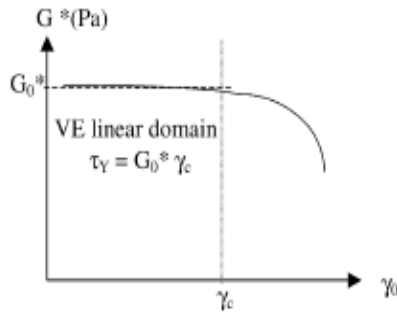


Figure 3.1 Calculation of yield stress from amplitude sweep tests (adopted from Seyssiecq et al., 2003)

3.1.1.2 Shear Sensitivity

Many researchers have measured particle or floc size in conditioned biosolids, using various methods such as light scattering (Spicer *et al.*, 1998) and image analysis (Wu *et al.*, 2003). With these methods, the size of particles or flocs is a relative index of floc strength in response to the amount of shear applied—i.e., the greater the applied shear, the smaller the particle size. But typically, this information is used neither to indicate the amount of free particulate material that will be released nor the physical structure of the biosolids during dewatering processes. Instead of dealing with particle size, Mikkelsen and Keiding (2002) have suggested a standardized shear sensitivity test for activated sludge that defines the primary particle concentration in terms of turbidity. This test is based on the adhesion-erosion (A-E) model developed by Mikkelsen and Keiding (1999) to describe the effects of solids content and

turbulent shear on sludge deflocculation. Dispersed mass concentration for varying total solids content for a given shear rate is defined by the equation

$$m_T = m_{d,\infty} + \frac{m_{a,\max} \cdot K_m \cdot m_{d,\infty}}{1 + K_m \cdot m_{d,\infty}} \quad (3.2)$$

where m_T is the total solids mass concentration, $m_{d,\infty}$ is the equilibrium dispersed mass concentration, $m_{a,\max}$ is the maximum mass concentration, and K_m is the equilibrium constant for the adhesion of primary particles to sludge flocs. From this model, they developed a “shear sensitivity” parameter k_{ss} for a fixed turbulent shear rate.

$$k_{ss} = \frac{m_{d,\infty}}{m_T} \approx \frac{1}{1 + K_m \cdot m_{a,\max}} \quad (3.3)$$

This parameter was successfully related to filterability, rheology and surface chemistry (Mikkelsen, 2001).

Mikkelsen and Keiding (1999) adopted the diffusion model by Crank (1975) for activated sludge desorption. A simplified diffusion model based on the first-order kinetics was used by Wahlberg and Mikkelsen *et al.* (1996). At a specified shear rate, dispersed mass concentration versus time data was fitted to Equation 3.4

$$m_{d,t} = m_{d,\infty} + (m_{d,0} - m_{d,\infty}) \cdot \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{N^2} e^{-N^2 D t} \quad (3.4)$$

where $m_{d,t}$ is the dispersed mass concentration at time t , and $m_{d,0}$ and $m_{d,\infty}$ are the dispersed mass concentrations initially and at equilibrium, respectively. N is an integer and D is an effective diffusion constant. The effect of shear can be investigated by

fitting Equation 3.4 to data, estimating $m_{d,\infty}$ and then calculating k_{ss} as given in Equation 3.3.

3.2 MATERIALS AND METHODS

3.2.1 Biosolid samples

Biosolid samples were collected from the Wilmington Wastewater Treatment Facility, which is a conventional activated sludge plant treating domestic and industrial wastewaters (Wilmington, DE, USA). Samples were collected from activated sludge tank and mesophilic anaerobic digesters at a typical retention time of 15-20 days.

3.2.2 Preparation of synthetic slurry

A standard synthetic surrogate was prepared based on a method developed by Muller (2002), using alginate, microcrystalline cellulose, fresh yeast, calcium and potassium salts. Alginate stock solution at a 5 g/L concentration as alginic acid was first allowed to completely dissolve. Then, 16.6 g cellulose and 7.3 g yeast were added into 540 mL 0.5% alginic acid solution, followed by the addition of 169 mL distilled water. The suspension was then gently stirred by magnetic stirrer for two hours to allow incorporation of alginate onto the particle surfaces. Next, 2 M 91 mL KCl solution was stirred into the sludge with a paddle stirrer at 300 rpm for 2 minutes, followed by 0.05 M 200 mL CaCl_2 for 3 minutes stirring at 500 rpm. To reduce the salt concentration, the surrogate was washed with distilled water at a 3:1 ratio. After a

minimum of 2 hours settling, the suspension returned to its original volume, so that the watery, salt-containing phase could be removed. Synthetic slurry samples were kept at 4°C until they were used, and all experiments were completed within 2 days. The solid content of final slurry was around 20 g/L. The amounts of the components were altered depending on the objective of the work.

3.2.3 Conditioning

A high molecular weight cationic organic polymer (Zetag 7557, Ciba Specialty Chemicals) was used. This is an acrylamide-based copolymer (quaternized 40/60 mole ratio AETAC/AM DMAEAQ: MeCl). A 0.5% stock polymer solution was prepared according to (Dentel *et al.*, 1993) for additions. Standard 1-liter beakers were used with 500-ml samples to perform the jar tests. Samples were subjected to rapid mixing at 300rpm for 2 minutes followed by slow mixing at 30rpm for 5 minutes.

3.2.4 Analysis of physical-chemical properties

The following provides brief descriptions of how the various physical-chemical properties were measured:

Total Solid Content (TS): TS content of sludge and synthetic gel were analyzed according to APHA American Public Health Association (1995).

pH: pH was performed according to Standard Methods (APHA American Public Health Association *et al.*, 1995).

Turbidity: The turbidity was determined after 30 minutes of settling of samples by using HIAC 2100P type of turbidity meter. Results were given in Nephelometric Turbidity Units (NTU).

Streaming Current: A Milton Roy Model SC 4200 streaming current detector was used for electrokinetic measurements.

Zeta Potential (ζ): Conditioned samples were centrifuged for 15 minutes at 3000 rpm, and the supernatant was used for the dilution. The zeta potential of samples was measured at least three times with ZetaSizer NanoZS (Malvern Instruments).

Surface Charge: Measurement of the surface charge of the synthetic slurry and the biosolids was accomplished using the colloid titration method described by Morgan *et al.* (1990).

Filterability: Filterability of samples was evaluated by measuring the capillary suction time (CST-Venture Innovations) minimum three times (APHA American Public Health Association, 1995). This test measures the required time to achieve filterability. Longer times show the samples with high resistance to filtration, and shorter times (low CST results) are favorable to obtain better filterability.

3.2.5 Swelling Ratio

The degree of swelling is the ratio of the mass of the swollen gel to that of the dry gel. The weight ratio of the filtered sludge over the dry matter was obtained after drying overnight at 105°C (Legrand *et al.*, 1998). Swelling experiments were

performed three times on both synthetic gel and sampled sludge, and average values were given. When considering weights, the swelling ratio was calculated by

$$q_w = \frac{w_s}{w_d} \quad (3.5)$$

where w_s = weight of swollen particles and w_d = weight of dry particles.

3.2.6 Rheological Analyses

Rheological measurements were carried out with an Anton Paar Physica MCR 500 dynamic mechanical rheometer coupled with US200 software. This software allows subsequent data analysis for the rheograms obtained from experiments. A CP 50-2 cone and plate sensor was used, with 49.94 mm diameter, 2° cone angle, and 0.05 mm gap. The temperature was maintained constant at 25°C by Peltier control.

Determination of yield stress was done by performing dynamic measurements; strain (amplitude) sweep tests were carried out at 1 Hz to obtain the critical amplitude of deformation above which the linear domain ends. After determining the yield stress and LVE with amplitude sweep tests, samples were also subjected to 0.1% strain value at various frequencies, and the corresponding storage and loss moduli were measured with frequency sweep tests.

3.2.7 Shear sensitivity

The samples were sheared in a baffled reaction chamber at 800 G for various time periods as described by Mikkelsen (2001). The degree of sludge dispersion was

characterized by the shear sensitivity parameter k_{SS} as defined by Mikkelsen (2001). A 1L sample was exposed to turbulent shear ($G=800\text{ s}^{-1}$) in a 105-mm-diameter baffled reactor. The use of a 5-mm (width) by 12-mm (height) single-bladed paddle corresponds to a stirring speed of 900 rpm. At suitable time intervals, 5-mL sludge samples were taken out for turbidity measurement. Supernatant turbidity was measured after 2 min centrifugation at 3000 rpm using an HIAC 2100P model turbidity meter; results were given in NTU. The dispersed mass concentration was estimated using the turbidity to solids mass conversion factor of $1.2\text{ mg SS}^{-1}\text{ FTU}^{-1}$ as reported by Wahlberg *et al.* (1994). The colloid content at equilibrium for a given shear test was estimated by fitting the data to Equation 3.4. Consequently, the shear sensitivity was estimated by Equation 3.3.

3.3 RESULTS AND DISCUSSION

3.3.1 Characterization of Synthetic Surrogate

The first series of experiments investigated the physical-chemical properties of different synthetic slurries prepared from the same components but at different doses. In these preliminary experiments, five main components of surrogate alginate, cellulose, yeast, and calcium and potassium ions were varied in order to observe the response of the slurry.

3.3.1.1 Effect of alginate concentration on surrogate characteristics

Alginate, which is the major component of the gel fraction, was used to simulate the polymeric substances in the actual biosolid structure. A 1-L surrogate sample was prepared at six different doses of alginate (0, 3%, 5%, 10%, 15%, 20% w/w). Alginate was shown to be an important component to form the homogeneous surrogate in which cellulose and yeast were embedded. In the absence of alginate, the particles can easily be separated, thus the CST value of this slurry was really low. Figure 3.2 summarizes the CST values for the entire experimental set. The first column set stands for the variation of alginate in increasing order: 0%, 3%, 5%, 10%, 15% and 20%, respectively. With increasing doses of alginate, the network structure was built, leading to higher CST results. Supernatant turbidity results that were measured after 2 min centrifugation at 3000 rpm indicated the specificity of the reactions between alginate and other components. For 3% and 5% alginate, the turbidity was noticeably higher (Figure 3.3). High concentrations of alginate affected the total solids content to some extent (Figure 3.4). The pH of the slurry varied between 4 and 5, and no significant difference was observed between the samples (Figure 3.5) with varied alginate content. More than 5% of alginate was required to lower the turbidity around 5 NTU. The charge content of the slurry was measured in terms of zeta potential and without alginate addition; the zeta potential was close to zero. Alginate decreased this value; however, there was no increasing/decreasing trend

observed with the variation of alginate amount. This again pointed out the specific reactions among alginate, ions, and others in the slurry.

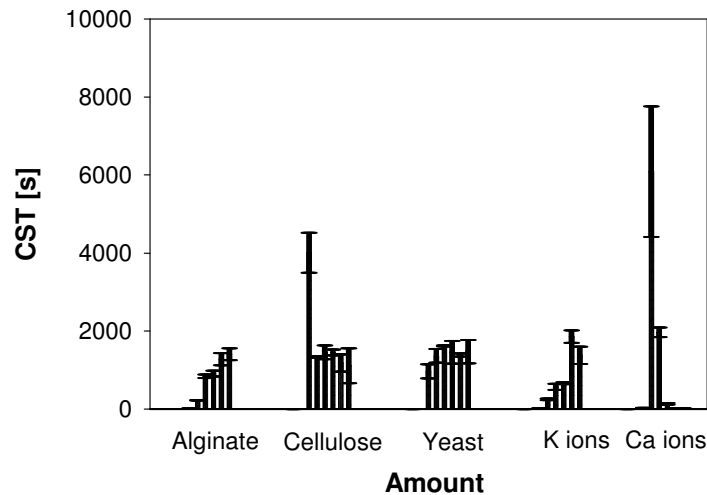


Figure 3.2 Change of filterability in terms of CST with increasing doses of the components from left to right

3.3.1.2 Effect of cellulose concentration on surrogate characteristics

Microcrystalline cellulose was selected to be used in the experiments because its size and shape are similar to those of filamentous organisms in the biosolids structure. Cellulose was added to the synthetic samples to give final concentrations of 0, 30%, 40%, 50%, 60%, 70% (w/w). The addition of cellulose helped the formation of flocs; as a result, the difference in filterability between 0% and 30% of cellulose was drastic (Figure 3.2). These results also supported the importance of cellulose in floc formation and the integrity of flocs that was suggested by Ormeci and Vesilind

(2000). As illustrated in Figure 3.3, the turbidity of the supernatant was also high with lower doses of cellulose; it started to improve with cellulose addition and reached the lowest value at 40%. After that point, the turbidity began to elevate, since a sufficient amount of cellulose was reached, and the residual amount did not take a part in floc formation, but rather stayed in the supernatant and increased the turbidity. The major component to increase the solid content of the slurry was found to be cellulose. The solid content was increased linearly from 0.6% to 3.7 % as the amount of cellulose added increased (Figure 3.4). The pH of the surrogate in the absence of cellulose was markedly different from the others (Figure 3.5), probably because the alginate and cations could not form a floc and were free to stay in the solution without restraint. The zeta potential of the samples was around the same value for the last four doses, but higher potentials were measured for the first two concentrations (0% and 30%). This was again linked to the formation of flocs. Varying the cellulose amount clearly affects the particulate fraction in the slurry.

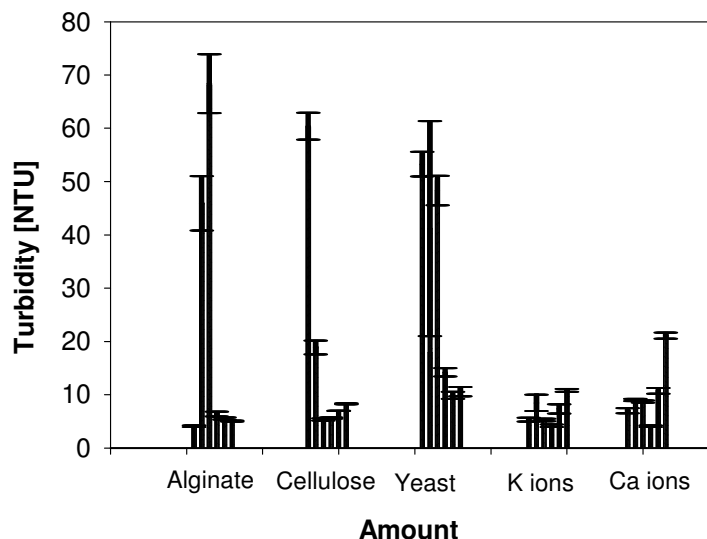


Figure 3.3 Turbidity results with increasing amounts of alginate, cellulose, yeast, K^+ and Ca^{2+} (from left to right)

3.3.1.3 Effect of yeast concentration on surrogate characteristics

Unlike other synthetic sludge formulations suggested by Vesilind and coworkers, who used polystyrene latex particles, baker's yeast was incorporated into this formula to simulate the bacteria. The average particle size of the yeast was reported as 2 μm (Siddiqi *et al.*, 1996), which was close to the actual value for individual bacteria in the biosolids structure (Li and Ganczarczyk, 1990). The aim of using the yeast in the prepared slurry was to change the particulate fraction. Yeast was introduced into the slurry in final doses of 0, 10%, 15%, 20%, 25% and 30% (w/w). It was observed that the yeast addition lowered the filterability up to a certain point

where alginate was attached onto the surface of yeast, and then no considerable difference was observed in CST for the last 3 doses applied (20%, 25%, 30%)—possibly because the alginate amount was not sufficient in the slurry (Figure 3.2). The turbidity results given in Figure 3.3 point out the importance of the yeast addition and its role in building the floc structure. The pH results showed the same pattern with cellulose results for the same reason (Figure 3.5). The zeta potential of the slurry oscillated from -10 to -14 mV, with the lowest value corresponding to the absence of yeast. It does not have a major contribution to the charge of the slurry.

3.3.1.4 Effect of monovalent cations on surrogate characteristics

The addition of cations into the slurry was necessary to form a gel-like structure in the synthetic surrogate. Murthy and Novak (1998) documented the effects of potassium ions on sludge settling, dewatering and effluent characteristics. Their later work (Murthy *et al.*, 1998) revealed the complex interactions between cations and biosolids and the influence of monovalent to divalent cations in the settleability of biosolids. Thus, monovalent ions were added in the form of KCl at various concentrations, corresponding to monovalent to divalent ratios of 0, 5, 10, 15, 20, 25. In the absence of K ions, long cellulose fibers were dominant in the slurry, which was not homogenous. The phase separation was observed after a short time. The filterability results given in Figure 3.2 show the low CST value (20 s) at 0 K⁺ concentration. The filterability of the slurry decreased (increasing CST results) with

increasing K^+ dose indicating the gelation of the solution. Cations enhanced the attachment of alginates onto the surfaces of cellulose and yeast by reducing the electrical double layer. Supernatant turbidity did not change much, ranging between 5 and 10 NTU (Figure 3.3). And the solid content increased only from 1.8 to 2.2% for the last two doses (Figure 3.4).

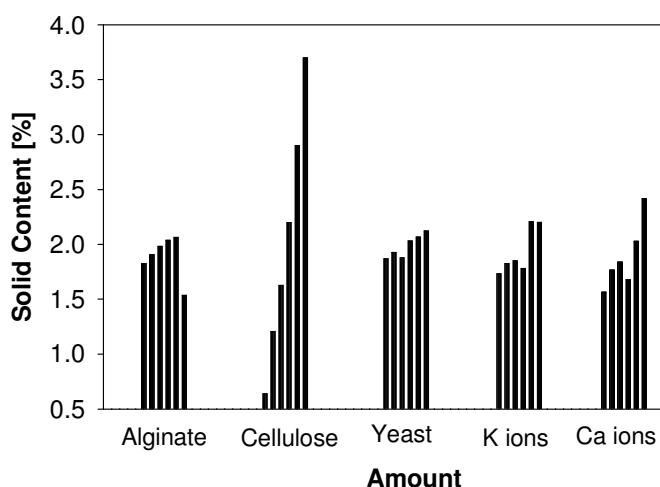


Figure 3.4 Contribution of each component of synthetic slurry to total solid content
(increasing amount from left to right)

The pH of the slurry without K^+ ions was more than 8, whereas the addition of K^+ ions lowered it to around 5 (Figure 3.5). As Figure 3.6 exemplifies, the zeta potential values of the slurry changed dramatically with increasing monovalent ions. This indicates the importance of the gel fraction in the charge content of the slurry.

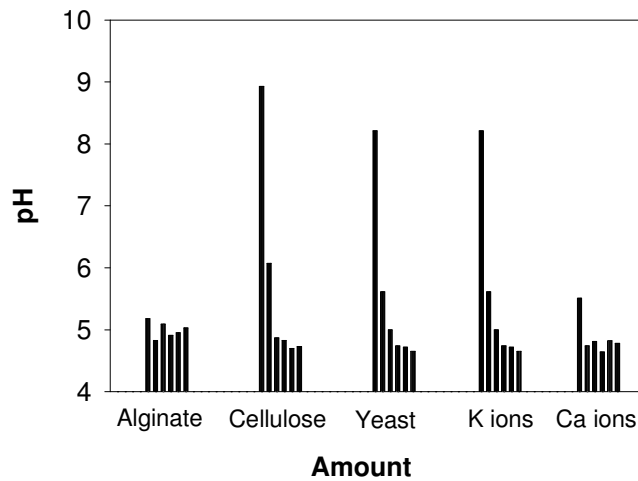


Figure 3.5 The change of pH as a function of the amount of each component

3.3.1.5 Effect of divalent cations on surrogate characteristics

The effect of cations on settling and dewatering of biosolids has been explored extensively by Higgins and Novak (1997a; 1997b). They have showed the importance of cations in building the floc structure by forming the bridges between particles and polymers. Sanin and Vesilind (1996) as well as Ormeci and Vesilind (2000) elucidated the role of Ca^{2+} in synthetic slurry. Hence, Ca^{2+} was added into the slurry in the form of CaCl_2 at divalent to monovalent ratios of 0, 0.03, 0.05, 0.1, and 0.2. The CST results given in Figure 3.2 indicate the effects of Ca^{2+} addition dramatically. The synthetic surrogate was a cloudy, milky homogenous solution without Ca^{2+} . There was no binding between cellulose and yeast and alginate. These findings showed that there is a need for both monovalent and divalent cations to form a gel-like network structure. With a small Ca^{2+} addition (0.03 Ca/K ratio = 33 $\text{K}^+/\text{Ca}^{2+}$ ratio), the CST

increased up to 6000 seconds. Increasing the Ca^{2+} amount changed the CST significantly by lowering the values back to 20 s. Although total solid content (Figure 3.4) and turbidity did not alter much, the pH (Figure 3.5) and zeta potential (Figure 3.6) values differed with the increase of $\text{Ca}^{2+}/\text{K}^+$. These changes were also found similar to the effects of $\text{K}^+/\text{Ca}^{2+}$ variation.

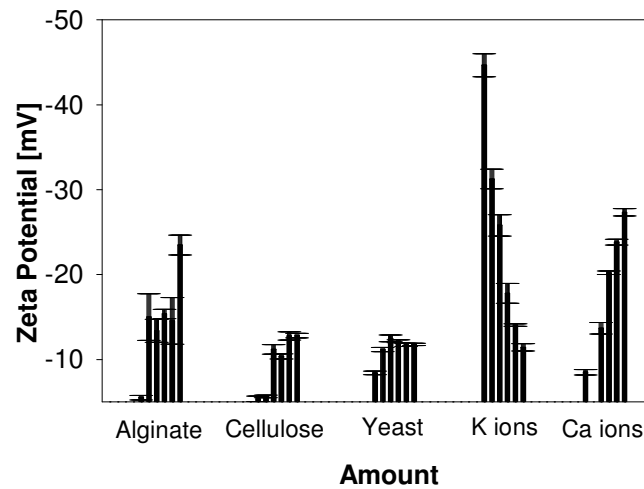


Figure 3.6 Zeta potential results with varying doses of the components of synthetic surrogate

These results showed that the gel fraction governed the filterability and charge content of synthetic slurry where the solid content and supernatant turbidity were mainly affected by the particulate fraction. Figure 3.7 emphasizes the filterability results using the inverse of the CST value on the y-axis. The reciprocal of CST [1/s] can be considered an indicator of filtration rate. In that case, higher points correspond to better filtration, whereas low values show lower filtration rates. Figure 3.6 clearly

reveals the significance of gel fraction in filterability. These experiments not only provided insight into the effect of each component and fraction on characteristics of the slurry but also provided a chance to prepare a synthetic slurry with the desired properties.

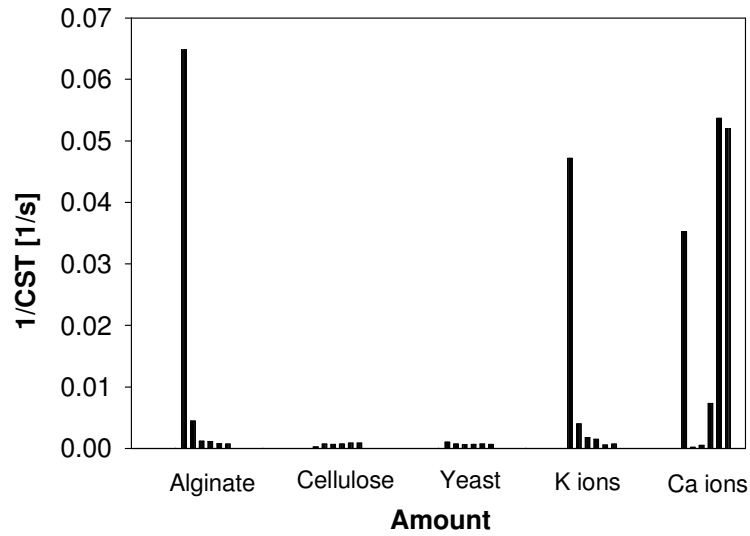


Figure 3.7 Effect of increasing amounts of each component (left to right) on filtration rate

3.3.2 Comparison of Conditioning Responses in Biosolids and Synthetic Surrogate

In this set of experiments, a synthetic surrogate with lower solid content was prepared. Details about the exact method can be found elsewhere (Dursun *et al.*, 2004). The general physical-chemical properties of this surrogate were compared to

those of the waste activated sludge (WAS). The response of these samples to conditioning was also investigated.

3.3.2.1 Analysis of raw samples

The characteristics of WAS and the synthetic surrogate were examined prior to conditioning experiments. The main physical and chemical properties of WAS and the synthetic surrogate are listed in Table 3.1.

Table 3.1 Characterization of Samples

	WAS	Synthetic Sludge
pH	6.26	5.14
Total Solids (TS), g/L	9.78	11.5
CST, s	103	1395
Streaming Current (SC)	-33.7	-36.7
Zeta Potential, mV	-28	-32

Table 3.2 Polymer Dose Conversions

Polymer Dose mg/L	WAS kg/ton	Synthetic Sludge kg/ton
0	0.00	0
50	0.51	0.43
100	1.02	0.87
150	1.53	1.30
200	2.04	1.74
250	2.56	2.17
500	5.11	4.35

It was found that WAS had a higher pH than the synthetic surrogate, due to the alginic acid in the synthetic surrogate. Even though the solids concentrations in the WAS and synthetic surrogate were similar, the CST's were quite different. And this was also linked to the alginic acid content and the abundance of cations. The TS of the suspension varied from the target of 10 g/L due to incomplete separation during the settling step.

Because solids concentrations differed, the conversions from mg/L polymer dose to kg/ton are also somewhat different for the synthetic sludges and WAS, as shown in Table 3.2.

The electrokinetic properties of the two samples were found to be similar. The SC is an indirect measurement of zeta potential, and the streaming current detector's (SCD) amplification was calibrated to give similar values to the zeta potential. Preliminary zeta potential measurements confirmed this (Table 3.1), and the SC measurement was thus used in this study due to its ease of use. Particle size analyses, though not reported here, showed the WAS and synthetic sludges to have similar size distributions, although the WAS was found more flocculated with somewhat fewer particles in the 15-25 μm sizes and more in the 25-100 μm range. The lower CST of WAS (Table 3.1) is also consistent with a more flocculated state than the synthetic sludge.

3.3.2.2 Analysis of conditioned samples

Zetag 7557 provided visually evident flocculation for both samples. To provide free water by sedimentation, a dose of at least 0.5 kg/ton was required for WAS and 1.3 kg/ton for the synthetic sludge.

Supernatant turbidity measurements (Figure 3.8) show that WAS had a much clearer supernatant than the surrogate, and, with both, overdosing led to increased supernatant turbidity values. Particle counts (not shown) agreed with this finding.

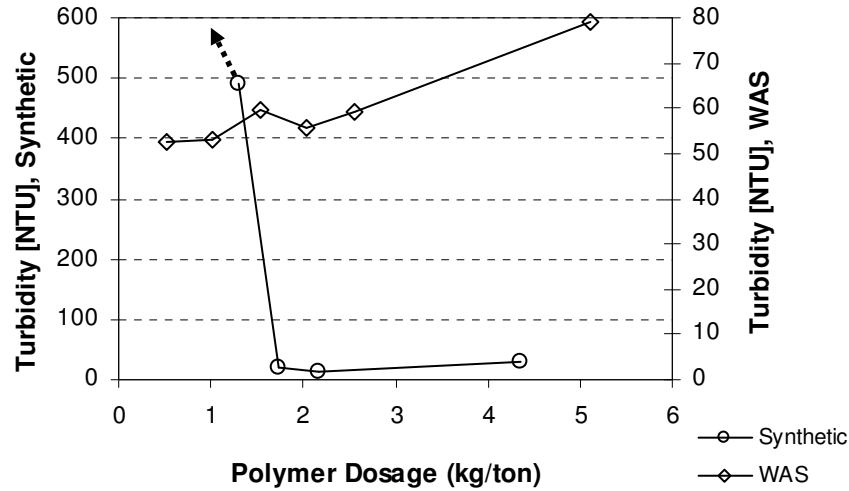


Figure 3.8 Residual Turbidity of WAS and Synthetic Surrogate after Conditioning

The CST results measured after conditioning are given in Figure 3.9. Different scales were required to show the features for the two types of sludge, although the trends of these two samples are similar. It is difficult to see the actual minimum CST on these plots, so the data were also transformed into reciprocals of CST, which can be considered as filterability rates. Figure 3.10 shows the data in this manner, with higher values on the ordinate indicating better filterability. The graph shows that improved WAS filterability can be accomplished using less polymer than the synthetic sludge, which requires a somewhat higher dose to attain the best filterability. The WAS results also indicate a broader dose range for satisfactory treatment.

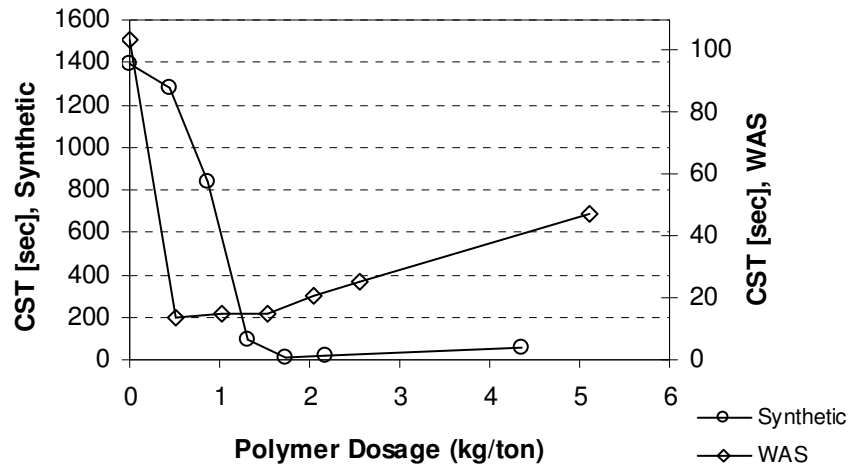


Figure 3.9 The actual results of CST measurements for synthetic and activated sludge

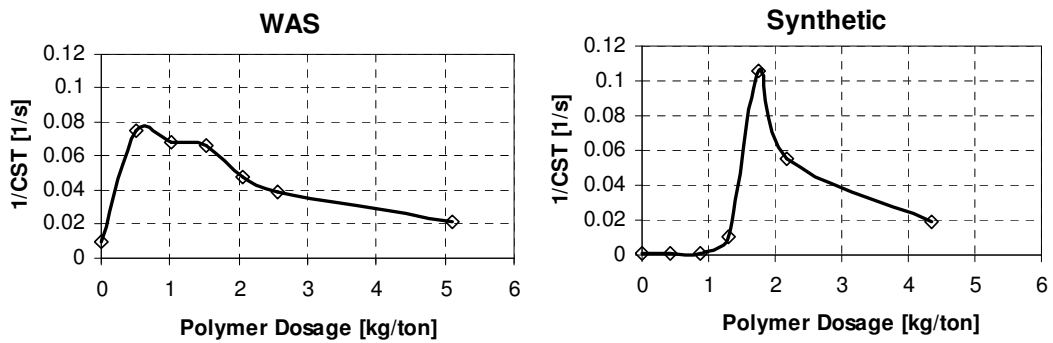


Figure 3.10 The rate of filterability for WAS and Synthetic Surrogate

Electrokinetic data show a strong resemblance between WAS and the synthetic surrogate. As shown in Figure 3.11, the addition of polymer leads the streaming current to become less negative, first reaching charge neutralization and then charge reversal. Although the WAS is neutralized at lower polymer doses, probably due to a

lower ratio of monovalent to divalent cations, the overall responses to polymer addition are very similar.

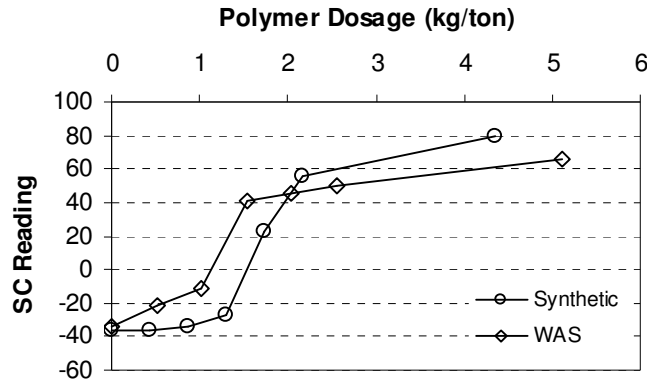


Figure 3.11 Comparison of polymer effects on SC

3.3.2.3 Optimum conditioner dose

In order to determine the optimum polymer dose for WAS and the synthetic surrogate, both filterability results and electrokinetic properties were taken into account. Additionally, “optimum” doses may be defined as somewhat below the amounts giving (for example) the absolute minimum CST, since small improvements in dewaterability may not justify a significant dose increase. The optimum dose ranges thus indicated are shown in Figure 3.12. The dose for WAS was from 1-1.5 kg/ton (100-150 mg/L), and a higher 1.5-2.0 kg/ton range (170-230 mg/L) for the synthetic surrogate. Plausibly, this difference is related to the initial filterability properties of the samples; the synthetic surrogate had a much higher initial CST, indicating a level of water retention requiring a greater amount of chemical conditioning. Based on

preliminary experiments in formulating the synthetic sludge, the alginic acid, especially in combination with the added calcium and potassium, was thought to provide the gel-like structure leading to these properties.

