The Effect of Cation Addition on the Settling and Dewatering Properties of an Industrial Activated Sludge

by

Michelle L. Smith

Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Environmental Engineering

APPROVED:

John T. Novak, Co-chair

Nancy G. Love, Co-chair

Gregory D. Boardman

January, 1996
Blacksburg, Virginia

Keywords: Activated Sludge, Cations, Extracellular Polymer, Settling, Dewatering

c.2

THE EFFECT OF CATION ADDITION ON THE SETTLING AND DEWATERING PROPERTIES OF AN INDUSTRIAL ACTIVATED SLUDGE

by

Michelle L. Smith

John T. Novak, Chairman

Department of Environmental Engineering

(ABSTRACT)

The purpose of this research was to examine the impact of cation addition on an industrial activated sludge system and to determine the applicability of the findings of a previous VPI&SU doctoral student (Higgins, 1995) to this industrial sludge. From this research, the implications on the full-scale industrial wastewater treatment system could be postulated.

The addition of sodium and potassium to the feed stream of a laboratory-scale activated sludge system improved sludge volume index (SVI), but produced high supernatant solids. Sodium addition resulted in weak flocs and a deterioration in sludge dewatering. Potassium addition also resulted in poor sludge dewatering but did not significantly affect floc stability. The addition of magnesium improved SVI, supernatant solids, and floc stability, but did not significantly affect sludge dewatering.

Increasing the monovalent/divalent cation ratio in the reactor feed stream, reduced SVI but produced high supernatant solids. The soluble and bound extracellular protein content was observed to increase with as this ratio increased. No trend was observed with soluble or bound extracellular polysaccharide content. Batch addition of both calcium and

magnesium improved sludge settling and dewatering, although this effect was not observed when sludge with low extracellular polymer content was examined.

This research confirmed that the effect of cations on activated sludge properties is highly dependent on the feed wastewater composition and starting and operating conditions. This implies the need for laboratory or pilot-scale testing before the effect of cation addition on a given sludge can be determined. For the industrial sludge studied here, the addition of 7 to 12 mM magnesium produced the most desirable sludge characteristics including improved SVI, supernatant solids and floc stability.

ACKNOWLEDGEMENTS

I would like to thank Dr. John Novak and Dr. Nancy Love for serving as co-advisors during the course of my research and for providing direction and support to a research project that was anything but cooperative. Thanks also to Dr. Greg Boardman for serving on my committee and to the rest of the Virginia Tech Environmental Engineering Faculty for making my stay in Virginia both enjoyable and educational. Special thanks to Julie Petruska, Bettie Windgate and Marilyn Grender for solving my numerous dilemmas of the past 16 months.

Thank you to the Virginia Water Research Project for making this project financially possible. Thanks to the Tennessee Eastman Chemical Company also for funding this project and to the Eastman Chemical staff for their interest and support through its duration. Special thanks to Cal Churn and John Barber for responding to my numerous questions. Thanks especially to Darryl Murphy and Lois Moles for supplying a constant flow of wastewater and biomass.

Finally, thanks to my family and friends for their support both emotionally and financially. Special thanks to Jay Meuser who put up with a year and a half of hundred dollar phone bills and 10 hour drives all for the sake of my education.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

The activated sludge process was pioneered by Ardern and Lockett in 1914 (Metcalf & Eddy, 1991). Since this time both our understanding of the biological and physical mechanisms of activated sludge and our ability to improve the process have grown significantly. Activated sludge is now the most commonly applied process in wastewater treatment and has become one of the most effective methods of stabilization of organic wastes. Fundamentally, the activated sludge units of today are very similar to those of 1914, relying on a two stage process. The first stage involves the stabilization of organic material by microorganisms through the conversion of substrate into energy and biomass, while the second step involves clarification in which liquid-solid separation is achieved through gravity settling in a quiescent zone. Liquid-solid separation is critical to the success of the activated sludge process, yet it poses one of the greatest obstacles in the wastewater engineering field. Researchers have studied biological flocculation processes for years; however, the theory behind it is still not well understood. Although several theories have been proposed, there is a clear lack of consensus in this area.

Closely related to the issue of sludge settleability is that of sludge dewatering capabilities. Sludge dewatering is important to treatment plant operators as sludge disposal can be one of the most expensive parts of the wastewater treatment process. As with sludge settling, determining and controlling the factors which produce good sludge dewatering is not easy.

Industrial sludges can be a particular challenge to settle and dewater as the chemical

nature of the wastewater and the variable nature of the influent flowrate and composition can seriously affect sludge behaviour. Chemical waste typically contains many easily degradable organic acids, alcohols and other solvents with a significant fraction of less degradable complexes.

Research to date has examined the effects of numerous factors on flocculation and sludge settling. It is generally accepted that divalent ions and the presence of extracellular proteins and polysaccharides impact settleability in some way, although many of the results are contradictory. It is also accepted that polymer content, particle size and bound water content impact sludge dewatering, but, again there is little agreement on the extent to which these factors are important.

Higgins (1995) investigated the effect of cation addition to a synthetic waste stream on a laboratory-scale activated sludge system. Higgins provided significant insight into the effect of cations on flocculation and their manifestation in sludge settling and dewatering. In particular, Higgins examined the relationship between monovalent and divalent ions and the production of soluble and bound fraction extracellular proteins and polysaccharides. Higgins reported that the monovalent to divalent cation ratio may be one of the most important parameters in the ability of a sludge to flocculate and settle well.

The objective of this research was to examine the principles developed by Higgins (1995) with respect to an industrial wastewater. This was done through the use of laboratory-scale activated sludge units seeded with biomass from the industry and continuously fed with wastewater supplied weekly by the industry. The addition of various

monovalent and divalent cations to the influent wastewater was used to test the universality of the theory that Higgins developed for a synthetic waste stream. This objective was achieved through a research plan consisting of two stages. The first stage of this research involved the characterization of the industrial sludge and wastewater over a one month period in an attempt to determine typical concentrations of soluble cations, soluble and bound extracellular proteins, particle size distribution, floc density, floc stability, optimum polymer dose, sludge settling and dewatering properties, and the degree of variation of each parameter in this time. The second stage of this research examined the effect of cations on the production of extracellular polymer, sludge settling and dewatering and various other sludge properties for comparison with current flocculation, settling and dewatering theories. Finally, through this research, a working knowledge was gained of the effect of feed cation levels on the properties of the specific industrial sludge. In the future, such knowledge may be applied to industrial wastewater treatment process on a full-scale level.

The industrial facility studied here was a large chemical plant which manufactures organic chemicals, plastics and fibres and which will be referred to from this point as the "Chemical Company". This large plant has over 10,000 employees and covers an area of 3600 acres. The plant utilizes a four train system of three activated sludge basins in series and employs step feed. The treatment plant operators switch the step feed to these 2.5 million gallon basins from 40:40:20 to 0:80:20 in the first, second and third basins, respectively, in response to sludge property changes and in an attempt to improve the

settling characteristics of the sludge. The activated sludge process operates at a dissolved oxygen concentration ranging from 1.7 to 2.0 mg/L with a hydraulic and solids retention time of 1 day and 11 to 13 days respectively. The influent wastewater contains a BOD_5 of 1200 mg/L and TOC of approximately 700 mg/L. The plant treats an average daily flow of 23 MGD and utilizes equalization, neutralization and nutrient addition prior to the activated sludge process. The activated sludge basins are followed by several large clarifiers. The effluent from the clarifiers is discharged to the South Fork of the Holston River and the settled sludge is dewatered by belt filter press. The solid fraction remaining after dewatering is disposed of by injection into the plant's coal boilers. The treatment plant often experiences difficulties in sludge settling as characterized by a sludge volume index (SVI) greater than 200. In addition, the sludge requires the addition of a cationic conditioning polymer at a dose ranging from 6 to 12 ppm for clarification, as well as 7 pounds per ton dry solids of another cationic polymer and 50 pounds per ton dry solids of bentonite clay to improve sludge dewatering. The addition of polymer at these levels to such a large wastewater stream is very expensive. Even with this addition, poor settling and dewatering is occasionally experienced.

The significance of this research therefore, is twofold. The first result is the confirmation or refutation of Higgins suppositions and the beneficial gain of information regarding the role of various operational factors in activated sludge. Secondly, this research will improve the understanding of interactions between the industrial wastewater and various cations, allowing the treatment plant operators to understand, if not improve

their sludge treatment process, possibly resulting in a reduction in treatment costs by reducing the need for synthetic polymer addition.

II. LITERATURE REVIEW

This section describes several currently proposed models for biological flocculation and their application to activated sludge properties. Also contained herein is a review of the current literature pertaining to the role of cations and extracellular polymers in bioflocculation and ultimately the settling, dewatering and conditioning properties of activated sludge. There is an overall lack of consensus regarding the effect of these factors on flocculation and the means by which the effects are generated. As a result, the varying laboratory results and proposed explanations are discussed here. Other factors thought to affect sludge properties, including floc density, bound water content, floc strength and particle size distribution are discussed and where possible, related to sludge settling and dewatering behaviour. This research follows the recent work of Higgins (1995) and therefore his findings are discussed in some detail.

2.1 Current Flocculation Theory

Several independent and interdependent models of bioflocculation have been developed over the past 100 years which attempt to describe the interactions between microorganisms, microbial excretions, water and inorganic materials which ultimately result in flocculation. Several theories previously considered, such as the *Zoogloea ramigera* theory described by McKinney (1953), the flagella interaction theory of Pijper (1938, 1941), the protozoa theory (Barker, 1946) and the poly-beta-hydroxybutyric acid (PHB) theory (Crabtree, 1966), have been discounted as viable flocculation models based

on several more recent discoveries (Pavoni *et al.*, 1972; Kato *et al.*, 1971). Currently, several distinct and interrelated theories are proposed which offer the most credible explanations of bioflocculation, although none can explain the flocculation mechanism in its entirety. The models discussed here include the polymer bridging theory and DLVO model as well as theories proposed by other researchers which examine a combination of several distinct flocculation models.

Each of the theories discussed is based on several well established principles of microbial behaviour and interaction. Many bacteria involved in activated sludge are known to produce polymers which can be exposed at the bacterial surface or excreted into the surrounding solution. Extracellular polymers may exist as a loose slime layer surrounding a cell or as a gelatinous capsule. Extracellular polymers are primarily composed of proteins, polysaccharides and smaller amounts of lipid, RNA and DNA (Forster, 1971; Coakley and Wilson, 1971; Tenney and Verhoff, 1973). Several researchers (Friedman *et al.,* 1969; Forster, 1971, Brown and Lester, 1979) have found that activated sludge surfaces are composed primarily of polysaccharides. In contrast, Tenney and Verhoff (1973), Urbain *et al.* (1993), and Higgins (1995) found that proteins constitute the largest portion of extracted biopolymer. The variations in relative biopolymer concentration can often be attributed to differences in the dominant microorganism species present in the sludge sample as well as the composition of the feed solution and the conditions under which they are grown (Gray, 1989). Kiff (1978) and Pavoni (1972) have shown that available nutrients, loading rate and sludge age can alter

the production of extracellular polymers. The method of extraction is also known to affect the amount of each polymer measured (Brown and Lester, 1980; Higgins, 1995). In general, extracellular polymers are found to contain functional groups which are primarily anionic or nonionic in nature and which tend to exert an overall negative charge at the cell surface. Extracellular proteins are hydrophobic in nature while polysaccharides create hydrophilic surfaces (Peter and Wuhrmann, 1970).

The work of numerous researchers has shown that flocculation does not occur to a large extent until the late logarithmic phase or early endogenous respiration phase of growth (Pavoni *et al.,* 1972). Tenney and Verhoff (1973) and Pavoni (1972) have provided convincing evidence that increasing production of polysaccharide and protein corresponds directly with the onset of the endogenous growth phase regardless of growth media or predominant microbial species. This helps to explain why an increase in solids retention time (SRT) tends to produce an increase in biopolymer production and improves sludge settling (Gray, 1989, Tenney and Verhoff, 1973). Gulas *et al.* (1979) attribute this increase in polymer to autolysis during the endogenous phase, and explain that significant polymer production also occurs during earlier phases of growth. In any case, the presence of high biopolymer concentration is not observed until this later stage. It is suggested that prior to the late logarithmic phase, the amount of extracellular polymer produced is not sufficient to cause flocculation. In view of the above information and supporting data, the following bioflocculation theories have been developed.

(1) Polymer Bridging Theory

(2) DLVO Theory

(3) "Combination" Theory

2.1.1 Polymer Bridging Theory

The theory of polymer bridging for bioflocculation as described by Tenney and Stumm (1965), Busch and Stumm (1968), and Ries and Meyers (1968), is a variation on the theory of the flocculation of colloids by polyelectrolytes developed by LaMer and Healy in 1963. According to this theory, a polymer molecule becomes attached to the available adsorption sites on the surface of numerous particles forming a bridge or polymer/particle network, destabilizing the particles and forming larger flocs. The aggregates which form are of sufficient size that they will settle quickly under quiescent conditions. Cations are thought to play an important role in this bridging mechanism, as they can bind negatively charged particle surfaces to the anionic functional groups found on extracellular polymers. The size of this polymer bridge is dependant upon the length and molecular weight of polymer. This controls the length to which the polymer branch can extend (or its effective radius) and the number of sites available for adsorption. Optimum destabilization occurs when a specific percentage of the available adsorption sites are occupied, resulting in a floc that is less prone to degradation and more resistant to shear forces (Smellie and La Mer, 1958). The presence of polymer in concentrations greater than that amount required for optimum destabilization will result in the restabilization of the particles. This can occur for several reasons. When the optimum

polymer dose has been exceeded, a polymer adsorbs to a particle surface but is unable to adsorb to other particles as all the sites have been consumed by other polymer molecules. In this way, the particle is not bridged to others in solution and will exist as a stable, free particle. The addition of polymer to an optimally destabilized solution may result in the polymer/particle network becoming very large and structurally unstable in solution. Any significant shear force exerted on the floc results in the rupture of the network producing floc fragments which, in the lack of close available binding sites, bind to other sites on the particle or particles to which it is already adsorbed. When restabilization occurs, the resultant particles are small, light and will not settle efficiently.

The rationale behind the polymer bridging theory implies that viable cells are not required for flocculation. The presence of a negatively charged surface and external polymers for bridging are essential to this model along with participating cations. In this way, a biological sample which is previously grown under floc inducing conditions should continue to flocculate even when the sample is rendered non-viable, at least until the microbial cells degrade such that their surfaces no longer hold their previous properties. This aspect is supported by the work of Tezuka (1969) and Hantula and Bamford (1991).

2.1.2 DLVO Theory

Several researchers have examined the differences between long range and short range forces which influence the aggregation of bacteria (Calleja *et al.*, 1984; Rose, 1984; van Loosdrecht *et al.*, 1989; Skvarla, 1993). At distances greater than 10 nm, long-range

forces including electrostatic and Van der Waals forces dominate. These forces are commonly known as Derjaugin, Landau, Verwey and Overbeek, or DLVO forces. Similar to the polymer bridging theory, the DLVO theory was originally developed to explain the behaviour of colloidal particles. It is been shown however, to also describe bacterial aggregation in certain systems (van Loosdrecht *et al.*, 1989; Zita and Hermansson, 1994). According to this theory, the electrolyte concentration or ionic strength of a wastewater is important in the degree of aggregation which can be achieved. Using this theory, the Gibbs free energy which exists at each particle surface forms a negative double layer and keeps the particles apart. A low ionic strength solution results in highly repulsive forces between particles and only weak aggregation can be achieved. As the electrolyte concentration increases, a net attractive force results from double layer compression which produces strongly bound flocs. According to the theory, all DLVO interactions are reversible. Short-range forces include hydrogen, ionic and covalent bonding. Unlike long-rang forces, short-range forces result in irreversible aggregation and are thought to involve the interaction of polymers and filaments.

2.1.3 "Combination" Theories

Although the previously discussed theories provide a basis on which bioflocculation can be based, they do not completely describe the flocculation process. Among the various flocculation models discussed here and the relative support that each model has received by some workers, it appears most likely that some combination of these theories may best

describe the mechanisms behind flocculation.

Calleja *et al.* (1984) consider a number of different theories which may combine to produce the observed flocculation processes. These workers distinguish between natural and artificial forms of microbial aggregation. According to Calleja *et al.* (1984), natural aggregation results from the natural metabolic processes of a microbial consortium whether grown under natural or laboratory conditions. Artificial aggregation is defined as aggregation which is invoked by the addition of synthetic substances or under non-physiological conditions, such as the batch addition of coagulant. It is suggested that the mechanisms which govern floc formation differ somewhat depending on what type of flocculation is occurring. Thus, the mechanisms of floc formation which occur naturally during the growth of a microbial consortium are not necessarily the same as those which occur as a result of polyelectrolyte addition or the addition of cations under non-growth conditions. This is supported by the work of Busch and Stumm (1968) who found that the sensitivity of flocs to shear forces is much higher in those produced by artificial flocculation or the addition of synthetic polymer.

According to Calleja *et al.* (1984), the nature of the activated sludge process creates such formidable conditions that some process beyond polymer bridging is required to produce floc formation and maintain floc integrity. These researchers suggest that activated sludge flocs have a more highly complex structure than other flocs grown under less tortuous conditions. Calleja *et al.* (1984) further postulate that due to these growing conditions, activated sludge floc formation requires the involvement of filamentous

microorganisms that both reinforce the floc and provide an increased surface area for microbial attachment. In the absence of filaments, flocs are small and spherical, and may lack sufficient weight to settle effectively.

The work of Calleja *et al.* (1984) does not diminish the importance of polymeric material in floc formation. They explain the flocculation process as a number of steps which begin with the collision of microbial surfaces causing weak aggregation by hydrogen bond formation or hydrophobic interactions. The flocs formed at this stage are highly sensitive to shear forces and other physical hardships. Covalent bonding then occurs as a post-aggregative event. This event produces flocs which are much more resistant to high temperature, excessive shear forces and polymer hydrolysing enzymes. The presence of polymeric material and the negatively charged cell surfaces is important in both levels of microbial aggregation. As described, Calleja *et al.* (1984) combined the ideas of several theories of flocculation in an attempt to explain the many phenomenon observed in the growth and flocculation of mixed activated sludge cultures.

In a similar fashion, Higgins (1995) proposed a biosurface floc model which also incorporates many aspects of other flocculation theories. This theory explains the flocculation of bacteria in terms of their surface characteristics, specifically surface area and filament length. Higgins suggested that there exists an optimum surface area which produces flocculation by cation mediated interactions between particles and extracellular polymers, resulting from polymer bridging. Higgins theory also accounts for aggregation due to hydrogen bonding, electrostatic and hydrophobic interactions. Although the above

models require expansion and enhancement, the "combination" theories combine many of the accepted mechanisms suggested by other bioflocculation models and are supported by the work of a number of researchers as discussed in the following sections.

2.2 Extracellular Polymers

The effect of extracellular polymer production on the settling and dewatering properties of numerous sludges has been examined by many researchers. As mentioned above, the results of this research generally show that extracellular polymers play an important role in bioflocculation although the mechanisms and the extent to which the influence occurs remains unconfirmed.

2.2.1 Effect of Total Extracellular Polymer

Studies by Beccari *et al.* (1980) with laboratory-scale activated sludge reactors report a varying correlation between total extracellular polymer content (ECP) and settling properties as measured by sludge volume index (SVI). At bound ECP concentrations greater than 130 mg/g suspended solid (SS), an increase in ECP correlated with an increase in SVI or a deterioration in settling properties. Below an ECP content of 130 mg/g, the converse relationship was observed. Beccari *et al.* (1980) attributed this effect to the existence of an optimum ECP dose required for sludge settling as described by the Polymer Bridging model. At ECP doses on either side of the optimum value, a deterioration in settling will be observed. Pavoni *et al.* (1972) examined the deflocculation of a bacterial

suspension by the extraction of extracellular polymers. The readdition of ECP to the microbial solution as well as to an inert particulate solution resulted in reflocculation and settling. Urbain *et al.* (1993) compared the results from 6 different studies in the literature and found that in each case except one, a good linear correlation existed between ECP and SVI. However, four of these studies showed a positive correlation between ECP and SVI and one showed a negative correlation (the negative correlation being the study by Goodwin and Forster, 1985). The last study showed no correlation. Goodwin and Forster (1985) suggested that the observed decrease resulted from the polymer becoming less amenable to extraction as SVI increased. Another explanation is the difference in the units used to express ECP, (mg ECP / mg TOC in the ECP as opposed to mg/g SS). Kang *et al.* (1989, 1990) studied the effect of the addition of previously extracted extracellular polymers to similar sludges and found that increasing ECP levels correlated well with deteriorating sludge dewaterability as measured by specific resistance to filtration (SRF). Conversely, Gulas *et al.* (1979) found that increasing extracellular polymer content enhanced thickening and dewatering capabilities of sludge.

The above trends relating ECP to sludge settling and dewatering properties fail to distinguish between extracellular proteins and polysaccharides and other components of ECP. This research confirms the importance of ECP in flocculation but does not specifically delineate between the roles of these various ECP fractions, nor does it examine the effect of the unbound polymer fraction. Many researchers have shown that different correlations between settling and dewatering characteristics are observed when different

components of the ECP are considered. The variance in the correlations observed above may therefore result from variations in relative polysaccharide and protein content between the sludges studied. Because many of the researchers did not report the breakdown of the ECP it is difficult to compare the data obtained during this study with that obtained by other researchers.

2.2.2 Effect of Proteins and Polysaccharides

Although the data by Beccari *et al.* (1980) discussed above showed good correlation between total ECP and SVI, when extracellular polysaccharides alone were considered, no correlation with SVI was observed. Similarly, studies by Barber and Veenstra (1986) showed no correlation between SVI and carbohydrate concentration on a percent dry weight basis in either laboratory or field data. Studies by Forster (1985) revealed that increasing soluble polysaccharide improved sludge settleability. Goodwin and Forster (1985) suggested that improved settling characteristics correlate well with lower bound polysaccharide fraction. In contrast to the above data, studies by Urbain *et al.* (1993) showed that the SVI of a given sludge increased with increasing bound polysaccharide concentration. Similarly, Randall *et al.* (1971) found that as total carbohydrate content increased, the bound water content also increased resulting in poorly settled sludge.

Barber and Veenstra (1986) found a good correlation between protein on a percent dry weight basis and SVI. Below a 35 percent sludge protein content, a constant sludge volume index was observed. Above this concentration, a sharp increase in SVI occurred

which continued up to approximately 47 percent dry weight. Similarly, Urbain *et al.* (1993) reported a deterioration in sludge settleability with increasing bound extracellular protein concentration. Randall *et al.* (1971) found an inverse correlation between cellular protein and water retention; therefore, high protein content contributed to improved settleability. Studies by Hantula and Bamford (1991) examined the influence of extracellular proteins on the growth and flocculation of *Flavobacterium* by the addition of protease to the growth medium. These researchers found that protease inhibited flocculation at significantly lower doses than required for flocculation prevention of other polymerases. In terms sludge dewatering, Barber and Veenstra (1986) found no correlation between either protein or polysaccharides and SRF.

The work of Bowen and Keinath (1984) related the conditioning properties of a sludge to its biopolymer concentration. These workers found that an increase in both extracellular polysaccharide and protein resulted in a decrease in the optimum polymer dose required, although polysaccharides were determined to have a much greater effect. They suggested however, that the decrease in optimum polymer dose required during the presence of biopolymers was due to the fact that biopolymer surfaces are very reactive and serve as good binding sites for the coagulant. This research is in direct contrast with the findings of Novak and Haugan (1980), who found that the optimum polymer dose increased with increasing bound polymer content.

In Higgins (1995) research, a distinction was made between soluble and bound fractions of both proteins and polysaccharides. Higgins postulated that if divalent cations

could bridge flocs together by attaching to the negatively charged sites of the extracellular polymer on the microbial surface, then an increase in bound polymer should result in improved settling and dewatering properties. Higgins found that the bound protein content of the activated sludge increased from 40 to 170 mg/g SS as the concentration of applied divalent ion increased. Little change in the bound polysaccharide content was observed. As an increase in the divalent cation concentration occured, both the settling properties, measured as SVI, and dewatering properties, measured as capillary suction time (CST) and SRF, improved. Higgins concluded that although bound polysaccharides was not significant in the bioflocculation process, bound protein content was. Higgins further substantiated this claim by the addition of pronase, a non-specific, proteolytic enzyme which degrades extracellular proteins without affecting the internal proteins of the cell. Similar to the results found by Endo *et al.* (1976) and Hantula and Bamford (1991), this research confirmed that in the presence of pronase, deflocculation occured and both settling and dewatering properties deteriorated. The addition of several other degrading enzymes such as catalase and RNAase did not affect flocculation.

