CHAPTER I

INTRODUCTION

INTRODUCTION

The digestion of waste sludge is an essential part of wastewater treatment system. The digested biosolids can be disposed of by incineration, land application or to a landfill, or be dumped into sea. The dumping of sludge in sea has been prohibited and as a result of which land application of this sludge is the predominant form of sludge disposal. To reduce the volume that must be hauled to land application sites and landfills, municipalities choose to dewater the biosolids. The digested biosolids typically have poor dewatering characteristics, requiring substantial amounts of conditioning chemicals and having dewatered cake with a solids concentration less than 25%. Hence the dewatering of sewage sludge is an important part of the waste handling and disposal system and can determine the economics of the entire wastewater treatment process.

Digestion of sludge can be carried out both aerobically and anaerobically. Though anaerobic digestion is more widespread, aerobic digestion in the form of autothermal thermophilic aerobic digestion has become popular over the last four decades.

In 1993 the USEPA regulation 40 C. F. R. Part 503 (Standards for the use and disposal of sewage sludge) for sludge management came into existence. The new regulations have promulgated a higher pathogen destruction and vector attraction reduction which is not possible by the conventional methods of sludge digestion(USEPA, 1990). Many municipalities do not have access to sites for disposal of class B biosolids. Because of the fewer restrictions to the land application of class A biosolids, municipalities are increasingly choosing to produce class A biosolids. Because of these new compliance parameters, it has become less beneficial from a cost and operation point for the municipalities to continue with their current biosolids management techniques so there is considerable interest in ATADs.

The ATAD process is classified as a high temperature aerobic digestion process. The ATAD process produces biosolids which meet the Class A biosolids definitions as per the USEPA 40 CFR Part 503 for reduction of VSS, pathogen and vector attraction (USEPA, 1990). Autothermal thermophilic aerobic digestion, or ATAD, was developed in the

1960's and has significantly developed ever since. It is at present successfully implemented in Europe and particularly in Germany.

The ATAD process has many benefits: a high pathogen destruction, low space and tank and energy requirements, and a high sludge treatment rate. ATAD systems are normally multistage aerobic digestion processes and are characterized by high temperature thermophilic conditions (40^{o} C to 80^{o} C) [1]. Generally no supplemental heat is required for this process. ATAD reactors typically operate at 55^{o} C and reach upto 72^{o} C in the second stage. Generally 2 ATAD reactors are operated in the series, with partially digested sludge being fed from first ATAD to the second ATAD. The ATAD reactors are followed by one or two holding tanks. In the two ATAD reactors aeration and complete mixing are provided while in the holding tank only mixing is provided. The SRT for the whole ATAD process ranges from 10-25 days.

Most digestion processes thicken the sludge prior to digestion to minimize the size of the digestion tanks and to limit the energy requirements for mixing and heating. Generally the sludge is thickened to 4-6 % TS concentration. Higher amounts of thickening, decreases the mixing efficiency and lower amounts of thickening increases the space and energy requirements. Thickening can be achieved by gravity thickening, rotary drum thickener, dissolved air floatation or co-thickening in the primary sludge clarifier. A polymer aid is also generally added to increase the thickening.

ATAD systems generally consist of covered, insulated reactors containing aeration, mixing, and off gas release equipment. Gases such as ammonia and carbon dioxide are produced in the digesters and are released by the off gas release equipment. Because of the high temperature generated in the digesters nitrification does not take place, thereby eliminating the oxygen requirement due to nitrification. The destruction of the volatile solids produces gases and heat energy which helps to sustain the process. The insulated systems help in retention of the heat which is released during digestion and results in high operating temperatures which in turn results in high degradation rates of volatile solids as well as destruction of pathogens. About 30 – 50 % of the volatile solids destruction takes place during the digestion process.

Most of the research pertaining to Autothermal thermophilic aerobic digesters has focused on process mechanisms, and pathogen and volatile solids destruction. The dewatering problems associated with ATAD sludges have also been the focus of some of the studies but the exact mechanism leading to the poor dewatering problems has not yet been completely understood. Previous experience has shown that the cost of chemically conditioning the thermophilic sludge for dewatering has increased by a factor of 20 -30 times over mesophilic sludge. Murthy et al [2, 3] found the cost of dewatering ATAD sludge to be in excess of $ 150 / dry ton of solids whereas for mesophilicly digested sludge it was found to be $20- $ 30/ dry ton of solids.