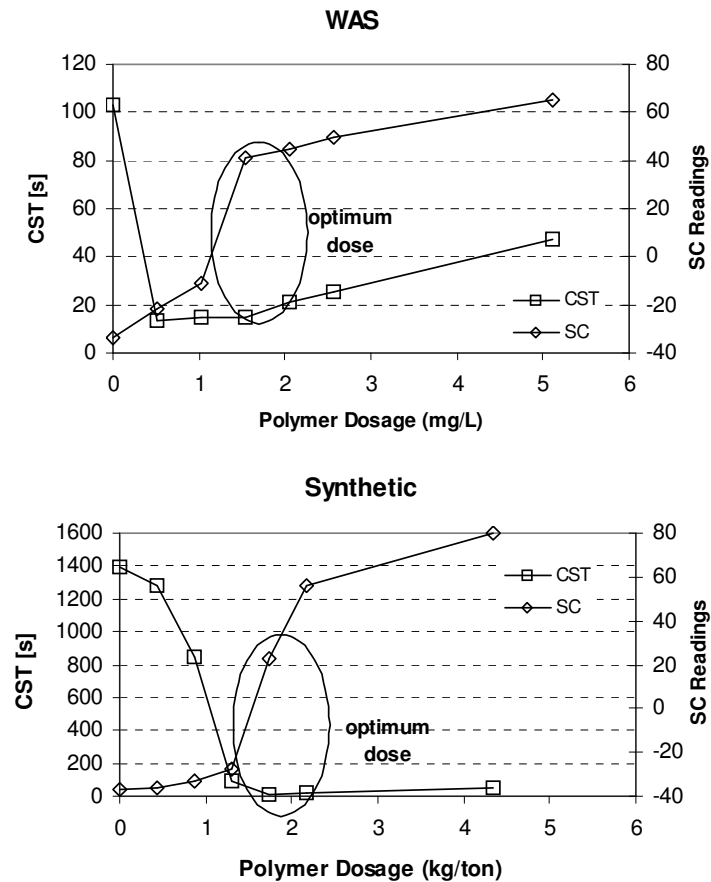


Figure 3.12 Optimum dose ranges for WAS and synthetic surrogate, relative to CST and SC results.

3.3.3 The use of swelling ratio and rheology to understand the gel-like properties

Broad gel characterization methods were used to characterize both the synthetic slurry and sampled biosolids. Samples were also subjected to conditioning to observe the rheological changes. Standard slurry as described in the Materials and Methods section was prepared, and *digested sludge* was sampled from the Wilmington Wastewater Treatment Plant. The experiments were combined with the surface charge measurements to understand the mechanism in the conditioning process.

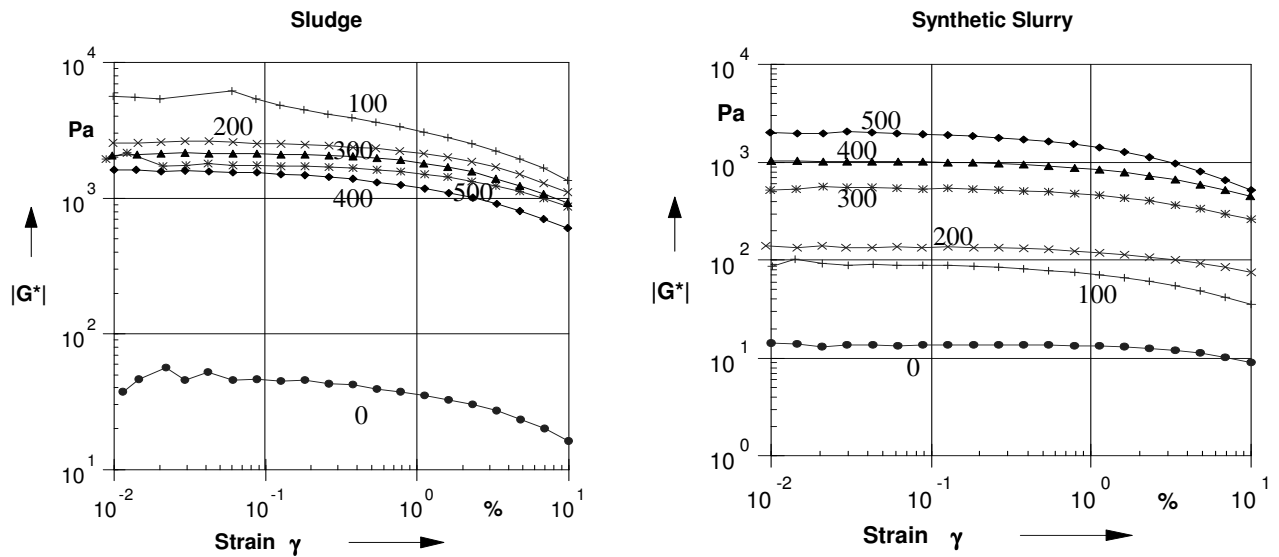


Figure 3.13 Results of amplitude sweep tests

(conditioner doses are given on the figures as mg/l)

3.3.3.1 Amplitude sweep tests to determine the yield stress and Linear viscoelastic range (LVE)

The change of complex modulus as a function of strain at constant frequency ($f=1$ Hz) is represented for the sampled sludge and the synthetic gel in Figure 3.13. A strain-independent complex modulus was observed with a constant plateau up to a critical strain value. The yield stress values of samples were determined by analyzing these curves as explained earlier (Figure 3.14). The complex modulus exhibited by both biosolid and synthetic samples increased as the conditioner amount increased. However, at higher conditioner doses, the critical strain value of the samples decreased at a greater rate than an increase in complex modulus. Therefore the decreasing trend of yield stress was observed with high doses of polymer addition (higher than 300 mg/l).

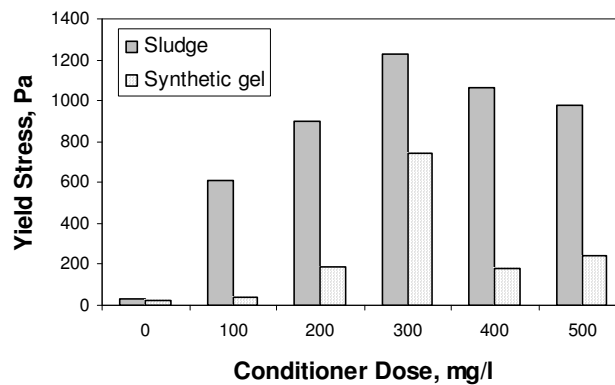


Figure 3.14 Yield stress values for sludge and synthetic slurry

3.3.3.2 Frequency sweep tests to understand the gel-like behavior

Followed by amplitude sweep tests, frequency tests were carried out at constant strain of 0.1% to examine the structure of the sample at rest. The results are given in Figure 3.15 for biosolid and synthetic slurry before conditioning. Storage modulus (G') dominates loss modulus (G'') for both samples, demonstrating a dominant elastic behavior ($G' > G''$) over viscous behavior. This result can be expected for solids or pastes, but for sludge which is low viscous at high shear rates, having $G' > G''$ in the LVE range, implies the gel structure. The similarity in response to conditioning of synthetic slurry and the sampled sludge also verifies the gel-like behavior of sludge.

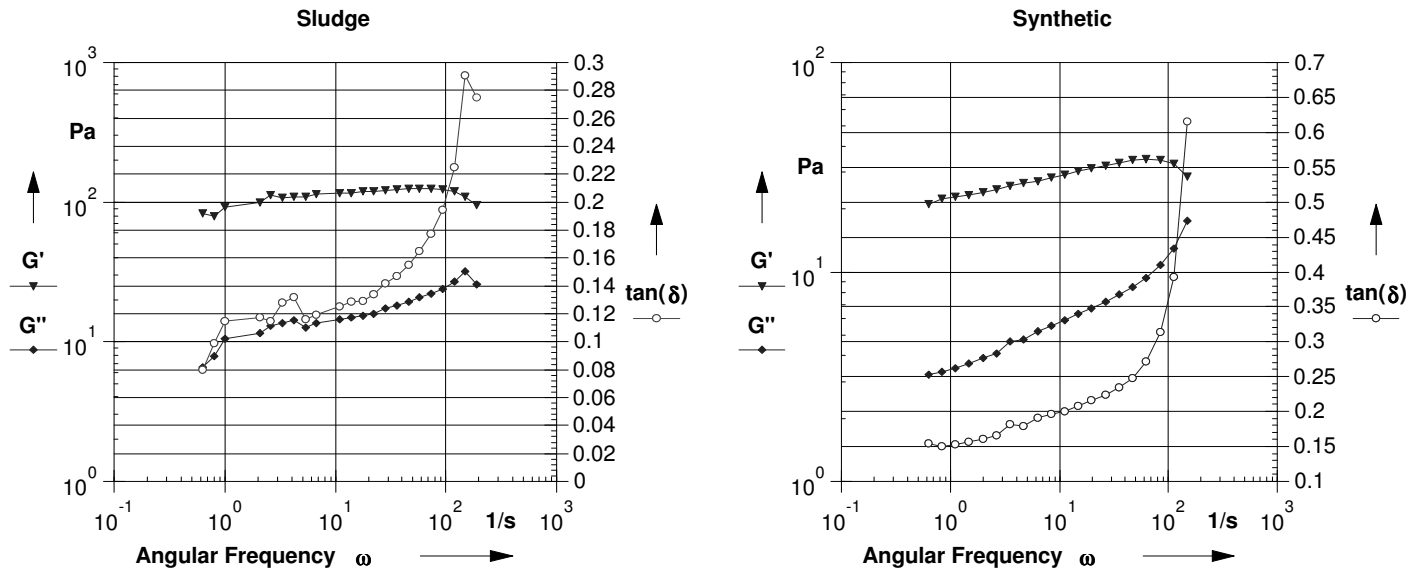


Figure 3.15 Frequency sweep test results for unconditioned samples

With an increasing conditioner dose, the internal structure of the sludge network becomes less flexible and more rigid. In this rigid structure, more deformation

energy is stored, and elastic behavior becomes increasingly dominant, leading to an increase in G' (Figure 3.16). Interestingly, the application of two low doses of polymer (50-100 mg/l) decreased the storage modulus for both the sludge and the synthetic slurry. This may be related to the amount of shear applied during conditioning. Application of shear might alter the structure of samples and disrupt the network structure; thus, low conditioner doses addition may not be sufficient to recover the effect of shear.

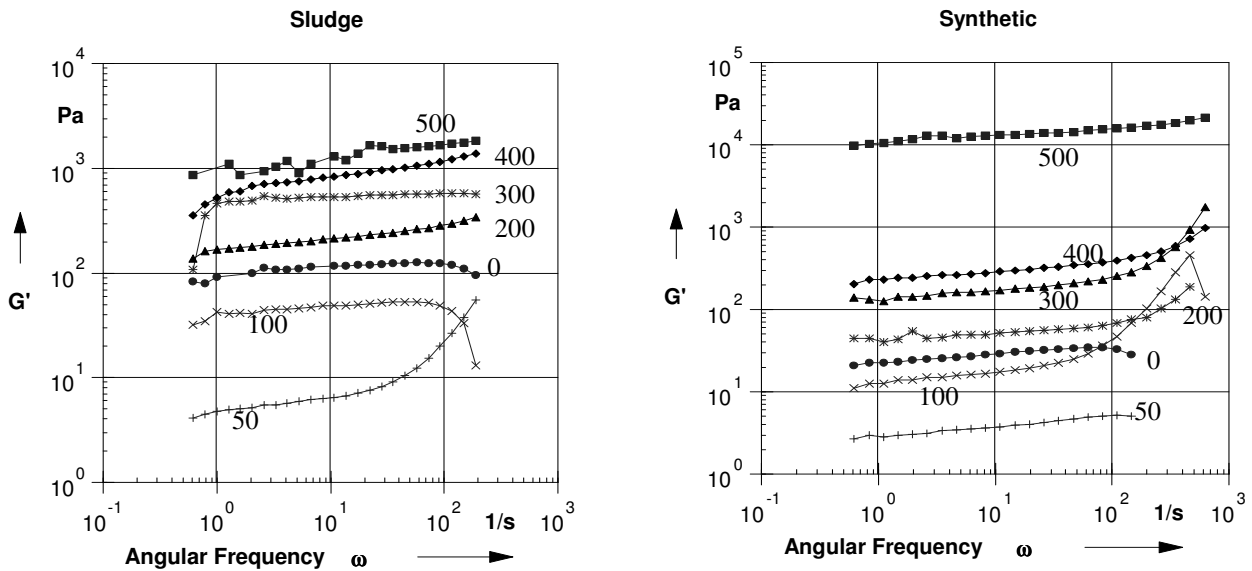


Figure 3.16 Effect of conditioning on elastic modulus

(conditioner doses are given on the figures as mg/l)

3.3.3.3 Relationship between surface charge, swelling ratio, filterability and rheological properties

The results of rheological measurements were combined with surface charge, swelling ratio and filterability analysis, and the characteristics of samples are summarized in Table 3.3. Without conditioning, due to the high water holding capacity of samples, measured as swelling ratio, G' was low and exhibited less elastic phase. As the swelling potential was decreased with conditioning, G' as well as yield stress values increased.

Table 3.3 Comparison of yield stress, swelling ratio, filterability and surface charge of synthetic slurry and biosolid

Biosolid					
Conditioner	Dose,	Yield Stress,	Swelling ratio,	CST,	Surface charge,
mg/l		Pa	g/g	s	meq/g
0		29.5	16.40	1181.3	-0.388
100		609.5	9.54	42.2	-0.104
200		896.2	9.48	28.3	-0.112
300		1224.3	7.36	13.7	-0.067
400		1067.4	7.60	30.4	-0.007
500		976.1	7.15	38.0	0.013
Synthetic Slurry					
0		21.0	15.97	485.7	-0.505
100		42.8	7.37	155.9	0.125
200		184.4	7.11	60.4	0.000
300		740.6	5.71	24.2	0.124
400		179.6	6.62	17.3	0.354
500		238.9	6.34	33.8	1.079

The results showed that swelling potential was significantly correlated with yield stress for the biosolid. Both for synthetic slurry and the sampled sludge, the relationship was described by an exponential equation (Figure 3.17). Comparing the biosolid and synthetic gel data indicated that, although the swelling potentials of the two samples were similar at the beginning, the yield stress exhibited by the biosolid was higher after polymer addition. This implies that the biosolid forms a more rigid substance with conditioner compared to synthetic slurry. Showing more resistance to filtration at the beginning also indicates a stronger gel fraction in digested sludge. The amount of gel fraction in the biosolid might be higher than in the synthetic slurry

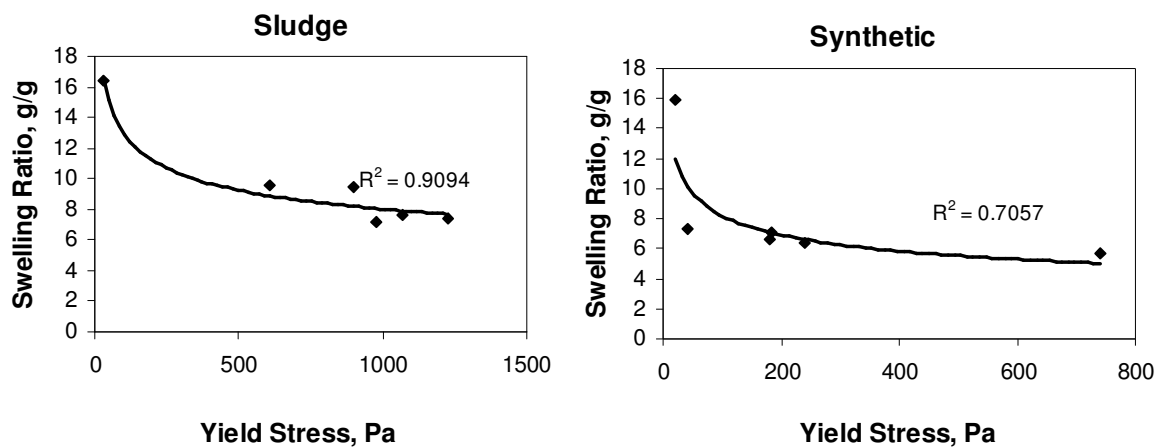


Figure 3.17 Relationship between yield stress and swelling ratio of samples

Previous study has shown the relationship between the surface charge characteristics of sludge and rheological properties (Forster, 2002). The values for the surface charge of samples are presented in Table 3.3, together with the yield stress

values calculated from the amplitude sweep tests. Although Forster related the higher surface charges to higher yield stress values, with conditioning, our results did not support their findings. We have observed higher yield stress values around zero surface charge (Table 3.3) but could not find an obvious correlation.

The CST values of synthetic slurry and biosolids are given in Table 3.3 and show that both samples have poor filterability, particularly for unconditioned samples. Rheological parameters can be suggested as an explanation of poor filterability such as low G' values before conditioning is correlated with high CST's. Like swelling potential, CST is also but exponentially correlated with yield stress for both samples indicating the sudden decrease at low doses of yield stress (Figure 3.18).

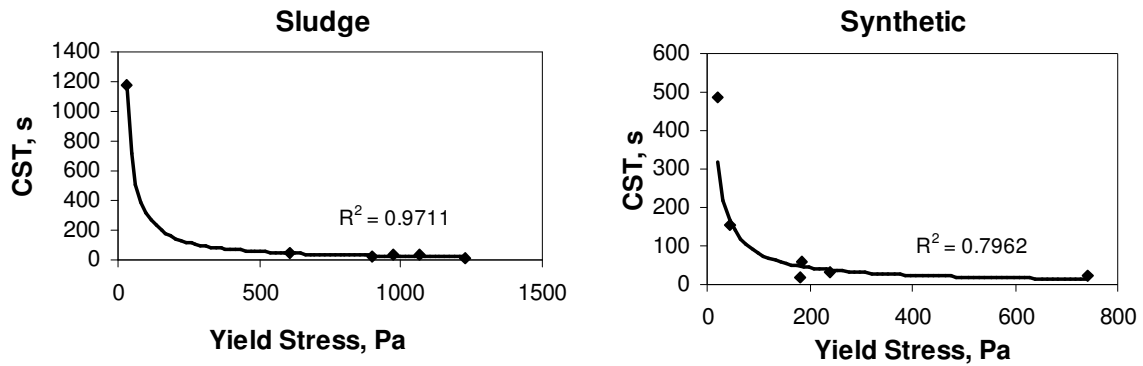


Figure 3.18 Relationship between yield stress and CST of samples

Since the CST of sludge was higher than that of synthetic slurry, it was expected that lower G' values would be obtained for sludge. However, this was not the case. The initial solid content of the samples was the same for both samples because

yield stress values were affected by the solid content of samples. Therefore, it is likely that different particle size distributions of samples or various constituents of polymeric fractions might cause these conflicting results.

3.3.4 Significance of Structural and Gel Fractions in Shear Sensitivity of Sludge

The structural (particulate) and gel (polymeric) fractions in biosolids were related to shear sensitivity. Synthetic slurries were used to simulate real samples, since the particulate and gel fractions in the slurry can easily be altered. The biosolids yield stress, which has previously been related to network strength (Yen *et al.*, 2002), was also used for characterizing shear sensitivity. Yield stresses of surrogates were measured by applying a dynamic rheological test (amplitude sweep tests).

Experiments allowed the A-E Model to be assessed. Figure 3.19 shows fitting results according to Equation 3.4 using Sigmaplot® nonlinear regression. Shearing effects on the dispersed mass concentration were essentially complete within 120 minutes, so shearing times were limited to 2 hours. The nonlinear regressions also gave the model parameters $m_{d,\infty}$ and D as given in the following sections for various synthetic surrogates. Regression coefficients (R^2) for the regressions are also tabulated.

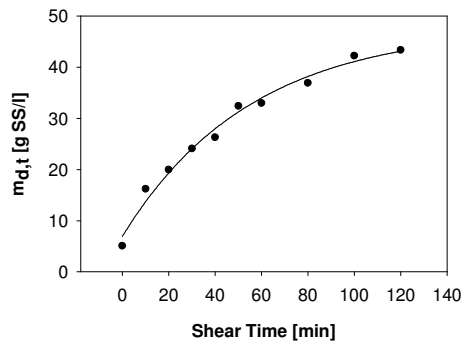


Figure 3.19 Typical graphs used to determine the shear sensitivity Dispersed mass concentration versus time

3.3.4.1 Effect of alginate content

Values of $m_{d,\infty}$ with varying alginate content, as estimated from the model, are given in Table 3.4. Using the model and Equation 3.3 gave the shear sensitivity results (k_{ss}) shown in Figure 3.20. The percentage of alginic acid used in formulating a synthetic sludge was found to be the major determinant in its gel-like behavior and shear sensitivity. A small percentage greatly increased shear sensitivity, but all further increases in alginic acid lessened the shear sensitivity of the samples. The slurry that was prepared without alginate addition (0%) also had low shear sensitivity (<0.01); this slurry did not exhibit gel-like behavior, and solids readily separated from the liquid phase. This led to fewer solids in the centrifuged supernatant and a low dispersed mass.

Table 3.5 shows that alginate content was also related to zeta potential. Increased alginate fractions gave less negative zeta potentials. In accordance with

DLVO theory, more neutral zeta potentials also resulted in stronger samples that were more stable and resistant to shear (Figure 3.21). However, although shear sensitivity (k_{ss}) correlated with initial CST, samples with high k_{ss} values actually gave low filterability (high CST values). A weaker structure may lead to floc disruption, structural collapse, and clogging.

Table 3.4 Model fitting parameters for alginate variation

Amount [%]	$m_{d,\infty}$ [mg/L]	D [s^{-1}]	R^2
0	49.31	0.0005	0.994
3	649.97	0.0002	0.947
5	546.04	0.0473	0.996
10	63.95	0.0147	0.991
15	53.04	0.0180	0.966
20	29.74	0.0165	0.976

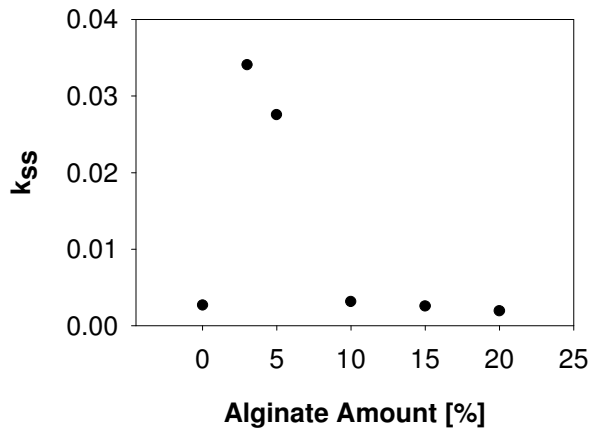


Figure 3.20 Variation of k_{ss} with alginate content of slurry

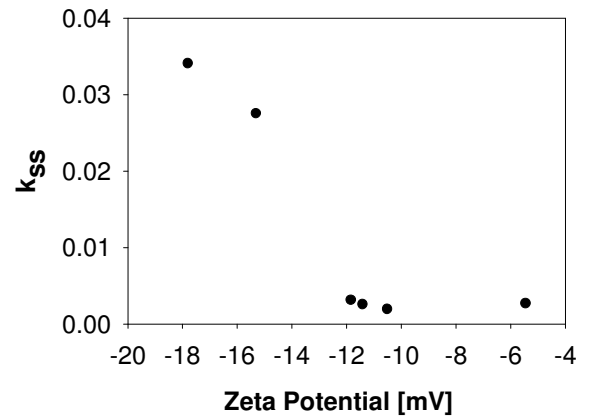


Figure 3.21 Zeta potential versus shear sensitivity for alginate variation

A moderate connection between yield stress and shear sensitivity is also suggested in Table 3.5. Actually, high shear sensitivity occurred only with very

negative zeta potentials, with nearly constant, low shear sensitivity for all zeta potential values approaching neutrality. Curiously, more negative zeta potentials and higher shear sensitivities were associated with higher yield stress values.

Table 3.5 Correlation coefficients (R^2) of linear regression between shear sensitivity and other measurements for alginate variation

	Zeta Potential [mV]	CST [s]	Yield Stress [Pa]	k_{ss}
Amount	0.8408	0.8821	0.0573	0.2614
Zeta Potential [mV]	X	0.0040	0.8285	0.7051
CST [s]	X	X	0.0126	0.1593
Yield Stress [Pa]	X	X	X	0.5660

3.3.4.2 Effect of cellulose content

Variation of cellulose content was the main parameter to change the solid content of the synthetic surrogate. Dispersed mass concentrations were raised with increased cellulose addition (Table 3.6). Increasing solid content formed a stronger network with alginate and other cations in the system, hence leading to more shear-resistant surrogates (Figure 3.22).

Table 3.6 Model fitting parameters for cellulose variation

Amount [%]	$m_{d,\infty}$ [mg/L]	D [s^{-1}]	R^2
0	319.17	0.0046	0.987
30	470.23	0.0011	0.980
40	678.58	0.0010	0.970
50	623.76	0.0017	0.953
60	725.86	0.0012	0.798
70	829.53	0.0019	0.844

The relationship between shear sensitivity and cellulose content was reasonably linear, decreasing from 0.05 to 0.02. The zeta potential of the surrogates was moderately related to shear sensitivity, but Figure 3.23 shows that shear sensitivity increased with more neutral zeta potentials, unlike the results from alginate variation.

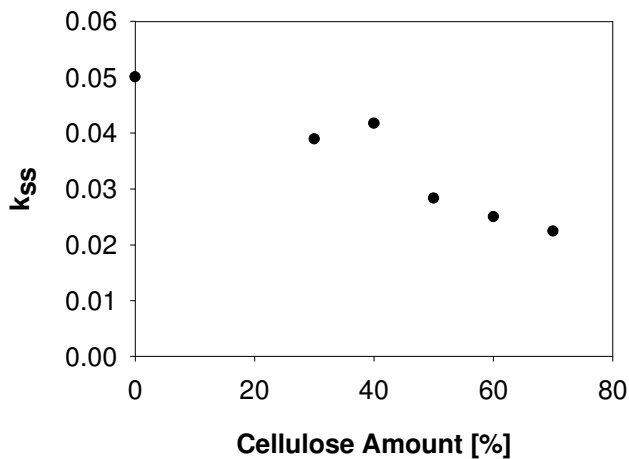
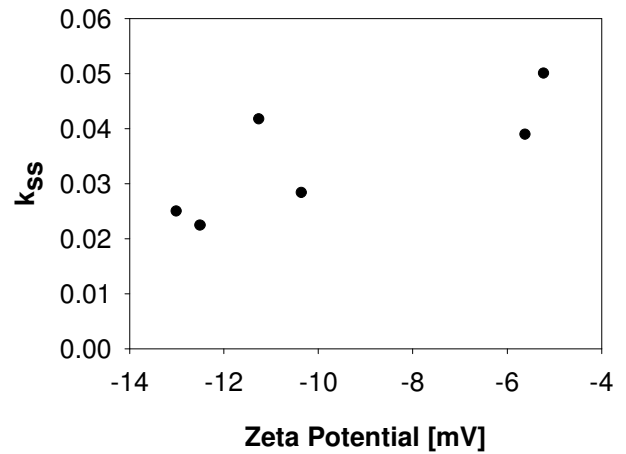


Figure 3.22 Variation of k_{ss} with cellulose content



3.23 Zeta potential versus k_{ss} for cellulose variation

These results suggest that the charge content of the slurry was not the governing factor in determining shear sensitivity. This is confirmed by the weak correlation of CST values to zeta potential (Table 3.7). The physical effects of cellulose were apparently more important, with strong effects on all measured parameters. Without any cellulose present, the slurry was a mix of alginate, cations, and a small amount of yeast—essentially a pure hydrogel with notably low filterability. As particle concentration increased with increasing amount of cellulose, a network of particles was formed by the increased number of particle interactions and the yield

stress increased (from 0 to 7 Pa). Table 3.7 summarizes the relationships among the parameters. As the yield stress of slurry increased shear resistant samples were appeared.

Table 3.7 Correlation coefficients (R^2) of linear regression between shear sensitivity and other measurements for cellulose variation

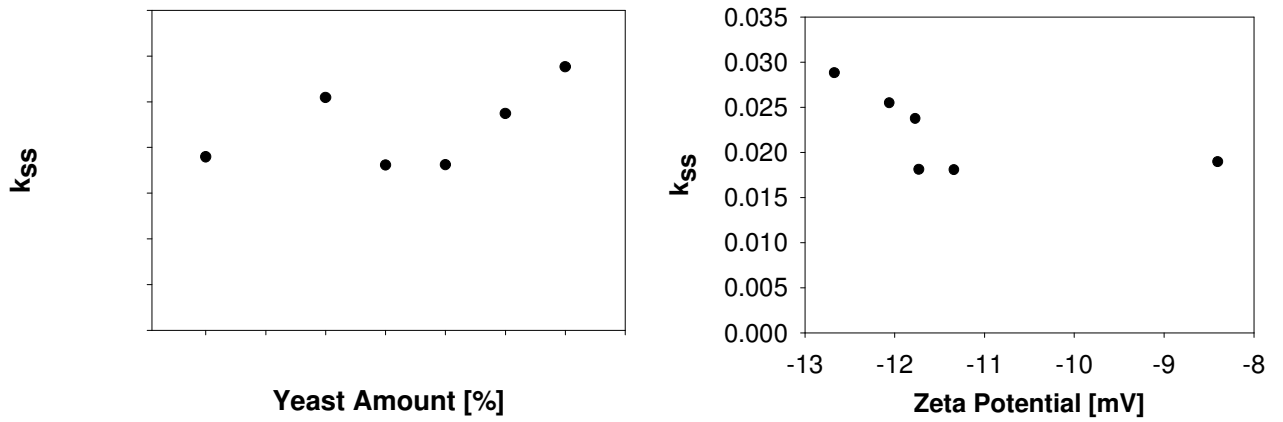
	Zeta Potential [mV]	CST [s]	Yield Stress [Pa]	k_{ss}
Amount	0.7904	0.7546	0.8888	0.9035
Zeta Potential [mV]	X	0.4519	0.7812	0.6203
CST [s]	X	X	0.4373	0.5869
Yield Stress [Pa]	X	X	X	0.8785

3.3.4.3 Effect of yeast content

Table 3.8 gives the model fitting parameters for variation of yeast content in the surrogate sludge. The estimates of $m_{d,\infty}$ with the addition of yeast were very similar with only insignificant variation. When yeast was added to surrogates, $m_{d,\infty}$ slightly increased, whereas there was no variation of the k_{ss} . Figure 3.24 gives the relationship between the estimates of k_{ss} —fluctuating between 0.018 and 0.029—and yeast amount. On the other hand, as the zeta potential slightly increased, k_{ss} decreased, resulting in shear-resistant surrogates at less negative zeta potentials (Figure 3.25).

Table 3.8 Model fitting parameters for yeast variation

Amount [%]	$m_{d,\infty}$ [mg/L]	D [s ⁻¹]	R^2
0	354.31	0.0052	0.933
10	490.63	0.0057	0.987
15	338.93	0.0172	0.953
20	367.52	0.0009	0.942
25	489.83	0.0015	0.823
30	611.39	0.0012	0.942

**Figure 3.24** Variation of k_{ss} with yeast content**3.25** Zeta potential versus k_{ss} for yeast variation

The correlation coefficients are shown in Table 3.9. The most significant relationship was the increase of yield stress as a function of yeast addition. However, the obtained yield stress values were relatively low (between 0.5 and 1.2 Pa); hence, it was difficult to draw a conclusion with this data set. As with the previous results, the predominant factor is simply the addition of the solids themselves. The use of initial CST as a shear sensitivity indicator is not possible for these samples (R^2 for CST- k_{ss}

was 0.014). This is probably due to the complicated nature of the CST test, which is affected by both the structure and primary particle concentration.

Table 3.9 Correlation coefficients (R^2) of linear regression between shear sensitivity and other measurements for yeast variation

	Zeta Potential [mV]	CST [s]	Yield Stress [Pa]	k_{ss}
Amount	0.6793	0.4656	0.8498	0.2703
Zeta Potential [mV]	X	0.6706	0.5394	0.3413
CST [s]	X	X	0.1653	0.0140
Yield Stress [Pa]	X	X	X	0.4126

3.3.4.4 Effect of monovalent/divalent ratio

Table 3.10 gives the effect of the monovalent to divalent (M/D) cation ratio on estimates of $m_{d,\infty}$. The M/D value (as well as the overall ionic strength) was increased with the addition of KCl into the slurry. As the M/D ratio increased, the samples showed a higher dispersed mass concentration and estimated k_{ss} values also increased from 0.003 to 0.01 (Figure 3.26). Although the addition of KCl ions into the slurry caused more shear-sensitive samples, the estimated k_{ss} values were still lower than the ones estimated for cellulose and yeast variation.