There is a great lack of consensus regarding the role of extracellular polymers in the research discussed above. Some of the discrepencies may be explained by variations in the method of extraction and measurement of biopolymers and the form in which polymer content is reported (i.e., bound vs soluble, and protein vs polysaccharides). More likely, differences in the feed composition and operating conditions are responsible for these effects. It generally appears that proteins play a larger role in flocculation with

increasing protein improving sludge settling and dewatering properties. Polysaccharides appear to play a less dominant role.

2.3 Role of Cations

The importance of cations in the activated process as both essential nutrients and as an important part of floc structure is not disputed. As with extracellular polymers, the extent to which cations are important and the means by which they act are not well established. It is generally agreed that polyvalent ions are an integral part of the floc structure involved in the aggregation of sludge particles by bonding to the anionic functional groups on the extracellular polymer surface.

Research by Bruss *et al.* (1992) found that the batch addition of magnesium ion to activated sludge resulted in the liberation of a large quantity of calcium ions (up to 3.5 mM). No significant release of sodium or potassium was observed. The addition of calcium ions however, did not affect the concentration of other cations in solution. The addition of monovalent ions, sodium and potassium, resulted in a minor release of calcium but not as significant as that seen in the case of magnesium. These researchers explain this as the presence of weakly bound calcium ions. Further, Bruss *et al.* (1992) found that any release in calcium from the sludge matrix by the addition of other ions resulted in the deterioration of sludge properties as measured by supernatant turbidity and SRF.

Kakii *et al.* (1985) examined the effect of batch addition of cations to a municipal activated sludge. These researchers found that the addition of calcium ion up to 1 mM

resulted in a decrease in both SVI and supernatant turbidity. Beyond 1 mM addition, no change in SVI or turbidity was observed. Kakii (1985) also noted that the bound calcium content of the sludge increased to a maximum concentration of approximately 14 mg/g SS which occurred at approximately 1 mM calcium addition. This would indicate that for a given sludge there is a limited number of calcium binding sites available. The number of sites appeared to be important in flocculation and therefore in the settleability of the sludge. The nature of the calcium binding site was not identified in this study. A later study by Kakii *et al.* (1990) examined the involvement of calcium ion in the flocculation of *Kluyvera* cryocrescens KA-103. These researchers found that flocs did not form when cultured on calcium-free media but flocculation improved with the increase in calcium up to a concentration of 1.5 mM. Above this concentration no further improvement in the extent of flocculation was observed. Kakii *et al.* (1990) also reported that the addition of sodium had a cooperative effect on calcium flocculation with improved flocculation above an NaCl concentration of 3.2 mM.

Angelbeck and Kirsch (1969) examined the effect of cations on non-slime forming strains of *Zoogloea ramigera*, a common microorganism found in activated sludge. Contrary to most other studies found in the literature, they found that both calcium and magnesium prevented floc formation when added to growth media in the range of 0.12 to 1.2 mM. Sodium was not found to affect aggregative growth. The addition of EDTA resulted in floc formation and suppressed the ability of calcium and magnesium to produce dispersed growth. Angelbeck and Kirsch (1969) suggested that aggregative growth is the

result of the deprivation of essential cations although the complete deprivation is known to be lethal. It light of the other studies discussed previously it seems unlikely that deprivation is a necessity for flocculation; however, there is no explanation for the effect of divalent ions reported by Angelbeck and Kirsch (1969).

Endo *et al.* (1976) studied six strains of floc-forming *Flavobacterium* isolated from activated sludge. The pure culture was grown in a low calcium medium which tended to prevent floc formation. Batch addition of calcium to these cells however, did not result in flocculation, implying that the flocculation process relies on the incorporation of calcium into the floc matrix during growth. This result was consistent with the findings of Higgins (1995). When a calcium concentration of 0.3 mM to 1.0 mM was added to the bacterial feed, adequate flocculation was achieved. Endo *et al.* (1976) showed that when these flocs were dispersed by suspension in distilled water, batch addition of calcium resulted in reflocculation, although complete reflocculation was not achieved. This result supports the theory that the presence of calcium during cell growth is necessary for the development of cellular components required for flocculation and thus the incorporation of cations into the floc matrix relies on physiological processes. Tezuka (1960) also studied the growth and flocculation of a *Flavobacterium* species commonly found in activated sludge. This worker found that the addition of both calcium and magnesium were required for flocculent growth and that the absence of either cation inhibited floc formation. Tezuka found that cells dispersed in distilled water could not only be reflocculated by magnesium and calcium but also by potassium, ammonium and sodium salts. In the research of Endo *et al.* (1976)

it was found that only one of six *Flavobacterium* strains examined could be deflocculated by EDTA. Research by Tezuka (1969) also found that cells dispersed in distilled water could be reflocculated by the addition of calcium and magnesium salts. In contrast to the work of Endo *et al.* (1976), this reflocculation effect was observed regardless of whether the cells had been killed by heat treatment or treatment with proteolytic enzymes and regardless of whether the cells were previously grown in a calcium containing media. However, Tezuka (1969) failed to explain that the media he considered to be calcium deficient contained 0.3 mM calcium as a background level in the polypeptone media. Therefore, the applicability of this study to calcium deficient sludges is not certain. Flocculation by dead cells lead Tezuka (1969) to suggest that flocculation mechanisms are physicochemical as opposed to physiological. However, the theory postulated by Endo *et al.* (1976) is still supported by Tezuka (1969)'s work. Endo *et al.* (1976) also found that cells grown at calcium levels less than 0.5 mM were susceptible to deflocculation by the addition of pronase. The addition of greater than 0.5 mM calcium to the feed however, produced a floc which was resistant to the effects of pronase as indicated by the lack of deflocculation and by a reduction in the level of free amino acids released into solution. Endo *et al.* (1976) also found that the amount of calcium ion in the feed affected the growth phase in which flocculation was observed. Higher calcium levels resulted in the delayed onset of floc formation. These workers suggested that higher levels of calcium protected the cell process through which flocculation occurs. It is also possible that calcium produces flocs which are more dependent on cations than protein content for their

structure.

Studies by Forster and Dallas-Newton (1980) found that the addition of magnesium ions to an activated sludge feed could be weakly correlated with improved SVI, although magnesium was not shown to bind to the sludge surface. Magnesium was added to a maximum concentration of 25 mg/L (1 mM). No correlation between calcium ions and SVI was shown although calcium was found to decrease the floc bound water content and to bind to the sludge surface, an effect not exhibited by magnesium. Calcium was added to a maximum concentration of 43 mg/L (1 mM). Forster and Lewin (1972) found that the addition of calcium ions to activated sludge lowered the bound water content while magnesium had no effect.

Hantula and Bamford (1991) also studied several pure cultures of *Flavobacterium*. These workers initially found that calcium and magnesium had different effects on the flocculation of bacteria with calcium enhancing and magnesium apparently inhibiting the process. Calcium and magnesium ions as high as 15 mM and 40 mM respectively were analyzed. Similar to the results found by Endo *et al.* (1976), further studies by Harantula and Bamford (1991) actually showed that magnesium did not inhibit flocculation but changed the growth phase required for optimum flocculation to the stationary phase instead of the late logarithmic phase as previously observed. Hantula and Bamford (1991) found that the addition of neither 40 mM EDTA nor NaCl as high as 500 mM resulted in deflocculation. Hantula and Bamford (1991) compared these results to the previous work of Endo *et al.* (1976) discussed above, who examined 6 different *Flavobacterium* species

and found that one strain of the bacteria was inhibited by EDTA. Hantula and Bamford (1991) postulated that the mechanisms by which different species of *Flavobacterium* flocculate are not identical although a protein dependency seems common. These workers also found that energy was not required for flocculation as the addition of energy depleting NaN_3 did not affect the process. This supports the work of Tezuka (1969) who found that flocculation could be induced in dead cells.

It is generally agreed that a limited number of binding sites exist for both magnesium and calcium and that up to this saturation dose, sludge settling and dewatering tend to improve with the addition of both ions. It is also agreed that the onset of floc formation is delayed by the addition of these cations. The role of monovalent ions has not been studied as extensively as divalent cations and therefore less is known of their roll in flocculation.

As mentioned previously, Higgins (1995) studied the addition of monovalent and divalent cations to the synthetic feed stream of a bench scale activated sludge system. Similar to the results of Tezuka (1969), Higgins found that the settling and dewatering properties of the activated sludge were optimal when both calcium and magnesium were added. The absence of either cation resulted in increased SVI and CST. Higgins later grew and identified two distinct activated sludge consortiums within his reactors, one which was sensitive to the ratio of calcium to magnesium and one which was not. As discussed by Higgins (1995), this agrees with the work of Tezuka (1969) and Endo *et al.* (1976) described above, that the sensitivity of activated sludge to various cations is

dependent on the bacteria present. This implies that each wastewater treatment plant may experience different results when cations are added and thus pilot tests are required before any conclusions can be drawn on the effects of cation addition. Further analysis by Higgins indicated that the absence of salts in the sludge feed stream resulted in the formation of small, light and weak flocs. Significant improvement in sludge settling and dewatering characteristics were observed in the presence of up to 2.0 meq/L (1 mM) of each cation. Optimum properties were observed around a Ca/Mg ratio of approximately 1.0. The presence of calcium and magnesium also resulted in the growth of denser flocs, possibly due to the reduction in bound water content as shown by Forster and Lewin (1972). The floc strength as measured by resistance to shear, also was shown to improve with an increasing calcium and magnesium concentration. Higgins further determined that the optimum polymer dose required for sludge conditioning decreased as divalent cation concentration increased which may be attributed to an observed decrease in colloidal particles (to be discussed in more detail later).

Studies on the effect of sodium and potassium addition by Higgins (1995) found that these cations also affected the settling and dewatering properties of the sludge. At a constant calcium and magnesium concentration, sodium was discovered to first improve settling characteristics of the sludge up to an NaCl concentration of 5 mM. Above this level, SVI and supernatant turbidity were shown to increase, although still being better than the control. Potassium was only studied to a limited extent and it was found that an addition of 1.5 mM resulted in improved SVI although it decreased the floc density.

Additionally, potassium at 1.5 mM was found to decrease sludge dewaterability. Sodium did not significantly affect dewatering properties or floc density up to 10 mM. After this point, dewatering properties deteriorated and the density of flocs decreased. At a sodium concentration of 20 mM, floatable sludge was produced and fine particles appeared in the supernatant. Here, the bound protein and polysaccharide contents decreased significantly. Higgins attributed the deterioration in sludge properties by sodium to the displacement of divalent cations from the floc matrix which, by the bridging model, would result in decreased binding between particles. The fact that floc strength greatly decreased at high sodium levels supports this theory. Observation of the flocs generated from the potassium fed reactor showed that a very different type of floc was produced when compared to that observed during sodium addition (Higgins, 1995). Potassium produced poorly dewatering sludge at levels much lower than sodium. This implies that these two monovalent cations play a different role in the flocculation of activated sludge although the extent to which this is true was not discussed by Higgins.

Higgins extended his analysis to consider the ratio of sodium over calcium plus magnesium, or the monovalent to divalent cation ratio on a milliequivalent basis, and its effects on the properties of the activated sludge. It was found that adjusting the Na/(Mg+Ca) ratio toward a value of one to two improved sludge properties even when the overall sodium concentration remained the same. The settling properties were therefore more a function of this ratio than of the absolute level of any one cation. This further supports the theory of competition between ions for binding sites on cell surfaces.

Higgins (1995) further examined the effect of batch addition of sodium, magnesium and calcium to previously cultured activated sludge samples. Cation addition was found to improve sludge settling in all cases while dewatering properties improved only with the divalent ions. The effects examined here were not as marked as those observed when the cations were added to the reactor feed. Higgins suggested that this was the result of the partial incorporation of cations into the floc matrix when not added to the growth media. Sodium addition tended to liberate previously bound calcium, magnesium and biopolymers from the flocs and produced a sludge with slightly higher SRF. Calcium and magnesium addition were also found to reduce the number of supracolloidal particles in the sludge.

To a limited extent, Higgins (1995) examined the effect of cations on industrial activated sludge in short-term laboratory studies and during full-scale operation. Generally it was found that the addition of divalent cations improved sludge settling and dewatering. This was particularly true for industrial wastewaters in which the ratio of calcium to magnesium was significantly different from one.

2.4 Other Factors

Beyond the models discussed above, numerous factors other than cations and extracellular polymer content have been reported to significantly effect the ability of a sludge to be settled and dewatered. Research by Randall *et al.* (1971), Forster and Dallas-Newton (1980), and Katsiris and Kouzeli-Katsiri (1987) indicated that bound water content is an important factor in both sludge settling and dewatering. Karr and Keinath (1978),

Novak and Haugan (1980), Novak *et al.* (1988), Barber and Veenstra (1986), and Bruss *et al.* (1992) have all reported that particle size distribution significantly affects the ability of a sludge to be dewatered. The research surrounding these findings are discussed below.

2.4.1 Particle Size Distribution

Many workers suggest that particle size distribution is the most important parameter affecting the dewatering of activated sludge (Karr and Keinath, 1978, Novak *et al.*, 1988). Karr and Keinath (1978) studied the effect of particle size of raw sludge, activated sludge and anaerobically digested sludge. These workers examined the size distribution of particles in each sample and determined the associated value of specific resistance. The particle size distribution was then altered to mimic the distribution of another sludge by the addition of the appropriate size particles. Karr and Keinath (1978) found that two samples from a completely different source had very similar dewatering properties when their particle size distributions were equal. The supracolloidal solids fraction (particles with diameter less than 100 μm) was found to be the most significant fraction affecting the dewatering of sludge. This was attributed to the ability of supracolloidal particles to cause blinding of the filter cake and media. Filter media has pores sizes ranging from 1 to 100 μm; therefore, smaller particles are able to pass through while larger particles stay on top of the filter forming a cake. Supracolloidal particles are of sufficient size that they can make their way into the filter media and clog it without passing through. These solids can also cause cake blinding by migrating through the cake and plugging critical pathways.

Research by Barber and Veenstra (1986) with activated sludge samples from 23 municipal treatment facilities and 5 bench scale units also found a direct correlation between the percentage of supracolloidal particles and SRF. This concept is supported in the work of Novak *et al.* (1988) who found that sludges with mean particle diameter less than 40 μm may cause blinding while blinding never occurs when the mean particle diameter is greater than 40 μm. These workers found that the degree to which blinding occurs can be quantified by using the equation,

$$r = \alpha V^{\beta}$$

where:

α =specific resistance measured for the initial filtrate volume

r = average specific resistance of the entire filtrate volume

V = volume of filtrate

ß = a contant which expresses the change in r with the change in V

ß is determined by plotting ln (time) versus ln V, the slope of this line being ß+2. A positive value of ß indicates that blinding has occurred.

Roberts and Olsson (1975) found that the optimum polymer dosage required by a sludge is dependent upon the particle size distribution. The optimum dosage was found to be independent of the original particle distribution and increased with increasing supracolloidal fraction.

The work of Karr and Keinath (1978) further examined the effect of dissolved

solids on dewatering and found them to have only a minor influence. The fragile settleable solid fraction was found to increase SRF; however, this was attributed to the shearing of these particles into smaller particles by the forces exerted during the SRF test. Rigid settleable solids were not found to influence sludge dewatering.

2.4.2 Bound Water Content

After particle size, Katsiris and Kouzeli-Katsiri (1987) identify particle surface properties as the most important factor in the dewatering of sludges. The presence of proteins, polysaccharides and DNA and the charge exerted by the cell surface result in the adsorption of water which lowers the specific gravity of the particle. Particularly high levels of hydrophilic polysaccharides tend to increase sludge water content (Randall, 1971, Forster and Dallas-Newton, 1980). According to Kauzmann (1959), water can either fill the voids within the polymer surface or become tightly bound due to the polarity of the cell surface. Water molecules which are tightly bound to the cell surface not only reduce the gravitational pull, thus inhibiting settling, but also reduce dewaterability by not readily releasing bound water. Katsiris and Kouzeli-Kitsiri (1987) showed that the addition of coagulant resulted in a sharp decrease in bound water content, with the minimum content occurring at the point of optimum coagulant dose. Friedman *et al.* (1969) postulate that the mechanism of flocculation by synthetic polyelectrolytes (which contain similar anionic groups such as $-COO^-$, and $-SO_3^-$ and nonionic -OH groups) is identical to that produced by natural biopolymers. This contradicts the theory of Calleja *et al.* (1984) which

distinguishes between the mechanisms of natural and artificial flocculation. Katsiri and Kouzeli-Katsiri (1987) postulate that the coagulant acts by replacing the bound water and that the optimum cell surface coverage occurs at this point of minimum bound water content. Studies by Randall *et al.* (1971) showed that the bound water content of a sludge increased with increasing concentration of total carbohydrates, although the ratio of these two factors is specific to each sludge. The presence of increasing amounts of protein decreased the ability of a sludge to adsorb water, likely due to its hydrophobicity. Unlike the relationship with carbohydrate, the ratio of increasing protein to decreasing bound water content seems to be constant regardless of the sludge source (Randall *et al.*, 1971). Similar results were found by Forster and Dallas-Newton (1980) although the work of Barber and Veenstra (1986) of 28 different activated sludges contradicts this theory.

2.5 Conclusion

The previous literature review confirms that although considerable research has been conducted to examine flocculation and the roles of various factors on flocculation, the process is very complex and not well understood. The research discussed above confirms that the effect of cation addition on sludge properties is highly dependent upon the sludge in question. It is generally agreed that divalent cations improve sludge settleability; however, the extent of the improvement cannot be predicted without laboratory or pilot-scale testing. In a similar way, the effect of cation addition on extracellular polymer production and the relationship between these polymers and sludge settling and dewatering

properties is highly variable. The operating conditions of treatment plants including sludge age, reactor feed composition and start-up conditions, appear to significantly affect the ultimate response of sludges to cation addition.

III. MATERIALS AND METHODS

The purpose of this study was to determine the effects of cation addition on a bench-scale industrial activated sludge reactor. Such effects were measured through an analysis of various settling, dewatering and conditioning properties. The techniques used for this study were acquired from the earlier work of a previous VPI&SU doctoral student (Higgins, 1995) with a few additions and minor modifications. These techniques are a compilation of several standard methods and methods previously developed by other researchers. The following discussion outlines the materials and procedures used in this study and the source of each test procedure.

3.1 Materials

3.1.1 Cation Source and Preparation

The addition of cations to the feed streams of each reactor was accomplished through the use of ACS grade, Fisher Scientific, chloride salts of Na^+, Mg^{++}, Ca^{++} and K^+. One molar salt stock solutions were prepared for cation addition to feed streams. These stock solutions were used in all cases except when the influent salt concentration exceeded 20 mM whereby direct salt addition was used. Similar materials were used for batch cation addition tests, although lower concentration stock solutions were prepared.

3.1.2 Biomass and Wastewater Source

The biomass used to originally seed the activated sludge reactors at the beginning

of each new trial was obtained from the Chemical Company. The second tank in the three stage activated sludge system was used as a biomass source to ensure that microorganisms accustomed to a lower food to microorganism ratio were obtained.

The wastewater used to feed each reactor was also obtained weekly from the Chemical Company. This wastewater was drawn from the wastewater treatment plant's equalization basin following neutralization, equalization and nutrient addition. When possible the feed was maintained at a temperature of 5° C for a maximum of 7 days. Feed solutions in use were kept at 20° C. New feed batches including added salts were made up every two days to avoid anaerobic growth in the feed containers.

3.1.3 Polymer Description and Preparation

The polymer used for conditioning studies was obtained from and identical to that used for conditioning at the Chemical Company. This was a CYTEC 496C cationic polymer. Stock solutions of 2000 mg/L, 500 mg/L and 300 mg/L were used for sludge characterization and conditioning. The solution was prepared from a powdered product which was mixed with distilled water for a minimum 12 hour period. Polymer solutions were stored at 5° C for a maximum of 3 days. This was done to avoid changes in polymer effectiveness with age, which is consistent with the polymer manufacturer recommendations.

3.2 Methods

3.2.1 Bench Scale Activated Sludge Reactor Configuration

Two differing bench-scale activated sludge reactors were used in this study. One reactor was operated as a completely mixed activated sludge (CMAS) reactor and the other as a continuous feed sequencing batch reactor (CFSBR) with distinct react, settle and decant stages but with a constant inflow during the react phase. This was done such that the batch reactor would more closely emulate a completely mixed system.

The 10 L CMAS reactors were constructed of clear Plexiglass sheeting with a completely mixed zone and quiescent zone to operate as a clarifier. A Plexiglass baffle was placed in the reactor to create these separate zones. The baffle height was adjusted such that optimum settling occurred in the quiescent zone while still maintaining a constant exchange of solids between the two zones. Four 4 L, clear glass jars were used for CFSBRs.

3.2.2 Bench Scale Activated Sludge Reactor Operation

Aeration for both reactor configurations was provided by porous stone diffusers and house air. In order that complete mixing be achieved through aeration, each reactor was operated at a dissolved oxygen concentration between 6.5 and 8.5 mg/L. Wastewater feed was provided through plastic tubing with the use of a peristaltic pump. The reactors were operated at a mean cell retention time (MCRT) of 13 days and ambient temperature of 20° $\pm 2°$ C. A hydraulic retention time (HRT) of 2 days (twice that of the industrial

wastewater treatment plant) was used in order to reduce wastewater consumption. It is generally accepted that a reactor must be operated for a duration of at least three SRT's to achieve steady state conditions. Due to time constraints, the reactors were operated until consistent sludge settling and dewatering properties over a minimum period of 3 days were observed, typically 14 to 25 days. The "steady state" data values were taken as the average of 3 to 7 data points during this time. Wasting of the CMAS reactors was accomplished through the daily removal of mixed liquor.

The CFSBRs were allowed to fill over the 2 day HRT to a maximum volume of 3 L. At this volume, the feed and aeration were turned off and the reactor was allowed to settle for a period of 3 hours. During this time, the mixed liquor would settle to approximately 750 mL. The supernatant was then decanted off manually and the fill cycle was started again. The CFSBR reactors were wasted once every two days just prior to the end of the react stage.

3.2.3 Wastewater Characterization

3.2.3.1 Cation Analysis

Sodium, potassium, magnesium, calcium and ammonium were analyzed using a Dionex Ion Chromatograph with CS12 column, Dionex 2010i conductivity detector and Dionex 4270 integrator. A 20 mM methane sulfonic acid eluent was used at a flow rate of 1.0 mL/min.

3.2.3.2 Microscopic Observation

The microbial population of each reactor was examined regularly by observation with an Olympus CH-2 microscope at 40x, 100x and 400x magnification to determine how flocs were distributed, to observe any growth of filamentous microorganisms and to determine what higher forms of life were present.

3.2.3.3 Settling Properties

Total suspended solids (TSS) and Sludge Volume Index (SVI) were determined using Standard Method 2540D and 2710D, respectively. Settling velocity was determined by placing a 250 mL or 1000 mL sample of mixed liquor (depending on the amount of sludge available) in a graduated cylinder and recording the interface height over time.

3.2.3.4 Dewatering Properties

Dewatering properties of the sludge were analyzed using capillary suction time (CST) and specific resistance to filtration (SRF). The CST procedure was performed as prescribed in Standard Method 2710G. The SRF was determined according to the procedure described by Christensen and Dick (1985). In this method, a 100 mL sample of mixed liquor was filtered through Whatman No. 2 filter paper at a pressure ranging from 10 psi to 16 psi. A pressure of 13 psi was typically achieved. The volume of filtrate (V) was then recorded with time (t) over a maximum period of five minutes. The value of specific resistance (r) was calculated by the equation,

$$r = \frac{2 \cdot P \cdot A^2 \cdot b}{\mu \cdot C}$$

where,

r = specific resistance to filtration (m/kg)

P = filtration pressure (N/cm^2)

A = area of filter paper (cm^2)

μ = viscosity of liquid (Ns/cm^2) [Assumed to be constant at 1×10^{-7}]

b = slope of the line obtained by plotting t/V vs V (s/cm^6)

and,

$$C = \frac{1}{\frac{(100-C_i)}{C_i} - \frac{(100-C_f)}{C_f}} \qquad (g/cm^3)$$

where,

C_i = initial solids concentration or MLSS (%)

C_f = cake solids concentration (%)

3.2.3.5 Conditioning Properties

During the initial stages of sludge characterization, the optimum polymer dose was determined by adding a known volume of 2000 mg/L stock polymer solution to 400 mL of biomass and adding distilled water up to a total of 500 mL. This solution was mixed at a Gt of 600 and the CST of the resulting mixture was plotted with polymer dose. During reactor operation, less biomass was available for the analysis, thus a known volume of 500 mg/L or 300 mg/L stock polymer solution was added to a 75 mL sample of mixed liquor with water added to a total volume of 115 mL. This mixture was stirred slowly for 12 seconds, just to mix the polymer with the biomass. The CST of the resulting mixture was plotted with polymer dose. Optimum dosage was determined as the dose which produced the lowest CST. An analysis of these two methods showed that optimum polymer dose varied little between these methods.