Several studies have investigated the mechanism leading to the poor dewatering in ATAD sludges. Different studies have attributed different reasons for this behavior. Most of the attention has focused on high temperature, sludge feed characteristics, biopolymer degradation and sludge retention time. Despite various theories suggesting different reasons for the poor dewatering, not much work has been done to improve the dewatering of ATAD sludges. Municipalities are still faced with the complex task of choosing between high dewatering costs associated with ATAD produced class A biosolids and stricter standards for the land application of class B biosolids. Hence further research is necessary to ascertain the mechanism for the poor dewatering of these sludges and to economically condition these sludges.

CHAPTER II

LITERATURE REVIEW

LITERATURE REVIEW

Water in activated and digested sludges exists in two states “free” water and “bound” water. The bound water has been defined as that portion of water that persists in the liquid phase at very low temperatures without freezing (Kyprianoff [4]). Vesilind (1994 [5]) defined bound water as that part of moisture which cannot be separated by mechanical means. Dewatering of waste sludges, particularly those containing secondary sludges without conditioning is not practical. The conditioning can either be physical or chemical. The chemical dewatering includes the use of organic and inorganic coagulants whereas physical dewatering includes heat treatment and freezing and thawing techniques (Katsiris and Katsiri [6]). The flocculation of those microorganisms and colloidal material which comprise the sludge surface is an essential prerequisite for the efficient and economical dewatering of sludge.

The Flocculation Process

The flocculation process is known to be a two step process, the transport process and the attachment process. The first step is the transportation step in which the particles come into contact with each other by collision. The rate of this process is determined by the velocities of the fluid and the particles present in it. Then in the next step depending on the short term forces, the attachment process takes place. The DLVO theory has been used to describe the interaction between two particles as the sum of additive forces resulting from the Van der Walls interactions (generally attractive), and the repulsive interactions from the overlap between the electrical double layer of the two particles. The difference in these two forces is the energy barrier which must be overcome for the attachment step to take place. A coagulant reduces this energy barrier by decreasing the electrostatic forces of repulsion.

La Mer and Healy [7] divided the destabilization of the sludge particles by chemical conditioners into two categories, those that aggregate colloidal particles into a floc structure by forming bridges with the coagulant and those that reduce the forces of interaction between two particles in the sludge. While coagulation by chemical salts such as ferric chloride and alum involve several steps in bringing the particles together, coagulation by polyelectrolytes involves direct inter-particle bridging.

Aluminum and iron salts are widely used as coagulants in water and wastewater treatment. Their mode of action is explained in terms of two distinct mechanisms; charge neutralization of the negatively charged colloids and sweep flocculation. The relative importance of these factors depends on factors such as pH and coagulant dosage (Duan and Gregory [8]). Polyelectrolytes are increasingly being used as coagulants for sludge conditioning. Polymeric additives can be used for aggregation of particles by polymer bridging or charge neutralization (Gregory [9]). At the optimum coagulant dose the zeta potential of the particles is close to zero [8]. At doses higher than the optimum dose, the electrophoretic mobility becomes positive because of charge reversal [8]. When iron and alum salts are used at high pH values, the optimum dosage increases because of the decreased positive charge of the adsorbed species.

FACTORS AFFECTING DEWATERING

Sludge settling and dewatering characteristics are affected by factors such as zeta potential, surface charge, and hydrophobicity, floc size distribution and the presence of divalent mineral cations (Liu and Fang [10])

Role of Biopolymer

The release of biopolymer in sludge has been found to occur due to microbial metabolism and release during cell lysis (Grady et al [11]). One reason for the difficulty in dewatering is the presence of exocellular polymeric substances (ECP), which entraps the water. Some of the functions of ECP matrix are adhesion to surfaces, aggregation of bacterial cells in flocs and biofilms, formation of a protective barrier that provides resistance to biocides or other harmful effects and retention of water. The ECP is believed to allow microorganisms to live at high cell densities (Laspidou and Rittmann [12]). Gehr and Henry [13] found that the large size of ECP made it difficult to compactly pack the sludge aggregates, which led to more interstitially bound water contained in the sludge and poor dewaterability (Forster and Lewin [14]). Soluble biopolymer has been found to have a greater impact on sludge dewatering properties than floc-bound biopolymer (Novak et al [15]).