Table 3.10 Model fitting parameters for various M/D ratios

Amount [ratio]	$m_{d,\infty}$ [mg/L]	D [s^{-1}]	R^2
0	47.79	0.0181	0.993
5	63.56	0.0048	0.990
10	103.97	0.0013	0.962
15	179.52	0.0020	0.969
20	221.03	0.0323	0.991
25	213.00	0.0254	0.980

Figure 3.27 indicates a close to linear relationship between zeta potential and shear sensitivity ($R^2 = 0.865$). This relationship is similar to that with cellulose addition. The zeta potential of samples became less negative with an increasing M/D ratio, probably due to double layer compression effects. This destabilization might be expected to flocculate and strengthen the solid phase, but shear sensitivity was also elevated, suggesting that the monovalent ions weaken, rather than strengthen, the sludge matrix.

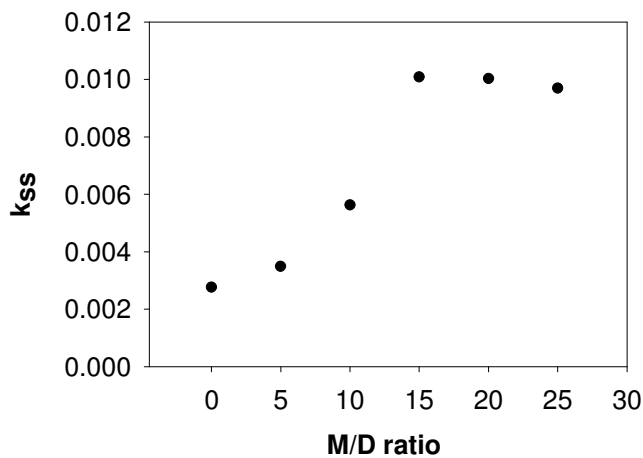
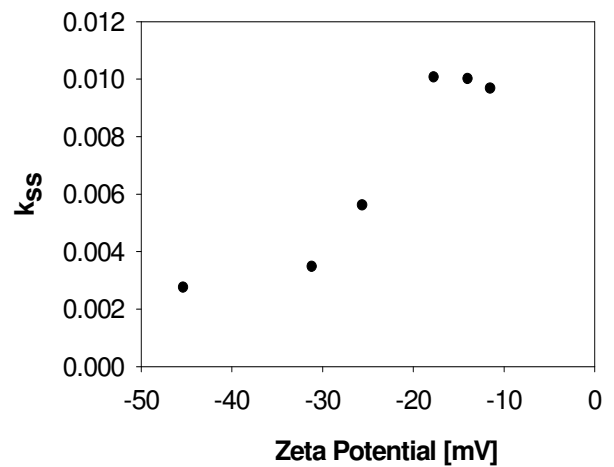


Figure 3.26 Variation of k_{ss} with M/D ratio



3.27 Zeta potential versus k_{ss} for M/D variation

Table 3.11 provides correlation coefficients between the experimental parameters. Filterability was decreased with increasing doses of KCl, which is in accordance with dispersed mass findings. The relationship between the yield stress and shear sensitivity is as expected, with shear-sensitive samples at low yield stress and shear-resistant samples at higher yield stress.

Table 3.11 Correlation coefficients (R^2) of linear regression between shear sensitivity and other measurements for M/D ratio variation

	Zeta Potential [mV]	CST [s]	Yield Stress [Pa]	k_{ss}
Amount	0.9277	0.8051	0.6992	0.8483
Zeta Potential [mV]	X	0.7339	0.6344	0.8645
CST [s]	X	X	0.5799	0.6913
Yield Stress [Pa]	X	X	X	0.8244

3.3.4.5 Effect of divalent/monovalent ratio

CaCl_2 was added into the surrogate sludge in order to increase the divalent/monovalent (D/M) ratio. Ca ions were found to be crucial in the formation of gel with alginate, since, in the absence of Ca ions, the synthetic surrogate was a cloudy, milky homogenous solution without binding among the cellulose, yeast and alginate. Thus, the solid/liquid separation was unproblematic, and the dispersed mass concentration was also low. The addition of a small amount of Ca formed a strong gel network with the alginate system, leading to high dispersed mass concentrations and high k_{ss} values. (Table 3.12).

Table 3.12 Model fitting parameters for various D/M ratios

Amount [ratio]	$m_{d,\infty}$ [mg/L]	D [s^{-1}]	R^2
0	18.08	0.0101	0.977
0.03	426.74	0.0279	0.998
0.05	336.35	0.0243	0.988
0.1	40.09	0.0178	0.988
0.15	51.52	0.0310	0.987
0.2	63.56	0.0048	0.982

Figure 3.28 depicts the variation of k_{ss} as a function of D/M ratio. The figure is remarkably similar to Figure 3.19, which shows the change of k_{ss} as a function of alginate content, thus indicating specific interactions of cations with alginate. The shear sensitivity was high when the D/M ratio was between 0.03 and 0.1 ($M/D = 33-10$), but additional divalent cations resulted in shear-resistant samples.

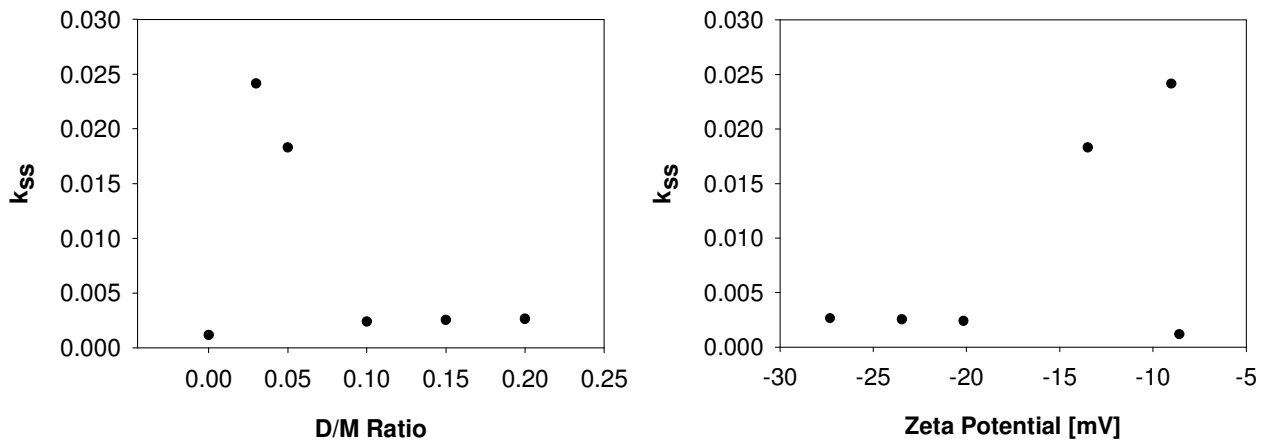


Figure 3.28 Variation of k_{ss} with D/M ratio

3.29 Zeta potential versus k_{ss} for D/M variation

Increasing the D/M ratio decreased the zeta potential linearly, again attributable to double layer compression. As can be seen in Figure 3.29, the tendency observed for D/M ratio variation was similar to changes accompanying the M/D ratio. The k_{ss} values were relatively low until a zeta potential of -20 mV was reached, after which k_{ss} was elevated. Only the sample without additional Ca ions was out of this pattern, since the lowest zeta potential, shear sensitivity, and yield stress were measured for that sample.

Table 3.13 Correlation coefficients (R^2) of linear regression between shear sensitivity and other measurements for D/M ratio variation

	Zeta Potential [mV]	CST [s]	Yield Stress [Pa]	k_{ss}
Amount	0.9683	0.2131	0.8075	0.2059
Zeta Potential [mV]	X	0.3358	0.7766	0.3043
CST [s]	X	X	0.2503	0.8605
Yield Stress [Pa]	X	X	X	0.2905

Based on Table 3.13, the most significant linear relationship is between the zeta potential and the ratio of D/M. Filterability was also enhanced after D/M=0.1. Yield stress was increased with increasing D/M ratio, and for the high yield stress values, shear sensitivity was low, whereas at small yield stress values, the shear sensitivity was high. This confirms that Ca ions were more effective than K ions in formation of the network structure, since the yield stress values obtained for Ca addition was higher than K ions, although the ratio was kept the same (Table 3.14).

Table 3.14 Yield stress values determined for variation of cations

M/D ratio with KCl addition	Yield Stress [Pa]	M/D ratio with CaCl ₂ addition	Yield Stress [Pa]
No K ions	200	No Ca ions	0.16
5	300	5	2600
10	75	6.7	3250
15	10	10	750
20	0.9	20	3

3.4. CONCLUSIONS

This work was necessitated by the fact that the mechanisms behind conditioning and dewatering remain unclear, and the idea of considering biosolids as gels might shed light on these processes. Biosolids properties change over time, primarily because of the active microbial content. It is precisely this property that confounds any attempt at comparative performance or research tests which require reproducibility. This study initially presented the development of a synthetic surrogate that simulates sampled biosolids' physical and chemical properties—instead of biological properties. In order to characterize the complex physical and chemical properties of biosolids, the reproducible synthetic surrogate can be helpful towards developing a model of WAS behavior, or optimization of conditioning and dewatering processes.

This work provides conclusions of three types: (1) in judging the validity of a “synthetic sludge” for the study of actual properties of biosolids; (2) in comparing rheological and swelling properties of biosolids to gels, relating them under the process of conditioning; and (3) in evaluating the shear sensitivity of synthetic slurry by changing each component deliberately.

The synthetic sludge may be considered an “adequate” surrogate for biosolids in many respects: its behavior was similar in terms of electrokinetic and rheological properties, with and without polymer addition. The filterability, as indicated by CST, and the supernatant quality, indicated by turbidity and particle size distribution, were

not the same, although the same type of response to polymer addition was seen. The material is judged acceptable for understanding trends in behavior: it does not “duplicate” biosolids properties and conditionability, but the relative trends in all of these measured parameters were similar, validating the use of this type of synthetic sludge for qualitative or mechanistic studies.

As one example of the utility of a synthetic sludge in studying conditioning, it may be noted that higher polymer doses were required in conditioning of the synthetic surrogate compared to WAS. We tentatively attribute this to the high alginate and calcium levels in the synthetic surrogate, leading it to be even less amenable to conditioning and dewatering than is the WAS. This hypothesis can easily be tested by varying the synthetic sludge formulation. Thus, the gel-like properties of WAS can be represented and modeled through the use of a reproducible surrogate sludge, since these are important aspects of WAS behavior.

In comparing rheological and electrokinetic measurements to the more-often measured CST and turbidity parameters, the electrokinetic properties agree reasonably well with turbidity and CST. The dynamic rheological analyses suggest essential advantages over rotational tests to understand the viscoelastic properties, as they allow separating the elastic and viscous characteristics of samples. Allowing the direct determination of the yield stress from amplitude sweep tests is also an advantage, as the uncertainty of classic regression models can be eliminated. Amplitude sweep tests point out that both sludge and synthetic slurry exhibit a constant plateau to a critical

strain. The yield stress of samples increases with the conditioner addition to a certain extent; however, with higher conditioner dosing, the yield stress values may be lessened. Frequency sweep tests indicate the gel-like behavior of sludge by showing the dominating effect of the elastic part over viscous part. In general, conditioning increases the elastic modulus, implying the increase in rigidity of samples. Both synthetic slurry and actual samples demonstrate the same trends in rheological analysis, although the values for actual samples were somehow found to be higher than the synthetic slurry. Rheological measurements also indicate the similarities of synthetic gel and sludge and their response to conditioning.

The rheological parameters in association with swelling potential and filterability measurements may be helpful in the definition of biosolids as gels. For both synthetic slurry and digested biosolids, the relationship between the swelling ratio and the yield stress was exponential. This explains the small resistance of samples to conditioning due to their polymeric fraction.

The synthetic surrogate recipe can be deliberately varied. Changing ingredient proportions changes the properties of the surrogate. For different scenarios, various synthetic slurries can be prepared (e.g., a specific activated or digested sludge). Therefore, the simulation could easily accommodate the variations in real sludge. Working with a synthetic surrogate thus has a tremendous advantage in determining which path to follow or what to do in these scenarios and understanding the response of conditioning.

Shear sensitivity measurements with variation of ingredients in a synthetic sludge showed important effects. The alginate content, in addition to Ca^{+2} and K^{+} ions formulating the surrogate sludge, were found to be the major components that alter shear sensitivity. These results indicate that the shear sensitivity is primarily controlled by the gel fraction, with alginate and the associated cations increasing the gel-like behavior. However, the particulate fraction effects on shear sensitivity should also be taken into account, since a linear increase was observed between cellulose amount and shear sensitivity. Shear sensitivity is thus a complex parameter including two types of responses: a resistance to dispersal of eroded or fractured material into the filtrate or centrate, and also maintenance of desired strength while the solids concentration increases in the shear field. Although alginate is not a constituent in actual biosolids, the importance of gel behavior itself in influencing dewaterability is suggested as a valid generalization.

ACKNOWLEDGMENTS

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Chapter 4

THE GEL APPROACH IN EVALUATING THE EFFECT OF ORGANIC AND INORGANIC ADDITIVES ON CONDITIONING EFFICIENCY AND SHEAR SENSITIVITY

Abstract

A new conceptual model of sludge structure—likening it to a colloidal gel—was assessed in this research as a means of interpreting conditioning mechanisms. Various conditioners (organic polymers, inorganic salts and a cationic surfactant) were introduced into anaerobically digested sludge, followed by filterability and surface charge measurements. Results indicated that inorganic conditioners formed precipitates and complexes thus collapsing the gel network and forming particulates, whereas organic polymers led to heterogeneous collapse with limited diffusion inside the gel. In this case, the biosolids' network was disrupted by polymer conditioning and the polymers' own structure acted as a backbone that supported and hold the network. Shear sensitivity of conditioned samples were tested by standard shear tests and novel rheological analyses. The filterability and surface charge of polymer conditioned samples were altered significantly by highly turbulent shear. However, neither the surface charge nor the CST were elevated notably with increasing shear for FeCl_3

conditioned samples. Thus, the inorganic conditioner led to the lowest shear sensitivity. With increasing molecular weight of applied polymers, the shear sensitivity also rose, due to the bridging of polymers that were disrupted under shear. The use of rheological analyses was also shown to be a useful tool for the determination of network strength and elasticity of samples. The gel approach, based on the osmotic pressure, was found reasonably successful in defining the filterability and conditioning efficacy. The discrepancies can be reduced by using pressure filtration tests instead of CST as an indicator of filtration rate. This approach was also shown to be beneficial in accounting for the shearing effects for polymer-conditioned biosolids where surface charge and porosity change with shearing time. However it failed to predict the shearing effects for biosolids conditioned with inorganic conditioners, due to the dominating effect of particles over gels.

4.1 INTRODUCTION

Inorganic additives and organic polymers can both be used for enhancing solid/liquid separation processes by forming entities that release the entrapped water easily. However, the dependence of the separation efficiency is based on the conditioner type and properties and also the characteristics of biosolids. The mechanisms of conditioning by using inorganic and organic conditioners appear to differ. Thus Chitikela and Dentel (1998) combined the use of both conditioner types to profit from the advantages of two mechanisms. Murthy *et al.* (2000) also suggested the

constructive effects of addition of inorganic conditioners before polyelectrolyte conditioning. Lee and Liu (2001) showed that sludge conditioned with dual polymers had better dewaterability with less chance of overdosing. Dual conditioning was found to be effective not only for wastewater sludges but also for water residuals (Ayol *et al.*, 2005).

Fundamentally, the inorganic agents such as FeCl_3 salts work chiefly by a sequence of hydrolysis, adsorption and precipitation reactions (Dentel, 2001a). Thus they are likely to function by the mechanism of charge neutralization. Precipitation reactions forming $\text{Fe}(\text{OH})_3$ (s) lead to a porous structure that is beneficial in the release of water from the biosolids network. Besides this usual mechanism, some other inorganic cations including Ca^{2+} and Mg^{2+} have been shown to cause more specific interactions that enhance bridging effects between polymers and flocs (Higgins and Novak, 1997a). Poxon (1996) indicated the destruction of biosolids structure with FeCl_3 addition that formed dense, structural aggregate regions separated by large void spaces. This collapse mechanism was later supported by Legrand *et al.*, (1998) where LaCl_3 addition caused full complexation of negative charges. It was intended to circumvent complications stemming from pH dependent hydrolysis of more commonly used ferric salts by using LaCl_3 .

Cationic surfactants are also used to improve the conditioning efficiency in solid/ liquid separation processes by promoting charge neutralization. Chitikela and Dentel (1998) added hexadecyltrimethyl ammonium bromide (HDTMA^*) as a first

step in their dual conditioning and showed significant reductions in optimum polyelectrolyte dose requirements. The role of surfactants in conditioning and dewatering was also considered in a study carried out by Chu *et al.* (1998). In this work, both cationic and anionic surfactants were added as a conditioner, but only the cationic surfactant enhanced the efficiency of filtration in consolidation stage.

Chemical conditioning is usually carried out by using various types, molecular weights and structures of cationic polymers since the required amount of a polyelectrolyte is notably less than that of inorganic additives such as lime and ferric chloride (Dentel, 2001a). The influence of polymer characteristics on dewatering was thoroughly investigated by Saveyn *et al.* (2005). Charge and molecular weight of polymers are generally considered the governing properties in conditioning. In the traditional coagulation/flocculation model, the charge accounts for charge neutralization, and the molecular weight for bridging. Thus it may be expected that low molecular weight but highly charged polymers be used for charge neutralization whereas high or very high molecular weight polymers of varying charge would be used for increasing the flocculation (Dentel, 2001b).

Using the “gel model” of biosolids suggests other polymer properties that may also be important. This approach may help to indicate what factors might be important in choosing an effective organic polymer for conditioning. Since the interaction of polyelectrolyte and anionic gel matrix is the main concept, charge neutralization should still be taken into account. The amount of negative charge in the biosolids

indicates how much cationic charge must be added – but in considering the biosolids as a gel, it may be advantageous to consider how, or whether, it is possible to measure this charge, since it includes interior sites (Dentel, 2004).

It has long been known that shear and the response to shear play a crucial role in conditioning and dewatering. Novak *et al.* (1988) have quantified mixing in terms of mean velocity gradient (G) and the mixing time (t). As the dimensionless product of these two terms ($G.t$) increases, the optimum polymer requirement increased. These findings were in accordance with the floc breakage and reformation concept introduced by Gregory and coworkers (e.g. Yukselen and Gregory, 2004), which consumes polymer as the flocs become stronger. The amount of shear may also be important in terms of gel approach since it helps to open up the gel network for polymer to access the inner sites. If the biosolids contain a significant amount of hydrophobic character, then the polymer might benefit from having a fraction of hydrophobic sites to increase its affinity for the gel.

Since the production of strong flocs is needed to increase the efficacy of separation processes, the description of floc strength becomes an area of interest. Many researchers have measured particle size or floc size in flocculated biosolids, but the size is really related to the amount of shear that has been applied. Thus, “floc size” becomes a relative index of floc strength. The more shear that is applied, the smaller the apparent floc size. Furthermore, a given amount of shear leads to more breakage when the physical structure is relatively weak. Rather than dealing with floc size,

Mikkelsen and Keiding (2002b) developed a standardized shear test based on the dispersed mass concentration at determined turbulent shear. Recently, Gray and Ritchie (2006) have investigated the effect of polyelectrolyte properties on floc strength by measuring critical mixing speed. Very low molecular weight polyelectrolytes have been shown to produce weaker flocs than did higher molecular weight polyelectrolytes.

It is also possible to evaluate the shearing effects without trying to define, or measure, floc size by using rheological measurements that analyze the entire sample rather than individual entities (Yen *et al.*, 2002). This approach fits well into the gel approach since it characterizes an overall matrix rather than its individual constituents. In fact, there are many rheological measurement techniques specifically developed to describe yield stress and gel-like behavior from both theoretical and practical standpoints (Ayol *et al.*, 2006).

The basis of the gel approach lies in the colligative properties that are altered by lowering of the solvent chemical potential by introducing a solute (Keiding *et al.*, 2001). Thus, these properties reflect the properties of the network rather than individual constituents. Keiding and Rasmussen (2003) used this insight to develop a conceptually simple model based on osmotic effects in biosolids. Their model has been used to explain the aspects of filtration dewatering. However, more work is required to see whether this approach can be used in explaining the conditioning mechanisms in the absence and presence of shear.

The apparent ability of various cations (both organic and inorganic) to penetrate and uniformly collapse sludge gels was related to cation size and surface charge, in this study. Determination of charge density by a titration procedure was primarily used to address this task. A Combination of filterability tests and charge measurements was used to explain the gel-collapse mechanism. Swelling measurements were performed to determine the collapsed state of the biosolids' network. With varying shear, the titration and filterability effects were also evaluated. Finally, all results were combined in a fairly new conceptual model in order to understand the use of the gel approach in predicting the conditioning efficiency.

4.2 MATERIALS AND METHODS

4.2.1 Materials

4.2.1.1 Sludge type

Anaerobically digested biosolids were sampled from the Wilmington, Delaware wastewater treatment facility, which is a conventional activated sludge plant treating domestic and industrial wastewaters. The primary and activated sludges are combined for mesophilic anaerobic digestion at a typical retention time of 15 to 20 days. Samples with 2.38% total solids and around 60% (of total TS) volatile solids were collected directly from the digester and transported to the laboratory, where all experiments were completed within three days of collection.

4.2.1.2 Conditioners

- o Ferric chloride (FeCl_3) was supplied from Fisher in hexahydrate form which is a common commercial form of FeCl_3 . The molecular weight of this inorganic additive is $270.30 \text{ g.mol}^{-1}$.
- o Lanthanum chloride (LaCl_3) purchased from Aldrich ($\text{mw}=245.26 \text{ g.mol}^{-1}$) was also used as an inorganic conditioner since widely used Fe^{3+} salts are known to give rise to colloidal species with valence lower than +3 at neutral pH. By using LaCl_3 the total positive charge can be assumed to be 3 between pH 6.5-7 (Legrand *et al.*, 1998).
- o Hexadecyltrimethylammonium bromide ($\text{HDTMA}^+ - \text{C}_{16}\text{H}_{33}\text{N}^+ (\text{CH}_3)_3\text{Br}^-$) is a cationic surfactant with mw 364.48 supplied by Spectrum (98-101% purity).
- o Zetag 7557 medium-high molecular weight cationic organic polymer was kindly provided by Ciba[®] Specialty Chemicals in microbead form. This is an acrylamide based copolymer of 65% (mole percent) acrylamide monomer and 35% acryloyloxyethyl trimethylammonium chloride (AETAC). A 0.5% stock polymer solution was prepared for additions. Figure 4.1 (a) gives the structure of monomers for Zetag 7557.
- o C587 is a polyDADMAC (poly-diallyl, dimethyl ammonium chloride) medium molecular weight, liquid, highly cationic organic polymer. It was supplied by Cytec Industries. The structure of DADMAC monomer is provided in Figure 4.1 (b)

o C591 has a similar polyDADMAC structure to C587. It is also a cationic organic polymer with high molecular weight, and was supplied by Cytotec Industries.

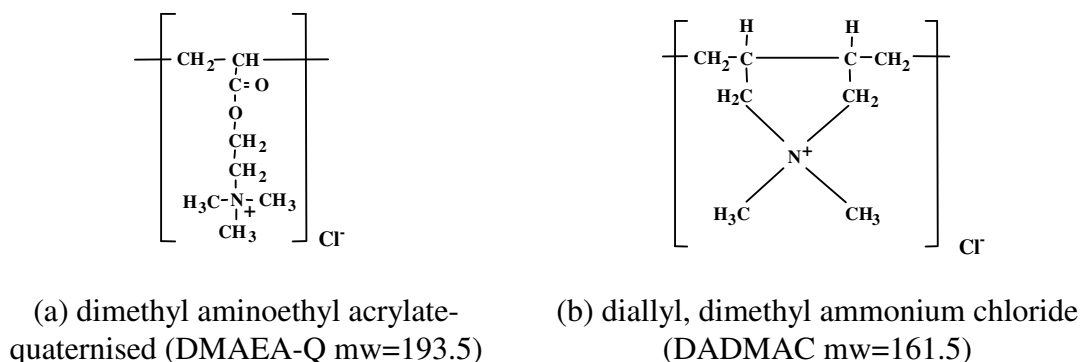


Figure 4.1 Structure of monomers used in organic conditioning agents

4.2.2 Methods

4.2.2.1 Physical-chemical analyses

Filterability was assessed using the Capillary Suction Time (CST) test as prescribed by Standard Methods (APHA American Public Health Association *et al.*, 1995) Section 2710G, using a CST meter (Venture Innovations, Lafayette, LA). Total solids content was also determined according to Standard Methods, performed on original samples in triplicate. Turbidity was measured by Standard Methods, using a HACH 2100P Turbidimeter.

The zeta potential was measured at least three times with a ZetaSizer NanoZS (Malvern Instruments) and surface charge was determined by using the colloid titration method described by Morgan *et al.* (1990). The charge densities of cationic organic

polyelectrolytes were analyzed by the ionic regain titration method (Dentel *et al.*, 1993). The degree of swelling is the ratio of the amount of mass of the swollen gel to that of the dry gel. It is the weight ratio of the filtered sludge on the dry matter obtained after drying overnight at 105°C (Legrand *et al.*, 1998). When considering weights, the swelling ratio was calculated by:

$$q_w = \frac{w_s}{w_d}$$

where w_s = weight of swollen particles and w_d = weight of dry particles.

4.2.2.2 Conditioning

For traditional jar tests a standard gang stirrer was used (Phipps and Bird, Richmond, Virginia), with common 1-liter beakers. Each beaker contained a 0.5 liter volume of digested sludge. Stirring paddles were the standard 30 mm x 80 mm dimension with no baffles employed. The paddle speed was set at 300 rpm during the initial 30-60 seconds while the polymer was added, using calibrated plastic syringes. After 2 minutes of continued rapid mixing, the paddle speed was slowed to 30 rpm for an additional 5 minutes.

4.2.2.3 Shear tests

Shear tests were carried out as proposed by Mikkelsen (2001) as described in Chapter 3 in detail. The sludge was sheared at a pre-determined shear rates (800G) in a baffled reaction chamber. The dispersed mass concentration was then determined by

measuring the turbidity. The degree of sludge dispersion was characterized by the shear sensitivity parameter k_{SS} as defined by Mikkelsen (2001).

4.2.2.4 Rheological analyses

Shear sensitivity was also assessed using a dynamic rheological method of determining yield stress, which has previously been related to network strength (Yen et al., 2002). Strain (amplitude) sweep tests at 1 Hz were used, using an Anton Paar Physica MCR 500 dynamic mechanical rheometer coupled with US200 software. A CP 50-2 cone and plate sensor was used, with 49.94 mm diameter, 2° cone angle, and 0.05 mm gap. The temperature was maintained constant at 25°C by Peltier control. The product of the complex modulus on the plateau and the deformation above which the linear domain ceases gave the yield stress as described in Ayol *et al.* (2006). Details of rheological analyses are given in Chapter 3. After determining the yield stress and linear viscoelastic range (LVE) with amplitude sweep tests, samples were subjected to 0.1% strain value at frequencies from 0.1 to 100 Hz, and the corresponding storage and loss modulus were measured with frequency sweep tests.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of different additives on conditioning efficiency

In this set of experiments, the characteristics of samples were determined with their response to conditioning as a function of the concentration of additives. The pH

of raw samples ranged between 6.8 and 7.1 and the surface charge was measured as -0.38 meq/g TS. The CST of the unconditioned sample was around 1100 sec. The total solids content varied from 22 g/L to 25 g/L depending on sampling time and conditions in the treatment plant.

4.3.1.1 Polyelectrolytes

The general characteristics of three polyelectrolytes used were summarized in section 4.2.1.2. Addition of polymers did not change the pH or total solids significantly. The pH ranged from 6.7 to 7.2 and total solids varied from 20 to 23 g/L. Zetag 7557 was estimated to have a medium-high molecular weight (10,000 to 100,000), and the charge density 3.93 meq/g TS that was determined by ionic regain titration method (Dentel *et al.*, 1993). C587, which is in the medium molecular weight range (1,000 to 10,000) has a different molecular structure and higher positive charge (5.18 meq/g TS) than does Zetag 7557. Although C591 has the same structure as C587, the molecular weight of this polymer was higher (100,000 to 1,000,000) with higher charge density (7.08 meq/g TS). The molecular weight estimates were obtained by the manufacturers.

Various doses of polymers were added into digested sludge and series of jar tests were conducted. The surface charges of samples after conditioning are shown in Figure 4.2. All polymers showed an increase in the surface charge with an increase in polymer dose from 0 to 25 g/kg TS. Zetag 7557 was the only polymer that inverted the

charge from negative to positive. PolyDADMAC polymers could not achieve zero net charge.

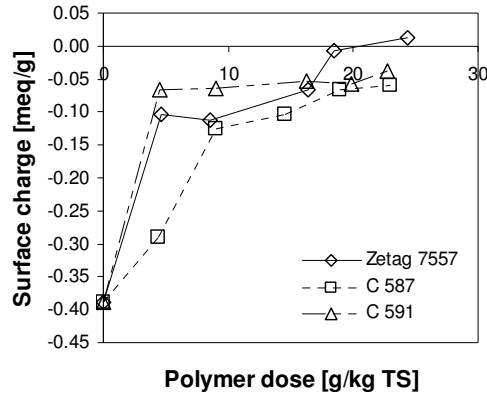


Figure 4.2 Surface charge of samples conditioned with polymers

Figure 4.3 compares the change of zeta potential with respect to polymer addition. n^+/n^- is the ratio between the number of positive charges brought into the system by polymer addition to negative charges carried by the biosolids. Less negative results were obtained as expected by increasing amounts of polymers. In accordance to the surface charge measurements, Zetag 7557 resulted in a steeper line compared to polyDADMAC type of polymers which exhibited almost the same line.

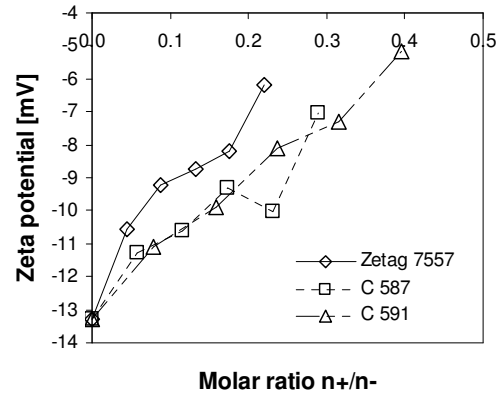


Figure 4.3 Influence of polymer addition on zeta potential

Figure 4.4 depicts the change of filtration rate in terms of $1/CST$ with the increase in molar ratio n^+/n^- for digested sludge conditioned with polymers. The optimum polymer dose –the point at which maximum filtration rate was observed– was achieved when n^+/n^- was equal to 0.1 for Zetag 7557, 0.25 for C591 and higher than 0.3 for C587 since there was no clear optimum seen in the n^+/n^- 0-0.3 range for C587.

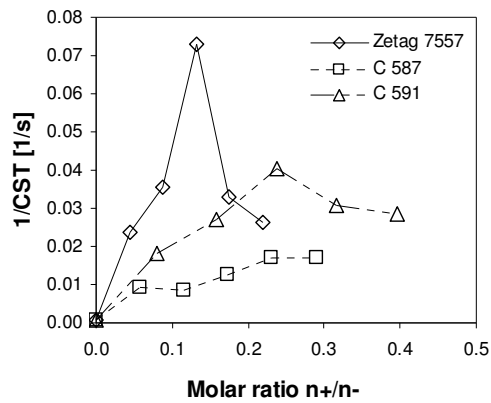


Figure 4.4 Variation of filtration rate with increasing amounts of polymer addition

Figure 4.5 gives the swelling ratio of biosolids as a function of n^+/n^- . The filterability and swelling ratio showed similar trends as one can expect since swelling results were obtained by filtration. An optimum dose could be seen for Zetag 7557 and also C591; however, it was difficult to determine the one for the C587 since the swelling ratio continued to decrease as the n^+/n^- ratio increased and no clear minimum was observed for C587.