3.2.3.6 Extracellular Polymer Extraction and Analysis

Extracellular polymer extraction was performed using the method described by Higgins (1995) with one minor modification. This method involved the extraction of the soluble polymer fraction by centrifugation at 10 g for 15 minutes. Once the supernatant had been decanted, the solid pellet remaining was resuspended in an NaOH/distilled water solution of pH 11. The pellet/NaOH solution was then mixed in a Waring blender for 10 seconds, instead of 3 seconds as prescribed by Higgins, to ensure complete break up of the pellet. The resulting solution was centrifuged at 10 g for 15 minutes. Soluble and bound

protein content was measured using the method described by Lowry *et al.* (1951) with Hartree (1972) modifications. The Dubois (1956) method was used for polysaccharide analysis As described by Higgins (1995), bovine serum albumin and glucose were used for protein and polysaccharide standards, respectively. Two sets of protein standard solutions were prepared, one at neutral pH and the other at pH 11. It was determined, however, that the resultant standard curves obtained were not significantly different when the accuracy of the extraction procedure was considered. A linear standard curve was obtained over the range of 0 to 120 mg/L and 0 to 100 mg/L for protein and polysaccharide, respectively.

3.2.3.7 Gel Filtration

Gel filtration was used to analyze the soluble polymer in mixed liquor samples before and after polymer addition. This analysis enabled the comparison of the molecular weight of polymer found in the supernatant of the untreated mixed liquor with that of the supernatant at optimum polymer dose in order that differences between optimum polymer dosages might be postulated. The approximate molecular weights of these soluble polymers were obtained by gel chromatography using a 15 mL, G-75 Sephadex gel column with an eluent containing 0.5 mM EDTA, 50 mM NaCl and 5 mM hydrogen phosphate buffered to a pH of 7.5. Approximately 3.5 mL of the eluent mixture were collected per 4 minute period over 2 hours. Each 3.5 mL sample was analyzed by spectrophotometer at a wavelength of 280 nm. The absorbance was then plotted against elution volume and

related to molecular weight as obtained from standards.

3.2.3.8 Other Properties

Floc density was measured by the isopycnic Percoll method described by Knocke *et al.* (1993). This method involved the addition of several drops of mixed liquor to a 10 mL sample of Percoll/distilled water solution at a known density. The mixture was then centrifuged at 12 g for 15 minutes which created a density gradient within the solution. Several drops of the solution at the level where the mixed liquor solids came to rest was analyzed with a Reichert ABBE MarkII digital refractometer. Higgins (1995) had previously correlated the refractive index to floc density by the equation,

$$\rho = 6.7862 \times \eta - 8.0426$$

where,

ρ = floc density (g/mL)

η = refractive index

Particle size distribution (PSD) was measured using a HIAC Model PC-320 particle size analyzer. Dilution of the mixed liquor samples were prepared at a ratio of 1:1000 with tap water to minimize any changes in particle size caused by changes in cell osmotic pressure. Floc stability was measured by mixing 400 mL of mixed liquor in a 1 L Plexiglass cylinder with baffles at a G of 500 s^{-1}. The CST was measured over a period of 20 minutes and plotted with time. For comparison of the various trials, each CST

obtained during the 20 minute duration was normalized with respect to the CST at time zero for that specific sample.

3.2.4 Batch Tests

Cation addition was performed on a batch basis by adding a known volume of stock salt solution to a 300 mL mixed liquor sample. The sample was then mixed for 30 minutes at 60 rpm at which time the CST, SRF and settling velocity were analyzed and recorded.

IV. RESULTS & DISCUSSION

The raw data acquired during this research are summarized in Appendix A.

4.1 Wastewater and Sludge Characterization

The wastewater obtained from the Chemical Company each week was analyzed by ion chromatography to determine the distribution and variation in cation concentrations. The average concentration and concentration range of each cation measured during the course of this research and the monovalent to divalent cation ratio on a milliequivalent basis are summarized in Table 1 below.

TABLE 1
Wastewater Characterization

Cation	Average Concentration (mM)	Concentration Range (mM)
Sodium	10.7	8.28 - 17.9
Ammonium (as Nitrogen)	1.43	0.60 - 3.50
Potassium	0.12	0.07 - 0.22
Magnesium	2.12	1.80 - 2.73
Calcium	3.66	0.52 - 5.90
Mono/Divalent Ratio (meq basis)	1.23	0.60 - 2.40

Each sample of mixed liquor received from the Chemical Company was analyzed with respect to solids concentration, settling and dewatering properties, pH, cations and particle size distribution. The average properties and the range are given in Table 2.

TABLE 2
Mixed Liquor Properties (as received)

Property	Average	Range
MLSS (mg/L)	3568	3312 - 3938
pH	7.83	7.8 - 7.85
SVI (mL/g)	257	241 - 274
CST (s)	16.3	13.5 - 21.6
SRF (m/kg)	1.06×10^{12}	5.8×10^{11} - 1.5×10^{12}
Soluble Protein (mg/L)	26.6	21.9 - 31.2
Bound Protein/MLSS (mg/g)	10.0	6.2 - 12.5
Soluble Polysaccharide (mg/L)	3.2	2.3 - 4.0
Bound Polysaccharide/MLSS (mg/g)	2.2	1.5 - 3.5
Optimum Polymer Dose (mg/L)	51	44 - 60
Sodium (mM)	10.7	10.5 - 10.9
Ammonium (as N) (mM)	0.30	0.08 - 0.62
Potassium (mM)	0.12	0.108 - 0.133
Magnesium (mM)	1.87	1.83 - 1.90
Calcium (mM)	3.82	3.62 - 4.19
Mono/Divalent Ratio (meq basis)	0.98	0.91 - 1.0

4.2 Batch Cation Addition

Batch additions of sodium, magnesium and calcium were performed to examine the effect of these cations under non-growth conditions. Sodium was added over the range of 1.0 to 25 mM while various additions of calcium and magnesium over the range of 1.0 to 15 mM were examined. Both calcium and magnesium were added simultaneously over the

range of 2.5 to 7.5 meq/L each. From this study, it was determined that the batch addition of sodium, calcium and/or magnesium did not significantly affect the settling velocity of the sludge or the dewatering properties as measured by CST and SRF. The results of this analysis contrast the work of Higgins (1995) who found that similar additions to several industrial activated sludges resulted in notable property changes. This difference may be attributed to the fact that the sludge, as received from the Chemical Company, contained a very low biopolymer concentration. According to the polymer bridging theory, the effect of cations on sludge properties relies on interaction between the ions and the polymer at the sludge surface. At such low polymer levels, there may not have been sufficient adsorption sites for notable property changes to be observed.

4.3 Cation Addition to Laboratory-Scale Reactors

The cations found in the wastewater were shown in Table 1 to vary over a wide range. This variation implies that the chemical composition of wastewater as received weekly from the Chemical Company also varied. This was also observed by physical differences in the wastewater obtained from one week to the next. The composition of the influent wastewater has been shown by many researchers to significantly affect sludge settling and dewatering properties. As the laboratory-scale activated sludge reactors were operated over a period of five months, the highly variable nature of the wastewater affected the results obtained during this time, making the results from each trial very difficult to compare. The variations in wastewater composition most significantly affected sludge

settling and conditioning, although other sludge properties were also affected. For this reason, the results from the control reactor operated for each data set were used to normalized the data for SVI and optimum polymer dose such that the relative effects of cation addition could be compared. For example, the settling characteristics of each sludge is presented as SVI of the sample over SVI of the control operated at the time of that trial (or SVI/SVIc). Sludge dewatering was less affected by the variability of the wastewater and this data was presented in raw form.

Additional difficulties were experienced as the reactor configurations used in this study selected for filamentous microorganisms. When filamentous bulking occurred, the reactors were kept in operation until the problem was controlled. In one case (when Na=50 mM) however, bulking could not be eliminated in the control reactor and thus no data exists with which to normalize. To compensate for this, the control from another trial (Na = 20 mM) which most closely approximated typical system performance was used to normalize the Na=50 mM data. A control reactor was not run alongside the magnesium-fed reactors; therefore, the data from these trials were not normalized.

Due to the large difference in reactor configuration and operating conditions, the biomass in the laboratory reactors demonstrated different properties than that of the sludge at the Chemical Company treatment plant. The typical steady state properties and range over which these reactors operated in this study are summarized in Table 3. Not shown in this table is the effect that laboratory conditions had on sludge biopolymer production. Although the addition of various cations affected both the bound and soluble biopolymer

concentration, in all trials, polymer production far exceeded that found in the sludge as received from the Chemical Company. Generally, the laboratory reactor sludge produced 3 to 13 times more extracellular polymer than the sludge at the full-scale treatment plant.

Table 3
Laboratory-Scale Reactor Operating Conditions

Property	Average	Range
MLSS (mg/L)	1800	1430 - 2453
pH	7.8	7.5 - 8.2
Dissolved Oxygen (mg/L)	7.2	6.5 - 8.0
Temperature (°C)	20	18 - 22

4.3.1 Effect of reactor configuration

An attempt was made initially to operate both CMAS reactors and CFSBRs , and to compare the results of these tests. In the early stages of this work, it was determined that the two configurations did not produce sludge with similar properties. The CFSBRs maintained a much lower solids concentration than the CMAS reactors and produced higher supernatant solids. Floc density was much lower in the CFSBRs and sludge settled and dewatered poorly in comparison, even when operated at the same cation feed levels. Additionally, the CFSBRs produced much higher concentrations of soluble polymers and lower levels of bound polymer. This possibly resulted from the increased shear forces caused by the aeration of very small sludge volumes. The CFSBRs produced extremely filamentous sludge. For this reason, the use of batch reactors was not continued beyond

the first stage of this research.

4.3.2 Effect of Sodium Addition

Sodium was added to the reactor feed at 4.4, 10, 20 and 50 mM concentrations. The addition of sodium did not affect the consumption of potassium or magnesium within the reactor. That is, the concentration within the reactor was the same as in the feed stream. Ammonium levels in the reactor were 0.5 to 1.6 mM less than found in the feed solution; this was not attributed to nitrification as shown by the lack of production of nitrite or nitrate. Calcium ion concentration was found to vary greatly with the addition of sodium, ranging from a consumption of up to 2.0 mM to a liberation of up to 2.5 mM. The variation however, did not correspond to changes in sodium addition, implying that some other factor influenced the consumption of calcium.

At sodium concentrations of 4.4 and 10 mM, the flocs appeared similar to those of the control reactor. Above this level, the sludge appeared somewhat granular and numerous unflocculated, unicellular bacteria were observed in the supernatant. The presence of filamentous organisms was much less common in the reactors with high sodium content. When filaments did occur, filamentous bulking was not experienced even when the filament concentration was extremely high. It appears that the presence of sodium ions prevented filamentous bulking.

As the sodium dose was increased up to 50 mM, the settling properties of the sludge, as measured by SVI, were dramatically improved. At the highest sodium dose, an

SVI of 72 was achieved which corresponds with a 60 percent reduction in SVI relative to the control reactor. This effect is shown in Figure 1.

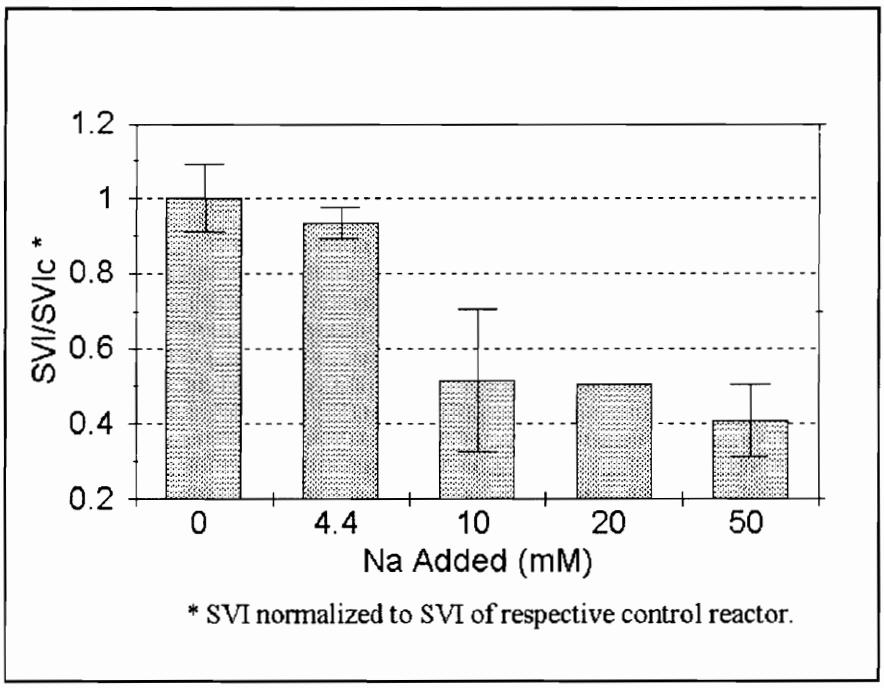


Figure 1: The effect of sodium addition to the wastewater feed on sludge SVI.
No control data are available for the Na=50mM trial; therefore, data from that trial are normalized with respect to the control for the Na=20mM trial.
Error bars represent one standard deviation.

These results are in contrast to the research of Higgins (1995) who found that increasing sodium above 5.0 mM resulted in a reduction in SVI. The large improvement in sludge settling resulted from an increase in the number of small, highly compressible particles, produced at high sodium levels.

Although SVI improved, a trend of increasing supernatant solids and SRF with sodium addition was observed, as shown in Figures 2 and 3. In this study, it was

determined that CST did not accurately quantify sludge dewatering and did not vary with SRF even when normalized to the supernatent solids concentration. Poduska (1981) also reported that the CST test was not a good indicator of the dewaterability of sludge from this Chemical Company. For this reason, the CST test will not be discussed in future sections and dewatering properties will be characterized by SRF only.

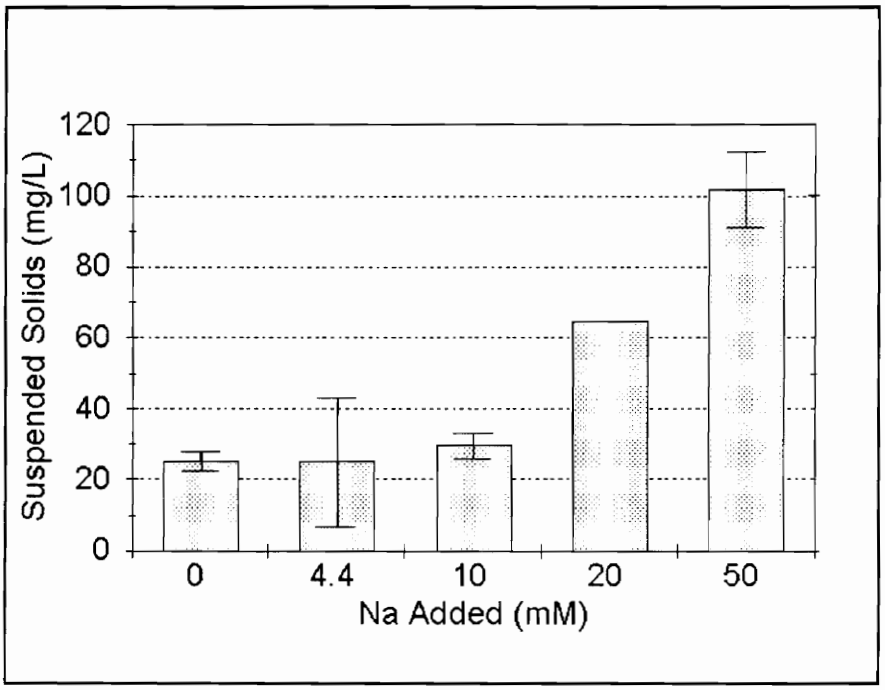


Figure 2: The effect of sodium addition to the wastewater feed on sludge supernatant solids.
No control data are available for the Na=50 mM trial; therefore, data from that trial are normalized with respect to the control for the Na=20 mM trial.
Error bars represent one standard deviation.

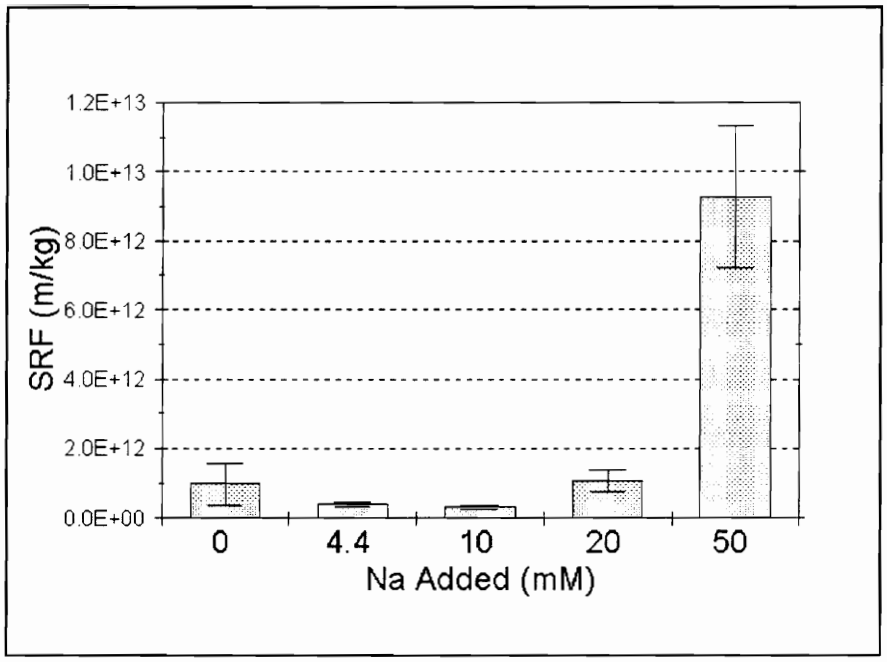


Figure 3: The effect of sodium addition to the wastewater feed on sludge SRF.
No control data are available for the Na=50mM trial; therefore, the data from that trial are normalized with respect to the control from the Na=20mM trial.
Error bars represent one standard deviation.

Both supernatant solids and SRF improved slightly with the addition of 4.4 mM sodium but deteriorated beyond this point. At a sodium dose of 50 mM, the supernatant solids concentration reached 102 mg/L, or 8 times that experienced without sodium addition, while SRF peaked at 9.3×10^{12}, or 14 times the SRF of the control reactor. Many free floating organisms were observed in the supernatant in this case, even after 3 hours of settling. Higgins (1995) also noted an increase in fine particles at high sodium levels. The correlation between fine particles and SRF was also reported by Karr and Keinath (1978).

A test for blinding was undertaken using the procedure described by Novak *et al.*

(1988) and it was determined that the increase in SRF was not the result of filter media or cake blinding. The deterioration in dewatering properties could be attributed to floc instability which resulted in floc break-up from shear forces applied during the SRF test. An increase in the number of small particles caused by floc shearing would render the sludge much more difficult to dewater. The floc stability was measured by the change in CST with the application of shear forces. Up to a sodium concentration of 4.4 mM, the floc structure was relatively unchanged with the applied shear. As sodium levels increased, flocs tended to break up with the mixed liquor fed 50 mM sodium being very unstable, as shown in Figure 4. The production of weak flocs by the addition of sodium was also observed by Higgins (1995).

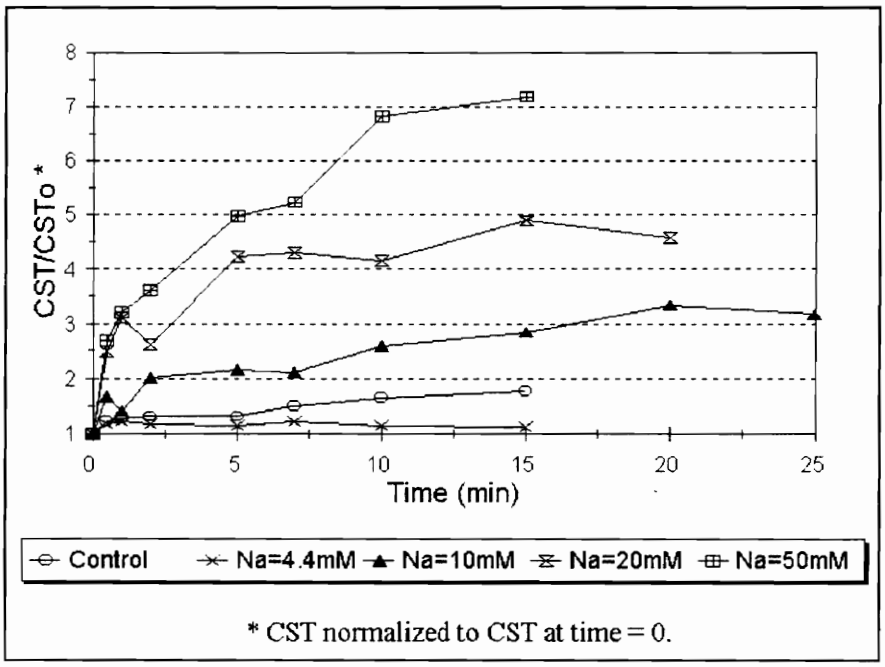


Figure 4: The effect of sodium addition to the wastewater feed on sludge floc stability.

In support of the above observations, the addition of increasing amounts of sodium was observed to have a significant effect on the particle size distribution of the sludge. As shown in Figure 5, increasing sodium resulted in an increase in the number of particles with diameter ranging from 5 to 50 μm. A notable decrease in the number of particles larger than 50 μm occurred at the same time. The exception to this is the Na=4.4 mM trial (not shown in Figure 5) in which a very small number of fine particles were present. The increasing number of fine, poorly settling particles correlated with high supernatant solids concentration seen at elevated sodium levels.

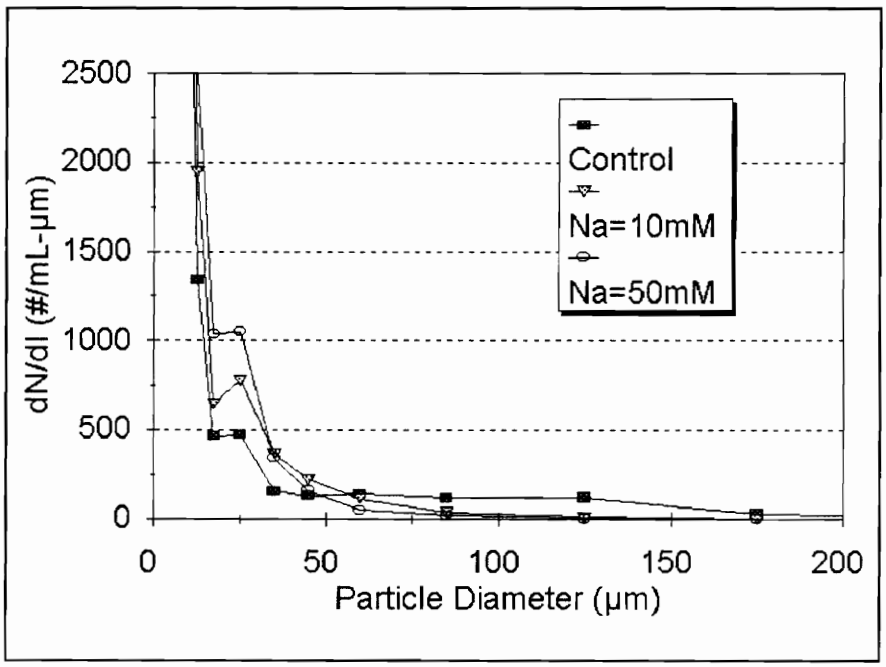


Figure 5: The effect of sodium addition to the wastewater feed on sludge particle size distribution.
Particles with diameter less than 10 μm and greater than 200 μm are not shown.
Trials for Na = 4.4 mM and Na = 20 mM are not shown.
N = number of particles, l = particle diameter (μm)

The optimum polymer dose required for sludge conditioning remained constant up to a sodium concentration of 10 mM. Increasing sodium beyond this point increased the polymer requirement as shown in Figure 6. At Na=50 mM, the optimum polymer dose had more than doubled that required in the absence of added sodium. This may be attributed to the presence of discrete particles which provide a large number of binding sites and therefore require more polymer in order to become aggregated. The increase in optimum polymer dose correlated well with increasing supernatant solids.

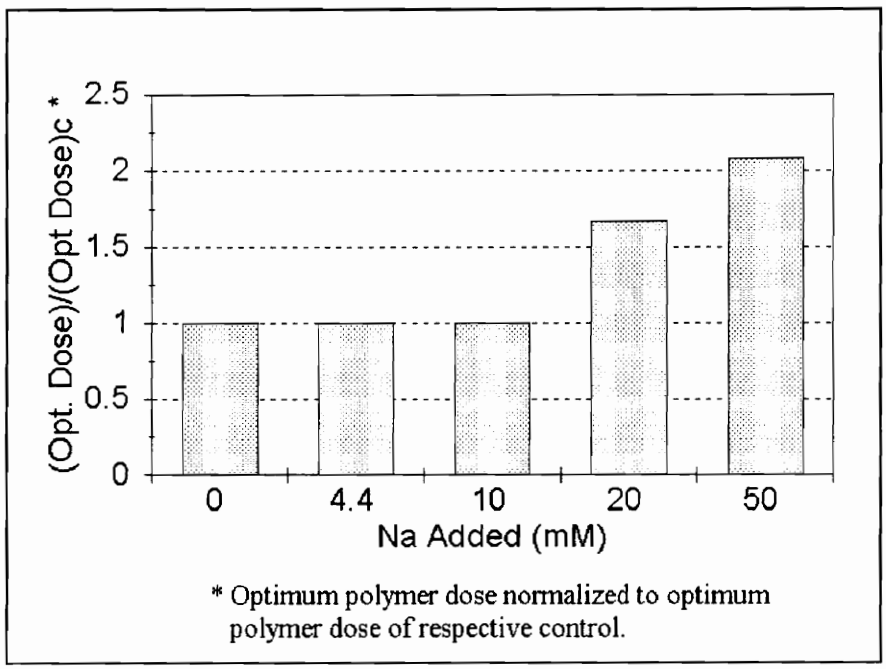


Figure 6: The effect of sodium addition to the wastewater feed on sludge optimum polymer dose.
No control data are available for the Na=50 mM trial; therefore, the data for that trial are normalized with respect to the control from the Na=20 mM trial.
No error bars are shown as each bar represents one analysis.

No significant trend was observed for extracellular protein or polysaccharide production with sodium addition. This observation does not agree with the works of Higgins (1995) who found that sodium addition resulted in a reduction in bound polymer and that bound protein fraction increased as sludge settling improved.

Gel filtration was performed on the supernatant from the sludge before and after the addition of conditioning polymer. The results of this analysis are shown in Figure 7.

With the exception of Na=20 mM, (not shown) the addition of sodium (Figures 7b and 7c) did not produce many low molecular weight polymers. The majority of the polymer produced during these trials had molecular weight greater than 45000 amu (elution volume less than 40 mL). This does not agree with the work of Forster (1985) who found that the presence of high molecular weight polymers was associated with poorly settled sludge as measured by SVI. In contrast, Kang *et al.* (1990) showed that the effect of extracellular polymer on dewatering was more a function of the type of polymer present than the polymer molecular weight. At the optimum polymer dose, the large molecular weight polymers were clumped to form molecules of molecular weight greater than 66000 amu (elution volume less than 30 mL).

The addition of sodium at 4.4 mM improved both sludge settling and dewatering properties, reduced supernatant turbidity and improved sludge resistance to shear. Above 10 mM, sodium produced granular sludge which settled extremely well but which was prone to shear and resulted in very high supernatant solids. An increase in 5 to 50 μm particles and a decrease in the number of 50 to 200 μm particles corresponded with an

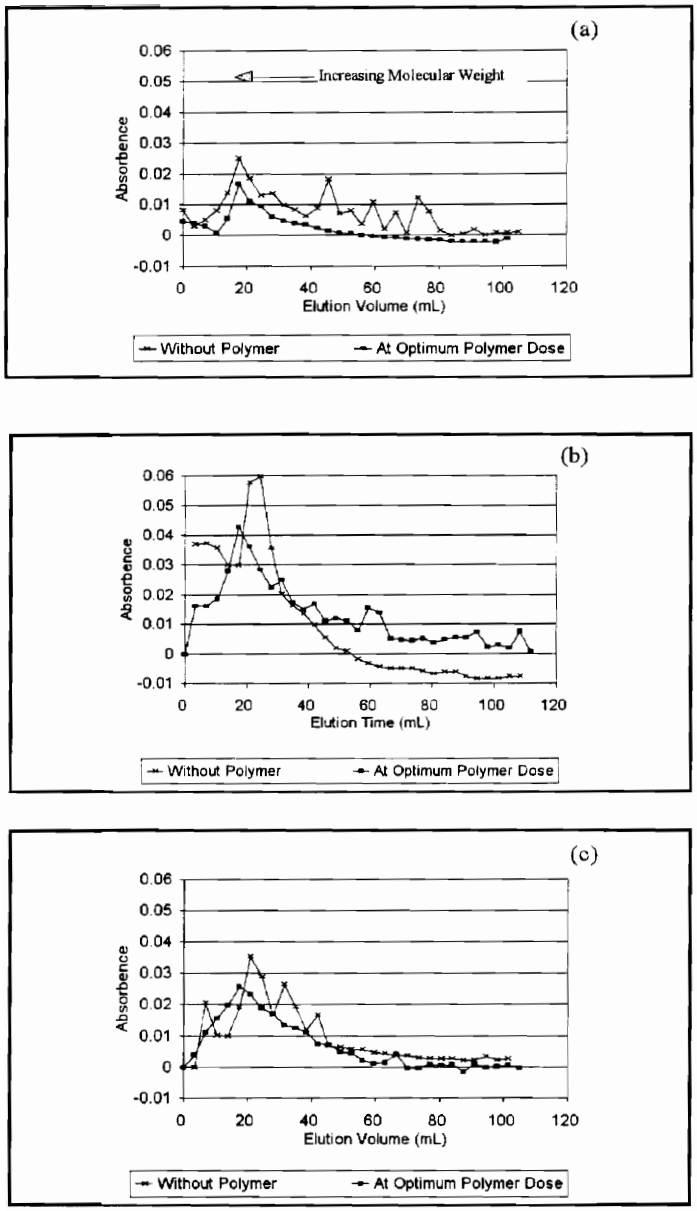


Figure 7: Gel fitration of the supernatant from sludge fed sodium enriched wastewater before polymer addition and at optimum polymer dose. (a) Control (b) Na=10 mM (c) Na=50 mM Data from the Na = 4.4 mM and Na = 20 mM trials are not shown. Exclusion volume = 25 mL.

increase in sodium concentration. Elevated sodium levels also resulted in a deterioration in sludge dewatering characteristics and an increase in conditioning polymer requirements. No pattern of extracellular polymer production with increasing sodium was observed. It is evident, however, that sodium addition resulted in the production of high molecular weight biopolymers of mass greater than 45000 amu. Few smaller polymers were produced.

4.3.3 Effect of Potassium

Potassium was added to reactor feeds at concentrations of 5.0, 10 and 17 mM. The addition of potassium did not affect the concentration of magnesium within the reactor which was found to be approximately equal to the influent magnesium concentration. Calcium consumption increased slightly with potassium addition at 5.0 and 10 mM while at a concentration of 17 mM the liberation of over 1.5 mM calcium was observed. This somewhat random fluctuation in calcium liberation was similar to that observed with sodium addition. Sodium was liberated at low potassium levels, but consumption was observed at a potassium concentration of 17 mM. The variations in these trends implies that other factors are involved in cation liberation.

As seen during the addition of sodium, a granular sludge was observed at 17 mM potassium addition. Slight granulation appeared in the K=10 mM sludge. The appearance of the sludge, however, was considerably different than for the sodium amended sludge, an observation also noted by Higgins (1995). The presence of filaments in the potassium

amended reactor did result in filamentous bulking. Also unlike sodium treated sludge, potassium addition at high doses produced floating sludge.

Improved sludge settling as measured by SVI was observed with the addition of 5.0 and 10 mM potassium as shown in Figure 8. The relative SVI at a concentration of 17 mM increased while still being better than the control. Based on the results found for sodium, it would be expected that the SVI would continue to improve with increasing potassium levels; however, this was not observed.

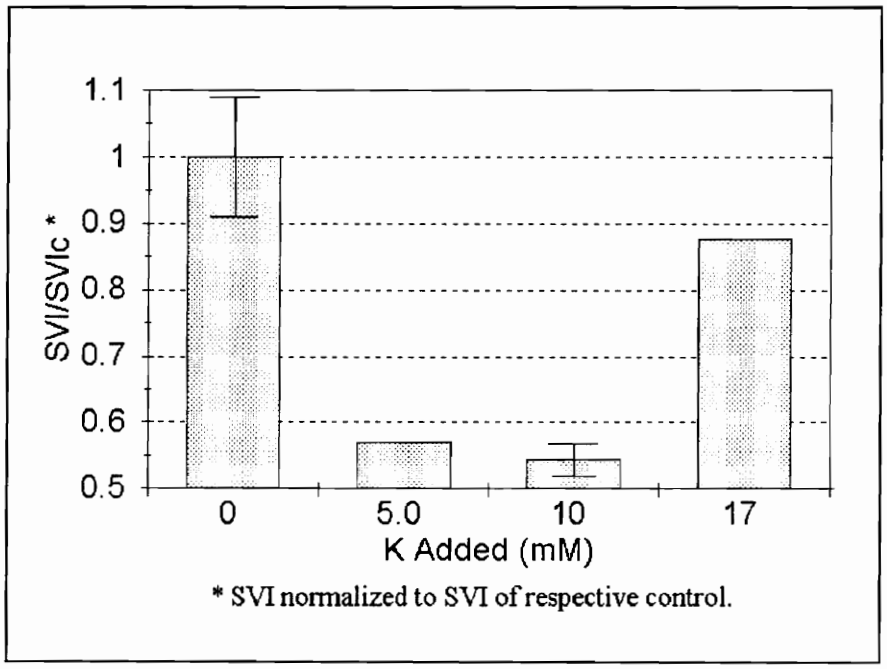


Figure 8: The effect of potassium addition to the wastewater feed on sludge SVI.
Error bars represent one standard deviation.

The fact that the 17 mM potassium trial did not fit with the other data points obtained for either settling or cation liberation suggests that some other factor played a dominant role in the properties of this sludge. Both K=5.0 mM and K= 17 mM trials were performed

at the same time; therefore, this observation cannot be attributed to variations in wastewater composition. No trend was observed between potassium addition and floc density or floc density and SVI.

Similar to those results seen during the addition of sodium, the addition of 5.0 mM potassium did not significantly affect the supernatant solids concentration. Above this level the solids concentration increased up to almost seven times the supernatant solids content of the control reactor when K=17 mM. This trend is shown in Figure 9.

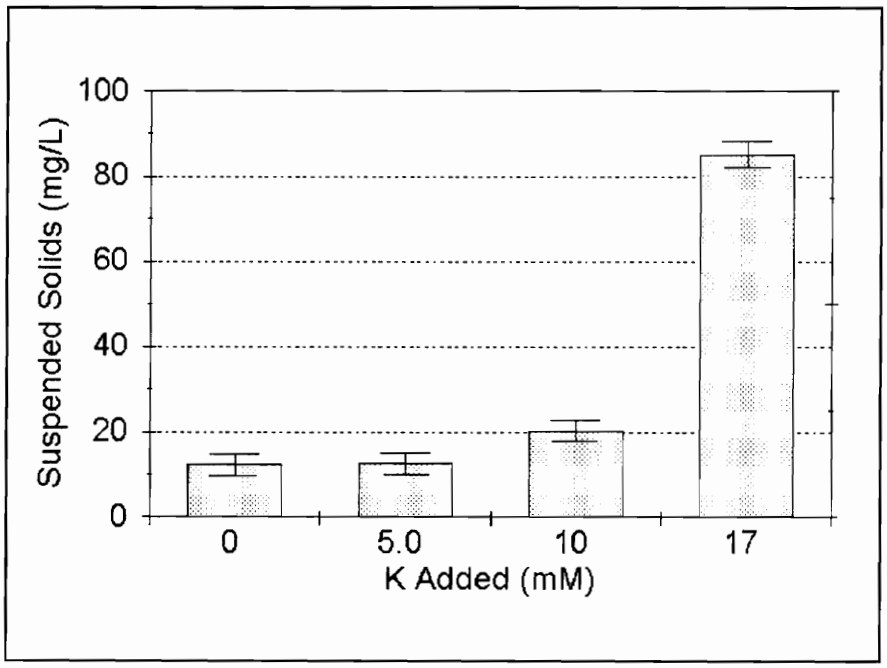
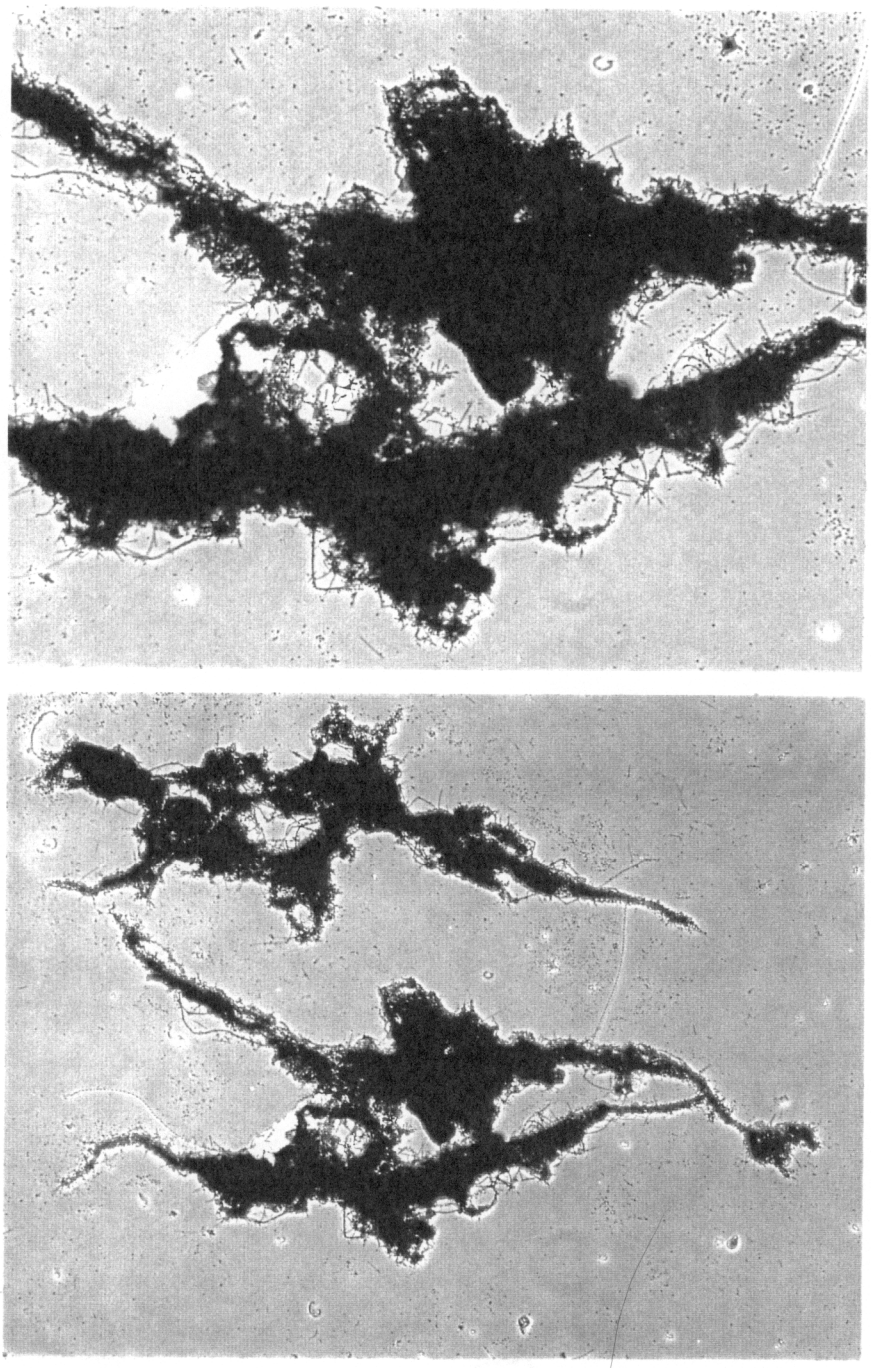


Figure 9: The effect of potassium addition to the wastewater feed on sludge supernatant solids.
Error bars represent one standard deviation.

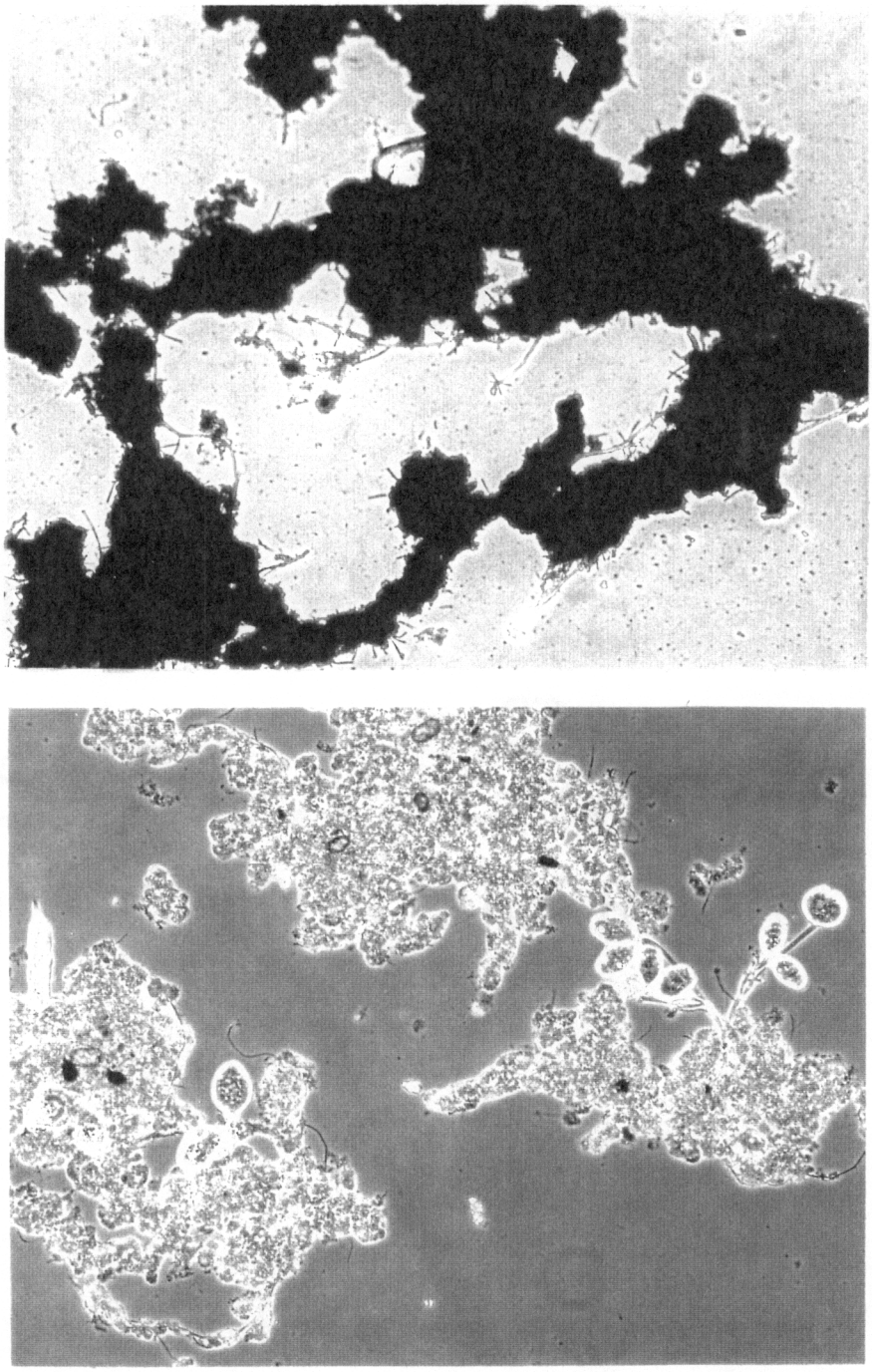
A microbial analysis, not performed by this author, was used to analyze the activated sludge samples receiving potassium amended feed at 5.0 and 10 mM. The representative micrographs of this sludge are shown in Figure 10 (a-d).



(a)

(b)

Figure 10: Micrographs of activated sludge produced by the addtion of 5.0 mM potassium added to the wastewater feed.
(a) 200 x Magnification: Phase Contrast, Scale: 1 cm = 50 μm
(b) 100 x Magnification: Phase Contrast, Scale: 1 cm = 100 μm
(Micrographs by Don Taylor.)



(c)

(d)

Figure 10: Micrographs of activated sludge produced by the addtion of 10 mM potassium added to the wastewater feed.
(c) 200 x Magnification: Phase Contrast, Scale: 1 cm = 50 μm
(d) 100 x Magnification: Phase Contrast, Scale: 1 cm = 100 μm
(Micrographs by Don Taylor.)

This analysis determined the cause of high supernatant solids to be the presence of a large number of individual bacterial cells. The presence of such cells may be the result of the adsorption of potassium ions into the polymer/particle bridge, resulting in the production of many unflocculated particles. The large increase in supernatant solids was observed at a lower molar concentration of potassium than sodium. This cannot be explained by the selective adsorption of potassium over sodium in the floc matrix as shown by Figure 11. The addition of similar molar concentrations of sodium and potassium resulted in virtually the same soluble ion concentration, indicating equal adsorption.

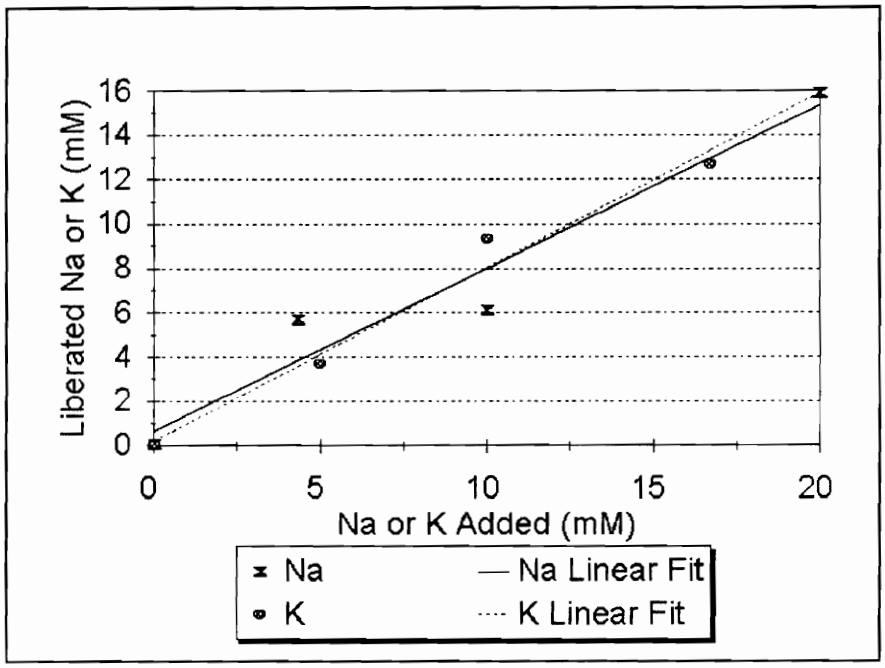


Figure 11: Monovalent cations liberated from sludge during the addition of sodium and potassium to the wastewater feed.

Unlike sodium, floc stability was improved by the addition of potassium above 5.0 mM, as shown in Figure 12. This implies that the increase in supernatant turbidity and

deterioration in sludge dewatering properties experienced during potassium addition did not result from the shearing of flocs to produce fine particles. An alternative explanation is that the addition of potassium affects the metabolic processes responsible for flocculation of activated sludge microorganisms. The process by which this effect occurs is not certain.

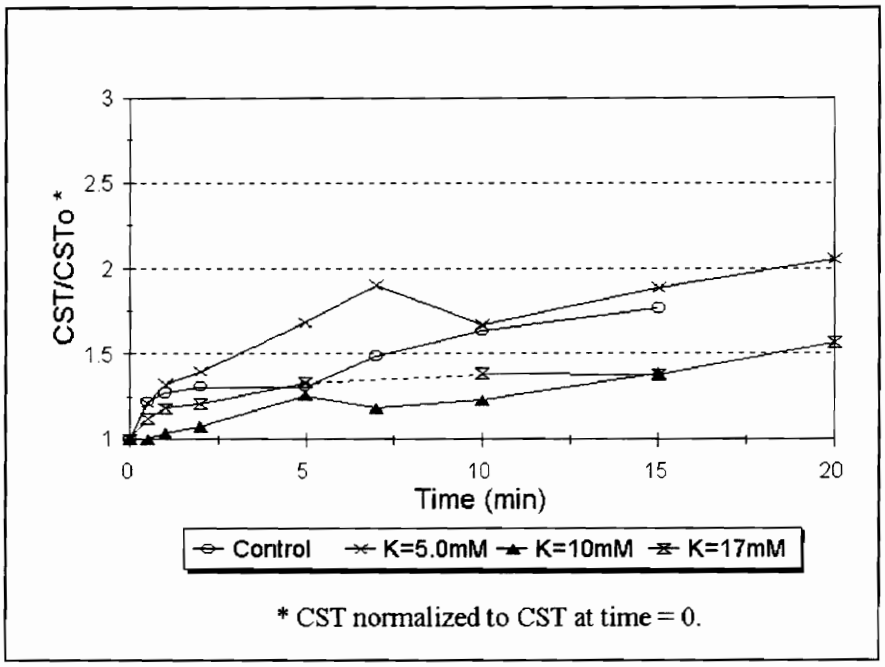


Figure 12: The effect of potassium addition to the wastewater feed on sludge floc stability.