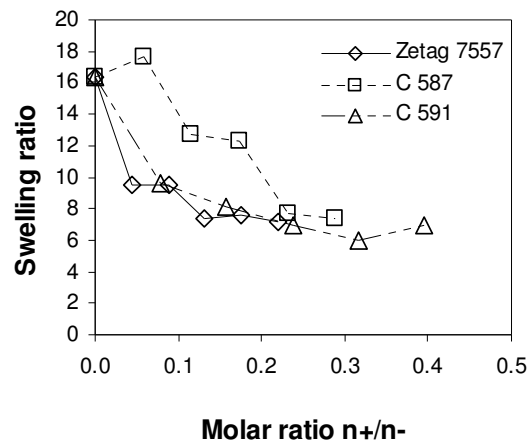


Figure 4.5 Change of swelling ratio with polymer addition

Addition of polymers to anaerobically digested sludge in very small amounts produced efficient conditioning with a mean CST lower than 50 seconds. At these concentrations, the attractive interactions were strong enough to build open spaces which allow the fast removal of interstitial water and caused deswelling. These results were also in agreement with charge neutralization. The available charges at the outer surface of the biosolids network affected the most from conditioning (Figure 4.2),

which is why the filterability of C591 is higher than C587. Highly charged C591 formed a dense layer on the outer surface due to charge neutralization. Zetag 7557 that has different structure led to the highest filtration rates probably due to higher diffusion rates into the network structure of biosolids. The dense layer formed by polyDADMAC type of polymers did not occur by AETAC type, thus letting the charges to diffuse into the network and then collapse the structure. Swelling results supported the collapse mechanism of cationic polymers in biosolids' negatively charged matrix structure (Figure 4.5). Later, this collapsed structure was presumably supported by the polymers' own structure in the network. The collapse mechanism was more likely to be heterogeneous due to uneven distribution of negative charges in the network. Thus structure, molecular weight and also charge density of polymers all affected the conditioning mechanism and efficiency. Higher dose of polymer was needed to reach efficient conditioning for low molecular weight polymers whereas the charge content of polymers were also shown to have a limiting effect on the diffusion and collapse mechanism.

4.3.1.2 Other Additives

As depicted in Section 4.2, FeCl_3 and LaCl_3 were selected as inorganic conditioners and HDTMA^+ was chosen as a surfactant in order to increase the efficiency of solid/liquid separation. These additives have significantly lower molecular weights compared to polymers. In contrast to polyelectrolytes, required

amounts to initiate the coagulation/flocculation process with these additives were significantly higher (around one order of magnitude) which was in accordance with the literature (Dentel, 2001a). Figure 4.6 illustrates the surface charge of samples after conditioning. FeCl_3 was the only additive that resulted in positive surface charge at extremely high additions (400g/kg TS). HDTMA⁺, a cationic surfactant with 1.73 meq/g TS charge density did not lead to charge reversal even at high doses. A steep increase in surface charge was observed for LaCl_3 , which was added in lower concentrations than FeCl_3 and HDTMA⁺.

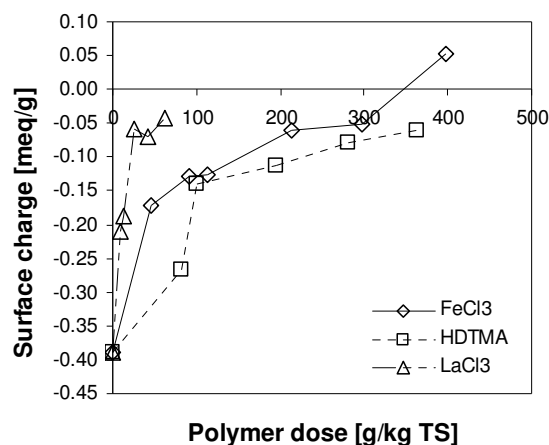


Figure 4.6 Surface charge of samples after conditioning with inorganic additives and a surfactant

The results were then converted into molar ratios, and the resulting variation of zeta potential vs molar ratio is shown in Figure 4.7. The zeta potentials became less negative in response to increasing additive amounts. Similar to the results obtained for

polymers, zeta potential did not go over 0 mV even if extremely high concentrations of HDTMA⁺ and FeCl₃ were added into biosolids.

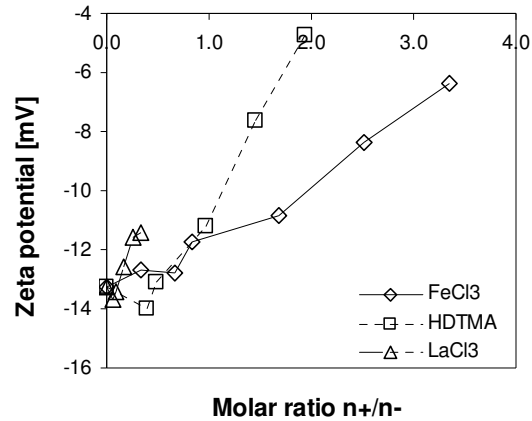


Figure 4.7 Change of zeta potential with increasing doses of inorganic additives and a surfactant

The filterability of samples evaluated with CST changed significantly but at higher doses (around 1.0 n^+/n^- ratio for FeCl₃ and HDTMA⁺) (Figure 4.8). Moreover attained filtration rates (0.001 to 0.0014) were still not as high as the ones reached with polymers (0.01-0.07). Both inorganic conditioners and surfactant did not signify optimum amount after which the additional increase of conditioner led to reduction in filtration rate.

The swelling ratios of conditioned samples given in Figure 4.9 demonstrate the decrease of swelling as a function of additive amounts. LaCl₃ exhibited a sudden decrease in swelling at very low molar ratios leading to almost the same final swelling ratio as with FeCl₃. The lowest swelling ratios were achieved with surfactant addition.

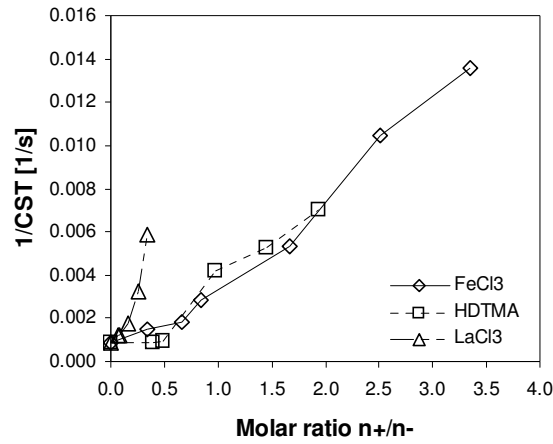


Figure 4.8 Variation in filtration rate with respect to molar ratio for inorganic additives and a surfactant

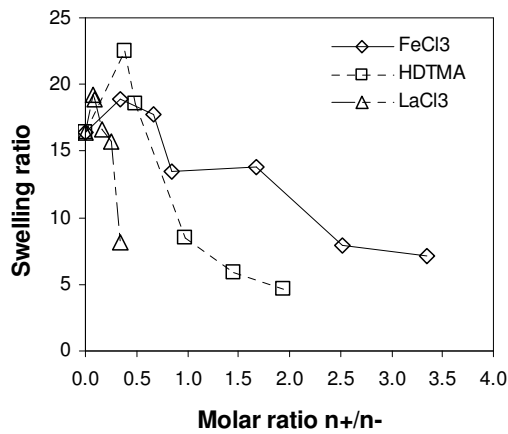


Figure 4.9 Swelling ratio as a function of molar ratio for inorganic additives and a surfactant

Addition of inorganic conditioners (FeCl₃ and LaCl₃) increased the sludge filterability since they penetrated into the biosolids network due to their small size and led to full complexation with negatively charged groups of biosolids. However, FeCl₃

and LaCl_3 responded in a similar way, reaching to optimal conditions or collapsed state at significantly different doses due to the different charge carried by the complexed ferric ion. As the n^+/n^- ratio increases, the complexation of the gel network of biosolids with cations results in continuous deswelling (Figure 4.9) and no reswelling is observed afterwards. Ricka and Tanaka (1984) extensively studied complexation mechanisms of carboxylic groups with metal ions. With complexation, the density of crosslinks was increased, reducing the net charge of the system and decreasing the attraction of water to polymeric matrix of biosolids. Therefore complexation induced by inorganic conditioners led to deswelling and collapse of the biosolids network.

A cationic surfactant HDTMA^+ was used and compared with other additives. The effect of HDTMA^+ was slightly different from FeCl_3 with a clear ramp in zeta potential by increasing HDTMA^+ concentration. Zeta potential measurements agreed with filterability and swelling tests, with optimum filtration at the lowest zeta potential. The use of a cationic surfactant was found effective in conditioning at doses comparable to ferric chloride. Overall, smaller cations required greater additions on charge-equivalent basis due to different abilities to penetrate the hypothesized gel structure. However, they caused lower swelling ratios relative to the larger cations, indicating the reduction in the structural volume of the biosolids network by freeing water.

4.3.2 Shear sensitivity of conditioned samples

Since shear has a strong influence on the optimum conditioner dose, filterability tests were combined with shear tests for direct comparison to the charge measurements. Another test was to apply shear and to repeat charge titration measurements to distinguish the effect of additives on conditioning efficiency based on their size and structure. For a constant cation type and structure (polymer, AETAC) at optimum polymer dose determined with jar tests, the measured surface charge decreased with the amount of applied shear, and at very high shearing times, the end points converged (Figure 4.10). The CST values were drastically ramped with increasing shearing time from 18 sec to 7000 sec. The surface charge and filterability appeared to be strongly dependent on the shear when the AETAC polymer was applied as a conditioner. It is therefore likely that biosolid flocs formed with Zetag 7557 addition consist of a large network with many hidden charges inside that only become available during shearing.

Figure 4.11 gives the same results for digested sludge conditioned with higher dose of Zetag 7557 (overdose). The same decreasing trend was observed for surface charge and a similar increasing trend was seen for CST results. The only difference between the two figures was the required shearing time to attain the same surface charge and CST results. Higher shearing time was needed to reach the negative charges and high CST values when higher dose of Zetag 7557 was added into the system since excess amount of polymer stayed in the system and, as the shearing

occurred, this excess polymer may penetrate into the network of biosolids in which more negative sites were available.

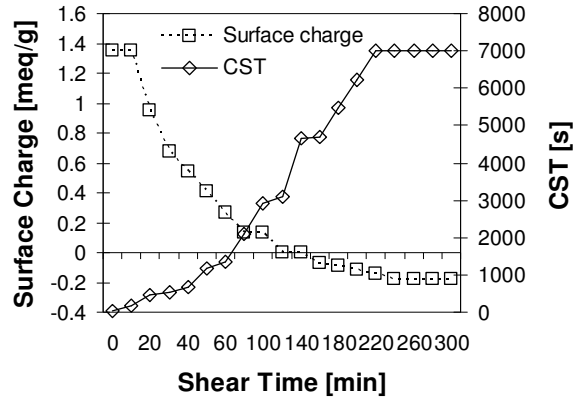


Figure 4.10 Shearing effect on surface charge and filterability of digested sludge conditioned with 16.4 g/kg TS Zetag 7557 (optimum dose)

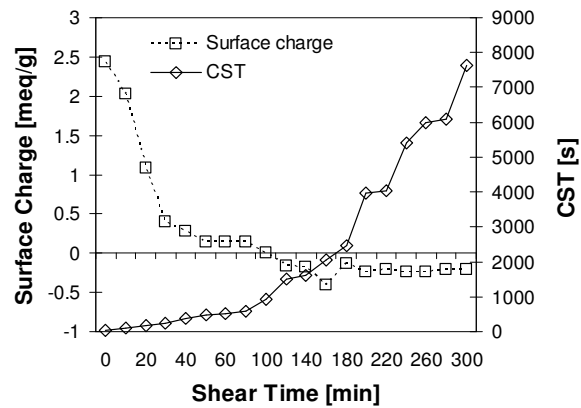


Figure 4.11 Shearing effect on surface charge and filterability of digested sludge conditioned with 24.4 g/kg TS Zetag 7557 (overdose)

The optimum polymer dose for the lower molecular weight and higher charge density polyDADMAC type of polymer was found significantly higher (34 g/kg TS)

than with the AETAC type, Zetag 7557 (16.4 g/kg TS). This result is parallel to the findings of previous researchers (Saveyn *et al.*, 2005). Having a higher charge led to higher degree of charge neutralization, thus only after really high shearing times (>220 sec), negative surface charge values were measured (Figure 4.12). Although CST values elevated with increasing shearing time, the values were almost half of the ones measured for Zetag conditioned sludge.

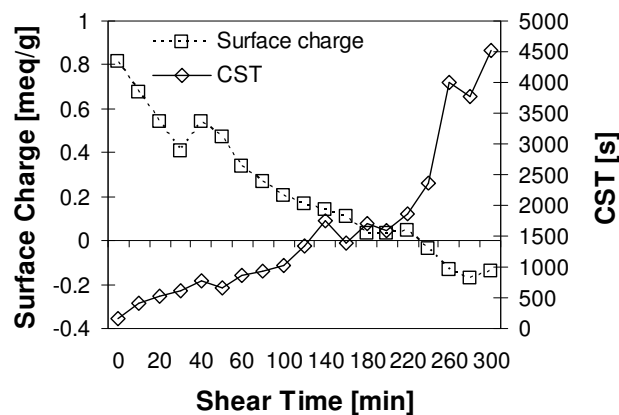


Figure 4.12 Shearing effect on surface charge and filterability of digested sludge conditioned with 34 g/kg TS C587 (optimum dose)

Increasing the concentration of C587 led to higher initial surface charge values. A net positive surface charge was observed for higher dose of C587, with the filtration rates also higher at overdose compared to optimum dose results (Figure 4.13). Conditioning with lower molecular weight, highly charged polymer required higher doses for effective flocculation. With a higher charge density polymer, more negative sites in the biosolids network were neutralized. Applying shear opened up some

negative surfaces, but the amount of negatively charged sites were not as many as of the ones created with Zetag 7557.

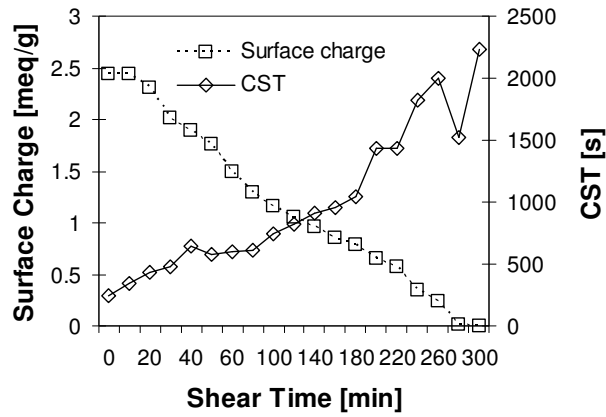


Figure 4.13 Shearing effect on surface charge and filterability of digested sludge conditioned with 45 g/kg TS C587 (over dose)

The optimum conditioner amount for C591—which has the highest molecular weight and charge density—was found to be higher than AETAC type of polymer but lower than C587. The response of C591 to shear was the same as for other polymers. As can be seen in Figure 4.14, no negative surface charge was achieved, even at high shearing times for the optimum dose. Capillary suction time showed a general increasing trend, indicating the change in filtration rate; however, the highest filtration rates were obtained with this type of polymer.

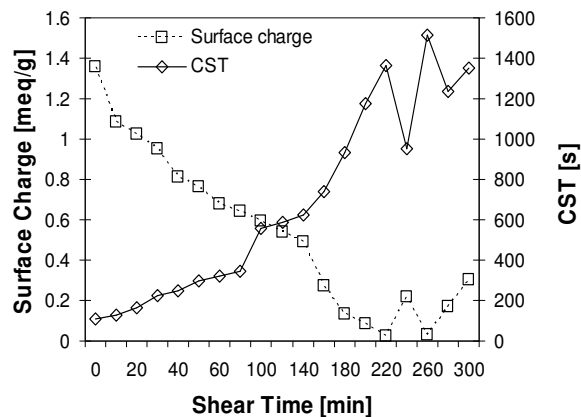


Figure 4.14 Shearing effect on surface charge and filterability of digested sludge conditioned with 22.7 g/kg TS C591 (optimum dose)

With overdosing of polymer C591, the final surface charge was found to be significantly higher than with either of the other two polymers applied (Figure 4.15). This result validates the influence of charge neutralization. More negative sites were neutralized by using highly charged C591 in jar tests. Previous researches demonstrated excess polymer in solution by using HNMR (Chang *et al.*, 2002) or viscosity measurements (Abu-Orf *et al.*, 2003). Application of shear tests after jar tests disrupted the formed flocs, but an excess amount of polymer in the system enabled reflocculation, with this leading to an overall positive surface charge.

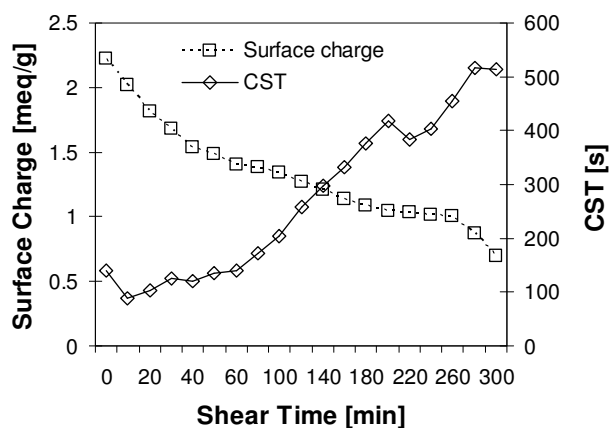


Figure 4.15 Shearing effect on surface charge and filterability of digested sludge conditioned with 34 g/kg TS C591 (over dose)

An inorganic conditioner— FeCl_3 —was also tested for shear sensitivity. Figure 4.16 gives the surface charge and CST values as a function of shear time for optimum FeCl_3 dose. There was a change of both surface charge and CST; however, the shearing effects for FeCl_3 -conditioned biosolids were not as pronounced as the polymer-conditioned biosolids. The surface charge decreased from 0.7 meq/g TS to 0.2 meq/g TS and stayed almost constant after 200 min shearing.

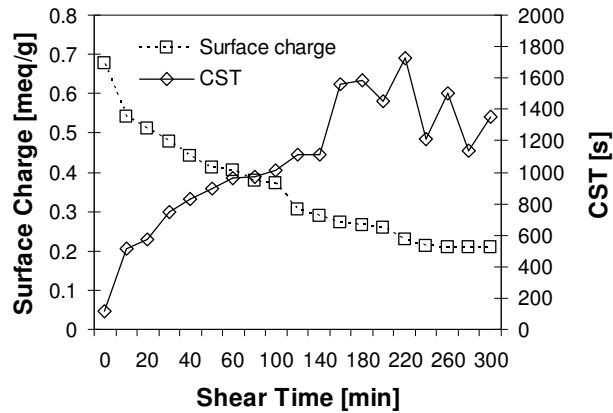


Figure 4.16 Shearing effect on surface charge and filterability of digested sludge conditioned with 213.7 g/kg TS FeCl_3 (optimum dose)

Higher surface charge values were measured as a consequence of the excessive amount of FeCl_3 addition. At initial shearing times, a decrease in surface charge was observed but again this decrease was not nearly as sharp as the one seen for polymers. After a certain point this response also lessened (Figure 4.17). Similar trends were observed for CST measurements. After 60 min of mixing, the CST ranged around 120 sec. It was also noteworthy to observe the lowest final CST results with FeCl_3 addition. When conditioning with inorganic additives, the surface charge of samples seems less affected by the application of shear. This is probably because of the complexation and precipitation process that occurs when inorganic conditioners are added into biosolids. It is therefore implausible that sludge conditioned with FeCl_3 consists of a network with many hidden charges inside, that become available during shearing. Thus conditioning with inorganic additives such as FeCl_3 formed a structure

where particles predominate over the network. This finding was also supported with electron micrographs (Poxon, 1996). After conditioning with FeCl_3 , it is possible to see biosolids as a collection of particles whose surface charges are neutralized by the adsorption and precipitation of FeCl_3 . Although smaller cations require greater additions on a charge equivalent basis, they can easily penetrate into the biosolids network and cause dense flocs with high shear strength and better filterability.

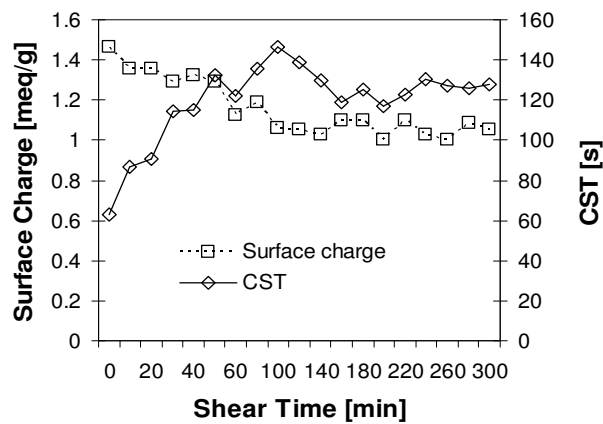


Figure 4.17 Shearing effect on surface charge and filterability of digested sludge conditioned with 297.6 g/kg TS FeCl_3 (over dose)

Following the application of turbulent shear to conditioned biosolids for 300 minutes in a baffled reactor, the shear sensitivity parameter k_{ss} was estimated based on the turbidity of supernatant by using Equation 3.3 and 3.4. Matlab was used to fit the dispersed mass concentrations into Equation 3.4 and to estimate the dispersed mass concentration at $t = \infty$ (infinite). Figures 4.18 and 4.19 give the estimated values derived from Equation 3.3 and 3.4.

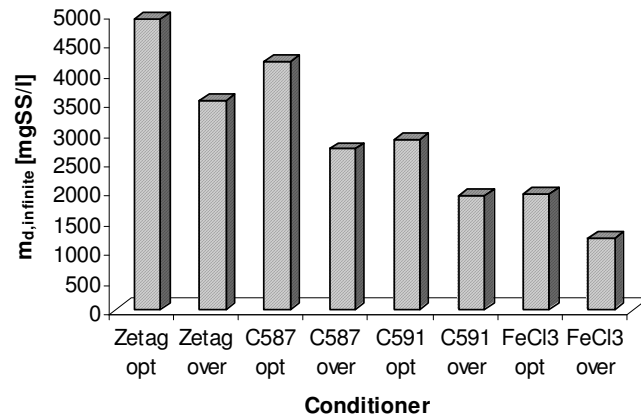


Figure 4.18 Dispersed mass concentrations at $t=\infty$ for conditioned biosolids

The highest amount of dispersed solids was estimated for the AETAC type of polymer. As the charge density of polymer increased, estimated $m_{d,\infty}$ values decreased for organic conditioners (Figure 4.18). These results were also parallel with the CST results given in Figures 4.10-4.17. Since FeCl_3 addition led to precipitation, shearing did not alter the structure, hence estimated $m_{d,\infty}$ values were found to be lower.

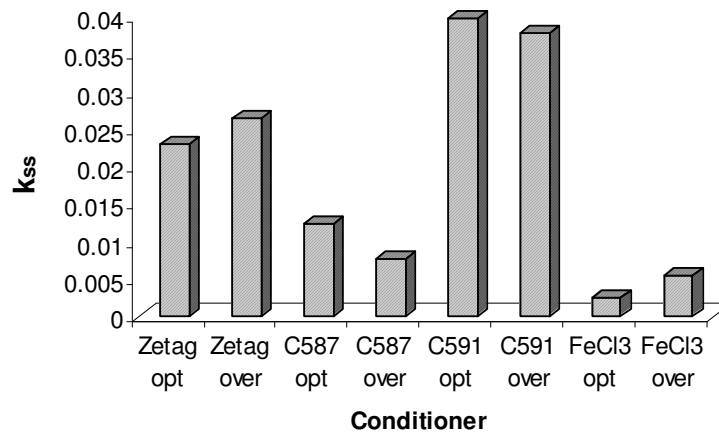


Figure 4.19 Shear sensitivity parameter as a function of conditioner type and dose

Figure 4.19 summarizes estimated k_{ss} values for different conditioners. The inorganic conditioner led to the lowest k_{ss} among 4 conditioners tested. The lowest molecular weight product, C587, provided the lowest value for k_{ss} compared to the other polymers. Since the bridging mechanism is governed by the molecular weight of polymers, shear sensitivity of C587 was the lowest among the other polymers due to its low molecular weight. By applying high molecular weight polymers, the shear sensitivity parameter increased.

Another method based on the dynamic rheological analyses was also tried to determine the shearing effects. Yield stress values calculated from amplitude sweep tests were shown in Figure 4.20. This graph indicates the network strength of samples after conditioning. At the optimum polymer dose, FeCl_3 led to the lowest stress followed by C587, Zetag and C591. Surprisingly, this result was in line with the shear sensitivity values k_{ss} estimated from standard shear tests and given in Figure 4.19.

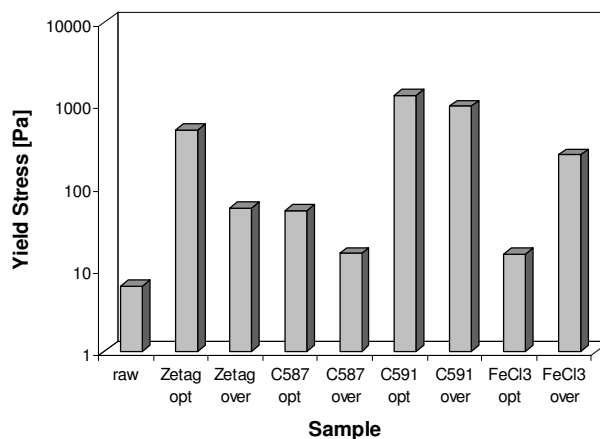


Figure 4.20 Yield stress values as a function of conditioner type

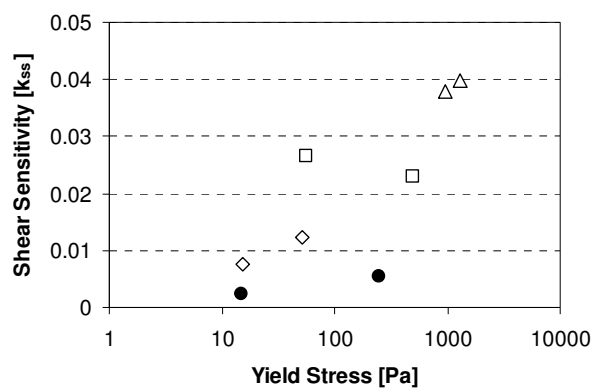


Figure 4.21 Relationship between shear sensitivity parameter and yield stress

Figure 4.21 gives the relationship between estimated shear sensitivity parameter and yield stress. One would expect lower k_{ss} values when yield stress is higher. But the results indicated the opposite, showing an increasing pattern for shear sensitivity as a function of yield stress. It should be kept in mind that the yield stress values were determined when sample was at rest and yield stress depicts the initial network strength before the disruption occurs. These results indicated that the disruption of shear was directly related to the network formed by conditioning.

The viscoelastic behavior of biosolids was investigated by using frequency sweep tests. This oscillatory test varies frequency at constant amplitude in the linear viscoelastic (LVE) range. All conditioned samples showed a gel character where G' (storage modulus) $> G''$ (loss modulus) (elastic behavior dominated over viscous behavior-data not shown in here). The storage modulus of samples, which represents the elastic behavior, is presented in Figure 4.22. In other words the rigidity of samples can be analyzed with this test. Conditioning in general increased the rigidity of samples by forming a network structure either with bridging or with increasing the

solid content. Only low molecular weight C587 showed a decrease in G' . Saveyn *et al.* (2005) also supported the decrease in elasticity with lower molecular weight polymer addition. FeCl_3 significantly increased the solid content (around 30%), hence the rigidity of samples was increased as the added FeCl_3 amount increased, and again particulate fraction became predominant. The total solid amount did not alter in polymer conditioning, therefore the increase in G' related directly with the network structure formed by polymers. Once more, C591 and Zetag 7557 formed stronger network due to their higher molecular weight. But shearing tests showed that under high turbulent shear the bridging mechanism easily disintegrated and shear sensitivity increased.

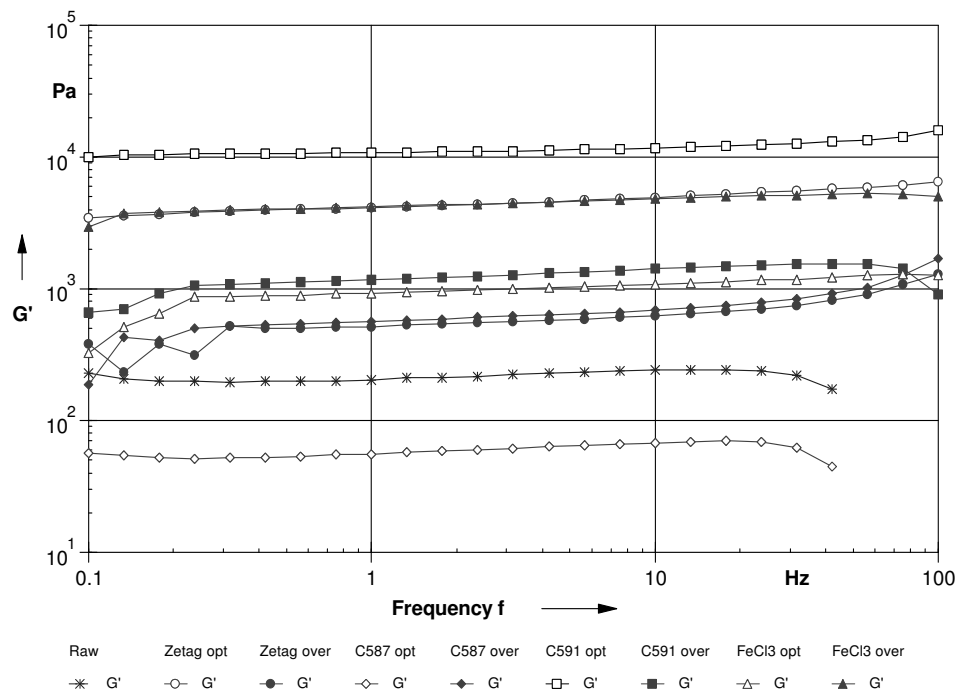


Figure 4.22 Change of storage modulus with conditioning

4.3.3 Application of gel approach in conditioning

Biosolids are composed of solid and liquid parts such as hydrogels. These parts stay together in a polymeric network or extracellular polymeric substances (EPS) and the water. Crosslinks inside the network structure of biosolids provide an elastic restoring force that counters the expansion of the network and the water prevents the network from collapsing (De and Aluru, 2004). On the other hand, the network retains the water and imparts solidity.

This approach assumes that the change of environmental conditions alters biosolids' properties due to the charged groups in biosolids. Addition of conditioners leads to an increased cation concentration that gives rise to an osmotic pressure and causes swelling or deswelling. As the concentration of the different ions inside the gel changes with conditioning, the osmotic pressure changes and thus deformation of the hydrogel (De *et al.*, 2002). Eventually, equilibrium is reached when the elastic force of the network balances the osmotic forces. With the addition of cationic conditioners cation concentration outside the biosolids network becomes higher than inside the network and hence osmotic pressure acts in the inward direction during deswelling.

Following the extensive research on conditioning efficiency of various additives, use of the gel approach to predict the conditioning efficiency was tested. The osmotic pressure and filterability effects were estimated by using Equation 2.7 and 2.9. The surface charge and CST results given in section 4.3.1 and 4.3.2 were directly used. A porosity term (β) was derived from swelling results.

The osmotic pressure values were estimated from Equation 2.7 for constant porosity as the surface charge varies with conditioning. Figure 4.23 shows the dependence of osmotic pressure on surface charge. The osmotic pressure increased significantly while the porosity values changed from 99% to 0.5%. At the same porosity value, the pressure lessened when the surface charge moved towards zero net charge. Figure 4.24 also illustrates how the pressure can change for constant surface charge as the porosity alters. Estimated osmotic pressure increased with decreasing porosity and increasing surface charge, but estimated pressure was 0 when the surface charge was 0.

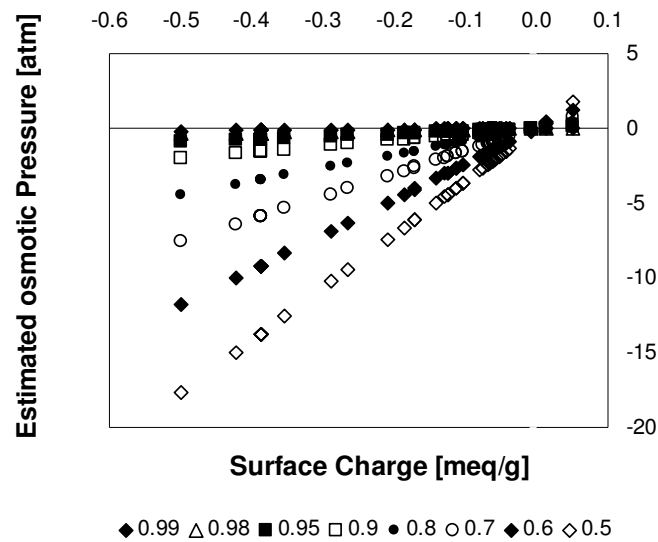


Figure 4.23 Estimated osmotic pressure values based on Equation 2.7 as a function of measured surface charge for constant porosity values

Unfortunately, both surface charge and porosity change with conditioning. As mentioned in previous sections, addition of conditioners led to less negative surface charge with lower swelling ratio (higher porosity). Figure 4.25 and 4.26 combine all results and present the dependence of surface charge and porosity on estimated osmotic pressure. The effect of surface charge was more pronounced on osmotic pressure.

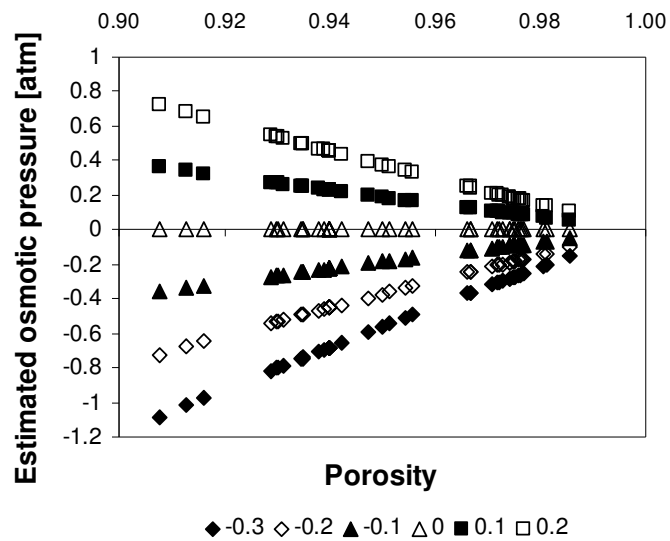


Figure 4.24 Estimated osmotic pressure based on Equation 2.7 as a function of porosity for constant surface charge

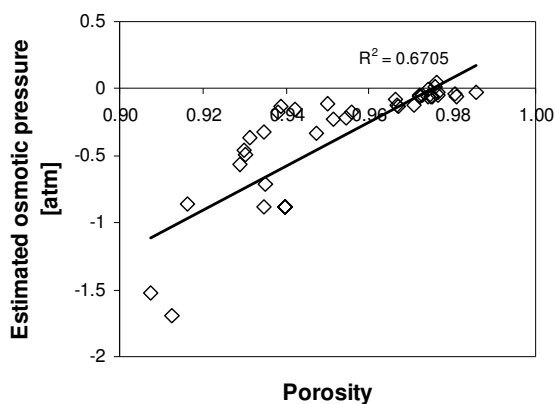


Figure 4.25 Dependence of osmotic pressure on porosity based on actual results

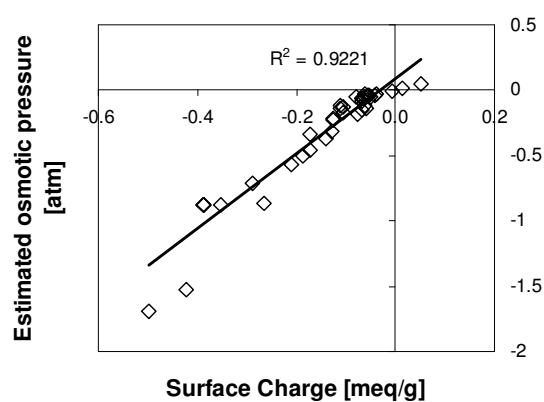


Figure 4.26 Dependence of osmotic pressure on surface charge based on actual results

These figures brought together the results from different types of conditioners, —organic, inorganic and surfactant— which were shown to have different conditioning mechanisms. For instance, inorganic additives produced more compact samples compared to organic polymers. Thus, Figure 4.25 and 4.26 are redrawn in Figure 4.27 and 4.28 respectively to separate the effect of each conditioner on estimated osmotic pressure. Significant correlations were found between osmotic pressure and surface charge ($R^2 > 0.91$) for all conditioners applied regardless of their type, molecular weight or charge.

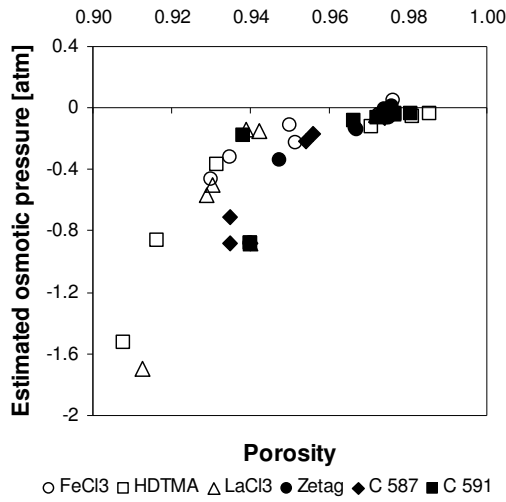


Figure 4.27 Dependence of osmotic pressure on porosity for different conditioners

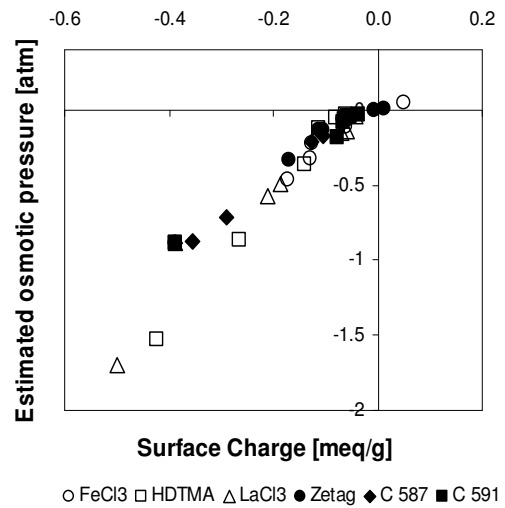


Figure 4.28 Dependence of osmotic pressure on surface charge for different conditioners

Although porosity affects the osmotic pressure to some extent, there was no considerable correlation observed especially for inorganic conditioners (for LaCl_3 $R^2=0.57$ for FeCl_3 $R^2=0.52$). For organic additives, the relationship between porosity and osmotic pressure was closer to linear ($R^2>0.8$).

Following to the estimation of osmotic pressure, the results were fitted to Equation 2.9 by choosing specific surface area (S_0) as an adjustable parameter. The lateral pressures on filter paper at various distances in CST cell were already investigated by several researchers (Smiles, 1998; Lin and Lee, 2001). These values were converted into vertical pressures in the filter cake by using a conversion factor which was the ratio of filter area/cylinder area. Estimated filtration rates in kg.s/m^2

were compared with actual flux values which were derived from CST tests. Figure 4.29 and 4.30 compares the actual values with estimated filtration rates based on this model when specific surface area is $4 \times 10^8 \text{ m}^{-1}$ (average particle diameter in sludge is 0.015 microns).

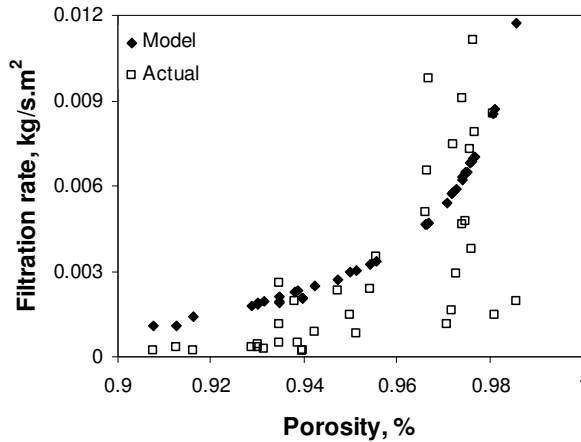


Figure 4.29 Filtration rate as a function of porosity for experimental and modeled values

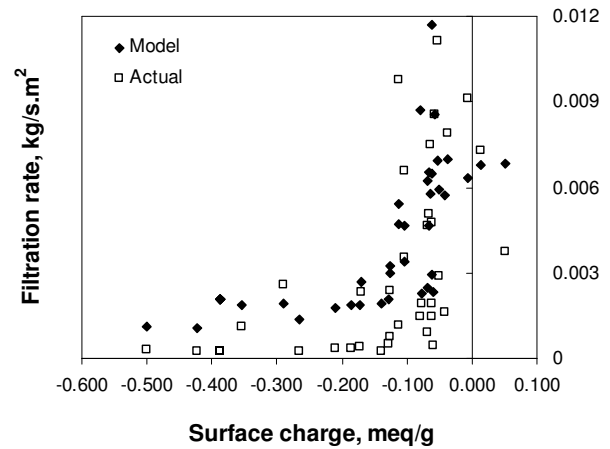


Figure 4.30 Filtration rate as a function of surface charge for experimental and modeled values

The filtration rate increased as the porosity increased and the charge got close to zero. The experimental results were varied in the same range when high specific surface area values were selected. This approach fits well when the particle size is small which is also in accordance to physical description of gel model that assumes polymeric substances with low particle size as the main component rather than particles forming the network. The difference between actual and modeled values was due to the use of $1/\text{CST}$ value as an indicator of filtration rate. The weaknesses of this test and the relationship of this test with actual filtration rate have been investigated by

number of researchers (Chen *et al.*, 1996; Smiles, 1998). The CST test fails to detect the measurable changes in filtration rate at higher conditioner doses (Christensen *et al.*, 1993). Thus in Figure 4.29 and 4.30, through the end of the x axis scale, where the conditioner dose is high, the difference between modeled and experimental values was high. CST is a useful, practical and empirical test, but constant pressure tests would be more beneficial to clear the uncertainty in this model.

With varying shear, the charge and filterability effects can also be used to test equations 2.6 and 2.7. In this manner, this approach may be beneficial to account for the shearing effects. Experimental results given in Section 4.3.2 enable estimation of the osmotic pressure for a total of 300 minutes when surface charge and porosity change. Figure 4.31 is given as a general example for illustrating the change of osmotic pressure with shear.

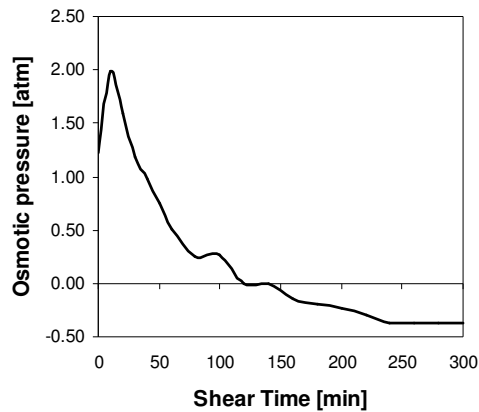


Figure 4.31 Effect of shear on osmotic pressure for optimum dose of Zetag 7557

The cross plots of modeled filtration rates with actual values were given in the following figures (4.32-4.35). The gel approach based on the osmotic effects was able to model filtration rate, thus the conditioning efficiency for polymers, since they also support the gel-like behavior by forming a network in biosolids.

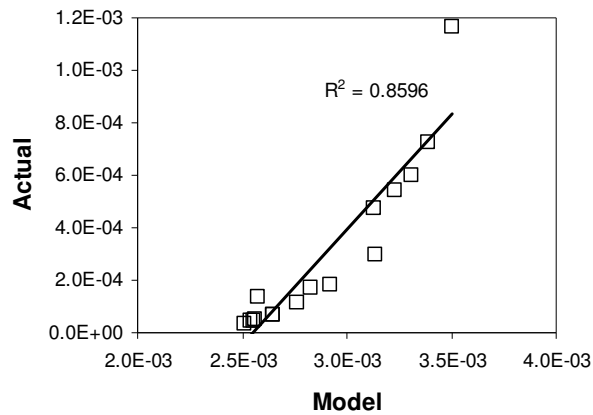


Figure 4.32 Measured values vs modeled filtration rate results for Zetag 7557

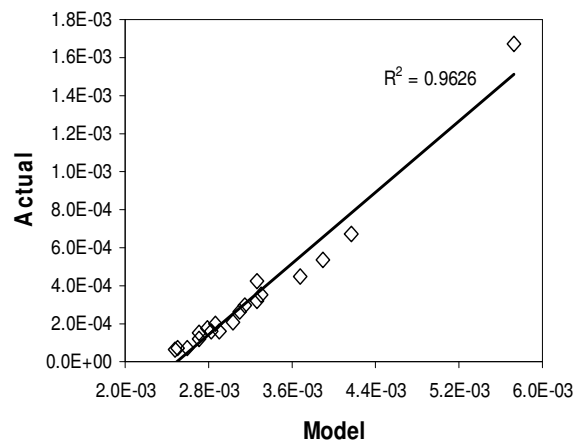


Figure 4.33 Measured values vs modeled filtration rate results for C587

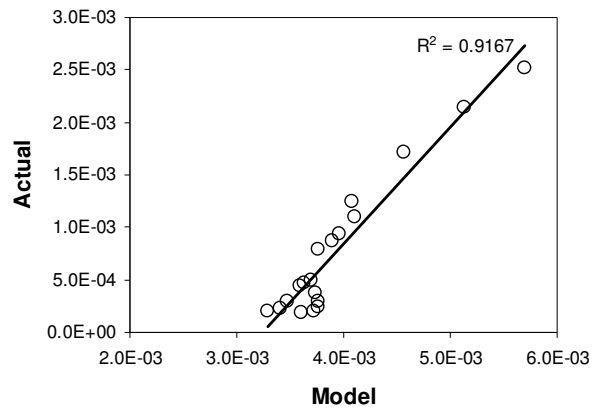


Figure 4.34 Measured values vs modeled filtration rate results for C591

However, for FeCl_3 , the linear correlation coefficient was low. This was related to the conditioning mechanism of FeCl_3 that lead to more compact materials. The network structure of biosolids was disrupted by precipitation, forming a rigid high particulate material. For that reason the gel approach failed to describe the conditioning effects of FeCl_3 .

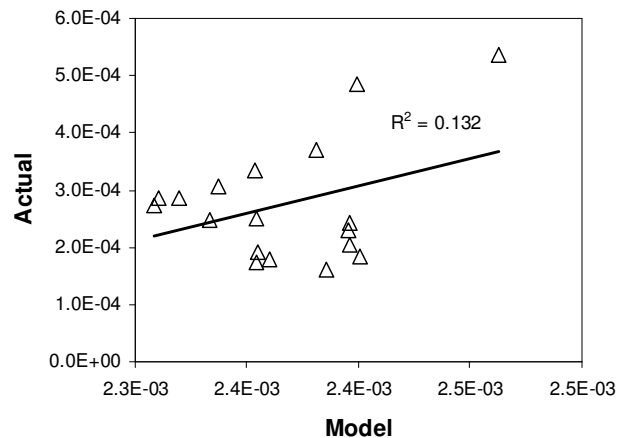


Figure 4.35 Measured values vs modeled filtration rate results for FeCl_3

4.4 CONCLUSION

The ability of various cations (both organic and inorganic) to penetrate and collapse biosolids' structure was related to cation size and surface charge. Different aspects of this approach suggested earlier have been combined and explored comprehensively. The mechanism of conditioning varied depending on the type, molecular weight, structure and charge content of the additives. Organic polymers diffused into biosolids network partially due to their high molecular weight. However, their own structures supported and hold the network. Smaller inorganic conditioners easily penetrated into the biosolids network and promoted complexation and precipitation by increasing the particulate fraction. Similar to small inorganic conditioners, a small cationic surfactant showed parallel responses under conditioning.

The shear sensitivity of conditioned samples was tested by standard shear tests and new rheological analyses. The filterability and surface charge of polymer-conditioned samples changed significantly under high turbulent shear. However, neither surface charge nor CST elevated notably with increasing shear for FeCl_3 conditioned samples. Thus, inorganic conditioners have exhibited the lowest shear sensitivity. As the molecular weight of polymers increased, the shear sensitivity also increased due to the network formed by polymers. This network easily disrupted under high turbulent shear. The use of rheological analyses was shown to be a useful tool to determine the network strength and elasticity of samples.

All experimental results were gathered into the new conceptual model based on a colligative property —osmotic pressure—. This model was found reasonably successful to define the filterability and conditioning efficiency. Use of pressure filtration tests instead of CST may also be valuable to clear the uncertainties in the model. The gel approach was also shown to be beneficial in accounting for the shearing effects for polymer-conditioned biosolids where surface charge and porosity change with shearing time. However, it failed to predict the shearing effects for biosolids conditioned with inorganic conditioners, due to the dominating effect of particles over gels.

Chapter 5

**EFFECT OF COMBINED SHEAR AND NORMAL FORCES ON
DEWATERABILITY OF BIOSOLIDS**

Abstract

The response of biosolids to shear under normal forces is of significance in solid/liquid separation processes such as filtration and dewatering. In this study, a novel technique was developed in order to simulate such dewatering processes. A special cell –called as the immobilization cell (IMC)– coupled with a dynamic mechanical rheometer enables to evaluate the effect of shear and normal forces as the filtration occurs. The limits of shear and normal forces to be applied to both digested sludge and a synthetic sludge before the collapse of samples' structure is established. The maximum normal force increases approximately linearly with the increasing solid content. However, the extent of the increase depends on the shear rate. As the shear rate increases, there is a decrease in the maximum normal force due to the rearrangement in samples structure. At constant shear rate, increasing the normal force leads to higher immobilization viscosity, but increasing the shear rate lowers the viscosity to some extent. No specific trend was observed for final solid content as a function of normal and shear forces. Depending on the type and the dose of

conditioner, the rate of water release and thus the final solid content changes. When the same type of conditioner and dose is applied, the responses of synthetic surrogate and digested sludge are found to parallel each other. The dewatering of biosolids is a complex phenomenon that is governed by the solid content, strength of the network structure, conditioning types and doses.

5.1 INTRODUCTION

Dewatering of biosolids based on solid/liquid separation has explained by filtration theory starting with Darcy's equation in 1800's. However, the behavior of biosolids under dewatering where both normal and shear forces apply still remains a major technological challenge in solid/liquid separation. Understanding the response of biosolids under these forces signifies a fundamentally important step in understanding and thus controlling the filterability of biosolids. Settling tanks, gravity thickeners, and mechanical dewatering processes are some of the operations in treatment plants that may lead to formation of a network structure subjected to normal and shear forces at different levels. The viscoelastic and rheological properties of biosolids under normal and shear forces are poorly understood, thus limiting the design and efficiency of these processes.

Although there has been a considerable increase in understanding the effects of compressive forces (Channell and Zukoski, 1997), much less attention has been paid where suspensions are subjected to combination of compressive and shear forces. In

this work, biosolids are subjected simultaneously normal and shear forces in a specifically designed filtration cell called an “immobilization cell” which is coupled with a dynamic rheometer.

Under normal forces, as the particle concentration increases due to filtration, the biosolids structure compacts to the point where it fully supports the applied load. The network structure is capable of transmitting pressure due to the particle concentration and polymeric fractions inside the network. At equilibrium, the normal force is entirely supported by the network force. When shear is applied, the network is disrupted; hence the equilibrium conditions must shift, leading to collapse into a more compact form.

Initial studies carried out by Buscall and his coworkers (e.g. Buscall *et al.*, 1987; Buscall and White, 1987) explored the theory of sedimentation by characterizing the compression of networks with compressive yield stress ($P(\phi)$) which is a function of particle concentration and the strength of interparticle forces. The particle network can support the normal load up to its compressive yield stress through elastic deformations, after which the structure collapses in order to support the applied force. After their work, numerous researchers investigated the compressive yield stress under different conditions for different materials (Aziz *et al.*, 2006; Green *et al.*, 1996; Miller *et al.*, 1996; Stickland *et al.*, 2006). At maximum forces (higher pressures), the maximum packing fraction is achieved. Higher solids yield to higher shear yield stress which defines the critical stress to be exceeded in order to initiate the flow of the

liquid phase in a normal direction. As the shear rate increases the shear stress also increases to a certain point where a stable viscosity is reached. However as the shear rate increases, the network structure of samples is degraded and the sample loses its ability to support the normal loads. This study investigates how the viscosity and solid content of samples alter as shear rate and normal force are varied.

More recently, Chenevert *et al.* (1994) have used a dynamic filtration device to impose shear while the suspension is being filtered through a porous outer wall. With the same idea, Channell and Zukoski (1997) have utilized a filtration cell in which filtration occurs through the base. However none of these cells allow rheological properties to be determined as normal and shear forces applied.

Willenbacher *et al.* (1999) developed a novel laboratory test to determine the immobilization and water retention of paper coating colors. They suggested the use of a device called an “immobilization cell” (IMC) that can adapt to many commercial rheometers for immobilization measurements (Willenbacher *et al.*, 2000). The IMC has porous base through which samples can be filtered. Coupling the IMC with a dynamic rheometer allows the rheological properties to be measured using a plate and plate geometry sensor at various shear and normal force variations. Although this device was developed and mainly used in paper and coating industries, Wollny (2001) related this method to the dewatering kinetics of suspensions. Two different test types—constant shear rate (CSR) and direct strain oscillation test (DSO)— were introduced for the IMC.

In contrast to traditional filtration tests such as CST and SRF, rheological analyses of biosolids enable analysis of the network of biosolids rather than of individual particles. Although there have been many studies relating rheological analyses to dewaterability, the rheological measurements and filterability tests have been carried out separately (e.g. Abu-Orf and Dentel, 1999; Mikkelsen, 2001). Recently, Ayol (2005) investigated the use of an immobilization cell in rheological characterization of biosolids during dewatering. However this study failed in application of normal forces. Shearing was found to decrease the immobilization time at which viscosity reaches to its maximum point and stays constant.

The objectives of this work were to develop the use of an immobilization cell for application of both normal forces and shear, investigating the maximum normal force that can be applied without disrupting the samples' structure at constant shear rates, evaluating the change of viscosity and solid content as a function of shear and normal forces, and comparing the behavior of sampled biosolids with synthetic surrogate in the IMC.

5.2 MATERIALS AND METHODS

5.2.1 Materials

5.2.1.1 Samples

Anaerobically digested biosolid samples were collected from the Wilmington, Delaware wastewater treatment facility, which is a conventional activated sludge plant

treating domestic and industrial wastewaters. In this plant, the typical retention time for mesophilic anaerobic digestion is 15 to 20 days. The total solid and volatile solid contents of samples were 2.2% and 60% (of Total Solids), respectively.

Synthetic surrogate samples were prepared by using alginate, microcrystalline cellulose, fresh yeast, Ca and K salts as described in (Dursun *et al.*, 2004) with a 2%-2.2% solid content.

5.2.1.2 Conditioners

A medium molecular weight cationic organic polymer Zetag 7557 supplied from Ciba[®] specialty chemicals in micro bead form was used for both synthetic surrogate and sampled biosolids. This is an acrylamide based copolymer 65% (mole percent) acrylamide monomer and 35% acryloyloxyethyl trimethylammonium chloride (AETAC). A 0.5% stock polymer solution was prepared for additions. Figure 4.1 (a) gives the structure of monomers for Zetag 7557.

An inorganic additive, ferric chloride (FeCl_3) as supplied by Fisher in hexahydrate form, was also used for conditioning of synthetic sludge.

5.2.2 Methods

5.2.2.1 Total Solids

Total Solid content of biosolids and synthetic surrogate were analyzed according to (APHA American Public Health Association *et al.*, 1995)

5.2.2.2 Conditioning

0.5 liter of samples were placed in a standard 1 liter beakers to conduct traditional jar tests with a standard gang stirrer (Phipps and Bird, Richmond, Virginia). Stirring paddles were the standard 30 mm x 80 mm dimension with no baffles employed. The paddle speed was set at 300 rpm during the initial 30-60 seconds while the polymer was added, using calibrated plastic syringes. After 2 minutes of continued rapid mix, the paddle speed was slowed to 30 rpm for an additional 5 minutes.

5.2.2.3 Description of Immobilization Cell

Figure 5.1 shows the schematic view of the immobilization cell (licensed by BASF AG). This cell is made from a stainless steel cylindrical metal tube with a punched metal plate that allows the drainage of water through samples. An appropriate base paper, selected from numerous types of filter paper, is placed on top of punched metal plate and the sample is situated on top of filter paper. By applying a vacuum with a vacuum pump, the sample's liquid phase is forced to penetrate into the base paper (Willenbacher *et al.*, 1999). A dynamic rheometer with parallel plate sensor is mounted to the IMC. The gap between the sample and the parallel plate sensor varies as the liquid drains from the sample in order to keep the tested material layer in contact with the upper plate. An initial normal force (F_N) is set in the measuring profile and then the applied normal force is adjusted by changing the gap between the sensor and

the sample. As the dewatering occurs, the normal force tends to decrease, however the rheometer compensates this decrease by moving to a smaller gap (Wollny, 2001).

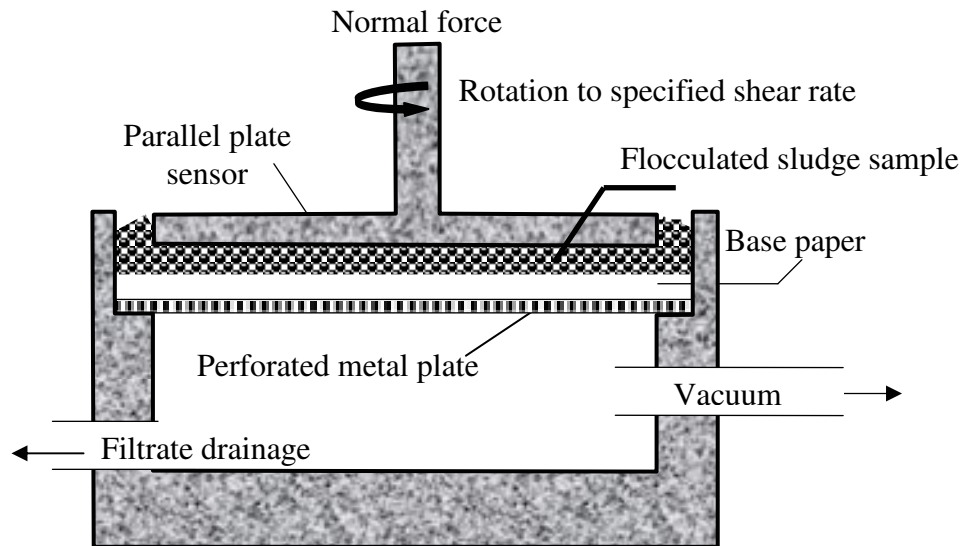


Figure 5.1 The Immobilization Cell (IMC) (Revised and redrawn from Brown, 2003)

5.2.2.4 Rheological analyses

Anton Paar Physica MCR 500 Rheometer with the IMC patented from BASF AG is used for rheological analyses throughout this study. The details of the IMC cell is described in the previous section. A parallel plate sensor (PP-50) with 50 mm diameter is employed to all samples for immobilization tests. The temperature is kept constant at 25°C.

Willenbacher *et al.* (1999) defines immobilization measurement as “measuring the increase of viscosity during dewatering of a coating layer into a sheet of base paper”. The IMC connected to a rheometer allows applying specific shear stress and

pressure to the samples that are placed on filter paper. The pressure gradient is held at 80 kPa by using a vacuum pump that removes the water from the samples, thus increase the solid content. As a function of shear and normal forces, after a certain point the flow from the samples decreases and eventually stops. At this point the viscosity of the samples remains steady. This point is termed the *immobilization point*, after which the sample is immobilized and there is no further change observed in the viscosity. Thus the analysis is stopped at this point (Ayol, 2005).

Previous researchers (Ayol, 2005) indicated the significance of the type of filter paper and the initial gap distance in immobilization experiments. Twelve different kinds of filter paper were tried at the beginning of this study to identify the best base paper for the samples. Most of them did not give meaningful results, due to either very high or very slow filtration rates. The most meaningful and reproducible results were obtained by using Whatman glass fiber (GF) filters, in accordance with previous findings. The initial gap distances were also evaluated with preliminary tests. This value was varied depending on the rheological test type and sample type. To determine the maximum normal force, the initial F_N set to zero and the effect of gap distance on normal force was observed. For conditioned samples due to floc formation, the initial gap distance required to attain zero normal force was higher than for unconditioned samples. The initial sample volume can significantly change the immobilization time. The volume was chosen as 4 ml and the duration of experiments kept at 200 seconds throughout this study.

Two types of tests were applied to samples: in the first test, the normal force was increased linearly by lowering the plate and decreasing the measuring gap until the point where the structure of the sample broke down. The maximum normal forces that can be applied to samples were determined at various constant shear rates. In the second type of test, selected normal force values were determined between zero and the maximum applicable normal force, and constant normal force and constant shear rate were applied to the samples. These tests can be called constant shear rate (CSR) tests. In each test the increases in the viscosity of a material versus time were determined during filtration process. The constant shear rates were kept fairly low (0.1-10 1/s) in order to observe the immobilization point clearly.

A semi-logarithmic plot of time vs. viscosity curves show the typical shape of viscosity increases with a linear increase at short times and a stable viscosity value when the samples reached the immobilization time as detailed in Willenbacher *et al.* (1999). This maximum viscosity when a sample reaches the immobilized stage is termed the immobilization viscosity.

The solid content of samples during filtration was calculated from the gap distance based on a mass balance using the known initial solid content. There was a linear relationship between the initial volume and the gap distance at constant normal force. Hence as the gap distance decreased, the solids content of the sample increased.

5.3 RESULTS AND DISCUSSION

5.3.1 Determination of Maximum Normal Force

In order to investigate the effects of an applied normal and shear forces on the viscosity and solid content of samples, it was first necessary to determine the range of normal forces that could be probed. At a constant shear rate, a linear increase in normal force will cause the sample to consolidate. In the same way, at a fixed normal force there is a limit to the shear rate which can be applied without causing the particle network to collapse. Figure 5.2 displays an example of the results obtained for an anaerobically digested sludge conditioned with Zetag 7557; the increase of viscosity as a function of increasing F_N and decreasing gap distance. The applied normal force led to close packing of sample solids, corresponding to decreasing gap distance. As seen in Figure 5.2, the steady state viscosity was achieved at constant shear rate after certain normal force. It should be noted that the maximum viscosity achieved depends upon the strength of the network structure in the sample, as does the shear rate. The intuitive picture is that continuous shear disrupts the network structure. The maximum normal force is determined as the normal force value corresponds to maximum viscosity at constant gap distance in order to eliminate the effect of having various solid contents.

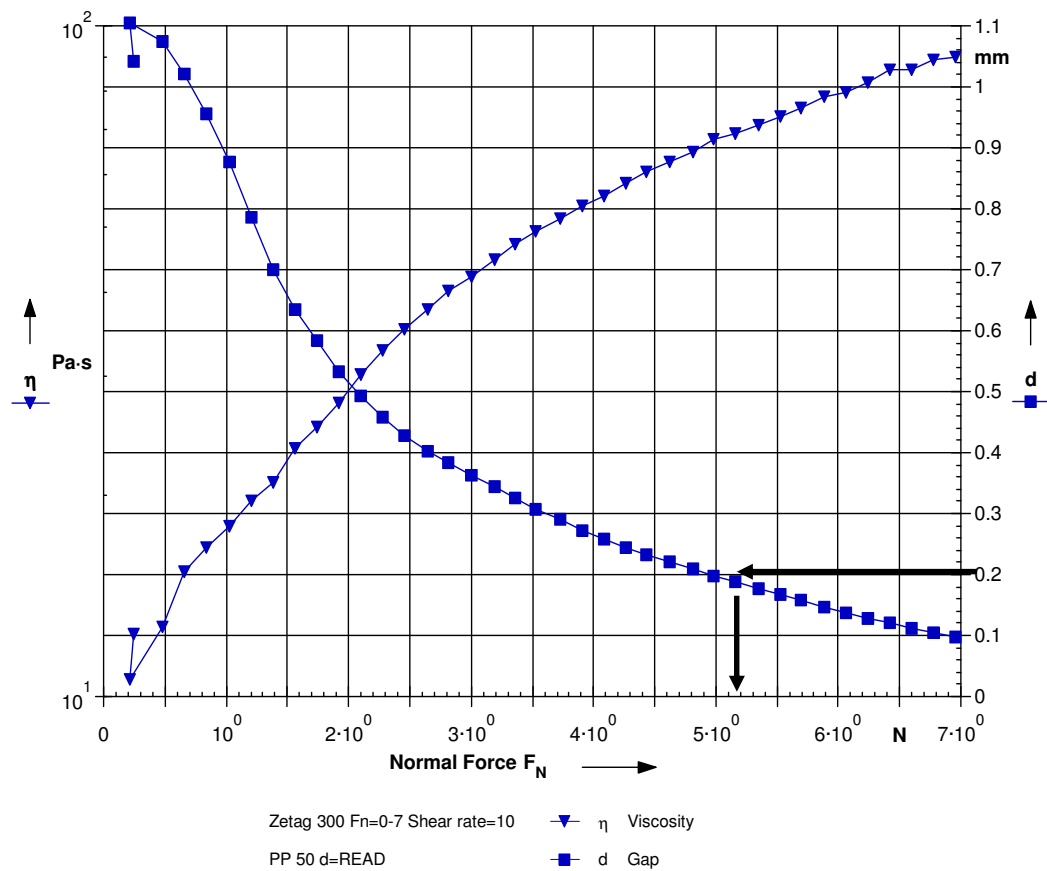


Figure 5.2 Determination of maximum normal force for digested sludge conditioned with 750 mg/L

In Figure 5.3 the effect of initial solid content on maximum normal force is given at different shear rates for digested sludge conditioned with Zetag 7557. Each point in Figure 5.3 represents normal force & shear force combinations above which the structure of sample will collapse. In all cases, the relationship between the maximum applicable normal force and the initial solid content of sludge is fairly linear: as the solid content increases, the maximum normal force that can be applied to

the sample increases at constant shear rate. Variation of shear rate from 0.1 1/s to 10 1/s reduces the amount of maximum normal force a sample can accept. The presence of shear alters the rate of bed collapse and probably the filtration rate due to the changes in the permeability of the bed.