Further microscopic analysis of the potassium amended sludge showed the presence of both extended and needle-like filaments extending from the floc surface. *Haliscomenobacter hydrossis* was determined to be the primary filament found in the sludge. Species identification was difficult due to large amounts of attached growth which hid the filaments (see Figure 10). Numerous amoeba were also present in the sludge, likely due to the large number of individual bacteria cells which serve as food for the

amoeba.

The effect of potassium on dewatering properties as measured by SRF were unclear, as shown in Figure 13. A general trend of increasing SRF with increasing potassium concentration was observed, although the data point for K=10 mM does not fit this trend. As mentioned previously, variations in wastewater composition from one trial to the next may be responsible for the inconsistencies in the data obtained. The deterioration of dewatering properties was expected to occur as a result of an increase in small particles. The effect of particle size is shown later.

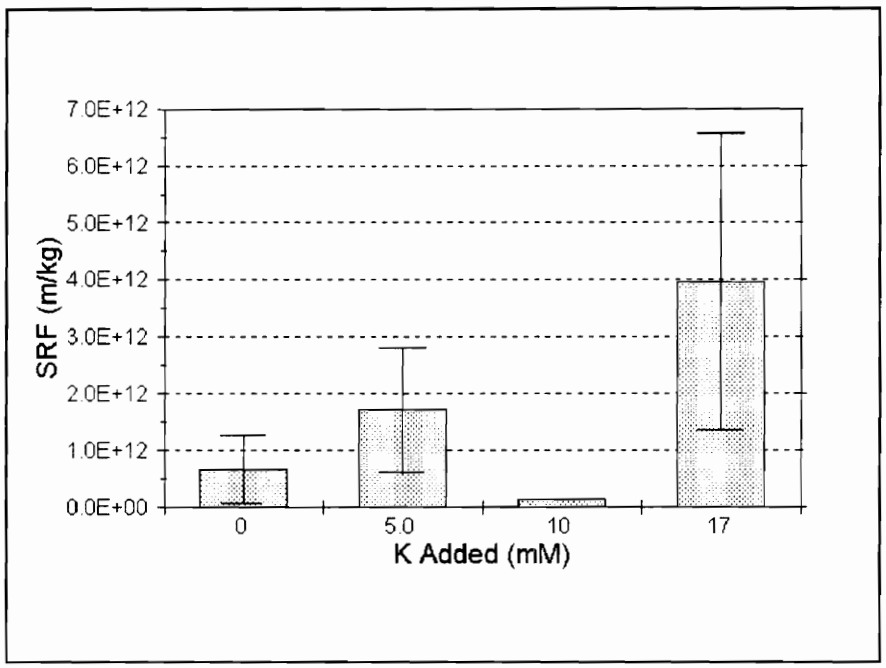


Figure 13: The effect of potassium addition to the wastewater feed on sludge SRF.
Error bars represent one standard deviation.

The addition of 5.0 mM potassium resulted in a reduction in the optimum polymer

dose required for sludge conditioning. After this level, the optimum polymer dose increased with increasing potassium as shown in Figure 14. Similar to the trend found for supernatant solids, increased optimum polymer dose was observed at a lower molar potassium concentration than sodium.

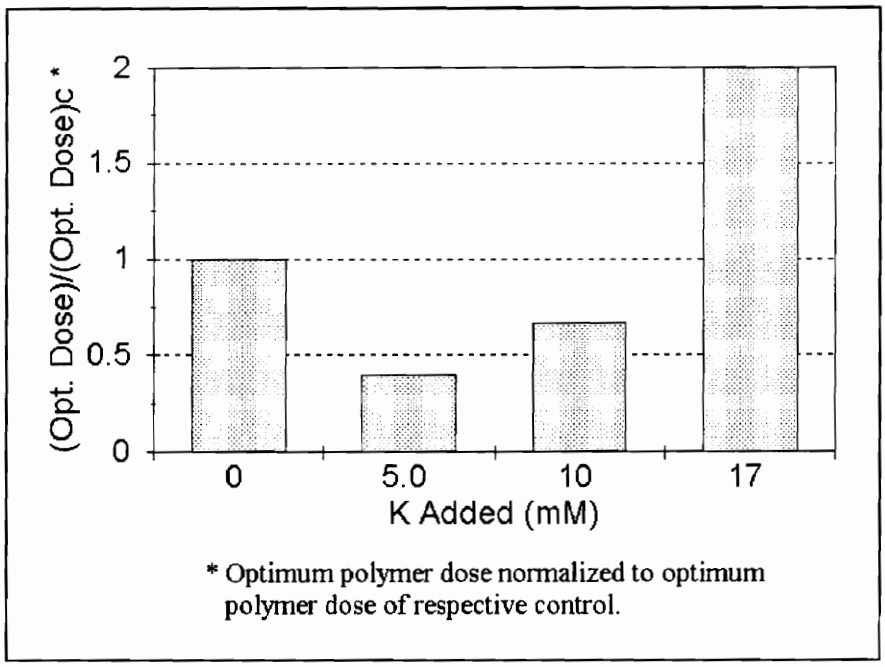


Figure 14: The effect of potassium addition to the wastewater feed on sludge optimum polymer dose.
No error bars shown as each bar represents one analysis.

No trend was found relating extracellular polysaccharide content with increasing potassium levels, similar to the result found for sodium addition. A general trend of decreasing bound and total protein content with improved SVI was observed. This is in contrast with the findings of Higgins (1995).

Like sodium, the addition of potassium produced changes in the particle size distribution of the activated sludge. As observed in Figure 15, the addition of potassium

(except at 17 mM) increased the number of particles of diameter 5 to 50 μm. Above 100 μm, there was a consistent decrease in the number of particles with the addition of potassium.

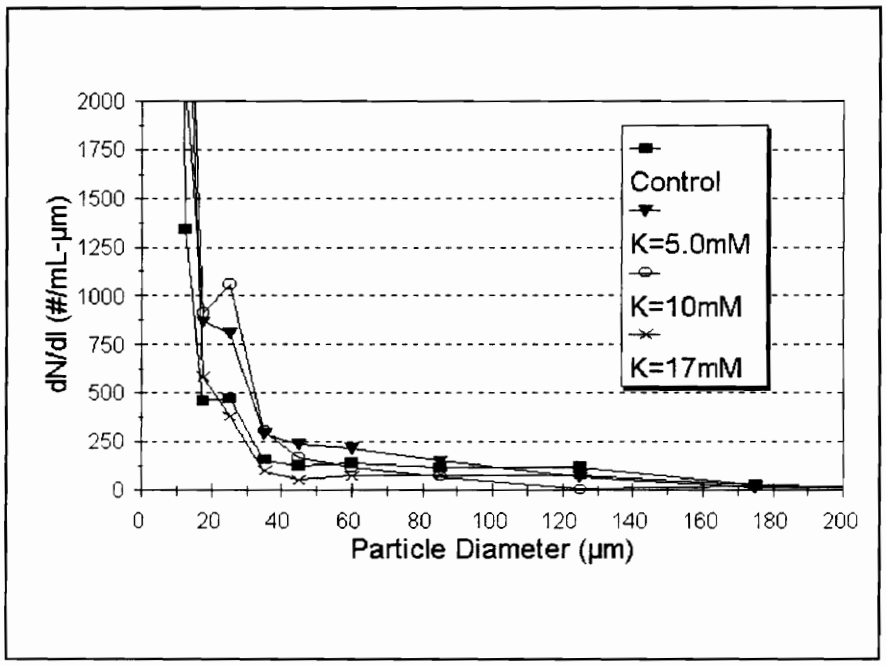


Figure 15: The effect of potassium addition to the wastewater feed on sludge particle size distribution.
Particles of diameter less than 10 μm and greater than 200 μm are not shown.
N = number of particles, l = particle diameter (μm)

This particle size change very closely mimicked that of sodium discussed previously. The increase in supracolloidal particles (diameter < 100 μm) did not correlate with deterioration in dewatering properties or increasing polymer dose as predicted by the work of Karr and Keinath (1978).

Gel filtration analysis of the potassium amended sludge showed that, like sodium, potassium addition resulted in the production of large molecular weight biopolymers. In

each potassium addition, a large peak representing a molecular weight greater than 66000 amu (elution volume < 30 mL) was observed as shown in Figure 16. Unlike sodium however, potassium fed sludge also produced a small quantity of biopolymer ranging in molecular weight from 29000 amu (elution volume = 50 mL) to less than 6500 amu (elution volume > 75 mL). This fraction however, was not as large as that found in the control reactor without potassium addition (Figure 16a).

The addition of conditioning polymer eliminated the small molecular weight fractions by coagulation into larger molecules. No significant trend between extracellular polymer molecular weight and sludge dewatering was observed.

The addition of potassium into the wastewater feed of the CMAS reactors up to 10 mM improved the settling characteristics and reduced the optimum polymer dose required for sludge conditioning. Supernatant solids and SRF deteriorated at lower molar potassium concentrations than experienced during sodium addition. This was not the result of selective adsorption of potassium over sodium. However, the production of strong flocs during potassium addition contrasts the weak flocs produced during sodium addition. This implies that another process, possibly metabolic, was involved in the varying effects between these two monovalent cations. The addition of potassium resulted in an increase in the number of particles of diameter 5 to 50 μm and a decrease in particles of diameter greater than 100 μm. Decreasing bound and total protein content was correlated with improved SVI. No other trend between ECP and increasing monovalent ions was observed. Like sodium, potassium produced mostly very high molecular weight

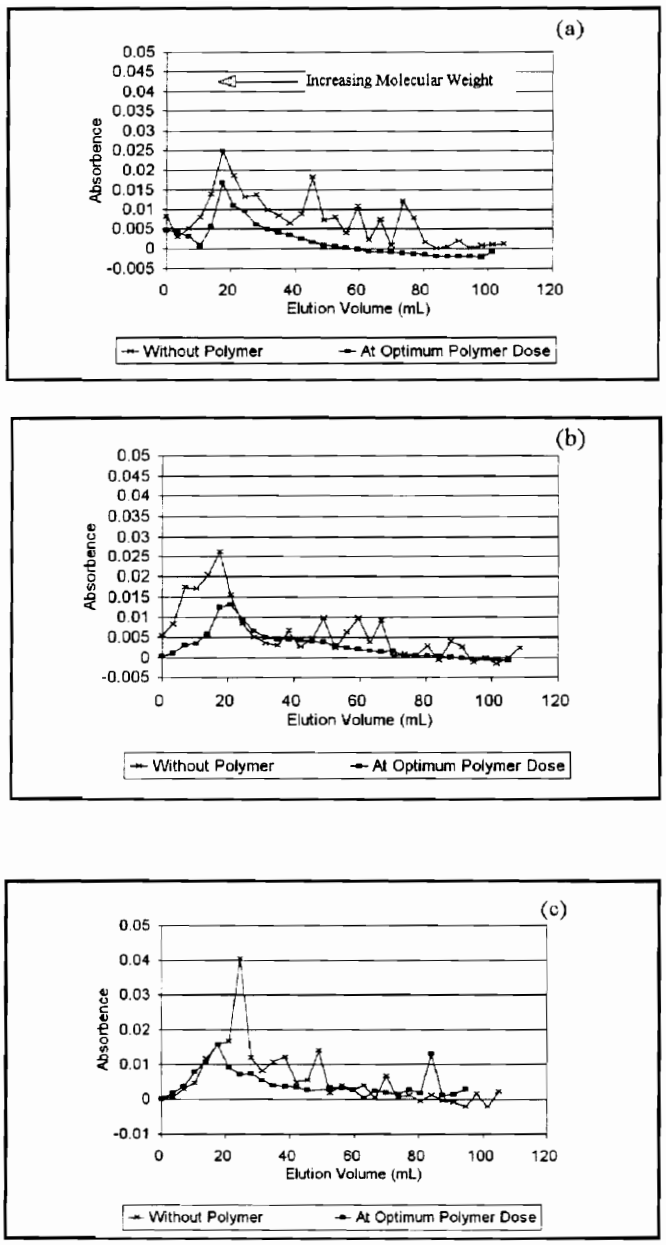


Figure 16: Gel filtration of the supernatant of sludge fed potassium enriched wastewater before polymer addition and at optimum polymer dose. (a) Control (b) K=5.0 mM (c) K=17 mM Data for the K = 10 mM trial are not shown. Exclusion volume = 25 mL.

biopolymers. In contrast to sodium, a small, lower molecular weight fraction was also produced during potassium amendment.

4.3.4 Effect of Magnesium Addition

Magnesium was added to the reactor feeds at concentrations of 3.8, 7.0 and 12 mM. Unfortunately the data points obtained for Mg=3.8 mM were significantly different than the others obtained in this series. This may have resulted from the variability of the influent wastewater which affected sludge properties. The lack of a control reactor during all magnesium experiments made it difficult to normalize this data set for comparison to other cation experimental trials. For this reason, the data points obtained for Mg=3.8 mM were not included in the analysis of the effects of magnesium addition on sludge properties, although they are still shown in the attached graphs. As both the 7.0 mM and 12 mM trials were operated simultaneously, these results were directly comparable to each other. The control reactor used for plotting purposes is representative of typical sludge properties observed when no cations were added to the reactor feed.

The addition of magnesium to the activated sludge feed resulted in an increased consumption of calcium ions and a liberation of sodium ions as shown in Figure 17. A maximum of 2.6 mM (2.6 meq/L) sodium was released and a maximum of 1.8 mM (3.6 meq/L) calcium was consumed during these trials. Potassium liberation increased slightly to a maximum of 0.3 mM (0.3 meq/L) with increasing magnesium addition.

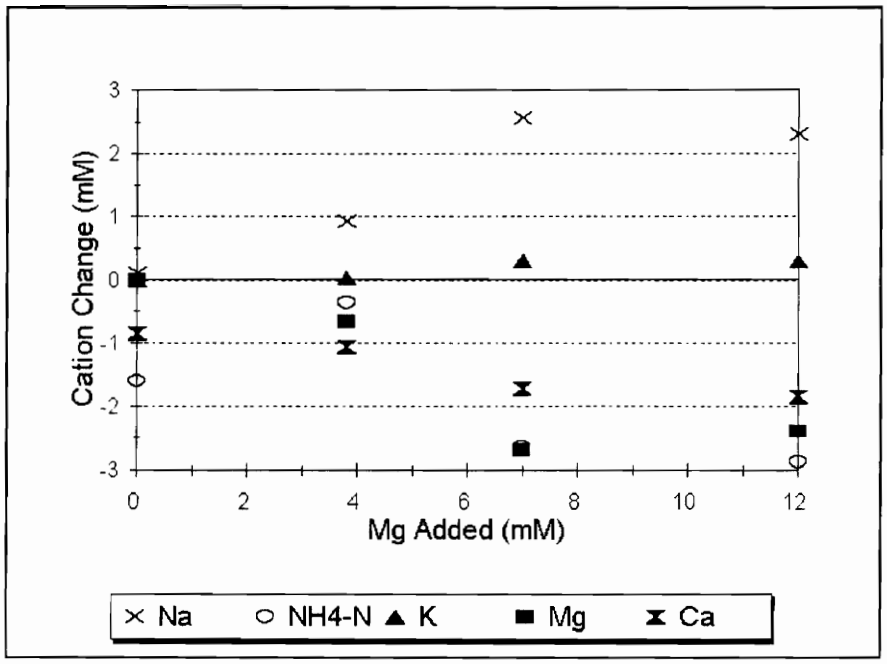


Figure 17: The effect of magnesium addition to the wastewater feed on the change in soluble cation concentration within the reactor.
Positive change represents cation liberation and negative change represents cation consumption.

These results are in direct contrast to the work of Bruss *et al.* (1992) who found that magnesium liberated calcium and did not significantly affect monovalent cation concentrations. It is possible that at higher magnesium levels, monovalent ions were displaced from the floc matrix and calcium was co-adsorbed. It should also be noted that a total of 8.5 meq/L of divalent cations were consumed while only 2.6 meq/L of monovalent ions were liberated. This implies that more binding sites are available for divalent cations than monovalent cations as suggested by the work of Forster (1985).

The addition of increasing levels of magnesium improved the settling properties of

the sludge as shown in Figure 18.

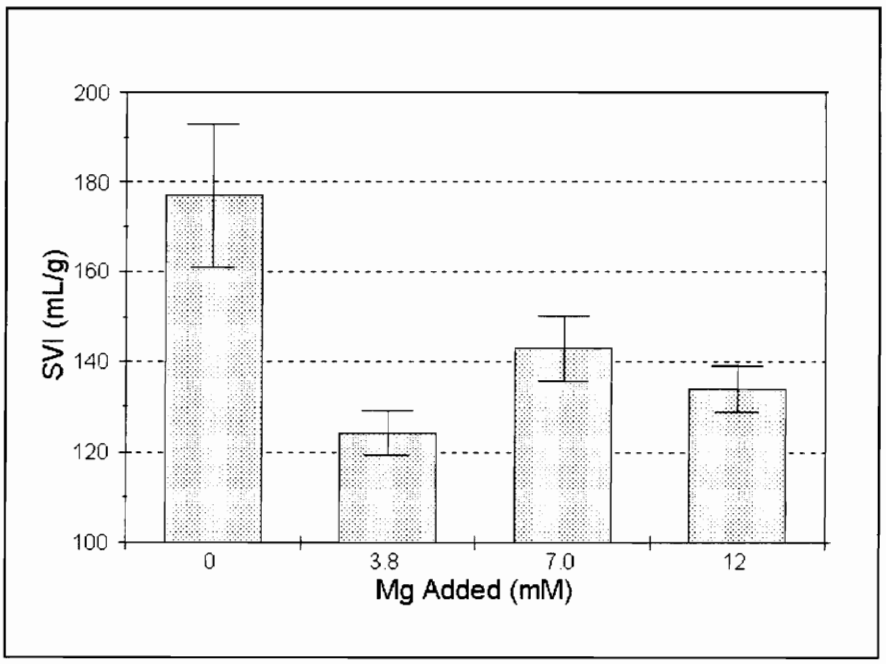


Figure 18: The effect of magnesium addition to the wastewater feed on sludge SVI.
Due to the lack of control data, the Mg=3.8 mM trial is not directly comparable to the Mg=7.0 and Mg=12 mM trials.
Control data from a previous trial is shown.
Error bars represent one standard deviation.

This result was similar to that observed by Forster and Dallas-Newton (1980) and Hantula and Banford (1991) who correlated magnesium addition with improved SVI. As discussed previously, the lack of control reactors during this trial results in this data being presented in raw form, and not normalized as shown for the previous SVI data. The decrease in SVI may have resulted from the incorporation of divalent ions into the floc matrix, which by the polymer bridging theory, would produce larger, more stable flocs. An increase in floc stability correlated with a decrease in supernatant solids at higher magnesium levels as

shown in Figures 19 and 20.

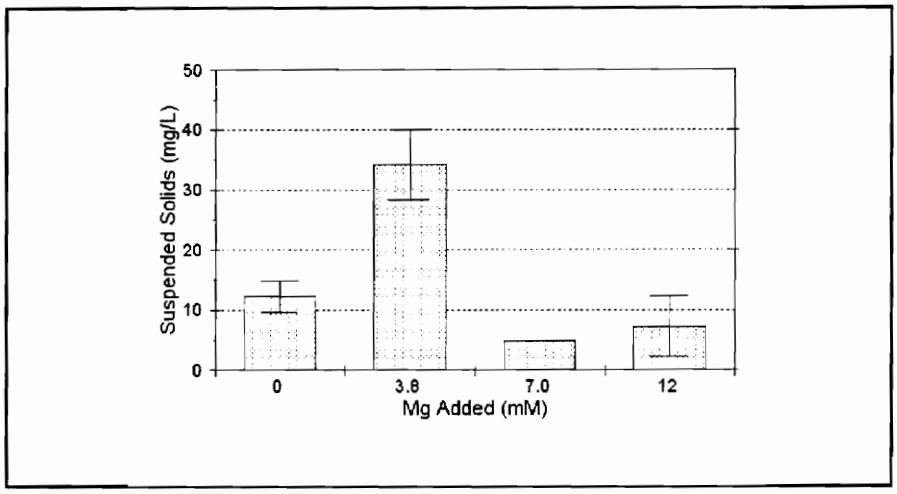


Figure 19: The effect of magnesium addition to the wastewater feed on sludge supernatant solids.
Due to the lack of control data, the Mg=3.8 mM trial is not directly comparable to Mg=7.0 and Mg=12 mM trials. The control from a previous trial is shown.
Error bars represent one standard deviation.

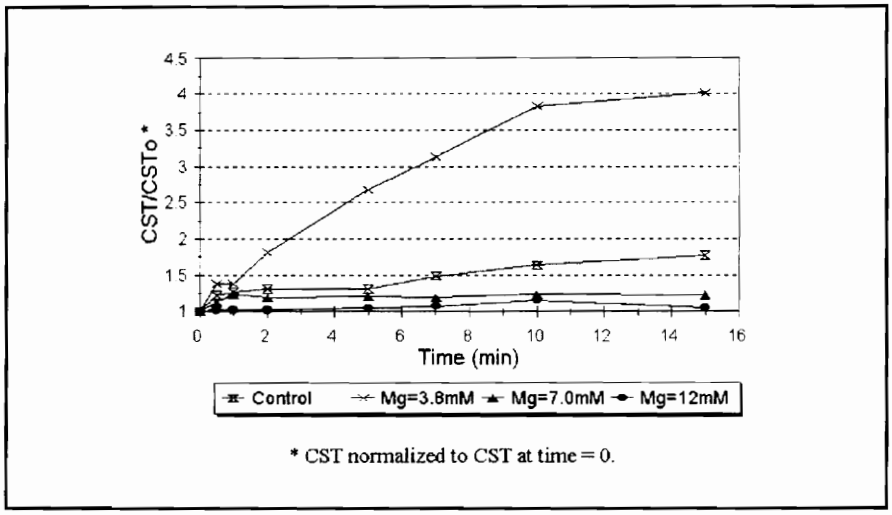


Figure 20: The effect of magnesium addition to the wastewater feed on sludge floc stability.
Due to the lack of control data, the Mg=3.8 mM trial is not directly comparable to the Mg=7.0 and Mg=12 mM trials. The control from a previous trial is shown.

This result supports the work of Higgins (1995) who also found that divalent cation addition produced flocs with a greater resistance to shear.

Particle size distribution was also affected by the addition of magnesium ions, as shown in Figure 21. Not shown in this figure is the fact that increasing magnesium addition resulted in a significant decrease in the number of particles of diameter 5 to 10 μm. Between 10 and 100 μm, a large increase in particle number was observed. Above 100 μm however, the number of particles decreased with increasing magnesium addition.