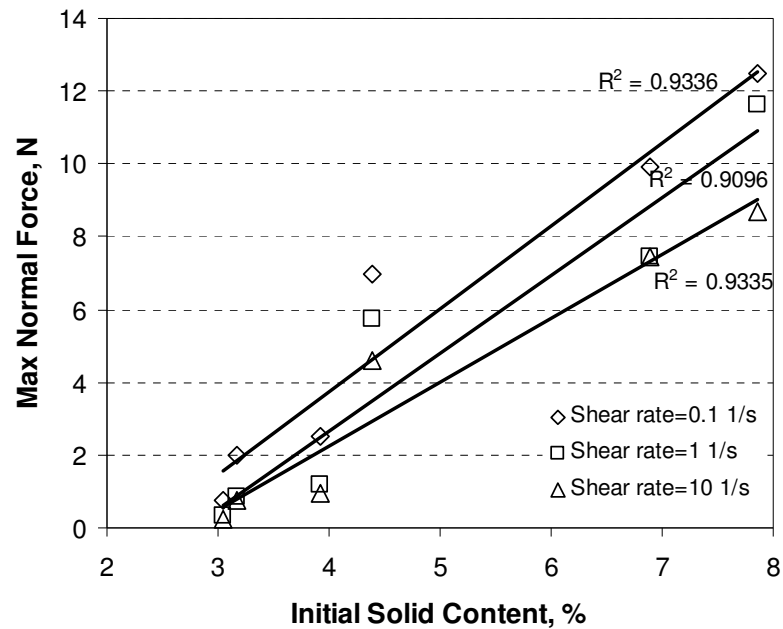


Figure 5.3 Maximum normal force that can be applied to a sample before it collapses as a function of shear rate and initial solid content for digested sludge conditioned with Zetag 7557

The corresponding viscosity values to maximum normal force are presented as a function of solid content and shear rate in Figure 5.4. Both Figure 5.2 and Figure 5.4 indicate the significant decrease in viscosity with increasing shear. However the dependence of viscosity on solid content remains uncertain for low shear rate (sample

at rest). As the shear rate increases the dependence between viscosity and solid content seems to be increased.

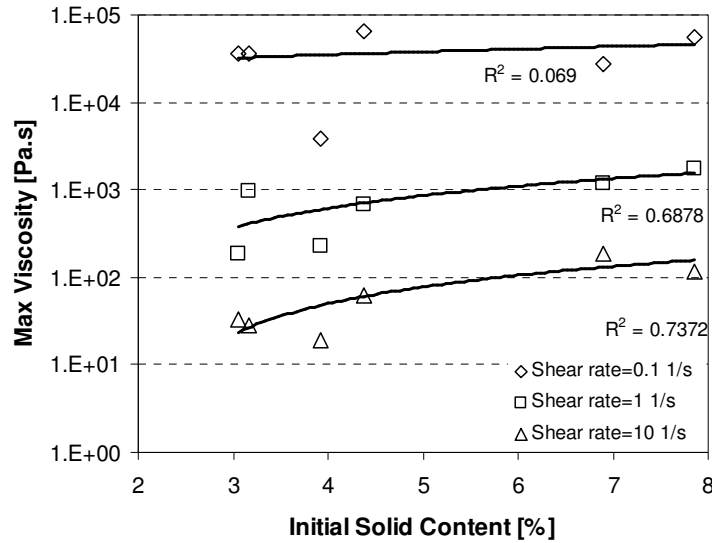


Figure 5.4 Maximum Viscosity as a function of shear rate and initial solid content for digested sludge conditioned with Zetag 7557

The same experiments were repeated for synthetic surrogate to determine the response of this substance to normal forces. Figure 5.5 depicts the change of applicable maximum normal force to synthetic sludge samples conditioned with Zetag 7557 as a function of solid content and shear rate. The relationship between solid content and the maximum applicable normal force was reasonably linear. Similar to digested sludge, the maximum normal force decreased with increasing shear rate.

Figure 5.6 demonstrates the increase of viscosity with increasing normal force and decreasing shear rate. Again at low shear rates, the linear correlation coefficient R^2

between solid content and the viscosity is lower relative to higher shear rates. When a flocculated sample is subjected to a shear, the load carrying structure within the sample network undergoes breaking and reformation.

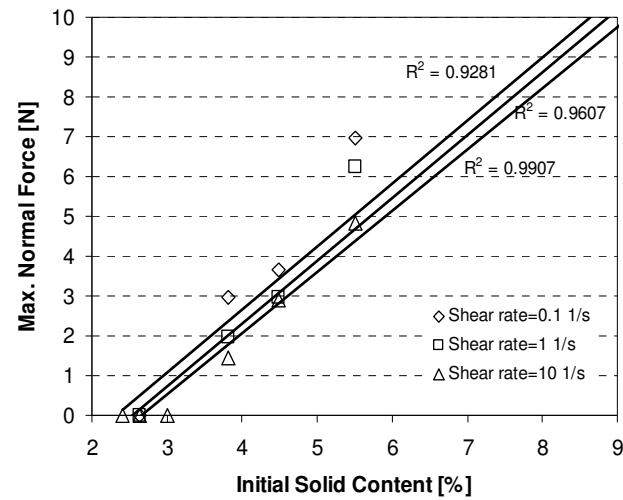


Figure 5.5 Maximum normal force that can be applied to a sample as a function of shear rate and initial solid content for synthetic sludge conditioned with Zetag 7557

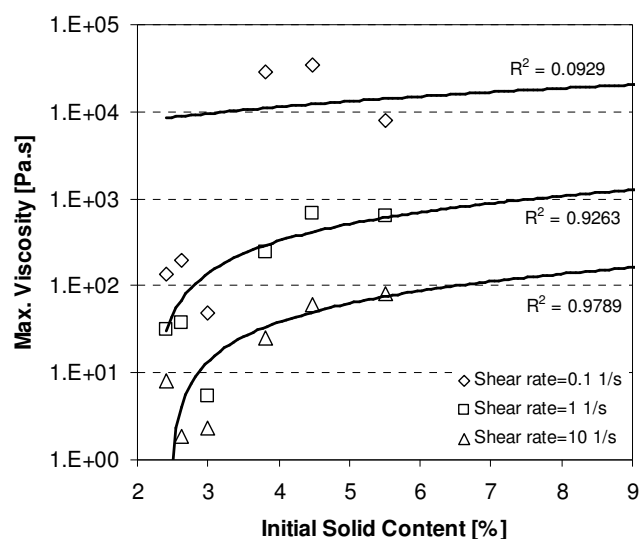


Figure 5.6 Maximum Viscosity as a function of shear rate and initial solid content for synthetic sludge conditioned with Zetag 7557

At low shear rates, the rate of structural rearrangement was greater than the rate at which load carrying structures were disrupted, thus the stress was passed through the particle network. As the shear rate increased, flocculated samples shear thinned and the stress transfer became dominated by viscous dissipation in the network. When normal forces were applied to a sample, the solid content of sample increases to a point where the sample is sufficient to support the applied force.

In order to investigate the effect of conditioning agent on the maximum applicable normal force, synthetic sludge was conditioned with an inorganic conditioner (FeCl_3). The results of maximum normal force as a function of shear rate and the solid content are given in Figure 5.7. Although the maximum normal force

significantly increased with increasing solid content, shearing did not alter the normal force. This indicates that after conditioning with FeCl_3 , the particulate fraction becomes dominant and carries the entire load. In Figure 5.8, the shear thinning behavior of the conditioned sample is shown. When sufficiently sheared, the particle network is degraded. This transition corresponds to a change in the stress transfer mechanism from energy dissipation due to structural rearrangements within the particle network to predominately viscous dissipation by the continuous phase. Hence the flow is enhanced in the immobilization cell.

The first part of this study defined the limits of shear and normal forces that could be applied in subsequent experiments without the collapse of samples' structure. As shown in Figures 5.3, 5.5 and 5.7, the maximum normal force applicable to a sample is a function of shear rate and solid content of the sample. From this point of view, compressive yield stress defined by Buscall *et al.* (1987) and maximum normal force shows strong resemblance.

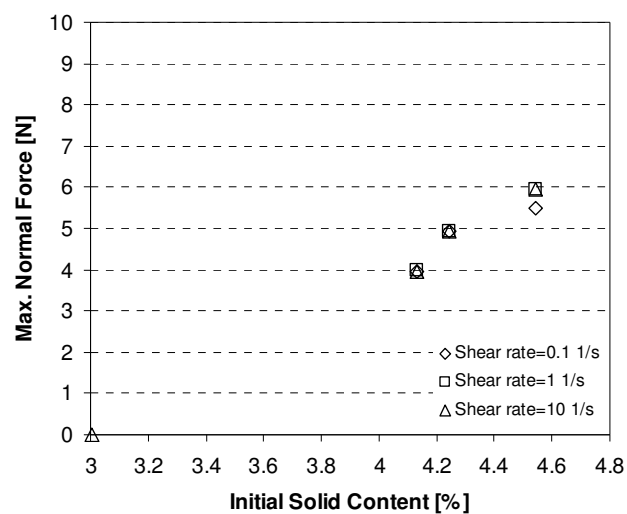


Figure 5.7 Maximum normal force as a function of shear rate and initial solid content for synthetic sludge conditioned with FeCl_3

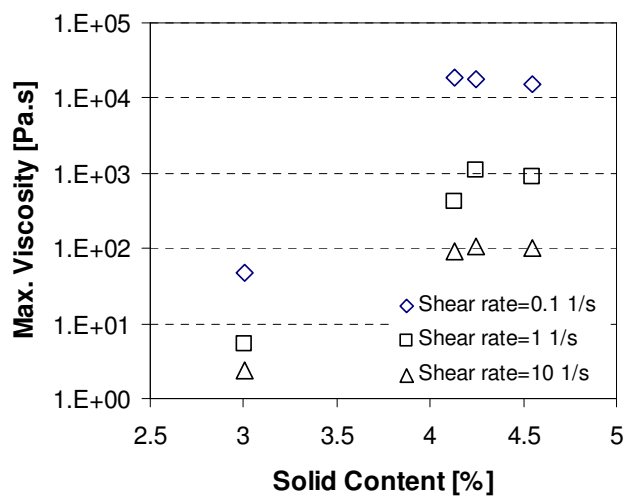


Figure 5.8 Maximum viscosity as a function of shear rate and initial solid content for synthetic sludge conditioned with FeCl_3

5.3.2 Effects of Normal and Shear Forces on Viscosity and Solid Content

After determining the range of normal forces at different shear rates, fixed shear rate and normal force were applied to samples and the change of viscosity and the gap distance as a function of time were monitored. The immobilization viscosity values were extracted from these plots and the solid content at the time when sample was immobilized was calculated based upon the gap distance. Immobilization viscosity values for anaerobically digested sludge conditioned with optimum doses (determined by preliminary jar tests) of Zetag 7557 are presented in Figure 5.9. The surface of this Figure represents a combination of shear rate and normal force when the sample is immobilized. It is evident that the viscosity increases with increasing amount of normal force and decreases with increasing shear rate. Using the IMC allows simulation of the change of flow properties in dewatering since it enables observation of the flow properties under normal forces & shear forces during filtration.

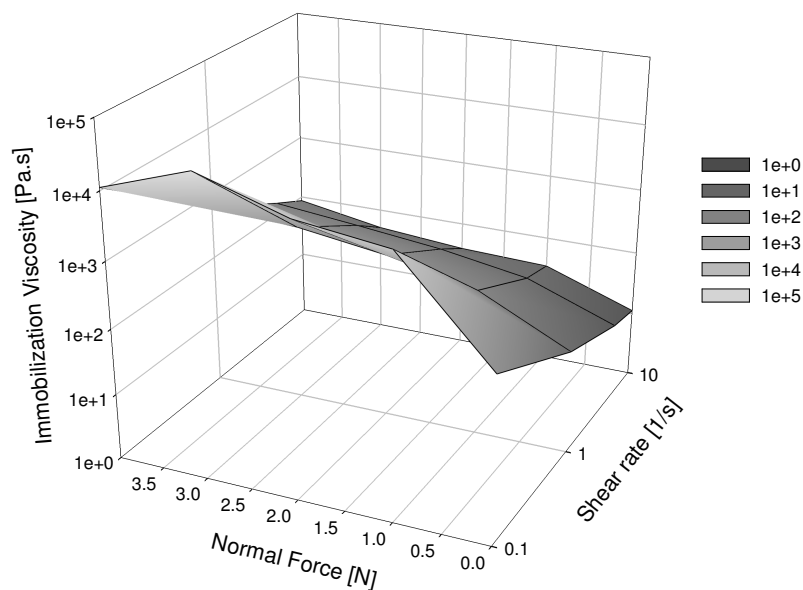


Figure 5.9 Immobilization viscosities as a function of shear and normal forces for digested sludge conditioned with optimum dose of Zetag 7557

Figure 5.10 shows calculated final solid content values when the sample was immobilized. The highest solid contents were achieved at higher normal forces when the shear rate was low. Conversely one might expect to have a higher solid content at high shear, due to higher filtration rate. However, the disruption of the network structure with high shear is more influential than the filtration for this sample. According to these results, in order to obtain a drier cake, application of normal force is more effective, because increasing the shear rate leads to disintegration of the sample and thus results in lower final solids.

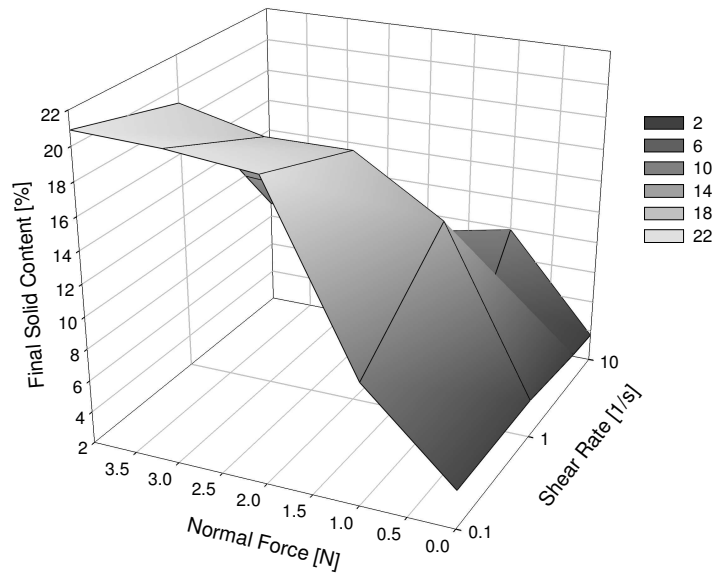


Figure 5.10 Final solid content of digested sludge samples conditioned with Zetag 7557 (optimum dose) as a function of shear and normal forces

Figure 5.11 displays the effects of normal and shear forces on the immobilization viscosity of digested sludge conditioned with a high dose of Zetag 7557. Based on results varying the amount of added polymer, this 500 mg/L addition is clearly definable as an overdose. The Figure is similar to Figure 5.9, with immobilization viscosities increasing as the applied normal force increases and the shear rate decreases. The viscosity values for overdosed sample were slightly higher than those obtained using the optimum polymer dose. But it was also noted that the amount of Normal Force (0 to 6 N) applied to that sample exceeded the amount applied with the optimum dose (0 to 3.5 N). If the viscosity values are compared for the same normal and shear forces, it can be seen that the immobilization viscosity

values are lower in overdose than optimum dose, which is parallel to the findings of previous researchers (Abu-Orf and Dentel, 1999).

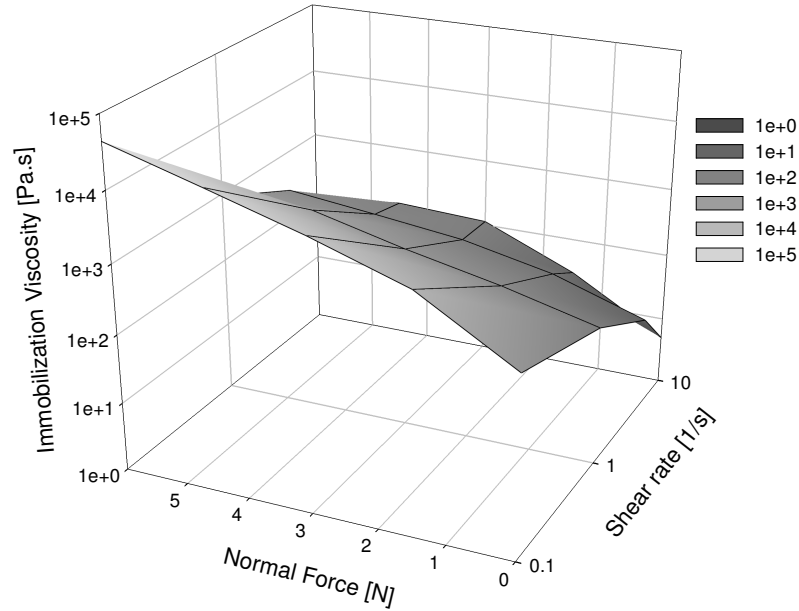


Figure 5.11 Immobilization viscosities as a function of shear and normal forces for digested sludge conditioned with Zetag 7557 (overdose)

Figure 5.12 shows the final solid content of digested sludge samples conditioned with 500 mg/L Zetag 7557. Although viscosity plots of digested sludge samples conditioned with different doses of conditioner look similar, this is not the case for final solid graphs. Figures 5.10 and 5.12 differ notably. The drier cakes were achieved at higher shear rates since excess polymer is consumed by the available sites inside the network structure of samples. In this case, shearing effects are more pronounced relative to optimum polymer dose.

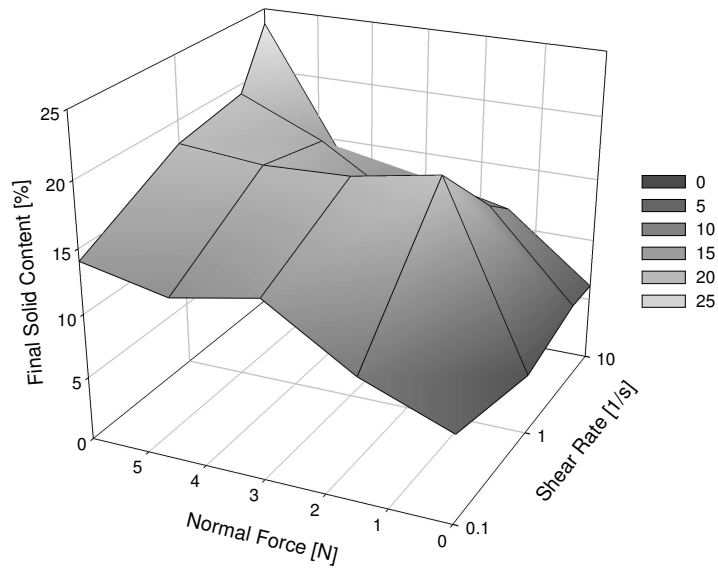


Figure 5.12 Final solid content of digested sludge samples conditioned with Zetag 7557 (overdose) as a function of shear and normal forces

In order to compare the response of sampled sludge with synthetic surrogate, the same experiments were carried out by using a synthetic surrogate conditioned with Zetag 7557. Figure 5.13 exemplifies the immobilization viscosity results obtained at the optimum polymer dose. The higher immobilization viscosities were observed at low shear rates and high normal forces which was in agreement with the results found for digested sludge—although the values for immobilization viscosity were lower than the digested sludge. Since the solid content of samples was the same, this difference stems from the network structures of the samples. Required normal force to immobilize digested sludge was found higher indicating the stronger structure of digested sludge compared to synthetic sludge.

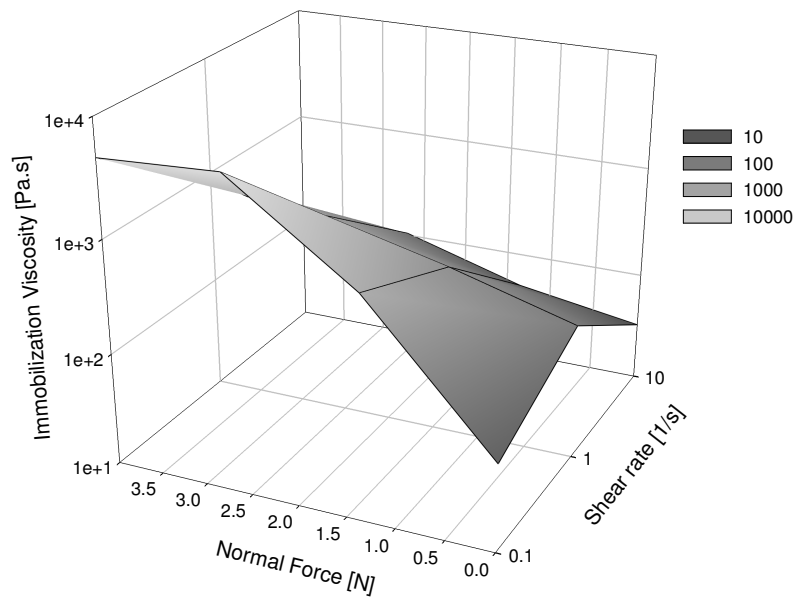


Figure 5.13 Immobilization viscosities as a function of shear and normal forces for synthetic sludge conditioned with Zetag 7557 (optimum dose)

As a result of the weaker structure of synthetic sludge, the amount of water released from the sample under shear and normal forces were relatively high. Using the optimum Zetag 7557 dose, low shear rate and high normal force led to a final solid content of over 40% (Figure 5.14). The viscosity pattern seen in Figure 5.14 is similar to that in Figure 5.10, demonstrating the similarity of digested sludge and synthetic surrogate in terms of their response to shear and normal forces. These results can be associated at least qualitatively by assuming that the water is pushed from the samples mainly by normal forces when applying the optimum polymer dose.

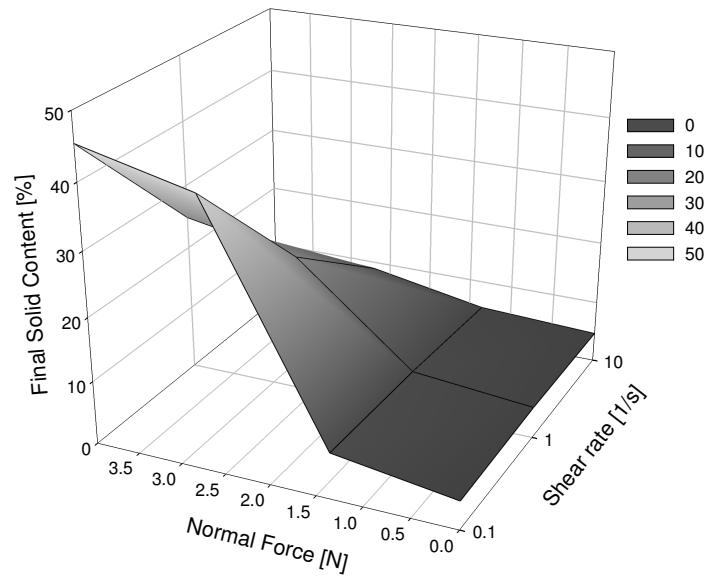


Figure 5.14 Final solid content of synthetic sludge samples conditioned Zetag 7557 (optimum dose) as a function of shear and normal forces

When a higher dose of polymer (over dose) was introduced into the synthetic surrogate, the maximum normal force that could be applied to this sample increased from 4N to 8N. The immobilization viscosities showed the same pattern as with digested sludge using the same amount of polymer (Figure 5.15). Regardless to the type of sample type and the amount of polymer added, immobilization viscosity vs. shear rate and normal force graphs reveal the influence of these two forces on flow properties during dewatering. Application of normal forces leads to higher viscosity values whereas shearing causes a thinning effect, probably due to disruption of the sample's network structure.

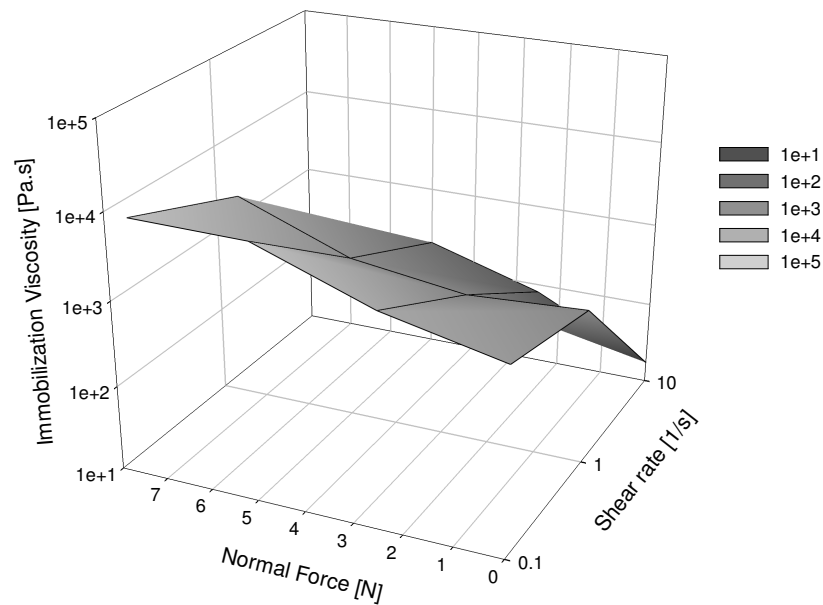


Figure 5.15 Immobilization viscosities as a function of shear and normal forces for synthetic sludge conditioned with Zetag 7557 (overdose)

The final solid content of synthetic surrogate conditioned with optimum and overdose amounts of polymer differed notably (Figure 5.14 and 5.16). As is evident from Figure 5.16, the highest amounts of solids were attained at higher shear rates, consistent with results for digested sludge. With overdose conditioning, the final solid contents were considerably less than those obtained at the optimum polymer dose. This finding is in accordance with the usual results of conventional filtration tests (capillary suction time and/or specific resistance to filtration) showing less satisfactory filtration when polymer is overdosed. It is also notable that digested sludge and

synthetic slurry showed similar responses to shear and normal forces, validating the use of these methods in characterizing mechanisms of dewatering.

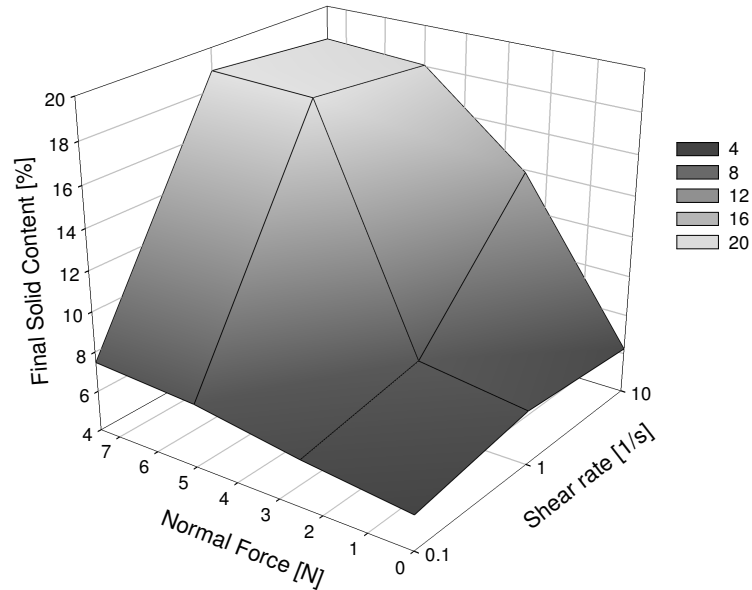


Figure 5.16 Final solid content of synthetic sludge samples conditioned with Zetag 7557 (overdose) as a function of shear and normal forces

An inorganic additive, FeCl_3 , was also used for conditioning of synthetic surrogate due to its different conditioning mechanism. As explained in the previous chapter, conditioning with FeCl_3 promotes complexation and precipitation, thus disrupting a sample's network structure. Hence the conditioned sample loses its gel-like properties. However, the rigidity of the sample still increases due to increasing solid content resulting from precipitation of ferric hydroxide species. Figure 5.17 displays the immobilization viscosity results for synthetic sludge conditioned with 500

mg/L FeCl_3 . The graph resembles previous graphs given for polymer conditioned samples (Figures 5.9, 5.11, 5.13, 5.15). This is because the solid content of the sample is strictly related to the immobilization viscosity.

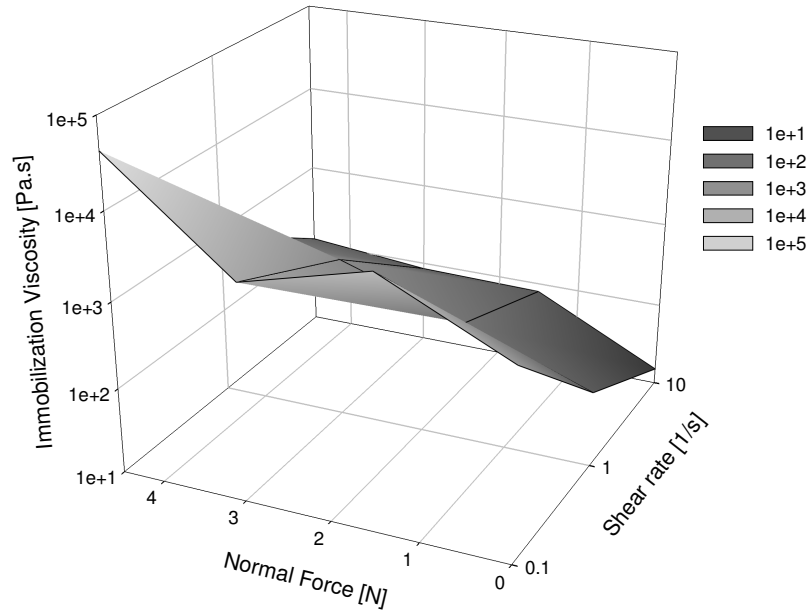


Figure 5.17 Immobilization viscosities as a function of shear and normal forces for synthetic sludge conditioned with FeCl_3

Figure 5.18 presents the solid content values of synthetic surrogate conditioned with FeCl_3 . For these samples, the combined effects of normal and shear forces do not seem to be pronounced since the differences in final solid content were fairly low, especially for shearing effects. Channell (1999) demonstrated that the characteristic shear rate is not a function of volume fraction but, rather, the strength of the interparticle bonds. Thus the strength of interparticle bonds may not be altered by

shear. These expectations are satisfied in Figure 5.18 where shear did not change the network strength and water release.

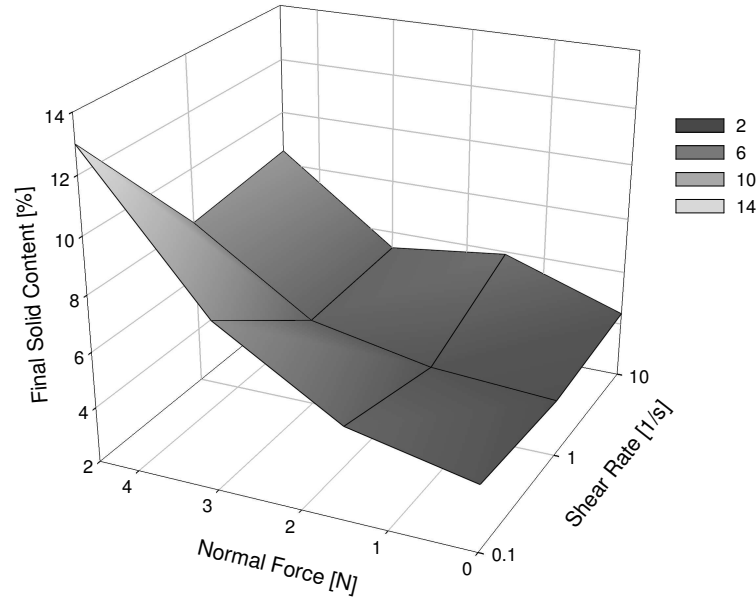


Figure 5.18 Final solid content of synthetic sludge samples conditioned with 500 mg/L FeCl_3 as a function of shear and normal forces

5.4 CONCLUSIONS

This study elucidates the limits of shear and normal forces that can be applied to both digested sludge and synthetic surrogate before the collapse of the samples' structure. The maximum normal force increases approximately linearly with the increasing solid content. However, as the shear rate is increased, there is a decrease in the maximum normal force due to the rearrangement in the sample's structure.

An applied normal force and shear rate during filtration alters the viscosity. It has been shown that sample viscosity elevates with normal force and decreases with shear rate. Application of normal force pushes the water through the filter paper and causes a more compact solid arrangement. Shearing also disrupts the structure of samples, leading to shear thinning behavior. These phenomena have been demonstrated for both digested and synthetic sludges, conditioned with different conditioner types and doses.

The final solid content of samples differed notably with normal and shear forces, although the trends could not be generalized. Depending on the type and the dose of conditioner, the rate of water release and the final solid content changed. When the same type of conditioner and dose were applied, the responses of synthetic surrogate and digested sludges were found parallel to each other.

The dewatering of biosolids is a complex phenomenon governed by the solid content, strength of the network structure, conditioning types and doses. The IMC can successfully be employed to define the dewaterability mechanisms of substances after careful preliminary tests to determine the initial parameters such as the base paper, sample volume, and initial gap distance. The results show that the IMC combined with rheological analyses provide a new insight into the understanding of dewatering mechanisms by applying both shear and normal forces.

ACKNOWLEDGMENTS

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Chapter 6

CHARACTERIZATION OF EXTRACELLULAR POLYMERIC SUBSTANCES IN BIOSOLIDS BY COMBINED ENZYME HYDROLYSIS AND SIZE EXCLUSION CHROMATOGRAPHY-INFRARED MICROSCOPY

Abstract

Previous research has established practical advantages to the enzymatic treatment of sludges, evidently through degradation of extracellular polymeric substances (EPS). In this study, EPS was characterized before and after enzyme treatment using size exclusion chromatography (SEC) coupled with infrared microscopy (μ FTIR). The EPS chromatograms were significantly altered using three different enzyme types, with an incubation time of 16h sufficient for most chromatogram trends. Application of either a commercial enzyme mix or an amylase/cellulase combination (to degrade polysaccharides) led to disappearance of molecular weight fractions above 0.5kDa. However protease application changed the chromatographic profile unexpectedly, forming very high molecular weight fractions (>4000 kDa). μ FTIR indicated that these large molecules result from mineral phase association with lower molecular weight organic molecules. Based on the chemical identification of EPS, it is apparent that specific enzymes degraded their target compounds. Although the effect of enzyme

treatment was observable using conventional sludge characterization methods, the SEC- μ FTIR method provided more specific information on chemical mechanisms responsible for enzyme effects.

6.1 INTRODUCTION

Wastewater sludges are complex aggregates consisting of microorganisms embedded in a polymeric network of extracellular polymeric substance (EPS) (Frolund *et al.*, 1996). The EPS consists of negatively charged macromolecules that provide cohesion and gel-like behavior to the floc structure (Keiding *et al.*, 2001; Wilen *et al.*, 2003a). Legrand *et al.* (1998) supported the gel analogy with comparative experiments, and Poxon (1996) presented scanning electron micrographs showing an extensive gel-like biocolloidal structure in digested sludge.

There are several problems observed in biosolids behavior stemming from EPS. First and perhaps foremost is that the gel structure of EPS leads to fairly tenacious retention of water within the sludge. Even with chemical conditioning using either inorganic cations or polymeric cationic flocculants, the flocculated EPS retains a significant volume of water within its gel-like matrix. This limits the solids concentrations that can be achieved in dewatering, with adverse effects on transportation, landfilling, and incineration costs.

A related problem is that the EPS apparently leads to significant increases in the amount of chemical conditioner that is required (Novak *et al.*, 2003). Conditioner

costs can be a significant component of overall operation and management costs in wastewater treatment. There are some other concerns with EPS's ability to increase viscosity and thus lead to higher pumping costs. Furthermore, the interaction of EPS and conditioning polymers might facilitate accumulation of organic chemicals and heavy metals within sludge.

EPS is composed of a variety of organic fractions (Frolund *et al.*, 1996). Early studies primarily examined the role of carbohydrates in EPS, but proteins have also been identified as significant (Wilen *et al.*, 2003b). Humic compounds, uronic acids, DNA (Wilen *et al.*, 2003b), and lipids (Goodwin and Forster, 1985) have also been characterized in EPS, though this information is inconsistent (Liu and Fang, 2002), perhaps due to different sludge sources and extraction methods.

Starting in the 1980's, researchers have investigated the use of enzymes to modify sludge properties. Forster (1983) showed an alteration in viscosity of both activated and digested sludges with various enzyme additions. Thomas *et al.* (1993) were apparently the first to report enzyme application for sludge pretreatment, using a mixed hydrolytic enzyme product including carbohydrase, proteinase and lipase to improve dewaterability in lab tests and in a full-scale belt press.

More recently, Zhou (2002) obtained a 13% improvement in the dewaterability of thermophilic biosolids in terms of capillary suction time (CST) by treating its liquid content with protease. This suggests that (a) different types of biosolids are treatable

using enzymes, and (b) both proteases and mixed enzyme products can be effective. Recent patents also suggest this idea (Sarkar, 2004).

Studies carried out in University of Delaware laboratories have confirmed the above findings and demonstrated more dramatic effects as well. The use of a commercially available enzyme formulation that contains protease, lipidase, and other hydrolytic enzymes gave significant improvements in final cake solid content (Ayol, 2005b; Dursun *et al.*, 2006a; Dursun *et al.*, 2006b). Analyses also showed that the enzyme formulation significantly decreased EPS levels. Results with samples from different treatment plants showed very similar trends, indicating the reproducibility of results (Ayol, 2005b).

Since the commercial product used has several enzymatic constituents, it should also be possible to improve the product formulation by identifying, and using, only the effective constituents. Also, “EPS” is a broad, vague, and operational definition only, so experiments with specific enzyme types should give a better idea of what chemical structures within “EPS” actually contribute to water retention and poor dewaterability. It is also conceivable that different enzymes will prove more effective on different biosolids, simply due to their different compositions. Thus, the use of specific enzymes provides this fundamental insight as well as leading to practical applications.

Previously Dursun and Dentel (2006) used specific types of enzymes: a protease, a lipase, and a carbohydrase mixture. The extensive results indicated that

none of these separate enzymes appear to be as effective as the combined formulation, so there is still work to be done in identifying the “active ingredient” or specific interactions necessary to optimize enzyme usage. Nonetheless, the enzyme treatment clearly succeeds in altering the EPS structure (Dursun and Dentel, 2006). However, this is still an overly broad conclusion when the enzyme-treated EPS has only been characterized using broad analytical methods.

A more incisive analytical approach for the characterization of activated sludge exopolymers has been developed by Gorner *et al.* (2003), combining size exclusion chromatography (SEC) with Fourier transform infrared micro-spectroscopy (μ FTIR). This analytical technique enables separation of the complex EPS mixture according to their macromolecular size and to provide information on the main EPS components' chemical nature by spectroscopic identification. In a more recent study, the same analytical method was used to determine the EPS chromatographic fingerprints of sludge from various origins (Garnier *et al.*, 2005). The results pointed out the validity of this method under different circumstances and the differences of the chromatographic fingerprints sampled from various treatment plants.

Enzyme treatment has been shown to be effective in the alteration of EPS components. Separation and identification of EPS with combined size exclusion chromatography and infrared microscopy has also been proven to be a successful method in showing differences between EPS from different plants. These methods were therefore combined to better characterize enzyme effects and the EPS properties

that govern dewaterability. Specific objectives were: (i) to characterize the extracellular polymeric substances originated from digested sludge by using SEC- μ FTIR; (ii) to identify the effect of enzyme treatment (both a commercial enzyme mixture and various specific enzymes) on extracellular polymeric substances; and (iii) to relate the components of polymeric substances to physicochemical properties of samples.

6.2 MATERIALS AND METHODS

6.2.1 Sludge Type and Collection

Digested sludge samples were collected from Maxeville wastewater treatment plant in Nancy, France. This plant has a capacity of 480000 population equivalents (the population of the greater Nancy area). The removal efficiency of the treatment plant is 91.5% for organic pollutants and around 50% for nitrogen. Biosolids originated from conventional activated sludge process are subjected to anaerobic digestion operated at 37⁰C with a 21 day retention time prior to mechanical dewatering. Biosolid samples were taken from anaerobic digesters and transferred to the nearby LEM (Laboratoire environnement et minéralurgie), where all experiments were completed within one week.

6.2.2 Physical-chemical Characterization

All samples were characterized for pH, conductivity, total solids (TS), volatile solids (VS) and specific resistance to filtration (SRF) according to Standard Methods (American Public Health Association, 1995). The pH was measured using a Tacussel Electronic PHM20 pH-meter. Conductivity was measured using an 810 Tacussel Electronic conductimeter.

To determine the SRF, a pressure filtration apparatus was fabricated with a support system, a metal cell holding up to 50 ml of sample, and a plastic beaker to hold the filtrate (Figure 6.1). A pressure of 1 bar was applied to the filtration cell using nitrogen gas. A punched metal frame with 3.5 cm diameter was placed inside the filter cell and a filter paper on top of this cell (Prolabo 08 314 716) was used to hold the solids. A 30 ml sample volume was poured into the filtration cell and the amount of filtrate was measured for one hour using an analytical balance. The results were recorded automatically to a computer. The SRF was calculated by using the slope of the filtration plot (volume of filtrate vs time/volume). Details about the method can be found in Christensen and Dick (1985).

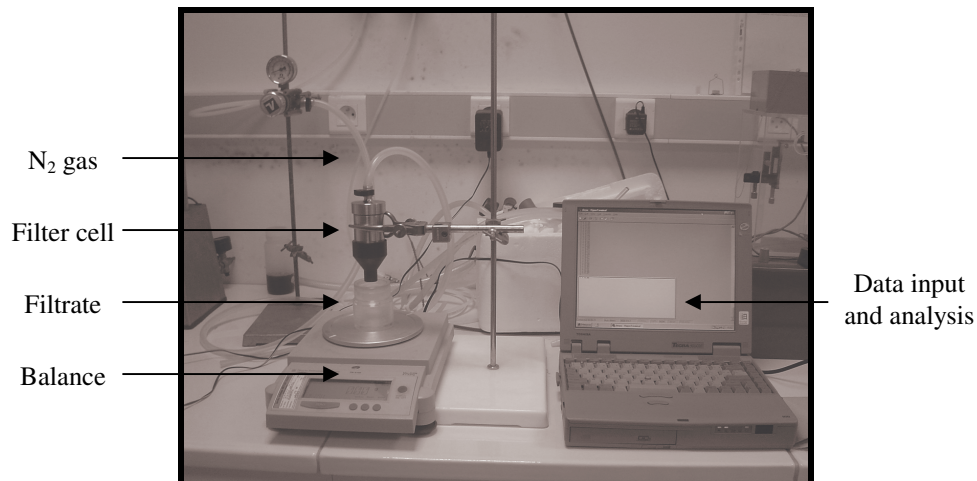


Figure 6.1 Filtration unit to determine SRF

6.2.3 Enzyme Treatment

A commercial multienzyme powder (Envirozyme 216, Winston Company, Tulsa, USA) containing protease, lipase, α -amylase, *Aspergillus oryzae*, and anaerobic bacteria was selected for the experimental studies. It was used at concentrations of 5, 15, and 25 mg/L. A protease and a combination of polysaccharide degrading enzymes were also used as treatments. The chosen protease (Sigma P6110-EC3.4.11.1) is a leucyl aminopeptidase from *Aspergillus oryzae* that can hydrolyze peptide bonds under the environmental conditions of anaerobic digesters. It was used at concentrations of 5, 15, and 25 mg/L. Another enzyme mixture, intended to degrade the various polysaccharides in sludge, combined α -amylase (2%) and cellulase (2%), to cleave α - and β -glucoside polysaccharide links, respectively. Amylase is a digestive enzyme, classified as a saccharidase, which hydrolyses long-chain carbohydrates (such

as starch) into smaller units. Cellulase is an enzyme complex which breaks down cellulose to β -glucose. This mixture was added to digested sludge in ratios of 1/100 (400 mg/l), 1/150 (300 mg/l), and 1/200 (200 mg/l) respectively.

Enzymes were prepared as a stock solution then added to digested sludge samples to give three different enzyme concentrations. Enzyme solution was mixed with biosolids for half an hour at medium speed. All samples were incubated at 40°C closed to atmosphere with their original head gas. No stirring or other agitation was used during incubation period. Incubation times were increased from 0 to 88 hours. Following the incubation period, the samples were analyzed as soon as possible (generally within an hour) since the enzymes were still active at room temperature.

6.2.4 EPS Extraction

The extraction procedure used in this study was based on the method of Frolund *et al.* (1996). This method has been widely used for EPS extraction from sludge, since it gives high extraction efficiency with little or no cell lysis or polymer disruption (Wilén *et al.*, 2003a). The EPS were extracted from the activated sludge by mixing with a cation exchange resin (Dowex, Aldrich-Fluka 44445) under turbulent shear. Digested sludge was mixed with Dowex (75 g/g VSS), previously washed in a buffer solution, and transferred to an extraction vessel. The suspension was stirred at 900 rpm for 4h. The extracted EPS was harvested by centrifugation at 12,000g for 2 x 15 min and filtered through a 0.22 μ m filter (Milipore) before size exclusion

chromatography. The extracted EPS was stored at -20°C. Carbohydrate measurements were determined as the equivalent glucose concentration, using Dubois' method with phenol-sulfuric acid (Dubois *et al.*, 1956). Protein was measured as bovine albumin equivalent using a protein assay kit Sigma P 5656 that is based on Lowry *et al.* (1951).

6.2.5 Size Exclusion Chromatography and Fourier Transform Infrared Micro Spectroscopy (SEC-μFTIR)

The method was used by Garnier *et al.* (2005) for characterization of EPS sampled from different wastewater treatment plants.

6.2.5.1 Chromatography (SEC)

Experiments were carried out with a Hewlett Packard 1100 Series chromatograph, equipped with a Zorbax Bio Series column (GF-250, 25 cm x 9.4 mm Agilent Technologies, France) thermostated at 25°C. The mobile phase was a solution of 0.005 M NaCl plus 0.005 M NaNO₃, with a pH of 7.3, ionic strength of 0.01 N, and flow rate of 1.0 ml/min.

The column was calibrated with proteins and polysaccharides. Five protein standards purchased from Sigma Aldrich, bovine r-nase, chicken albumin, bovine serum albumin, α-amylase, and thyroglobulin (molecular weights 13700, 45000, 67000, 200000 and 670000 Da respectively) were injected. Furthermore, in order to create a calibration curve, the polysaccharide standards (180, 738, 5900, 11800,

22800, 47300, 112000, 212000, 404000 and 788000 Da.) were also injected. Two different kinds of detector, diode array UV detector and refractive index detector (Agilent 1100 Series) were used at 25°C. Several wavelengths (210, 260 and 280 nm) were systematically followed and the chromatograms at 280 nm are presented in this work. All samples were filtered with 0.22 μm filters (Millipore) prior to injection (100 μL).

6.2.5.2 Infrared Microspectroscopy (μFTIR)

The chromatographic fractions corresponding to the peaks obtained in HPLC chromatograms were used for infrared microscopy. One drop of each chromatographic fraction separated was placed on a CaF_2 slide and dried at ambient temperature and crystallites of EPS thus obtained. Spectral analysis was performed with an IRScope I, Bruker A590 device connected to a FT-IR spectrometer (Bruker IFS55). All measurements were made in transmission mode in the $4000\text{-}600\text{ cm}^{-1}$ range (200 point scans, resolution $\pm 2\text{ cm}^{-1}$). The obtained crystalloids were observed by optical microscopy and analyzed in the mid IR range ($4000\text{-}600\text{ cm}^{-1}$). The aperture of the IRScope was adjusted to the size of the chosen crystalloids (8 to 60 μm). Results were evaluated with OPUS software. The biomolecules were identified from the specific IR profiles of -N-C=O ($1690\text{-}1500\text{ cm}^{-1}$) and -C-O- ($1300\text{-}1000\text{ cm}^{-1}$) valence vibrations. This micron scale specific analysis allows considerable sensitivity in chemical identification of EPS constituents.

6.2.6 Resin Embedding

The method developed by Deneux-Mustin *et al.* (1997) was used with minor modification to perceive the structural changes with enzyme treatment. Control and enzyme-treated samples were fixed with 2.5 ml of 2.5% glutaraldehyde for 24h and then with 2% osmium tetroxide for 1h in order to preserve the samples in their original state. The samples were dehydrated with series of acetone additions then transferred to mixtures of acetone-Epon 812 (Josdelville Technology) of increasing resin content and then polymerized in moulds at 60 for 12h.

6.3 RESULTS AND DISCUSSION

6.3.1 Effect of Enzyme Treatment on Molecular Weight Distributions

6.3.1.1 Commercial enzyme mixture

Changes in molecular weight due to the treatment were determined by size exclusion chromatography, with reproducibility tested vigilantly for each sample. We applied 3 different concentrations of the enzyme preparation, followed by 88 total hours of incubation. The same extraction time and method were used for other types of enzyme used. EPS extracted from raw digested sludge (incubated without enzymes), which was used as a control, exhibited no significant difference in its chromatogram over the 88-h incubation time (Figure 6.2). The peak values (retention times) of samples were almost the same with a slight increase in intensity with increasing

incubation time. The retention times of 11.6, 12.3, 13.7 and 15.1 min correspond to 7, 2.5, 0.4 and 0.05 kDa respectively based on the calibration curve of proteins.

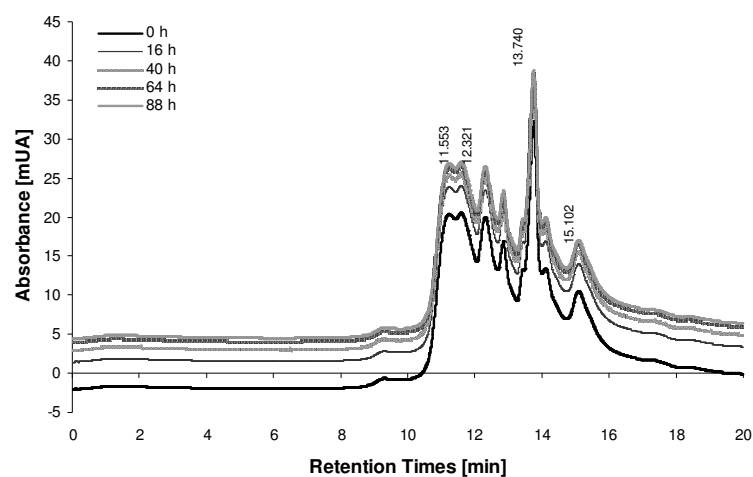


Figure 6.2 Effect of incubation time on EPS chromatograms

Figure 6.3 depicts the alteration of chromatograms with Envirozyme 216[®] treatment at four different incubation times (16, 40, 64, 88 h). As with the control, the effect of incubation was minor for samples without enzyme addition. All chromatograms at time 0 were found to be identical to the control sample given in Figure 6.2, thus Figure 6.3 excludes 0 hours of incubation. Figure 6.3 also points out that incubations exceeding 16 hours resulted in minimal additional degradation at any enzyme concentration. Table 6.1 summarizes results after 16 hr incubation, which is similar to those at longer times.

Compared to the control (without enzyme), Envirozyme 216[®] addition caused significant changes in the chromatograms (Figure 6.3). Increasing Envirozyme 216[®] concentrations led to fewer chromatogram peaks, and at longer retention times. At 5 mg/l, Envirozyme 216[®] decreased the molecular weight of all four EPS fractions, and at higher concentrations, only 2 main peaks remained, with longer retention times indicating significant decreases in molecular weight. With the 25 mg/l Envirozyme 216[®] treatment, the molecular weight was decreased from the raw EPS fractions at 7 and 2.5 kDa (Table 6.1) to only 0.3-0.1 kDa. Thus, the commercial enzyme mixture led to a lower molecular weight distribution.

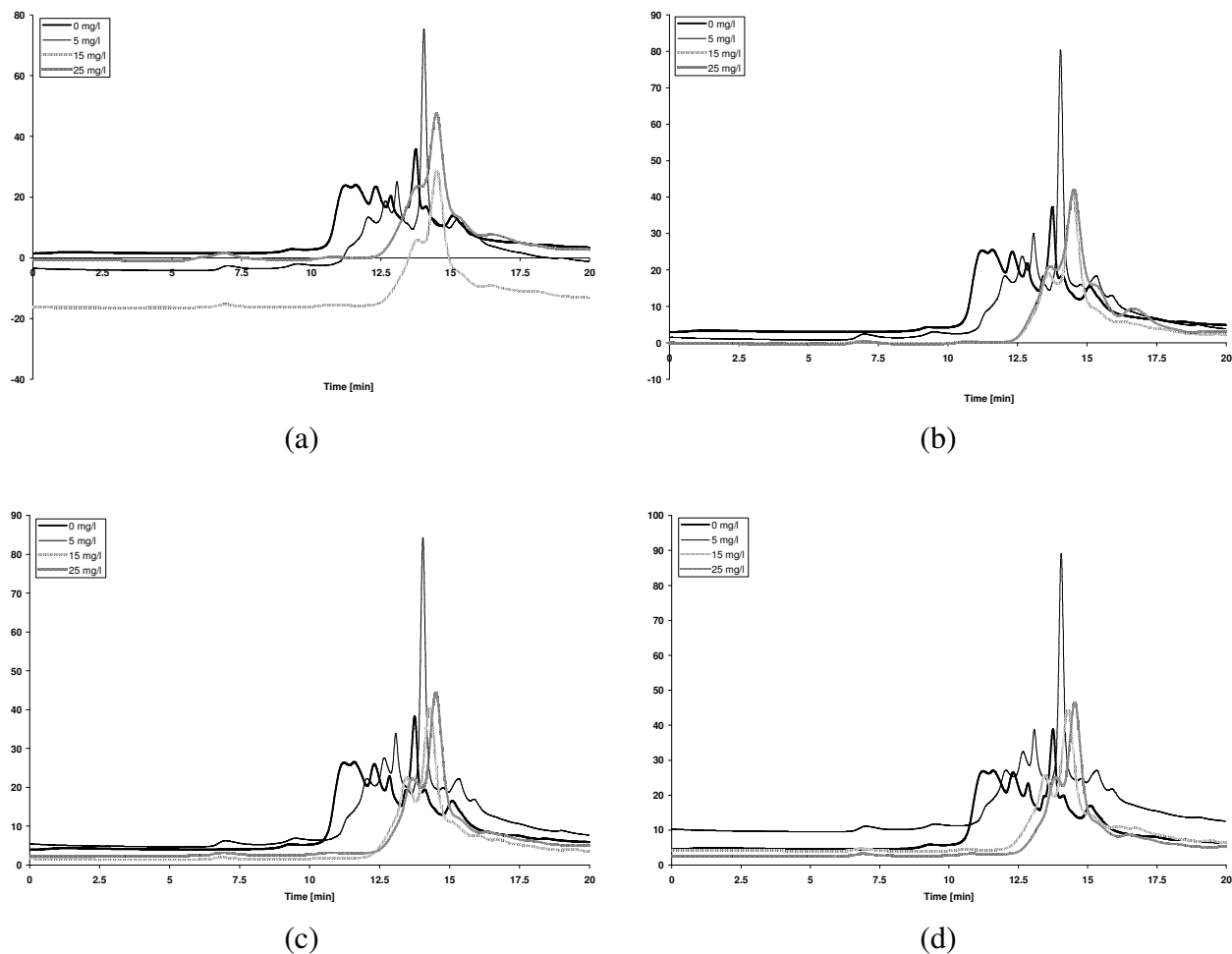


Figure 6.3 EPS chromatograms obtained from samples incubated with Envirozyme 216[®] for (a)16h (b)40h (c)64h (d)88h at different concentrations

Table 6.1 Effect of Envirozyme 216[®] on molecular weight distribution (after 16 h of incubation)

Enzyme Type	Enzyme Concentration [mg/l]	Retention times [min]	Molecular weight [kDa]
Control (No enzyme)	0	11.5, 12.3, 13.7, 15.1	7, 2.5, 0.4, 0.05
Envirozyme 216	5	12.7, 13.1, 14.1, 15.3	1.4, 0.8, 0.2, 0.04
Envirozyme 216	15	13.5, 14.4	0.5, 0.2
Envirozyme 216	25	13.9, 14.5	0.3, 0.1

6.3.1.2 Polysaccharide degrading enzymes

Polysaccharides represent a major component of EPS. In order to selectively degrade this fraction, an enzyme mixture including α -amylase (2%) and cellulase (2%) was prepared. Based on previous studies of Dursun and Dentel (2006) and patent literature (e.g. Sarkar, 2004), the concentrations of these enzymes were selected as 200, 300 and 400 mg/l.

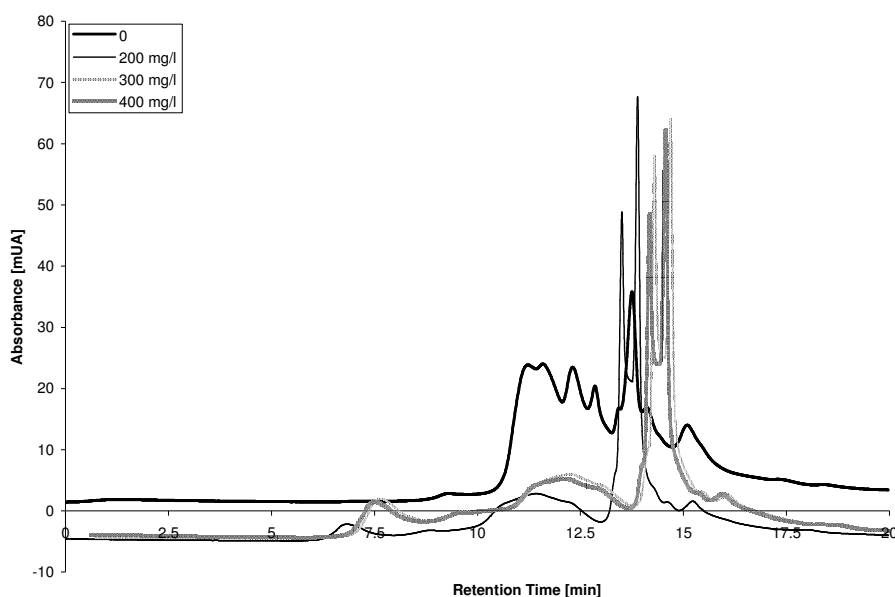


Figure 6.4 Typical EPS chromatograms for samples treated with various concentrations of polysaccharide degrading enzymes for 16h of incubation

Figure 6.4 shows that the chromatograms after use of the polysaccharide degrading enzymes resemble those using the commercial enzyme mixture. Enzyme application shifts the leftmost peaks in the control sample towards the right, and the

fractions at shorter retention times disappear, indicating the degradation of complex polymeric substances into simple ones with lower molecular weights. Table 6.2 presents the main fractions and molecular weight range of EPS samples treated with polysaccharide degrading enzymes.

Table 6.2 Effect of polysaccharide degrading enzymes on molecular weight distribution (after 16 h of incubation)

Enzyme Type	Enzyme Concentration [mg/l]	Retention times [min]	Molecular weight [kDa]
Control (No enzyme)	0	11.5, 12.3, 13.7, 15.1	7, 2.5, 0.4, 0.05
Amylase+Cellulase	200	13.5, 13.8	0.5, 0.3
Amylase+Cellulase	300	14.3, 14.6	0.2, 0.1
Amylase+Cellulase	400	14.2, 14.6	0.2, 0.1

6.3.1.3 Protease

Since proteins are reported to be one of the major components of EPS, a protease was used alone for comparison to other enzyme mixtures. Three different concentrations of protease (5, 15 and 25 mg/l) were applied to anaerobically digested sludge, with EPS extracted after 16 hours of incubation. Figure 6.5 gives the EPS chromatograms of samples treated with protease compared to the control sample, and Table 6.3 summarizes the results.

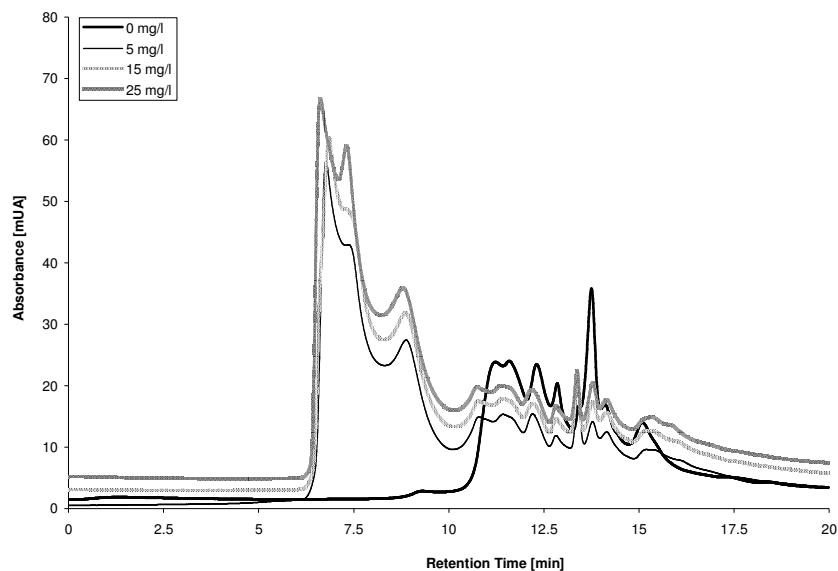


Figure 6.5 Typical EPS chromatograms for samples treated with various concentrations of protease for 16h of incubation

Table 6.3 Effect of protease on chromatographic fractions and molecular weight distribution (after 16 h of incubation)

Enzyme Type	Enzyme Concentration [mg/l]	Retention times [min]	Molecular weight [kDa]
Control (No enzyme)	0	11.5, 12.3, 13.7, 15.1	7, 2.5, 0.4, 0.05
Protease	5	6.8, 8.9, 13.4, 13.8	4350, 275, 0.6, 0.3
Protease	15	6.7, 9.0, 13.8, 15.4	5500, 240, 0.3, 0.04
Protease	25	6.6, 8.6, 13.8, 15.3	5900, 370, 0.3, 0.04

Unexpectedly, the chromatograms after protease treatment differed significantly from those using the commercial enzyme mixture and polysaccharide degrading enzymes, with very high molecular weight polymers appearing (around

5000 kDa, shown by the high intensity at ~6.5 min). Although smaller weight polymers were expected after protease treatment, the results instead suggest a molecular weight increase of three orders of magnitude due to the protease. These results were quite reproducible and unchanged even with the longer incubations up to 88 hours. The very high molecular weight peaks could not be attributed to the protease itself, as shown by injections of an enzyme control giving peaks at 6.6 min and 12.9 min with intensities of only 0.35 and 0.6mUA respectively (negligible compared to the intensities in Figure 6.5).

Since the protease is only capable of reducing molecular weight, it was hypothesized that degradation products from the EPS can be joined or bridged by inorganic substances, such as divalent cations. FTIR analyses presented in the following section appear to confirm this hypothesis.

The molecular weight of EPS after treatment with commercial enzyme mix, and amylase + cellulase mixture was generally lower than 0.5 kDa. However, the chromatograms of these samples also exhibited small rises at retention times of 6-7 min, where much larger peaks were seen in protease-treated samples. The intensity of this rise increased to some extent with increasing enzyme concentration. The very high molecular weight of this slight fraction might be explained with the same hypothesis cited for the protease results.

6.3.2 Infrared Characterization of Enzyme Treated EPS

The main fractions obtained in chromatographic separation of EPS samples were collected for μ FTIR analyses in order to define their chemical composition. This analysis is based on the microscopic examination of obtained crystallites with an infrared beam. Around 30 scans were made for each fraction collected after chromatographic separation; thus only 4 samples were chosen (named control, envirozyme, protease and carbohydrase) for μ FTIR analyses with 16 total fractions. More than 600 scans were made throughout this study, requiring considerable effort in the identification of chemical species predominating in each fraction. The infrared spectrum was considered in terms of spectral regions and major spectra-structure correlations were made based on special regions.

The main chemical species found in each fraction of samples were classified as shown in Table 6.4. Although pure chemical species were observed in some crystallites, most of the species were in association with others. Additionally in the same fraction, various chemical groups were determined. Main families and subfamilies are presented in Tables 6.4 and 6.5. Data is arranged in accordance with abundance of chemical species; for instance, PS+MP means the spectra indicated more polysaccharide than mineral phase was present.

Table 6.4 reveals that the chemical composition of EPS changes by enzyme treatment. The complex nature of EPS can be seen in the chemical composition of the control sample due to a wide range of chemical species of various hydrodynamic sizes.

In the higher molecular weight range, a carbonate mineral phase is dominant, with a significant amount of protein also present. In the lower molecular weight range, polysaccharides are prevalent although the polysaccharides associated with a mineral phase exhibit larger size.