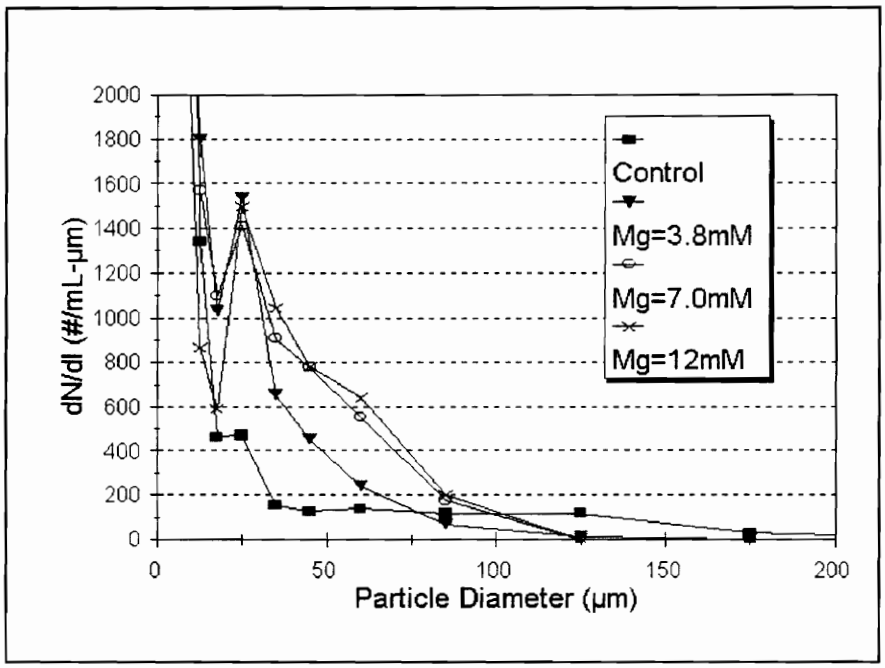


Figure 21: The effect of magnesium addition to the wastewater feed on sludge particle size distribution.
Due to the lack of control data, the Mg=3.8 mM trial is not directly comparable to the Mg=7.0 and Mg=12 mM trials. The control from a previous trial is shown.
Particles of diameter less than 10 μm and greater than 200 μm are not shown.
N = number of particles, l = particle diameter (μm)

Also not shown in Figure 21 is the fact that in all magnesium additions, the number of particles greater than 300 μm was somewhat higher than the control reactor. This particle size distribution does not appear to correlate with optimum polymer dose or sludge dewatering properties, although it does correlate well with sludge stability and supernatant solids. No significant trend was observed between magnesium addition and floc density, sludge dewatering or optimum polymer dose.

A decrease in bound protein and polysaccharide concentration was observed with increasing magnesium addition. Soluble polysaccharide was also found to decrease with increasing magnesium. No trend was found relating magnesium to soluble protein concentration. These results do not agree with the theory of polymer bridging which implies that an increase in bound polymer content resulting in the increased adsorption of divalent cations should produce improved flocculation and settling. In this study it appears that some other mechanism was influential.

The curves produced by gel filtration of the magnesium amended sludge are very different than those produced during the addition of monovalent ions. As shown in Figure 22, magnesium addition resulted in the production of biopolymers widely ranging in molecular weight.The addition of conditioning polymer dampened the large fluctuations in polymer molecular weight; however, many small polymer fractions existed even at the optimum polymer dose. The presence of small molecular weight biopolymers correlated well with the reduction in supernatant solids concentration. Unlike sodium, these results

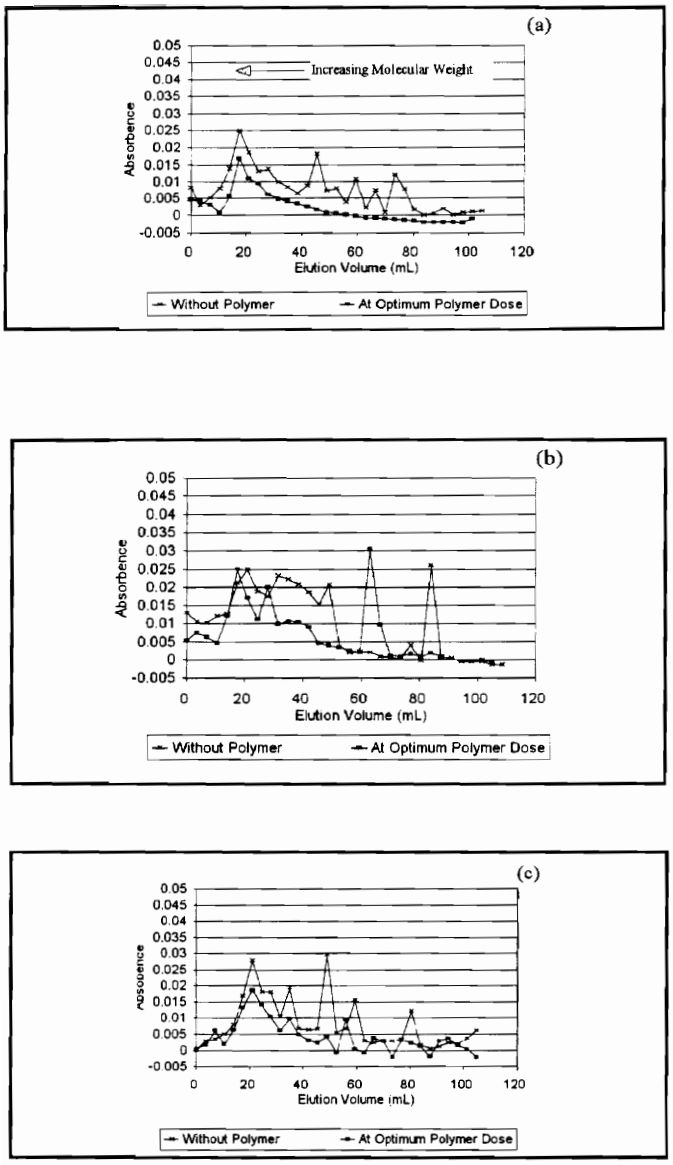


Figure 22: Gel filtration of the supernatent of sludge fed magnesium enriched wastewater, without polymer addition and at optimum polymer dose.
(a) Control (b) Mg=7 mM (c) Mg=12 mM
The control from a previous trial is shown. The Mg = 3.8 mM data is not shown.
Exclusion volume = 25 mL.

agree with the findings of Forster (1985) who suggested that the presence of lower molecular weight polymers improve sludge settling.

The addition of magnesium improved sludge settling, reduced supernatant solids and decreased the amount of total extracellular polymer produced. This is supported by the work of Hantula and Bamford (1991) who found that higher magnesium levels delay the onset of polymer production which may be observed as a decrease in production if the reactor is not operating at a sufficiently high SRT. Monovalent ions were displaced by magnesium, and calcium appeared to be co-adsorbed. Floc stability was also slightly improved by magnesium addition. No other correlation between magnesium addition and any other sludge characteristic was found. It is possible that the ratio of divalent cations in the activated sludge is near optimum, as defined by Higgins (1995) when no cations are added. This would mean that any additional divalent cations would have only marginal effect on sludge properties.

4.3.5 Summary of Cation Addition Studies

In general, it was found that sodium and potassium addition to the feed of the laboratory-scale activated sludge units at levels greater than 5 mM resulted in granulation of the sludge which occurred with improved SVI and a large increase in supernatant solids. High sodium and potassium levels were associated with poor dewatering. Sodium addition produced very weak flocs that were prone to shear while potassium addition did not significantly affect floc stability. It appears that there are similarities in the way that these

monovalent cations interact with microorgansisms to affect flocculation. Several subtle differences in the effects produced by these two ions imply that the mechanisms by which flocculation occurs do not rely identically on potassium and sodium. Some of these differences may result from metabolic processes which are selective to one cation.

Magnesium addition improved sludge settling and supernatant solids, but did not affect sludge dewatering. Floc stability was also improved by magnesium addition. Divalent cation addition which resulted in the small property changes seen in this research is indicative of a wastewater cation balance near the optimum value. Magnesium addition may enable the displacement of sodium ions from the floc matrix and enhance bridging between particles.

4.3.6 Varying Cations with Time

In order to examine the effects of consecutive changes in cation feed concentration, the influent feed solution was varied from the natural background cation level to 20 mM sodium to 3.8 mM magnesium and back to 20 mM sodium within a three week period. Only the settling properties of this sludge were analyzed during this time and are shown in Figure 23.

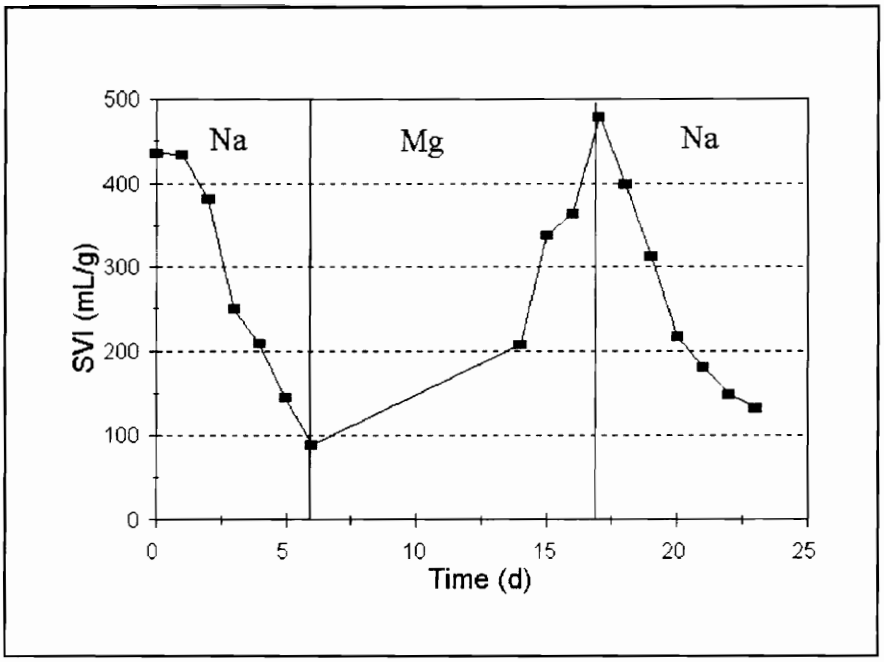


Figure 23: The variation of sludge SVI with changes in added cations to feed wastewater from Na = 20 mM to Mg = 3.8 mM to Na = 20 mM.
Filamentous microorganisms were present after t = 10 d.

The rapid changes in feed cations produced a sludge with a large filamentous population. As observed in the above research, the presence of filaments during background cation levels and during magnesium feed resulted in filamentous bulking. Sodium addition did not eliminate the presence of filamentous organisms, but did prevent bulking, as shown in the figure.

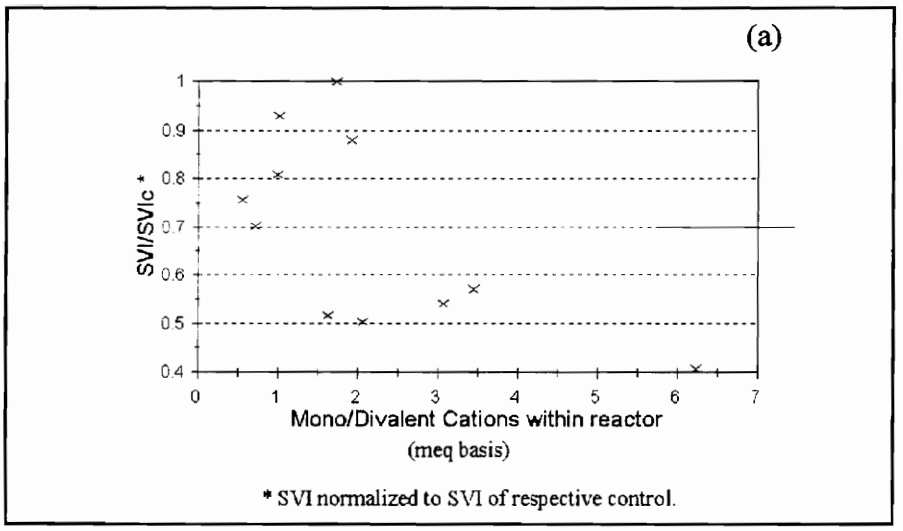
4.3.7 Effect of Monovalent/Divalent Cation Ratio on Sludge Properties

Higgins (1995) suggested that the ratio of sodium to calcium plus magnesium in the

feed solution may often represent a more accurate account of the resultant sludge properties than the actual concentration of any one cation added. For this reason, the effect of monovalent/divalent cation ratio (meq basis) in the feed and observed within the reactors were analyzed with respect to sludge settling and dewatering properties. For the purpose of this analysis, monovalent/divalent cation ratio is defined as:

$$\frac{\text{Monovalent Cations}}{\text{Divalent Cations}} = \frac{(Na + K + NH_4)}{(Ca + Mg)} \text{ (meq basis)}$$

The settling properties of the activated sludge improved with increasing monovalent to divalent cation ratio both within the reactor and in the feed solution as shown in Figure 24, although the correlation was somewhat weak for the feed ratio.



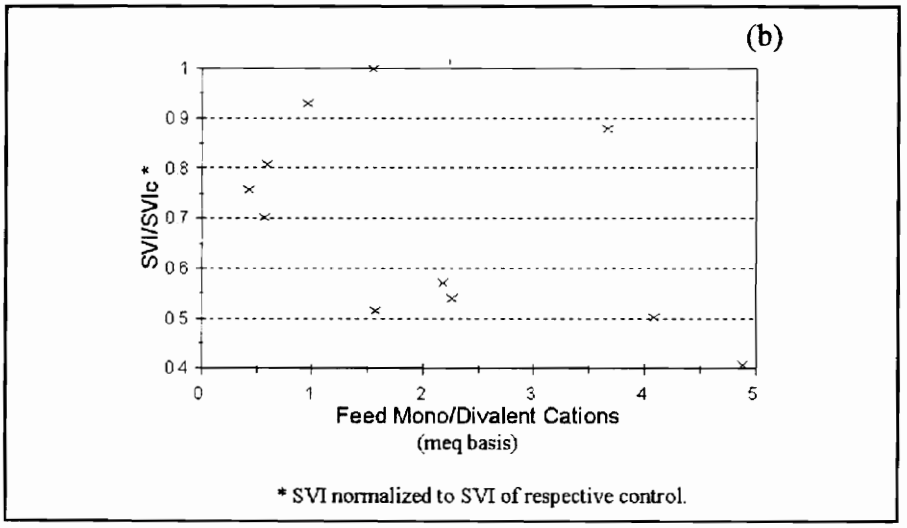


Figure 24: The effect of monovalent/divalent cation ratio (meq basis) on sludge SVI.
(a) Ratio within reactor (b) Ratio within feed
Data points are obtained from the Na, K and Mg addition trials. Mg trial data are normalized to the SVI of a previous control. Na = 50 mM data point is normalized to the control from the Na = 20 mM trial.

Similar to the work of Higgins (1995), increasing the monovalent/divalent cation ratio in the feed above 2.0 resulted in high supernatant solids concentration, shown in Figure 25. In this case the ratio in the feed solution correlated well while the ratio within the reactor did not correlate.

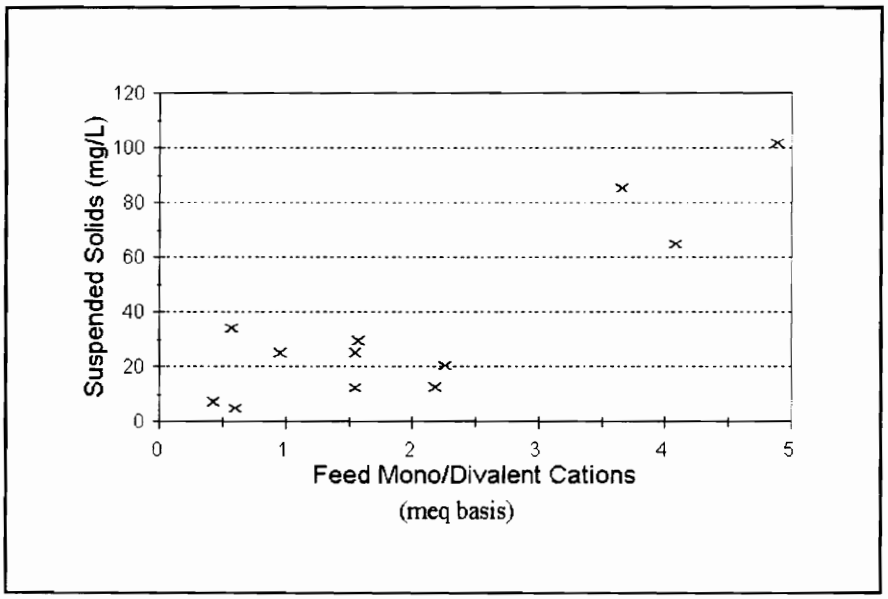


Figure 25: The effect of monovalent/divalent cation ratio in the wastewater feed on sludge supernatant solids.
The data points were obtained from the Na, K and Mg addition trials.

No correlation was found between monovalent/divalent cation ratio and SRF, floc density, or optimum polymer dose. No significant correlation was found between extracellular polysaccharide concentration and monovalent/divalent ratio with either the bound or soluble fraction. As shown in Figure 26, a trend of increasing bound and soluble protein levels with increasing monovalent/divalent ratio in the feed stream was observed.

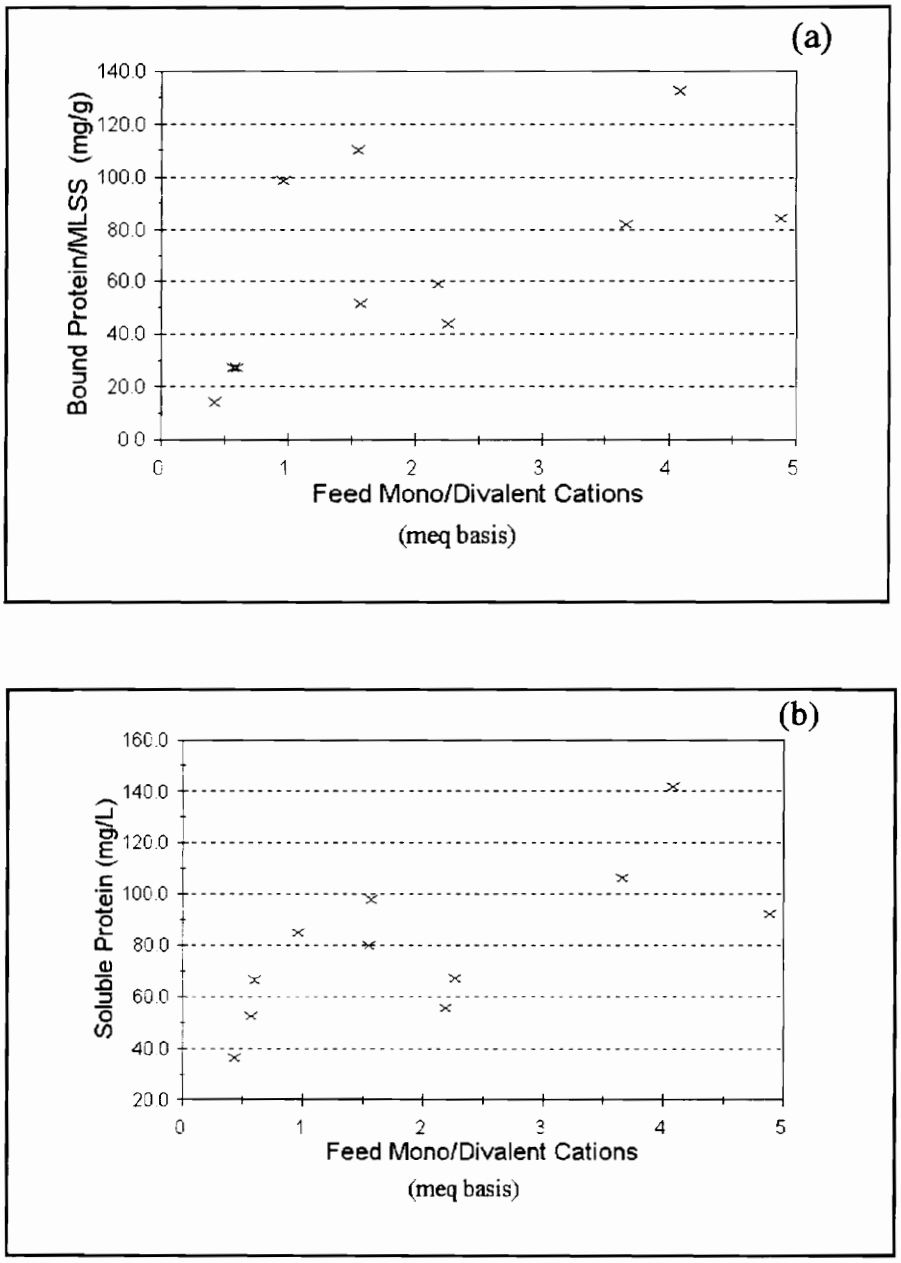


Figure 26: The effect of monovalent/divalent cation ratio (meq basis) in the wastewater feed on extracellular protein.
(a) Bound Protein (b) Soluble Protein
The data points were obtained from the Na, K and Mg addition trials.

The same trend was not observed for the ratio within the reactor.

4.4 Batch Tests Repeated

As discussed in Section 4.2, no correlation was observed when cations were added in batch mode to the activated sludge samples obtained from the Chemical Company. Higgins (1995) found batch cation addition to affect sludge properties. To confirm the previous results, further batch cation addition tests were undertaken with activated sludge removed from the Na=20 mM reactor after "steady state" had been reached. The rationale behind this was that with the increased biopolymer level that resulted from growing the sludge in laboratory reactors, the effects of cation addition may be more evident than in the previous tests where low biopolymer concentrations existed. Calcium was added at 5.0 and 10 mM doses while magnesium was added at 2.5, 5.0 and 10 mM. The CST and settling velocity of these samples were analyzed following 30 minutes of mixing. SRF was not analyzed during this test. As shown in Figures 27 and 28, increasing levels of divalent cation result in increased settleability.

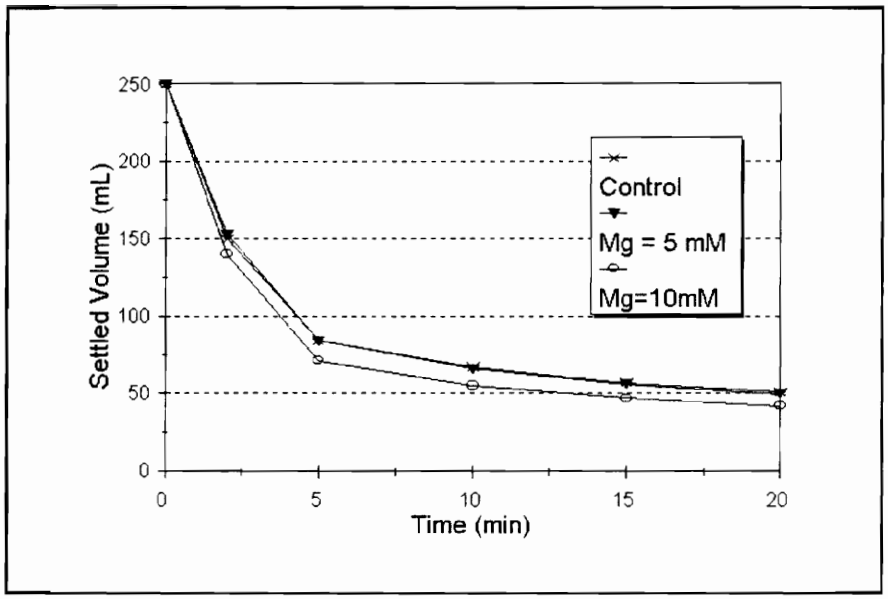


Figure 27: The effect of batch magnesium addition on the settling of sludge fed wastewater with 20 mM sodium added.
Data from the addition of 2.5 mM Mg are not shown.

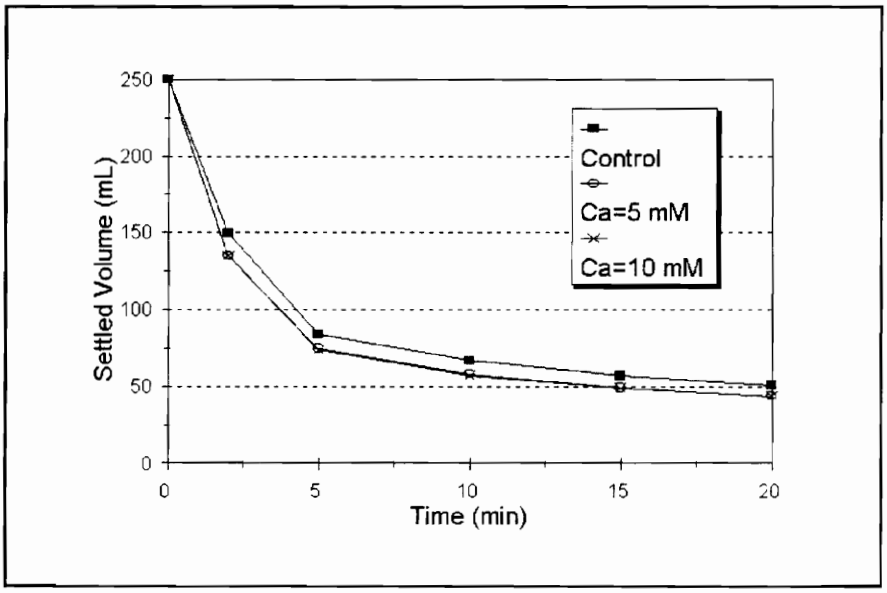


Figure 28: The effect of batch calcium addition on the settling of sludge fed wastewater with 20 mM sodium added.

Sludge dewatering also improved with divalent cation addition as the sludge CST decreased with increasing divalent cation addition, shown in Figure 29. Here, calcium exhibited a greater improvement than magnesium.