Table 6.4 Summary of main chemical families in four different EPS samples

EPS Origin	Retention Time [min]	Molecular weight [kDa]	Family	Subfamilies		
Control (No enzyme, 16 h incubation)	11-12	15-4	Mineral phase	PS+MP	MP+PS	MP
	12-13	4-1	Protein	PR		
			Protein	PR		
			Mineral phase	MP	PS+MP+OA	
			Polysaccharide	PS	PS+OA+MP	MP+PS
Envirozyme- treated (15 mg/l Envirozyme 216, 16h incubation)	14.5-15.5	0.2-0.03	Protein	PR	PR+PS	
			Polysaccharide	PS+OA+MP		
			Mineral phase	MP		
	12.5-13	2-1	Mineral phase	MP+OAS	MP+PS+OAS	
	13-13.5	1-0.5	Protein	PR+LI+PS	PS+PR+OA	
			Polysaccharide	PS+OAS	OAS+PS	
	13.5-14.5	0.5-0.13	Protein	PR		
			Protein	PR+MP	PR+PS	
			Organic acid	PS+OAS	MP+PS+OAS	
	14.5-15.5	0.12-0.03	Organic acid	PS+OAS	MP+PS+OAS	
Protease-treated (25 mg/l protease, 16h incubation)	6-7	13500-3500	Mineral phase	MP+PR	MP+PS	
	8-9	880-225	Lipid	LI		
			Unidentified	Unidentified+PR+PS		
	13-14	1-0.25	Organic acid	OA+MP		
	14.5-15.5	0.12-0.03	Polysaccharide	PS+MP+OA	PS+OAS	
Carbohydrase- treated (400 mg/l amylase+ Cellulose, 16h inc)			Organic acid	OA		
	6-7	13500-3500	Protein	PR	PR+PS	
	10-11	57-15	Mineral phase	MP		
			Protein	PR	PR+LI	
	13.5-14.5	0.5-0.12	Mineral Phase	MP		
			Mineral phase	MP		
			Organic acid	OAS+PS		
			Lipid	LI		
	14.5-15.5	0.12-0.03	Organic acid	OA	OA+MP	
			Mineral phase	MP		
			Protein	PR+LI		

PS= polysaccharide PR=protein MP=mineral phase OA(S)=organic acid (salts) LI=lipids

After Envirozyme treatment, organic acid salts become the main species associated with others (MP,PS,PR). These associations could be the result of humic acids (Stevenson, 1982) which arise by the microbial degradation of biomolecules e.g. lipids, proteins, and polysaccharides. Since Envirozyme is an unpurified enzyme broth including not only enzymes but also bacteria and constituents, the EPS composition is complicated with different families, subfamilies and associations.

The species after protease and polysaccharide degrading (amylase+cellulase) enzyme treatment are also shown in Table 6.4. A simpler chemical composition is apparent, mainly formed from organic acid and mineral phase associations compared to control sample. It can be noticed that no pure proteins were identified after protease treatment, with the only observed proteins being those associated with a mineral phase at very high molecular weight (13500-3500 kDa). This indicates the association of carbonate species with the degradation products of complex protein molecules.

In the samples treated with polysaccharide degrading enzymes, the major species in EPS were again organic acids and mineral phase(s) with a small amount of high molecular weight proteins, partially associated with polysaccharides (with no other polysaccharides being detected). Only in protease and amylase+cellulase-treated samples lipids were detected. The chemical characteristic of amylase+cellulase-treated sample is also less complicated, with fewer associations. These results show that the specific enzymes degrade the target components in EPS.

Table 6.5 groups the whole data set for the main chemical families and subfamilies with IR band positions. The source and the molecular weight range where this family was identified is also given in the last two columns of Table 6.5. The typical IR spectra for each subfamily are also given in Figure 6.6. Proteins were found in pure form and also in association with other species. Four subfamilies were identified where they are dominant and associated with other species. A total of six subfamilies were distinguished for polysaccharides, with only one not in association with other compounds. Only 2 spectra were found for lipids throughout this study. A mineral phase was identified in every EPS sample regardless of the molecular weight range. Five different subfamilies were determined (associated with PR, PS, OAS and PS+OAS). Pure organic acids were only present in specific enzyme-treated samples at the smallest molecular weight range (0.12-0.03 kDa).

Total protein and polysaccharide amounts were also measured by using widely used methods (Lowry and Dubois, respectively). Figures 6.7 and 6.8 illustrate the change of total protein and polysaccharide amount as a function of incubation time and enzyme concentration. Sesay *et al.* (2006) developed an EPS extraction method by using enzymatic hydrolysis and showed significant increases in extracted polysaccharide and protein amounts determined with Lowry and Dubois method. This point of view was also supported in our chromatograms (Figure 6.3, 6.4 and 6.5) where the peak heights of enzyme-treated samples are higher than those in the control sample, indicating an increase in concentration of polymeric substances.

Table 6.5 IR band positions of EPS samples with and without enzyme treatment

Family	Sub family	IR band position [cm ⁻¹]	EPS source	Mw range [kDa]
Protein	PR	PR[3287;1645;1537;1400]	Control	15-4
			Control	4-1
			Control	0.2-0.03
			Envirozyme	1-0.5
			Carbohydase	13500-3500
			Carbohydase	57-15
			Control	0.2-0.03
	PR+PS	PR[3280;1647;1541;1400] PS[1037]	Envirozyme	0.5-0.13
			Carbohydase	13500-3500
			Envirozyme	0.5-0.13
	PR+MP	PR[3277;1622;1587] MP[1363;1349]	Carbohydase	57-15
	PR+LI	PR[3278;1647;1539] LI[2937;2914;2847]	Carbohydase	0.12-0.03
	PR+LI+PS	PR[3280;1653;1558] LI[2916;2848] PS[1043]	Envirozyme	2-1
Polysaccharide	PS	PS[1052]	Control	0.5-0.13
	PS+OAS	PS[1010] OAS[1579]	Envirozyme	1-0.5
			Envirozyme	0.12-0.03
			Protease	0.12-0.03
	PS+MP	PS[1038] MP[1408;878]	Control	15-4
	PS+MP+OA	PS[1042] MP[1369;838] OA[1703]	Control	4-1
			Protease	0.12-0.03
	PS+PR+OA	PS[1020] PR[3276;1635;1560] OA[1703]	Envirozyme	2-1
	PS+OA+MP	PS[1039] OA[1683] MP[1441]	Control	0.5-0.13
			Control	0.2-0.03
Mineral Phase	MP	MP[1435;864]	Control	15-4
			Control	4-1
			Control	0.2-0.13
			Carbohydase	13500-3500
			Carbohydase	57-15
			Carbohydase	0.5-0.12
			Carbohydase	0.12-0.03
			Control	15-4
			Control	0.5-0.13
			Protease	13500-3500
	MP+PS	MP[1416;879] PS[1170;1110;1034]	Protease	13500-3500
			Protease	13500-3500
	MP+PR	MP[1433;864] PR[3346;1635;1537;1406]	Envirozyme	2-1
	MP+OAS	MP[1341;1005] OAS [1608]	Envirozyme	2-1
	MP+PS+OAS	MP[1338] PS[1011] OAS[1594]	Envirozyme	2-1
			Envirozyme	0.12-0.03
Organic Acid (Salts)	OA	OA[1713]	Protease	0.12-0.03
			Carbohydase	0.12-0.03
	OAS+PS	OAS[1593] PS[1044]	Envirozyme	1-0.5
			Carbohydase	0.5-0.12
	OA+MP	OA[1693] MP[1414;843]	Protease	1-0.25
			Carbohydase	0.12-0.03
Lipids	LI	LI[2916;2845;1385]	Protease	13500-3500
			Carbohydase	0.5-0.12
Unidentified	Unidentified	Unidentified PR[3290;1647;1560] PS[1088;1041]	Protease	880-225

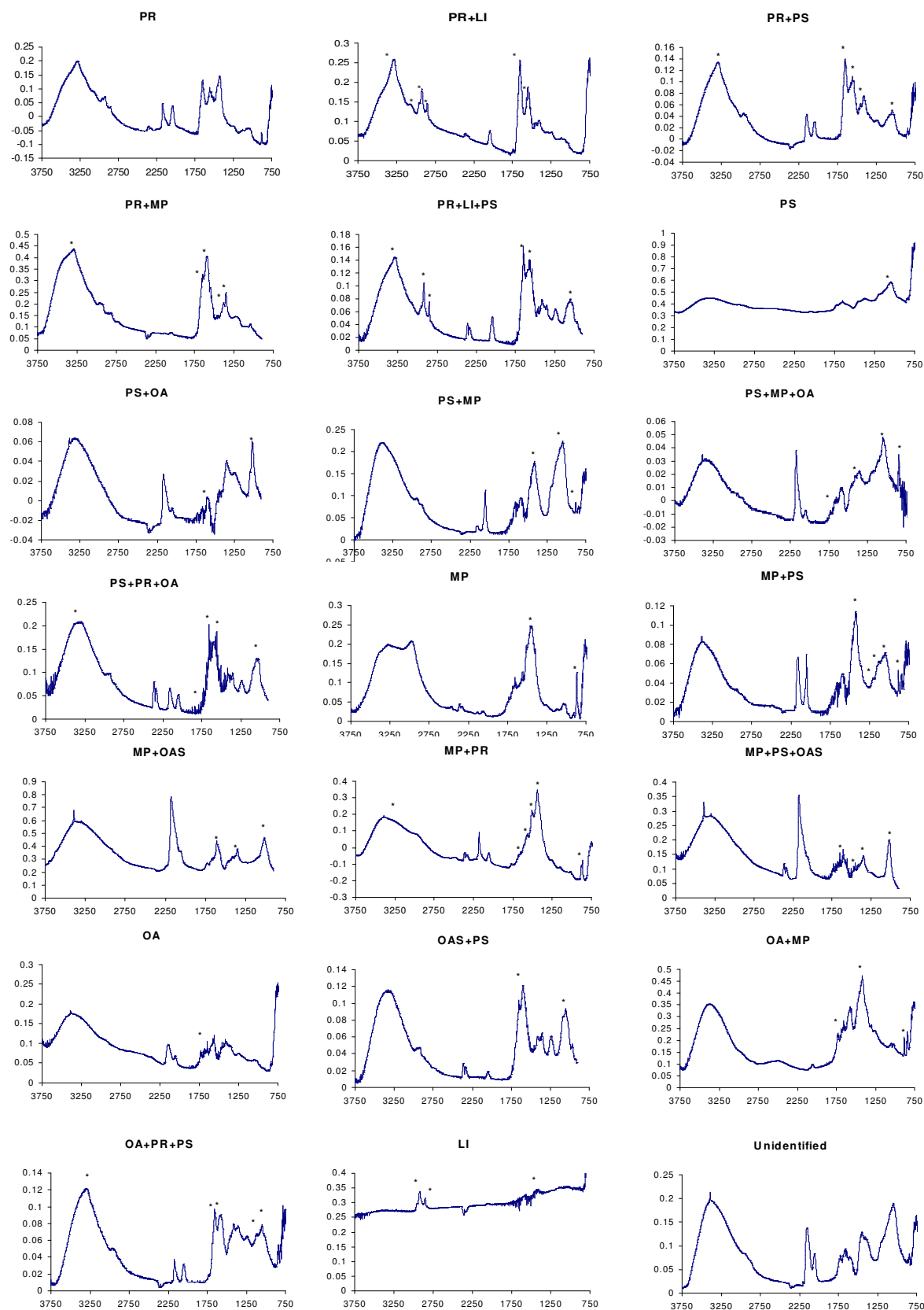


Figure 6.6 IR spectra of identified families in EPS

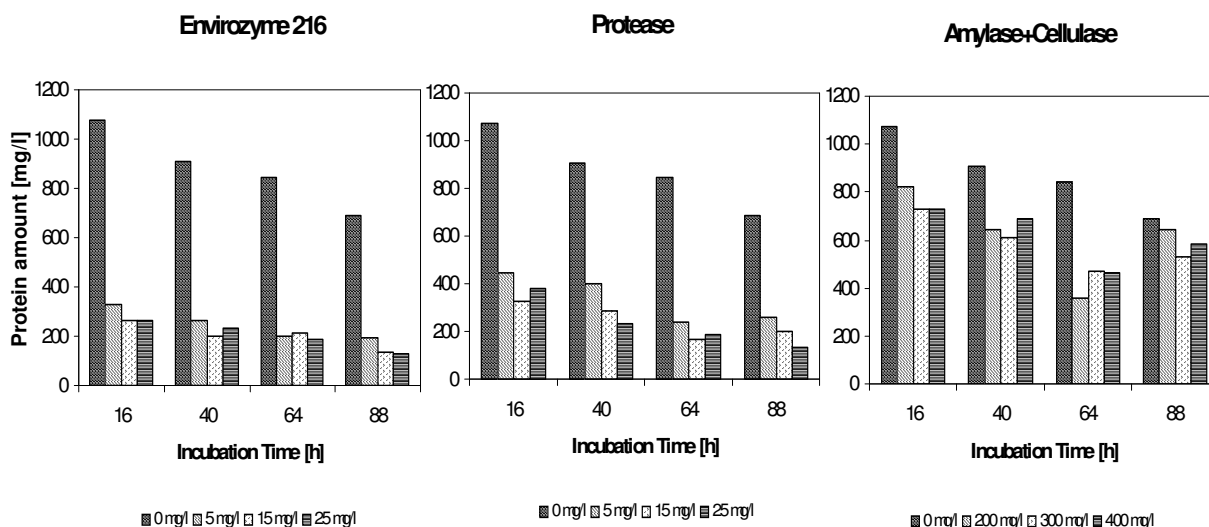


Figure 6.7 Total protein amount after enzyme treatment

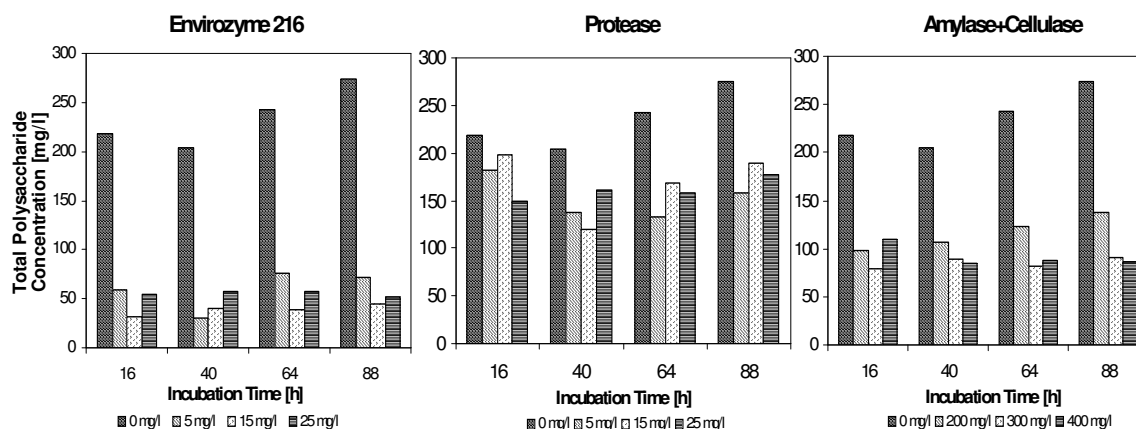


Figure 6.8 Total polysaccharide amount after enzyme treatment

However, surprisingly, Figure 6.7 and 6.8 show significant decreases in total protein and polysaccharide concentration with enzyme treatment which was also in accordance with Ayol (2005). The smaller molecules released outside the flocs formed by enzymatic degradation may be more available for microorganisms and these polymers may be easily consumed by microorganisms. The chromatographic method does not only measure proteins or polysaccharides. Another reason might be due to the

selected method for protein and polysaccharide determination. These methods are known to interfere with specific types of proteins, surfactants and Ca^{2+} and Mg^{2+} ions (Lowry *et al.*, 1951; Morrissey and Woltering, 1989). Thus they might not be appropriate to determine the degradation products of enzyme treatment. And since μFTIR findings showed that most degradation products were associated with organic acid salts and mineral phase, it is more likely that the associated species could not be detected with these analytical methods.

6.3.3 Effect of enzyme treatment on physical-chemical properties

Although considerable decreases in pH were observed for all samples after 16h of incubation, the final pH after 88h of incubation actually increased from 8.15 up to 8.60. During the initial 16h of incubation, hydrolysis evidently produces acidic products, as previously noted by Wawrzynczyk *et al.* (2003). The increase in conductivity at 16h indicates that the acidification process also produces more charged species. After 16h of incubation, it is possible that produced acids were converted into methane and carbon dioxide, leading to an elevation in pH and drop in conductivity (Table 6.6 and 6.7).

Table 6.6 pH change as a function of enzyme concentration and incubation time (h)

Dose/inc time	0	16	40	64	88
No enzyme	8.15	7.56	7.7	8.04	8.16
Envirozyme 5 mg/l	8.15	7.55	7.76	7.91	8.38
Envirozyme 15 mg/l	8.15	7.55	7.88	7.92	8.44
Envirozyme 25 mg/l	8.15	7.55	7.76	8.16	8.58
Protease 5 mg/l	8.15	7.52	7.96	8.22	8.58
Protease 15 mg/l	8.15	7.54	7.79	8.05	8.29
Protease 25 mg/l	8.15	7.61	7.83	8.31	8.60
Carbohydrase 200 mg/l	8.15	7.47	7.73	8.08	8.52
Carbohydrase 300 mg/l	8.15	7.69	7.88	8.15	8.41
Carbohydrase 400 mg/l	8.15	7.48	7.79	8.23	8.44

Table 6.7 Conductivity values (mS) as a function of enzyme concentration and incubation time (h)

Dose/inc time	0	16	40	64	88
No enzyme	6.36	9.83	5.67	4.21	5.83
Envirozyme 5 mg/l	6.36	9.41	7.15	6.81	5.07
Envirozyme 15 mg/l	6.36	9.21	7.02	6.63	5.23
Envirozyme 25 mg/l	6.36	8.37	6.93	5.89	4.61
Protease 5 mg/l	6.36	6.90	7.34	6.01	4.32
Protease 15 mg/l	6.36	6.77	5.96	5.44	3.82
Protease 25 mg/l	6.36	6.82	5.54	5.71	4.83
Carbohydrase 200 mg/l	6.36	7.04	5.69	4.36	2.59
Carbohydrase 300 mg/l	6.36	6.83	5.88	4.51	4.24
Carbohydrase 400 mg/l	6.36	6.90	5.94	4.70	3.32

The volatile solid content increased with incubation time for all enzyme-treated samples (Table 6.8). The highest values were acquired for a commercial enzyme mix. Enhanced hydrolysis of complex polymeric substances by enzyme treatment would improve the solubilization of biosolids, thus higher organic matter amount measured with volatile solids was observed. The significance of these results would be the indication of increased gas production after enzyme treatment (Roman *et al.*, 2006;

Wawrzynczyk *et al.*, 2003). The total solid content of all samples remained around 23-25 g/l, generally with a slight decrease with enzyme treatment.

Table 6.8 The change of volatile solids (% of TS) with enzyme concentration and incubation time (h). The original TS content was 24 g/L.

Dose/inc time	0	16	40	64	88
No enzyme	54.26	54.80	55.20	54.32	54.39
Envirozyme 5 mg/l	54.29	59.78	60.20	62.13	63.97
Envirozyme 15 mg/l	54.29	58.79	60.00	61.97	62.51
Envirozyme 25 mg/l	54.31	59.40	59.90	61.64	62.64
Protease 5 mg/l	54.29	56.44	59.78	60.06	60.47
Protease 15 mg/l	54.29	57.38	58.79	60.88	61.00
Protease 25 mg/l	54.31	58.00	59.40	61.13	62.20
Carbohydrase 200 mg/l	54.29	55.76	56.36	57.44	57.93
Carbohydrase 300 mg/l	54.29	55.40	56.18	57.13	57.76
Carbohydrase 400 mg/l	54.31	54.98	55.59	56.40	57.90

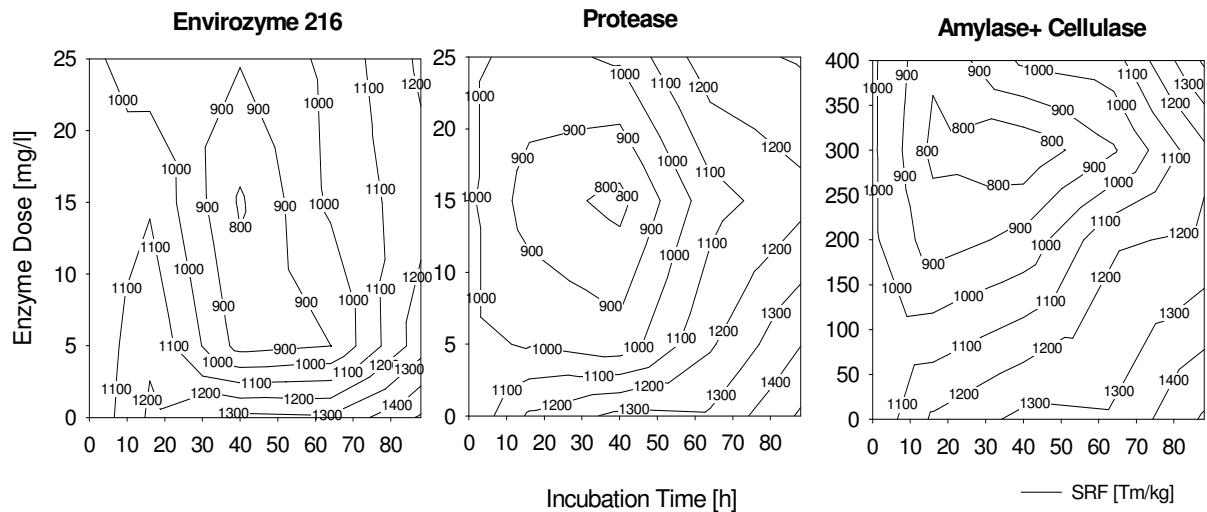


Figure 6.9 Effect of enzyme treatment on Specific Resistance to Filtration (SRF)

The role of enzymes in filterability was evaluated by measuring specific resistance to filtration (SRF). Figure 6.9 gives the SRF values as a function of

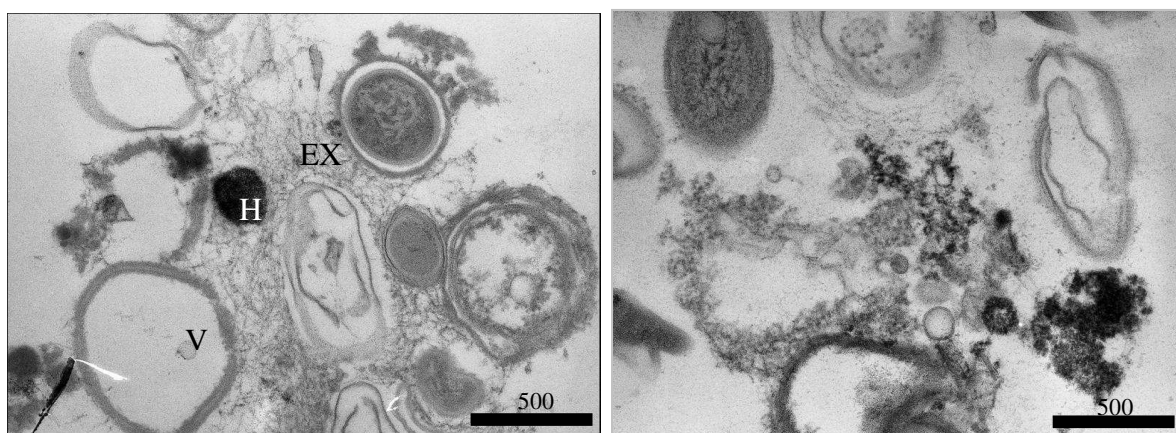
incubation time and enzyme concentration. Samples incubated without enzyme exhibited decreasing rates of filtration (higher SRF values). Enzyme treatment increased the filtration rate to a minor extent at lower incubation times, but this was reversed with further incubation.

The significant effect of proteins on filterability, as previously noted by Dursun and Dentel (2006), is also evident in these results. Protease-treated sample that has a higher molecular weight than other samples and in which no pure proteins were identified with FTIR, resulted in the highest filterability. On the other hand, the filterability of Envirozyme and carbohydrase-treated samples did not differ significantly. The presence of high molecular weight polymers in EPS might help to increase the filterability where reduced filterability conditions were prevailed for the EPS with smaller molecular weight. However the difference in filterability between enzyme-treated samples was not nearly as clear as in previous studies in which CST were used to evaluate filterability (Ayol, 2005; Dursun *et al.*, 2006a). Thus, the role of the EPS molecular weight on filterability still remains ambiguous and needs further exploration.

6.3.4 Structural Changes with Enzyme Treatment

Figure 6.10(a) shows the ultrathin section transmission electron micrographs of sludge (without enzymes) sampled from a digestion tank. This typical anaerobic sludge floc composed of bacteria, EPS (EX), Humics (H) and Virus (V). Although

viruses were observed in the control sample, they were really abundant in the sample treated with Envirozyme. This was related to the ingredients of enzyme mixture. The EPS was darker in the Envirozyme treated sample indicating that they were fixed with osmium, which was associated with humics. In protease-treated sample, the network of EPS seems more degraded on the whole (Figure 6.10(b)). Small viruses were seen, the majority was black osmiophiles masses related with bacterial remains formed by the degradation of EPS.



(a) (b)
Figure 6.10 TEM Micrographs of resin embedded samples (a) raw sludge (b)
 protease-treated sludge

6.4 CONCLUSIONS

Size exclusion chromatography, coupled with μ FTIR spectroscopy, was successfully used to characterize EPS extracted from anaerobically digested sludge. Five main constituent families were identified: polysaccharides, proteins, mineral

phase, organic salts/acids, and lipids. All were chiefly found in association with other constituent types rather than as pure species, illustrating the complexity of EPS.

EPS chromatograms after enzyme treatment showed clear evidence of enzyme effects, varying in characteristics according to the enzyme used. Enzyme effects were mostly completed during the first 16h of incubation, and although enzymes should act in a catalytic manner, greater enzyme concentrations generally led to greater effect.

Sludge treatment using Envirozyme or carbohydrase (amylase+cellulase) decreased the molecular weight distribution of the EPS. However, significantly higher molecular weight compounds were formed with protease use. μ FTIR results suggest that the association of protein degradation products with a mineral phase explains this phenomenon. This finding highlights the advantages of size exclusion chromatography followed by Fourier Transform Infrared micro spectroscopy, with these coupled techniques revealing much more on a molecular basis than could be obtained by the more traditional analytical methods.

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Chapter 7

CONCLUSIONS AND FUTURE DIRECTIONS

7.1 CONCLUSIONS

Biosolids have complex structures including particles, microorganisms, and inorganic substances embedded in a polymeric network. Although conditioning increases the efficacy of dewatering, the addition of chemicals to biosolids also increases the complexity of the biosolids' structure. Treatment of biosolids—especially conditioning and dewatering—are costly operations in treatment plants; thus, increasing the effectiveness of these units will be beneficial. In this study, the biosolids were considered as gels (at least in part) to investigate the conditioning and dewatering processes.

The early step in this research was the synthesis of a synthetic surrogate that behaved like a gel due to its natural biopolymer (alginate) content. The synthetic sludge was considered an “adequate” surrogate for biosolids in terms of characterizing physical-chemical properties and their behavior under conditioning. Following the development of a stable, standard gel system, rheological analyses and swelling tests were used to provide evidence for the gel-like behavior of biosolids. Shear had an influence on conditioning requirements and efficiency of dewaterability. Shear

sensitivity measurements were initially carried out in a synthetic surrogate with variation of its components. It was shown that the shear sensitivity was primarily controlled by the gel fraction, with alginate and the associated cations increasing the gel-like behavior. However, the effect of particulate fraction on shear sensitivity should also be taken into account. Accordingly, shear sensitivity was explained as a complex parameter including two types of response: the resistance to dispersed mass concentration into centrate and the maintenance of desired strength while the solids concentration increases in the shear field.

The apparent ability of various cations to penetrate and uniformly collapse sludge gels was related to cation size and surface charge. Organic polymers diffused into the biosolids network and collapsed the structure; however, afterwards the structure of the polymers supported and held the network. Inorganic conditioners promoted complexation and precipitation by increasing the particulate fraction in the biosolids network. Similar to inorganic conditioners, the cationic surfactant showed parallel responses under conditioning.

High turbulent shear altered the filterability and surface charge of polymer-conditioned digested sludge samples. However, neither surface charge nor CST rose notably with increasing shear for samples conditioned with inorganic additives. Thus, inorganic conditioner resulted in the lowest shear sensitivity. As the molecular weight of polymers increased, the shear sensitivity was raised due to the bridging mechanisms of polymers that were disrupted under high turbulent shear. The use of rheological

analyses was also shown to be a useful tool to determine the network strength and elasticity of samples, which may be related to shear sensitivity.

All experimental results were gathered into the new conceptual model based on a colligative property—osmotic pressure. This model was found reasonably successful in explaining the filterability and conditioning efficiency. The gel approach was also shown to be able to account for the shearing effects for polymer-conditioned biosolids in which surface charge and porosity change with shearing time. However, more care should be given when inorganic additives are used for conditioning, since the particulate fraction dominates over the gel fraction, and conditioned samples behave more like particles than gels.

The effect of shear on normal forces is crucial in dewatering. A special cell called the immobilization cell, coupled with a dynamic mechanical rheometer, was used to evaluate the effect of shear and normal forces on viscosity and solid content during filtration. Limits of normal forces that could be applied to both digested sludge and synthetic surrogate before the collapse of the sample structure were established at various shear rates. The maximum normal force increased approximately linearly with the increasing solid content. However, as the shear rate increased, there was a decrease in the maximum normal force due to the rearrangement in the structure of the samples. The combination of normal force and shear rate altered the viscosity during filtration. It was shown that viscosity increased with normal force and decreased with shear rate. The application of normal force pushed the water through the filter paper and formed a

more compact arrangement. On the other hand, shearing disrupted the structure of samples, leading to shear thinning behavior. Depending on the type and the dose of conditioner, the rate of released water, and thus the final solid content, changed. The responses of the synthetic surrogate and digested sludge to shear and normal forces were found to parallel each other.

Altering the structure of biosolids by targeting the polymeric substances with enzymatic treatment changed the structure of the biosolids. Size exclusion chromatography, coupled with Fourier Transform Infrared spectroscopy, was successfully employed to characterize extracellular polymeric substances extracted from anaerobically digested sludge. Five main constituent families were identified: polysaccharides, proteins, mineral phase, organic salts/acids, and lipids. All were chiefly found in association with other constituent types rather than as pure species, illustrating the complexity of EPS. EPS chromatograms after enzyme pretreatment showed clear evidence of enzyme effects, varying in characteristics according to the type of enzyme used. Sludge pretreatment using Envirozyme 216[®] or carbohydrase (amylase+cellulase) decreased the molecular weight distribution of the EPS. However, protease treatment led to the formation of compounds with significantly higher molecular weights. FTIR results suggested the associations of protein degradation products with a mineral phase to explain this phenomenon. This finding highlighted the advantages of size exclusion chromatography followed by FTIR spectroscopy. This

technique revealed much more on a molecular basis than could be obtained by the more traditional analytical methods.

7.2 FUTURE DIRECTIONS

This thesis aims to develop a better understanding of the behavior of biosolids under conditioning and dewatering processes. Although the significant findings of this research extend our knowledge notably, there are still various directions that need to be further explored. Increasing production of biosolids and strict land application regulations require more careful selection of conditioning additives and more efficient dewatering equipment. Therefore, understanding the mechanisms of conditioning and dewatering will become more important throughout the years.

This study mainly concentrated on the gel-like behavior of biosolids originating from wastewater treatment plants. Another task addressing water treatment residuals can also be useful. Water treatment residuals which are known to be gelatinous in character and difficult to dewater (Bache and Papavasiliopoulos, 2003) originate as a result of the coagulation process using generally aluminum sulfate. Although a significant amount of work has investigated the characteristics of alum sludge and the effect of organic and inorganic conditioners on dewatering efficiency (Papavasiliopoulos and Bache, 1998; Wu *et al.*, 1997; Zhao *et al.*, 2002), there is limited information on gel-like properties of this sludge type (Johnson *et al.*, 2000). This approach may enhance understanding of the ability of additives to condition

water treatment residuals, and this may lead to improvement of the analogy to the gel-collapse mechanism. It might also be valuable to combine widely investigated physical properties of alum sludge such as floc size, density and fractal dimension (Chu *et al.*, 2005; Zhao, 2003) with polymeric properties in order to comprehend the significance of the gel approach.

This work has briefly discussed the application of existing dewatering models based on osmotic effects and validated the use of this model under shear. However, the use of capillary suction time as an indicator of filterability limited further development of this model. The next step can be to conduct pressure filtration tests where the pressure and surface area can be determined exactly to eliminate the uncertainties in the model. Recent rheological findings on the combined effect of normal and shear forces might also be combined with dewatering models originally developed by Buscall and coworkers (Buscall, 1990; Buscall *et al.*, 1987) and then developed by Scales and coworkers (e.g., Usher and Scales, 2005).

Enzyme pretreatment was found to be effective in laboratory-scale tests to change the structure of biosolids. The promising results warrant further investigation on this topic. Recently, a significant amount of work which investigated various aspects of enzyme treatment has been published (Kim *et al.*, 2006; Roman *et al.*, 2006). Practical implications of this treatment should be further explored after determining the optimum conditions for enzyme treatment. Due to the costly nature of enzymes, feasibility analyses should be conducted. The cost of enzymes might be

offset by reducing the amount of required conditioning agent and/or producing less solids.

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