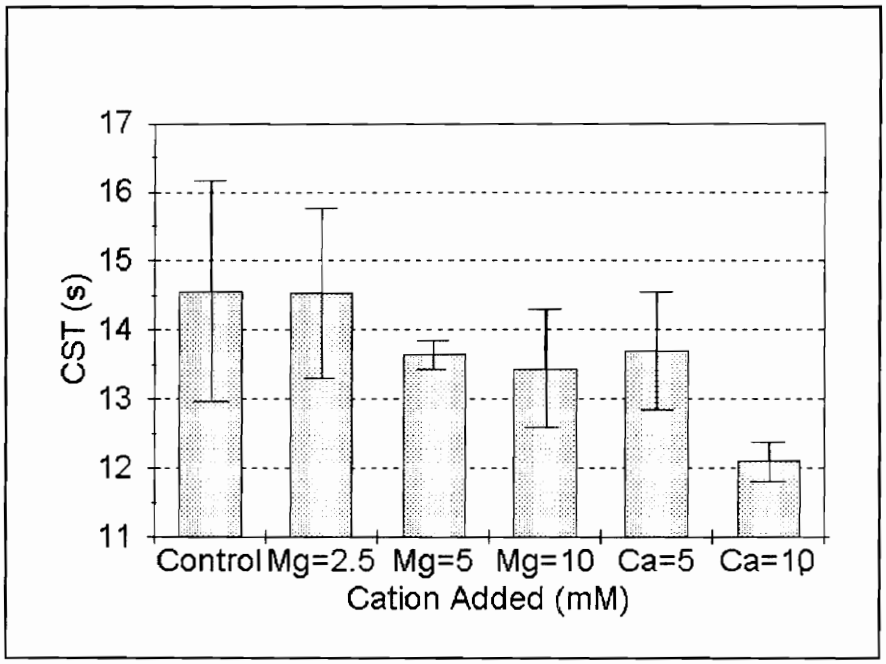


Figure 29: The effect of batch divalent cation addition on the CST of sludge fed wastewater with 20 mM sodium added. Error bars represent one standard deviation.

The results of this test are questionable as CST was previously shown not to adequately represent sludge dewatering properties. However, the CST test was used here to represent sludge dewatering properties due to the lack of other available data. A comparison of the previous batch cation addition tests with the results of this test supports the theory that the presence of biopolymers is important in the effect of cations on flocculation and settling. The second batch tests performed in this research agree with the work of Tezuka (1969) and Higgins (1995) who found that the presence of divalent cations during growth was not

necessary for improvement of sludge properties. This implies that the mechanisms by which divalent cations improve sludge properties are in place, to some degree, even when the sludge was not grown on the high divalent cation media. Higgins (1995) showed that more marked effects were observed when cations were added to the sludge feed than when added in batch mode. The lack of data in this research made such a comparison difficult. The fact that Higgins found a higher degree of improvement when cations were added to the reactor feed implies that the mechanisms involved in flocculation may be a combination of physical-chemical and physiological processes.

4.5 General Trends

In each study it was observed that calcium consumption was largest when extracellular polymer production was low. This trend is shown in Figure 30.

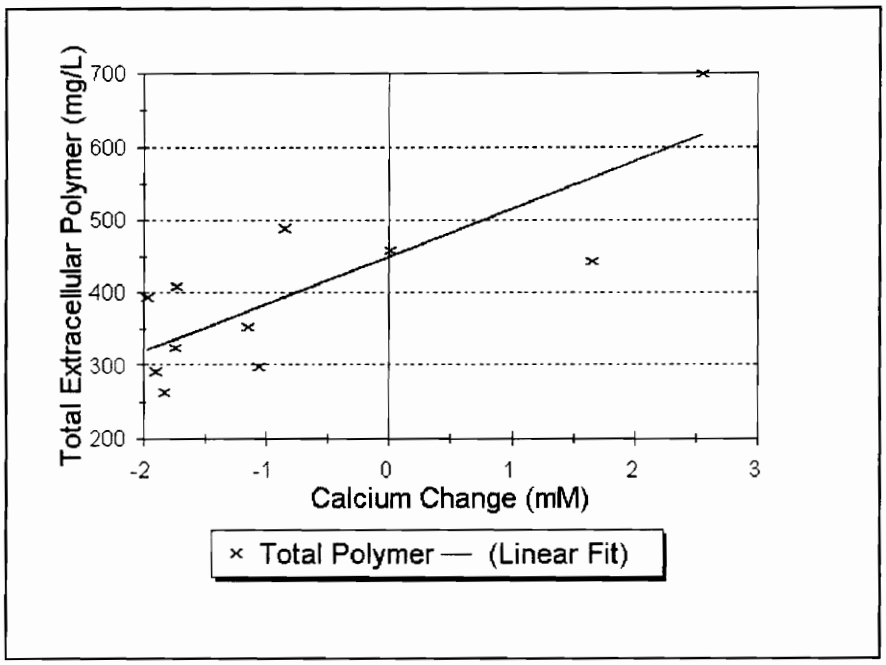


Figure 30: Variation of total extracellular polymer content with changes in soluble calcium concentration.
Positive change represents calcium liberation, while negative change represent calcium consumption.
Data points were obtained from Na, K and Mg addition trials.

When considered in terms of the two different polymer fractions, a similar trend was observed for both bound and unbound protein fractions. No trend was observed relating either the bound or unbound polysaccharide fraction with the liberation of calcium or sodium.

An examination of the soluble cation conconcentrations within the reactor in comparison with the feed soluble cation also showed several trends. The consumption of calcium ions occured with a subsequent release of sodium ions as shown in Figure 31.

Similar trends were not observed with potassium or sodium addition.

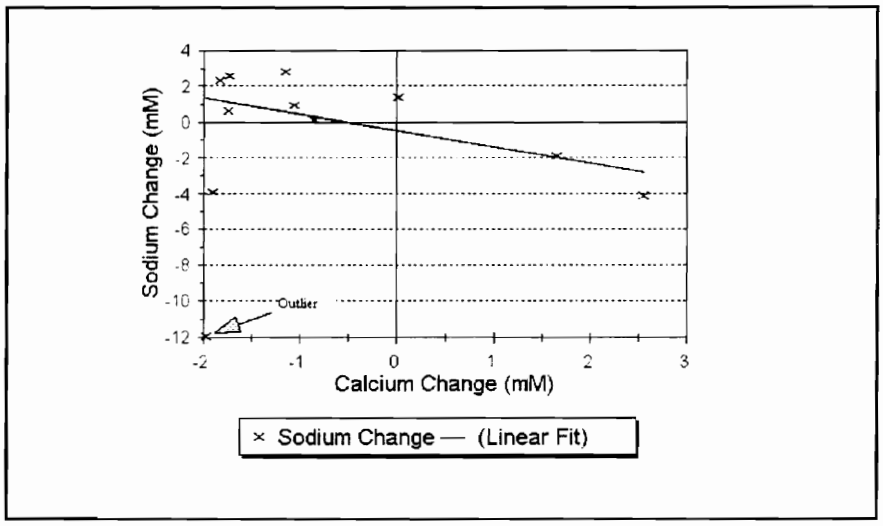


Figure 31: Change in soluble sodium concentration within reactor with change in soluble calcium concentration. Data points obtained from Na, K and Mg addition trials.

The addition of sodium to the wastewater feed stream showed that the sludge had the ability to consume a considerable amount of cations. As the sodium concentration was raise up to 50 mM, sodium ion consumption as high as 12 mM occured. The sludge also consumed potassium when these ions were added to the feed wastewater. At a feed potassium concentration of 17 mM, 4.2 mM of potassium ions was consumed. A maximum consumption of 2.7 mM of magnesium ions were consumed during the magnesium addition trials. These results show that the sludge has a significant cation sorption ability.

4.6 Implications to Operation of the Chemical Company Full-Scale Plant

Approximately 10 days (or one MCRT) after the feed was changed from the

original cation level, changes in the sludge characteristics were generally observed. This implies that the Chemical Company need not be concerned with any "shock" additions of sodium or other cations which may enter the activated sludge system. Any production process modifications which produce a significant, long-term change in the concentration of any one ion, however, may have a significant impact on sludge properties. Such changes should therefore be examined in terms of their effect on wastewater treatment before being put in place.

The Chemical Company currently operates their system using sodium bentonite for improved dewatering. At the levels experienced in their wastewater, it appears that no detrimental effect is experienced. The results from the laboratory-scale studies described herein, show that an increase of approximately 10 mM sodium (or double their current level) is required before increased supernatant turbidity is experienced An even greater increase in sodium is required before any deterioration in sludge dewatering occurs. The monovalent/divalent cation ratio of the Chemical Company wastewater fluctuates around a value of 1.0, which is approximately the optimum value for sludge settling as described by Higgins (1995). Although sodium addition was shown to improve the sludge SVI, the increase in fine particulates and the production of weak floc which accompanies this improvement suggests that sodium addition would not benefit the wastewater treatment process. The research discussed herein suggests that some improvement in sludge settling, floc stability and supernatant solids may be achieved through the addition of magnesium to the influent wastewater stream at a concentration ranging from 7.0 to 10 mM. No

significant improvement in sludge dewatering is expected by this addition. This increase in magnesium concentration could be achieved through the substitution of sodium-based chemicals for magnesium-based chemicals in either the wastewater treatment process or within the production processes themselves.

The laboratory reactors operated during this research however, do not closely approximate those conditions experienced at the Chemical Company's wastewater treatment plant. Although the seed biomass and wastewater feed are identical, differences in food:microorganism ratio, dissolved oxygen, shear forces and substrate gradient experienced by the bacteria may seriously influence the results of cation addition. To further understand the effect of these cations on the full-scale industrial wastewater treatment system, studies must be undertaken to more closely simulate those conditions experienced at the plant. Both laboratory scale and pilot scale testing are recommended.

The addition of calcium to the reactor feed was not examined during this research. Due to the extensive data showing that calcium addition improves sludge properties, it is recommended that this addition be examined. The addition of more than one cation is also recommended to examine the relative effects of cation dosage and monovalent/divalent cation ratio. Further examination is recommended to determine the mode of interaction of both sodium and potassium during floc formation. This examination may also provide some insight into the mechanisms involved in floc stability and settling.

V. SUMMARY

The purpose of this research was to analyze the effect of cation addition on the settling and dewatering properties of an industrial activated sludge. Through this research the applicability of the previous work of Higgins (1995) to other sludges were assessed. Also through this objective, implications of cation addition to the Chemical Company whose sludge was examined, were determined.

5.1 Conclusions

From the results of this research, the following conclusions can be made.

1. Both monovalent and divalent cations significantly affect the physical properties of activated sludges. It can also be concluded that although different monovalent ions produce many similar sludge characteristics when added to the influent wastewater, the mechanisms by which they interact with microorganisms and within the floc matrix are not identical.

2. As suggested by Higgins (1995), it was found that the ratio of monovalent to divalent cations was important in determining sludge properties. It was determined that for this sludge, no one optimum ratio of monovalent/divalent cations could be applied to all sludge properties. In general, most of the sludge properties reached optimum levels below a feed ratio of 2.0.

3. Through an analysis of the results found by Higgins (1995) and numerous other researchers, in comparison with the results found here, it was determined that the

absolute effect of various cations on activated sludge properties is highly dependent on the sludge being considered and conditions under which they are operated. Many of Higgins findings are not universal and cannot be applied to all sludges.

4. For this industrial sludge, the most significant improvement in sludge properties was achieved through the addition of 7.0 to 12 mM magnesium. Although a significant decrease in SVI was achieved through sodium addition, the deterioration in other properties which accompanies this decrease make sodium addition an unattractive alternative for sludge improvement.

5.2 Engineering Significance

The results of this research provided significant insight into the effect of cations on laboratory-scale activated sludge systems. From these results, the implications of cation addition on full-scale industrial sludge treatment systems could be postulated. From this research, several concepts important in the field of wastewater engineering were developed and are listed below.

1. The results of this research showed that the effect of various cations on activated sludge properties is highly dependent on the sludge in question. This result suggests that in order to determine how cation addition will affect the properties of a given sludge, laboratory and pilot-scale studies must be undertaken. In terms of industrial activated sludges, any process modification which results in the long term alteration of either the absolute concentration of one cation or in the monovalent/divalent cation ratio may

significantly alter the efficiency of the wastewater treatment system. Any such changes are therefore, important to treatment operators and should be examined so that the implications to the treatment system can be addressed prior to implementation of the process change.

2. In terms of the sludge examined in this research, it was determined that some improvement in sludge properties could be achieved by an increase in the soluble magnesium concentration by 7.0 to 12 mM. Such an increase could be achieved through the substitution of wastewater treatment chemicals from sodium or potassium-based chemicals (i.e., NaOH) to magnesium-based chemicals (i.e., $Mg(OH)_2$). Substitutions of chemicals in the production process could also be used to achieve this goal. Although such a substitution may result in an increase in the cost of raw chemicals, the savings achieved through the reduction in conditioning polymer requirements which would result from increased magnesium levels could be more than offset this cost.

5.3 Recommendations

Based on this research, the following recommendations for further work in this area are suggested.

1. This research confirmed that different monovalent ions do not interact identically when added to the wastewater feed of an activated sludge system. It has not been confirmed to what degree these differences can be attributed to physical/chemical or physiological interactions. Further studies are recommended examine the different roles

of monovalent ions in activated sludge and to determine the nature of the interactions of these ions.

2. Previous studies have shown that calcium addition can significantly improve activated sludge properties. Calcium addition was not examined during this research, although magnesium addition was shown to improve sludge properties. Further studies are recommended to examine the effect of calcium on the industrial sludge properties.

3. There were significant differences between the operating conditions of the laboratory-scale activated sludge units used in this research and the full-scale wastewater treatment system operated by the Chemical Company. Therefore, pilot-scale studies are recommended to confirm the applicability of the results of this research to the full-scale treatment system.

VI. REFERENCES

Angelbeck, D.I. and Kirsch, E.J. (1969) Influence of pH and Metal Cations on Aggregative Growth of Non-Slime-forming Strains of *Zoogloea* ramigera. *Applied Microbiology,* **17**, 435-440.

Barber, J.B. and Veenstra, J.N. (1986) Evaluation of Biological Sludge Properties Influencing Volume Reduction. *Journal of the Water Pollution Control Federation*, **58**, 149-156.

Barker, A.N. (1946) The Ecology and Function of Protozoa in Sewage Purification. *Annals of Applied Biology,* **33**, 314-325.

Beccari, M., Mappeli, P. and Tandoi, V. (1980) Relationship between Bulking and Physicochemical-Biological Properties of Activated Sludges. *Biotechnology and Bioengineering,* **22,** 969-979.

Bowen, P.T. and Keinath, T.M. (1979) Sludge Conditioning: Effects of Sludge Biochemical Composition. *Water Science and Technology,* **17**, 505-515.

Brown, M.J. and Lester, J.N. (1979) Metal Removal in Activated Sludge: The Role of Bacterial Extracellular Polymers. *Water Research,* **13**, 817-837.

Bruss, J.H., Nielsen, P.H. and Keiding, K. (1992) On the Stability of Activated Sludge Flocs with Implilcations to Dewatering. *Water Research,* **26**, 1597-1604.

Busch, P.L. and Stumm, W. (1968) Chemical Interactions in the Aggregation of Bacteria Bioflocculation in Waste Treatment. *Environmental Science and Technology*, **2**, 49-53.

Calleja, G.B. (1984) Aggregation. In Microbial Adhesion and Aggregation (Marshall, K.C. Ed.), Springer-Verlag:Berlin.

Christensen, G.L. and Dick, R.I. (1985) Specific Resistance Measurements: Methods and Procedures. *Journal of Environmental Engineering,* **111**, 258-271.

Coakley, P. and Wilson, F. (1971) Flocculation with Special Reference to Water and Waste Water Engineering. *Filtration and Separation,* 61-65.

Crabtree, K., Boyle, W., McCoy, E. and Rohlich, G.A. (1966) A Mechanism of Floc Formation by Zoogloea ramigera. *Journal of the Water Pollution Control Federation,* **38**,

1968-1980.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956) Colorimetric Method for Determination of Sugars and Related Substances. *Analytical Chemistry,* **28**, 350-357.

Endo, T., Nakamura, K. and Takahashi, H. (1976) Pronase-susceptible Floc Forming Bacteria: Relationship between Flocculation and Calcium Ion. *Agricultural and Biological Chemistry,* **40**, 2289-2295.

Forster, C.F. (1971) Activated Sludge Surfaces in Relation to the Sludge Volume Index. *Water Research,* **5**, 861-870.

Forster, C.F. (1985) Factors Involved in the Settlement of Activated Sludge-I. *Water Research,* **19**, 1259-1264.

Forster, C.F. (1985) Factors Involved in the Settlement of Activated Sludge-II. *Water Research,* **19**, 1265-1271.

Forster, C.F. and Dallas-Newton, J. (1980) Activated Sludge Settlement - Some Suppositions and Suggestions. *Water Pollution Control,* **79**, 338-351.

Forster, C.F. and Lewin, D.C. (1972) Polymer Interactions at Activated Sludge Surfaces. *Effluent and Water Treatment Journal,* **12**, 520-525.

Friedman, B.A., Dugan, P.R., Pfister, R.M. and Remsen, C.C. (1969) Structure of Exocellular Polymers and Their Relationship to Bacterial Flocculation. *Journal of Bacteriology,* **98**, 1328-1334.

Goodwin, J.A.S. and Forster, C.F. (1985) A Futher Examination in the Composition of Activated Sludge Srufaces in Relation to their Settlement Characteristics. *Water Research*, **19**, 527-533.

Gray, N.F. (1989) Biology of Wastewater Treatment. Oxford Science Publications:New York.

Gray, N.F. (1990) Activated Sludge Theory and Practice. Oxford Science Publications:New York.

Gulas, V., Bond, M. and Benefield, L. (1979) Use of Exocellular Polymers for Thickening Activated Sludge. *Journal of the Water Pollution Control Federation,* **51**, 798-

807.

Hantula, J. and Bamford, D.H. (1991) The Efficiency of the Protein-dependent Flocculation of *Flavobacterium* sp. is Sensitive to the Composition of Growth Medium. *Applied Microbiology and Biotechnology,* **36**, 100-104.

Hartree, E.F. (1972) Determination of Protein: A Modification of the Lowry Methad That Gives a Linear Photometric Response. *Analytical Biochemistry,* **48**, 422-427.

Higgins, M.J. (1995) The Roles and Interactions of Cations, Proteins, and Polysaccharides in the Settling and Dewatering of Activated Sludge. Ph.D. Dissertation. Virgnia Polytechnic Institute and State University.

Kakii, K., Kitamura, S. Shjirakashi, T. and Juriyama, M. (1985) Effect of Calcium Ion on Sludge Characteristics. *Journal of Fermentation Technology,* **63**, 263-270.

Kakii, K., Hasumi, M., Shirakashi, T. and Kuriyama, M. (1990) Involvement of Ca^{++} in the Flocculation of *Kluyvera* cryocrescens KA-103. *Journal of Fermentation and Bioengineering,* **69**, 224-227.

Kang, S., Kishimoto, M., Shioya, S., Yoshida, T., Suga, K. and Taguchi, H. (1989) Dewatering Characteristics of Acitivated Slduges and Effect of Extracellular Polymer. *Journal of Fermentation and Bioengineering,* **68**, 117-122.

Kang, S., Kishimoto, M., Shioya, S., Yoshida, T. and Suga, K. (1990) Properties of Extracellular Polymer Having an Effect on Expression of Activated Sludge. *Journal of Fermentation and Bioengineering,* **69**, 111-116.

Karr, P.R. and Keinath, T.M. (1978) Influence of Particle Size on Sludge Dewaterability. *Journal of the Water Pollution Control Federation,* **50**, 1911-1929.

Kato, A., Izaki, K. and Takashi, H. (1971) Floc-Forming Bacteria Isolated from Activated Sludge. *Journal of General Applied Microbiology*, **17**, 439-456.

Katsiris, N. and Kouseli-Kitsiri, A. (1987) Bound Water Content of Biological Sludges in Relation to Filtration and Dewatering. *Water Research,* **21**, 1319-1327.

Kauzmann, W. (1956) Some Factors in the Interpretation of Protein Denaturation. *Advanced Protein Chemistry*, **14**, 1-57.

Kiff, R.J. (1978) A Study of the Factors Affecting Bioflocculation in the Activated Sludge

Process. *Water Pollution Control*, **77**, 464-468.

Knocke, W.R., Dishman, C.M. and Miller, G.F. (1993) Measurement of Chemical Sludge Floc Density and Implications Related to Sludge Dewatering. *Water Environment Research,* **65**, 735-743.

La Mer, V.K. and Healy, T.W. (1963) Adsorption-Flocculation Reactions of Macromolecules at the Solid-Liquid Interface. *Review of Pure Applied Chemistry*, **13**, 112-132.

Lowry, O.H., Rosebrough, N.J., Farr, A.L. and Randall, R.J. (1951) Protein Measurement with the Folin Phenol Reagent. *Journal of Biological Chemistry,* **193**, 265-275.

McKinney, R.E. and Weichlein, R.G. (1953) Isolation of Floc-Producing Bacteria from Activated Sludge. *Applied Microbiology,* **1**, 259-261.

Metacalf & Eddy Inc. (1991) Wastewater Engineering: Treatment, Disposal and Reuse. New York: McGraw-Hill Inc.

Novak, J.T. and Haugan, B.E. (1980) Mechanisms and Methods for Polymer Conditioning of Activated Sludge. *Journal of the Water Pollution Control Federation,* **52**, 2571-2579

Novak, J.T., Goodman, G.L., Pariroo, A. and Huang, J. (1988) The Blinding of Sludges During Filtration. *Journal of the Water Pollution Control Federation,* **60**, 206-214.

Pavoni, J.L., Tenney, M.W., and Echelberger Jr., W.F. (1972) Bacterial Exocellular Polymers and Biological Flocculation. J*ournal of the Water Pollution Control Federation,* **44**, 414-431.

Peter, G. and Wuhrman, K. (1970) Contribution to the Problem of Bioflocculation in the Activated Sludge Process. *Proceedings of the 5th International Conference on Water Pollution Research.*

Pijper, A. (1938) Dark-Ground Studies of Flagellar and Somatic Agglutination of B. Typhosus. *The Journal of Pathology and Bacteriology,* **47**, 1.

Pijper, A. (1941) Microcinematography of the Agglutination of Typhoid Bacilli. **42**, 395-409.

Poduska, R.A. and Stroupe, R.C. (1981) Belt-Filter Press Dewatering Studies, Implementation and Operation at the Tennessee Eastman Company Industrial Activated Sludge Wastewater Treatment System. *Proceedings of the 35th Industrial Waste Conference*, 437-455.

Randall, C.W., Turpin, J.K, and King, P.H. (1971) Activated Sludge Dewatering: Factors Affecting Drainability. *Journal of the Water Pollution Control Federation,* **43**, 102-122.

Ries, H.E. and Meyers, B.L. (1968) Flocculation Mechanism: Charge Neutralization and Bridging. **160**, p.1449-1450.

Roberts, K. and Olsson, O. (1975) Influence of Colloidal Particles on Dewatering of Activated Sludge with Polyelectrolyte. *Environmental Science and Technology,* **9**, 945-948.

Rose, A.H. (1984) Physiology of Cell Aggregation: Flocculation by Saccharomyces cerevisiae as a Model System. In Microbial Adhesion and Aggregation (Marshall, K.C. Ed.), Springer-Verlag: Berlin.

Skvarla, J. (1993) A Physico-chemical Model of Microbial Adhesion. *Journal of the Chemical Society - Faraday Trans.*, **89**, 2913-2921.

Smellie, R.H. and La Mer, V.K. (1958) Flocculation, Subsidence and Filtration of Phosphate Slimes. *Journal of Colloid Science,* **23**, 589-599.

Standard Methods for the Examination of Water and Wastewater. (1992) American Public Health Association, Washington D.C.

Tenney, M.W. and Stumm, W. (1965) Chemical Flocculation of Microorganisms in Biological Waste Treatment. *Journal of the Water Pollution Control Federation,* **37**, 1370-1387.

Tenney, M.W. and Verhoff, F.H. (1973) Chemical and Autoflocculation of Microorganisms in Biological Wastewater Treatment. *Biotechnology and Bioengineering,* **15**, 1045-1073.

Tezuka, Y. (1969) Cation-dependent Flocculation in a *Flavobacterium* Species Predominant in Activated Sludge. *Applied Microbiology,* **17**, 222-226.

Urbain, V., Block, J.C. and Manem, J. (1993) Bioflocculation in Activated Sludge: An Analytic Approach. *Water Research*, **27**, 829-838.

van Loosdrecht, M.C.M., Lyklema, J., Norde, W. and Zehnder, A.J.B. (1989) Bacterial Adhesion: A Physicochemical Approach. *Microbial Ecology,* **17**, 1-15.

Zita, A. and Hermansson, M. (1994) Effects of Ionic Strength on Bacterial Adhesion and Stability of Flocs in a Wastewater Activated Sludge System. *Applied and Environmental Microbiology,* **60**, 3041-3048.

VITA

Michelle Smith was born on December 6, 1971 in Oshawa, a small city in southern Ontario, Canada. In 1974 she moved to the small hamlet of Garden Hill, Ontario where she lived and was educated for the next 16 years. Michelle attended the University of Guelph in Guelph, Ontario from 1990 to 1994 and earned a Bachelor of Science degree in Environmental Engineering, graduating with distinction. Immediately after obtaining this degree she decided to undertake a Master of Science degree in the same field at Virginia Tech.

APPENDIX A

TRIAL: **Na = 4.4 mM**

DATE: Date: July 5/95 to July 24/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Mg	Ca
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	388.7	36	2E+12	0.008232	90.9	50.4	28.8	8.7		1.016					
12	529.1	40	1.1E+12	0.007024	102.9	96.5	29.2	19		1.019					
13	517.5			0.00675											
14	517.8		3.6E+11	0.00611											
16	501.3	10	3.5E+11	0.00576											
18	471.4		4.6E+11	0.00471	60.3	100.6	10.8	28.5	20	1.023	14	0.13	0.14	2.2	4.8

Floc Stability
(t=18 days)

Time	CST
(min)	(s)
0	9.8
0.5	11.4
1	12.0
2	11.5
5	11.2
7	11.9
10	11.2
15	11.0

TRIAL: **Na = 10 mM**

DATE: July 24/95 to August 14/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	526.7	2		0.006239											
10	514.7	16	7.1E+11	0.006342	98	86.9	7.87	15.3		1.017					
12	452	58	3.5E+11	0.00623	93.1	84.9	8.01	15.1		1.012					
14	359	254	3.3E+11	0.008792	85.7	54.2	18.3	11.7							
16	126.3	26.8		0.007129	114.2	48.4	13.3	9.8		1.017					
18	88.3	28	3.4E+11	0.007321											
20	59.6	33.8	2.5E+11	0.007634					20	1.02	17.8	0.3	0.17	2	3.6

Floc Stability
(t=20 days)

Time (min)	CST (s)
0	12.9
0.5	21.4
1	18.1
2	26.1
5	28
7	27.3
10	33.5
15	36.8
20	43.2
25	41

TRIAL: **Na = 20 mM**

DATE: September 8/95 to October 3/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
13	386.1	2.4	5.4E+11	0.006335	60.1	53.1	20.5	13.4		1.0177					
15	352	2.4	6.1E+11	0.00537											
16	345.3	1.2	3.4E+11	0.00505	46.8	54.1	32.1	11.7		1.0177					
17	426		3.8E+11	0.006553											
18	407.5	1		0.004917											
19	400.8	3.1	3E+11	0.00481	29.7	82.8	97.1	15.7		1.0177					
20	433.2														
22	436.2	1.1		0.004772											
23	434.7	2	4.2E+11	0.005077						1.0197					
24	380.9	10.3	4.5E+11	0.005084	66.8	71	54.4	12.9		1.0197					
25	249.6	17	2.9E+11	0.004137	65.5	62.3	44	12.7		1.0197					
26	207.6	27.6		0.004958											
27	143.8	27.2	1.3E+12	0.004822	99.6	121.9	66.3	22.3		1.0204					
28	89.1	64.8	5.9E+12	0.006497	142	143.3	76.5	22.8	20	1.021	26.1	0.8	0.16	1.8	4.7

Floc Stability
(t= 28 days)

Time	CST
(min)	(s)
0	13.5
0.5	33.6
1	42
2	35.3
5	57.2
7	58.2
10	56.3
15	66.1
20	62

TRIAL: **Na = 50 mM**

DATE: August 15/95 to September 8/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	452.4	16.8	1.4E+12	0.005695											
10	529.1	15.8	7.2E+11	0.008089											
12	191	42	1.7E+12	0.008703	65.2		34.7	16.4		1.017					
13	124.2	104	3.8E+12	0.009606	62.7	101.1	39.5	12.3		1.0129					
14	96	110	7.9E+12	0.011008											
15	71.8	84	9.6E+12	0.010202	86.4	78.3	37.3	9.7		1.0129					
16	63.7	100	7.5E+12	0.010915	89.9	86.9	38.3	14		1.0143					
17	56.9	110	1.2E+13	0.011013	100	87.8	42.7	14.7	33	1.0095	48.2	0.63	0.11	1.7	2.2

Floc Stability
(t= 17days)

Time	CST
(min)	(s)
0	22
0.5	59.1
1	70.9
2	79.4
5	109.6
7	115.4
10	150.3
15	158.2

TRIAL: K = 5.0 mM

DATE: September 8/95 to October 3/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
10	242.9	1.4		0.007301											
12	251.3	19.4	1.1E+12	0.006754											
13	313	18	1.2E+12	0.007324	61.4	68.6	28.7	14.9		1.0115					
14	426		1.3E+12	0.009125											
15	450.7	35.1		0.008466											
16	516.3	84.5	1.6E+12	0.010386	37.8	73.5	88.2	13.7		1.0109					
17	585.9														
19	517.9	4		0.007114											
20	497	1.1	1.3E+12	0.006751						1.0122					
21	473.5	14.7	4.4E+12	0.006568	63	56.7	50.5	12.9		1.0143					
22	380.9	11	1.6E+12	0.005824	48.3	58.1	39.8	13.4		1.017					
23	351.3	10	1.4E+12	0.004993											
24	339.6	10.9	1E+12	0.005216	47.1	66	41.4	15.3		1.0149					
25	309.7	15.8	2.8E+12	0.004884	64.4	56	33	12.7	8	1.0149	13	0.6	3.8	1.5	1

Floc Stability
(t= 25 days)

Time	CST
(min)	(s)
0	13.4
0.5	12.8
1	13.5
2	13.8
5	15.2
7	
10	15.8
15	15.7
20	17.9

TRIAL: **K = 10 mM**

DATE: October 4/95 to October 23/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	123.2	27.4													
10	124	17	2.5E+11	0.00407											
12	105.8	13.2	1.3E+11	0.003846	66.3	28	108	6.6		1.0129					
13	100.4	20.4	1.6E+11	0.003877						1.0149					
14	101.3	23.5	1.4E+11	0.003703	85.9	34.1	66.1	8.6		1.0156					
15	92	17.2	1.4E+11	0.003586	67.9	41	71	6.6		1.0156					
16	93.3	20.4	1.4E+11	0.003875	58.2	39.6	80.8	8.7		1.0156					
17	98.7	20	1.2E+11	0.00432	56.4	61.5	113	11.2	8	1.0149	11.9	0.13	9.5	2.4	1.2

Floc Stability
(t= 17 days)

Time	CST
(min)	(s)
0	10.4
0.5	10.4
1	10.8
2	11.2
5	13.1
7	12.3
10	12.8
15	14.4

TRIAL: **K = 17 mM**

DATE: September 8/95 to October 3/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
10	478.7	3.8		0.007737											
12	435.9	18.8	6.4E+11	0.00689											
13	475.7	2.2	5.7E+10	0.007023	59.8	72.8	22.5	14.3		1.0109					
14	579.4		6.8E+10	0.008553											
15	535.9	15.8		0.008361											
16	518.9	2.3	3.6E+11	0.008839	38.2	93.1	88.9	18.1		1.0143					
17	604.2														
19	566.9	12.2		0.006305											
20	556.1	11	4.1E+11	0.006818						1.017					
21	504.2	16.1	1.5E+12	0.006789	51.4	83.7	101.3	15.2		1.0177					
22	275.9	38	5.8E+11	0.005578	65.3	93.3	93.4	15.5		1.0183					
23	258.2	52.6	1.5E+12	0.005682											
24	219.7	83	6.7E+12	0.005937	98.1	76.6	76.8	17		1.0109					
25	155.1	87.3	3.7E+12	0.005645	106.3	74.3	56.2	16	24	1.0156	8.3	0.6	12.8	1.8	3.8

Floc Stability
(t= 25 days)

Time	CST
(min)	(s)
0	11.4
0.5	12.8
1	13.5
2	13.8
5	15.2
7	
10	15.8
15	15.7
20	17.9

TRIAL: **Mg = 3.8 mM**

DATE: August 15/95 to September 8/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	280	26	1.1E+12	0.006021											
10	519.2	20	1.7E+12	0.007346											
12	284.6	16	2.5E+12	0.008353	47.8		21.9	13.5		1.0177					
13	173.6	32	1.6E+12	0.008358	51.1	55.2	24.6	9.5		1.0177					
14	128.7	42	2.9E+12	0.007853											
15	131.2	26	1.2E+12	0.007722	50	52.6	7.4	1.3		1.0149					
16	117.4	36	1.3E+12	0.007596	52.8	68	0.94	3.6		1.0156					
17	119.4	35	1.3E+12	0.007571	56.1	61.7	0.01	6.9	10	1.0143	11.1	0.8	0.13	5.2	3.2

Floc Stability
(t= 17 days)

Time	CST
(min)	(s)
0	13.5
0.5	18.7
1	18.7
2	24.5
5	36.1
7	42.2
10	51.7
15	54.2
20	64.8

TRIAL: Mg =7.0 mM

DATE: October 4/95 to October 23/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	301.6	21.5													
10	274.2	2.6	2.8E+11	0.004007											
12	194.9	32.6	1.7E+11	0.004412	48.4	41	48.9	12.4		1.0231					
13	185.8	39	4.3E+11	0.00473						1.0244					
14	141.9	30	5.1E+11	0.005589	60.1	66.4	60.1	19.1		1.0244					
15	135.9	38.5	7.4E+11	0.005664	66.7	68.5	52.5	18.7		1.0238					
16	141.1	4.5	6.7E+11	0.005108	73.8	64.5	42.2	19.1		1.021					
17	153.1	5.1	6.8E+11	0.00638	64.9	85.6	32.8	23.5	28	1.0204	13.8	1.3	0.5	6.9	1.2

Floc Stability
(t=17 days)

Time (min)	CST (s)
0	13.8
0.5	15.5
1	17
2	16.4
5	16.7
7	16.4
10	17
15	16.9

TRIAL: **Mg = 12 mM**

DATE: October 4/95 to October 23/95.

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	315.3	19.3													
10	313.5	1.9	2.4E+11	0.004276											
12	234.8	44	2.5E+11	0.003958	38.4	42.7	30.2	10.8		1.0238					
13	179.8	15.4	1.9E+11	0.003991						1.0238					
14	129.2	5.6	2E+11	0.003869	32.3	48.6	25.6	9.5		1.0244					
15	132.9	9.7	2.2E+11	0.003983	37	47	26.1	11.5		1.0244					
16	133.1	12.5	2.2E+11	0.003897	40.6	42.2	24.4	8.9		1.0244					
17	141.2	1	1.7E+11	0.004156	36.7	56.3	31.4	9.7	12	1.0238	13.6	0.94	0.44	12.2	1.1

Floc Stability
(t= 17days)

Time	CST
(min)	(s)
0	11.5
0.5	11.7
1	11.8
2	11.8
5	12
7	12.3
10	13.3
15	12.1

TRIAL: Control (filamentous)

DATE: July 5/95 to July 24/95

Day	SVI	Supern. Solids	SRF	CST/MLSS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	380.9	40	2.1E+12	0.00766	68.3	40.8	29.3	8.3		1.016					
12	556.2	56	1.3E+12	0.007938	102.5	96.1	31.6	15.4		1.02					
13	543			0.00705											
14	559.1		7.1E+11	0.00703											
16	536.4	14	5.5E+11	0.00613											
18	522		3.1E+11	0.00561	68.5	124.5	23.3	34.9	20	1.02	10.8	0.28	0.14	1.8	4

Floc Stability
(t= days)

Time	CST
(min)	(s)
0	11.3
0.5	12.1
1	11.6
2	13.2
5	11.4
7	11.7
10	12.6
15	12.7

TRIAL: Control (slightly filamentous)

DATE: July 24/95 to August 14/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
8	467.3	30		0.005176											
10	502.5	34	7E+11	0.005785	93.6	116.6	6.94	19.1		1.016					
12	456.6	27	3.5E+11	0.005553	87.9	104.2	7.73	18.4		1.016					
14	456.4	12	2.7E+11	0.005771	72.5	67.1	19.5	13.5							
16	471.9	30.5		0.006359	81.5	66.6	12.9	14.2		1.017					
18	507.6	41	3.3E+11	0.00625					N/A						
20	566.3	84.9	2.1E+11	0.006744						1.016	N/A	N/A	N/A	N/A	N/A

Floc Stability
(t= 20 days)

Time	CST
(min)	(s)
0	11.3
0.5	12.1
1	11.6
2	13.2
5	11.4
7	11.7
10	12.6
15	12.7

TRIAL: Control

DATE: September 8/95 to October 3/95

Day	SVI	Supern. Solids	SRF	CST/MLS	S. Prot	Bd Prot.	S. Poly	Bd Poly.	Polymer	Floc Dens	Na	NH4-N	K	Ca	Mg
	(mL/g)	(mg/L)	(kg/m)	(mg/mg)	(mg/L)	(mg/g)	(mg/L)	(mg/g)	(mg/L)	(g/cm3)	(mM)	(mM)	(mM)	(mM)	(mM)
13	377.6	2	6.1E+11	0.006378	64.5	39.6	15	11.2		1.0163					
15	397.1	13.2	5.9E+11	0.006261											
16	429.6	1.1	5.6E+11	0.006338	50.7	52.4	27.8	11.3		1.0163					
17	460.6		5.1E+10	0.00715											
18	399.7	1.1		0.005047											
19	434.1	2.1	4.1E+11	0.005759	44.1	72.9	83.3	14.1		1.017					
20	488.8														
22	409.8	1.1		0.006139											
23	415.9	1.1	4.1E+11	0.005824						1.0177					
24	317.8	9.2	3.4E+11	0.006144	61.6	59.5	69.7	12.8		1.018					
25	250.2	11.1	5.6E+11	0.005406	44.4	63.3	66.3	12.1		1.019					
26	186.9	14.3		0.005457											
27	158.8	11.6	7.7E+11	0.00498	46.7	84	87.9	15.5		1.0183					
28	185.4	15.7	2.3E+12	0.006074	77.5	86	81.4	15	12	1.0183	10.3	0.4	0.13	1.8	1.3

Floc Stability
(t=28 days)

Time	CST
(min)	(s)
0	1
0.5	1.224
1	1.273
2	1.308
5	1.308
7	1.49
10	1.636
15	1.769

Batch Cation Addition

Settling Volume

Cation: Control

SS (mg/L)	2791	1953	2333
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	240	212	238
10	232	141	222
15	222	121	206
20	214	110	190
25	205	102	175
30	196	97	162
35	188	92	151
40	180	88	142
45	171	84	134

Cation: Ca = 2.5 mM

Conc(mg/L)	50	50	50
SS (mg/L)	2900	2360	2550
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	242	236	236
10	234	192	223
15	225	145	209
20	216	126	194
25	207	116	182
30	198	108	170
35	190	102	159
40	182	96	150
45	174	92	142

Batch Cation Addition

Cation: Ca = 5 mM

Conc(mg/L)	100	100	100
SS (mg/L)	2612	2622	1975
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	244	226	234
10	236	186	218
15	230	151	193
20	222	132	188
25	215	120	172
30	208	111	158
35	200	105	146
40	192	100	137
45	185	95	129

Cation: Ca = 7.5 mM

Conc(mg/L)	150	150	150
SS (mg/L)	2720	2568	2729
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	248	240	240
5	236	222	226
10	228	202	211
15	220	181	195
20	212	162	180
25	204	146	166
30	197	134	154
35	190	124	143
40	182	116	133
45	175	109	125

Batch Cation Addition

Cation: Ca = 10 mM

Conc(mg/L)	200	200	200
SS (mg/L)	3150	2478	2788
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	240	232	233
5	230	213	221
10	220	191	206
15	211	171	191
20	202	154	176
25	193	140	163
30	184	129	151
35	176	119	139
40	168	112	130
45	161	104	122

Cation: Ca = Mg = 2.5 meq/L

Conc(meq/L)	2.5	2.5	2.5
SS (mg/L)	2682	1975	2438
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	243	235	235
10	234	208	203
15	226	186	148
20	220	167	132
25	212	152	121
30	204	141	113
35	196	130	106
40	190	123	102
45	182	116	97

Batch Cation Addition

Cation: Ca = Mg = 5 meq/L

Conc(meq/L)	5	5	5
SS (mg/L)	2553	2114	2176
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	246	246	245
5	238	231	228
10	230	202	210
15	222	156	191
20	214	134	176
25	204	120	161
30	196	112	150
35	188	104	139
40	180	99	131
45	173	94	122

Cation: Ca = Mg = 7.5 meq/L

Conc(meq/L)	7.5	7.5	7.5
SS (mg/L)	2600	2363	2693
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	242	242	240
5	230	226	228
10	222	207	210
15	212	189	183
20	201	172	162
25	191	158	147
30	181	145	134
35	172	133	124
40	164	124	116
45	155	116	99

Batch Cation Addition

Cation: Mg = 1.25 mM

Conc(mg/L)	30.4	30.4	30.4
SS (mg/L)	3082	2442	2711
Time	Mg	Mg	Mg
(min)	(mL)	(mL)	(mL)
0	250	249	248
5	244	212	216
10	235	147	152
15	216	125	131
20	209	114	118
25	186	106	111
30	170	100	104
35	158	96	99
40	148	91	95
45	140	88	91

Cation: Mg = 2.5 mM

Conc(mg/L)	60.8	60.8	60.8
SS (mg/L)	3091	2100	2707
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	244	240	238
5	237	212	221
10	230	174	181
15	222	138	136
20	214	122	119
25	206	112	110
30	198	104	103
35	190	98	97
40	181	91	92
45	173	89	88

Batch Cation Addition

Cation: Mg = 3.75 mM

Conc(mg/L)	91.1	91.1	91.1
SS (mg/L)	3188	2507	2720
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	238	234	233
5.3	224	210	210
10	218	189	196
15	210	149	178
20	200	129	164
25	190	114	151
30	180	107	138
35	172	99	129
40	162	94	120
45	154	89	112

Cation: Mg = 5 mM

Conc(mg/L)	121.5	121.5	121.5
SS (mg/L)	2643	2578	2662
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	242	230	233
10	234	151	179
15	226	126	140
20	216	114	125
26.5	204	103	112
31.5	195	97	106
35	189	94	102
40	180	90	97
45	171	86	93

Batch Cation Addition

Cation: Na = 5 mM

Conc(mg/L)	115	115	115
SS (mg/L)	3038	2425	2600
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	248	248
5	242	214	221
10	212	146	154
15	169	126	132
20	150	114	120
25	138	106	111
30	129	101	105
35	123	96	100
40	117	91	95
45	112	88	92

Cation: Na = 10 mM

Conc(mg/L)	230	230	230
SS (mg/L)	2960	2513	2313
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	246	245	244
5	237	223	228
10	230	161	188
15	220	130	148
20	211	116	129
25	202	107	118
30	193	101	110
35	184	95	104
40	176	91	98
45	168	87	94

Batch Cation Addition

Cation: Na = 15 mM

Conc(mg/L)	345	345	345
SS (mg/L)	2905	2538	2613
Time	Na	Na	Na
(min)	(mL)	(mL)	(mL)
0	244	240	240
5.3	230	218	214
10	222	181	200
15	211	146	181
20	200	129	163
25	190	118	148
30	181	109	135
35	172	102	124
40	163	97	116
45	155	92	109

Cation: Control

Conc(mg/L)	0	0	0
SS (mg/L)	2825	2684	2725
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	244	236	234
10	238	178	211
15	231	138	204
20	224	122	190
26.5	214	110	172
31.5	206	104	159
35	190	100	152
40	191	95	142
45	183	91	133

Batch Cation Addition

Cation: Control
Conc.: 0 meq/L
0 mg/L

SS (mg/L)	3480	3180	3000
CST (s)	12.95	14.25	12.6
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	243	239	227
10	237	204	171
15	227	162	135
20	219	143	122

Cation: Control
Conc: 0 meq/L
0 mg/L

SS (mg/L)	3199	3095	2870
CST (s)	12.2	12.4	11.8
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	240	234	234
10	228	206	212
15	212	170	193
20	195	148	130

Cation: Ca++
Conc.: 1 meq/L
20 mg/L

SS (mg/L)	3055	2890	2769
CST (s)	13.1	12.75	12.15
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	249
5	240	238	230
10	228	224	210
15	212	209	190
20	202	196	178

Batch Cation Addition

Cation: Ca++ Repeat
Conc.: 1 meq/L
20 mg/L

SS (mg/L)	3560	3140	2900
CST (s)	13.63333	13.1	12.05
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	252	250	250
5	244	241	239
10	236	226	196
15	228	212	146
20	220	198	128

Cation: Ca++
Conc.: 2 meq/L
40 mg/L

SS (mg/L)	3055	2890	2679
CST (s)	13	12.3	12.3
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	236	234	234
5	228	223	223
10	220	214	199
15	211	204	193
20	202	194	179
25	194	184	166

Cation: Ca++ Repeat
Conc.: 2 meq/L
40 mg/L

SS (mg/L)	3340	3020	2980
CST (s)	12.3	11.3	11.95
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	240	242	246
5	230	228	229
10	220	214	211
15	210	191	194
20	200	189	178

Batch Cation Addition

Cation: Ca++
Conc.: 5 meq/L
100 mg/L

SS (mg/L)	3300	2920	2880
CST (s)	11.95	11.65	11.4
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	226	226	234
5	218	214	218
10	210	191	201
15	202	188	183
20	194	176	166

Cation: Ca++
Conc.: 7.5 meq/L
150 mg/L

SS (mg/L)	3260	2980	2820
CST (s)	11.8	11.4	11.5
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	192	200	212
5	182	186	196
10	173	174	179
15	164	161	162
20	156	148	146

Cation: Mg++
Conc.: 1 meq/L
12.15 mg/L

SS (mg/L)	3420	3060	2840
CST (s)	12.75	11.8	12.2
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	243	237	231
10	237	201	169
15	223	157	134
20	212	139	121

Batch Cation Addition

Cation: Mg++
Conc.: 2 meq/L
24.3 mg/L

SS (mg/L)	3260	2940	2840
CST (s)	12.5	12.95	12
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	241	237	246
5	234	225	234
10	228	213	172
15	221	201	139
20	215	189	123

Cation: Mg++
Conc.: 5 meq/L
60.75 mg/L

SS (mg/L)	3240	2900	2720
CST (s)	11.5	11.53333	11.45
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	229	230	240
5	220	218	224
10	211	195	208
15	202	192	191
20	194	178	175

Cation: Mg++
Conc.: 7.5 meq/L
91.125 mg/L

SS (mg/L)	3220	2960	2840
CST (s)	13.15	12.2	11.9
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	202	196	217
5	193	186	192
10	184	176	186
15	175	166	170
20	166	155	154

Batch Cation Addition

Cation: Na+
Conc.: 1 meq/L
23 mg/L

SS (mg/L)	3420	3180	3020
CST (s)	13.05	12.75	12.75
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	251
5	242	238	240
10	234	226	195
15	226	212	146
20	218	199	129

Cation: Na+
Conc.: 2 meq/L
46 mg/L

SS (mg/L)	3400	3260	3040
CST (s)	12.65	12.35	12.45
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	244	238	236
5	235	228	220
10	227	216	201
15	220	196	184
20	211	177	167

Cation: Na+
Conc.: 5 meq/L
115 mg/L

SS (mg/L)	3620	3200	3280
CST (s)	13.53333	13.1	12.15
Time	Volume	Volume	Volume
(min)	(mL)	(mL)	(mL)
0	250	250	250
5	243	238	235
10	236	225	165
15	227	209	138
20	218	179	124

Batch Test Data

Added to sludge from Na =20 mM trial at steady state.

CST

Cation Added	Control	Mg=2.5 (mM)	Mg=5 (mM)	Mg=10 (mM)	Ca=5 (mM)	Ca=10 (mM)
Mean	14.56667	14.53333	13.65	13.43333	13.7	12.1
High	12.96667	13.30333	13.44	12.57333	12.85	11.82
Low	16.16667	15.76333	13.86	14.29333	14.55	12.38

Settling Volume

time (min)	Control (mL)	Mg=2.5 (mL)	Mg=5 (mL)	Mg=10 (mL)	Ca=5 (mL)	Ca=10 (mL)
0	250	250	250	250	250	250
2	150	130	153	140	135	135
5	84	81	84	71	75	74
10	67	64	66	55	58	57
15	57	55	56	47	49	49
20	51	49	50	42	44	44