Houghton et al [16] found that there is an optimum level of ECP at which each type of sludge exhibits maximum dewaterability. They suggested ECP values of 20 mg ECP/ g SS for raw sludge, 35 mg ECP/ g SS for activated sludge and 10 mg ECP/g SS for digested sludge. They suggested that by altering the process parameters, such as sludge age, retention time, digester feed composition and operation temperature it may be possible to manipulate the level of ECP produced.

It was earlier believed that EPS is predominantly composed of carbohydrates. The recent studies have however shown EPS to be primarily composed of proteins (Dignac et al [17]) and hence are important compounds affecting floc structure. Frolund et al [18] found the exocellular polymeric substances (EPS) to be composed of protein, polysaccharides, humic acids and nucleic acids. Recent studies have also indicated the presence of other substances such as humic acids, uronic acids and DNA. (Jorand et al [19] , Nielsen et al [20]. Higgins and Novak [21, 22] categorized these substances into bound and dissolved. The dissolved EPS can be extracted by centrifugation while the bound EPS requires additional treatment.

Eriksson and Hardin [23] proposed the unifying model of flocculation which suggests that during the initiation of flocculation, exocellular polysaccharide is responsible for bridging the distance between electro-statistically stabilized cells to form a weak elongated floc. Up to a certain level, further polysaccharide synthesis produces stronger flocs by bridging cells more firmly, after which they will have a dispersing effect. Karr and Keinath [24] suggested that floc size and particle size distribution are the two most important physical parameters in sludge dewatering. Flocculation changes the particle size distribution of the sludge by binding smaller particles together. They also found that the higher the fraction of the particles in the size range of 1 – 100 μm, the poorer was the dewatering. Novak et al. [25] showed that small particles tend to blind the sludge during filtration. The reason for the appearance of smaller particles is not clear. Rasmussen et al [26] reported mechanical disruption and anaerobic storage to be responsible for the appearance of these particles. Novak et al [27] studied the effect of aerobic and anaerobic digestion on floc destruction. They found that biopolymer was released during both aerobic and anaerobic digestion. In particular there was more protein released during anaerobic digestion than aerobic digestion. The dewatering rate was found to directly depend on the total biopolymer in solution.

Sludge is generally thickened and stored prior to digestion. Nielsen et al [20] and Bura et al [28] found that during thickening and storage the EPS underwent biological transformations and lost some of its bound water during the thickening process resulting in the reduction of sludge dewaterability. Novak et al [27] found that sludge dewaterability decreased by 16 – 95 % after anaerobic storage. Rasmussen et al [26] found that during anaerobic storage EPS was slowly degraded, with an increase in the turbidity and the concentrations of cations such as calcium, potassium, ammonium,

Role of Cations

Studies have found that sludge containing high concentrations of calcium and magnesium have generally better sludge settling and dewatering properties. Mineral cations tend to complex with EPS affecting bioflocculation, settling and sludge dewaterability. Two models of bioflocculation have been suggested: double layer compression and cation bridging. In the double layer model flocculation improves at increased ionic strength due to the decrease in the double layer thickness and surface potential (Zita and Hermansson [29]). In the cation bridging model, the cations serve as a bridge between the negatively charged EPS. The bridging stabilizes the floc network thereby improving the sludge settling and dewatering (Forster and Lewin [14], Higgins and Novak [21, 22]).

Higgins and Novak [21, 22] found out that the ratio and concentration of cations can have a major impact on the dewatering properties of activated sludge. They studied the effect of the calcium to magnesium ratio; the effect of increasing divalent cation concentrations; and the effect of increasing monovalent cation concentrations. Their study found that the settling and dewatering properties of activated sludge were dependent on both the ratio and the concentration of the cations in the feed. They concluded that a ratio of sodium to divalent cations greater than two resulted in deterioration in settling and dewatering characteristics, and a minimum concentration of calcium and magnesium for good settling and dewatering was in the range of 0.72 – 2.0 meq/l of each. Bruus et al [30] studied the stability of activated sludge flocs and their relation to dewatering. They found that approximately half of the calcium was associated with exopolymers. When the calcium was extracted from the sludge it led to an increase in the number of smaller particles and subsequently to an increase in the specific resistance to filtration.

Murthy and Novak [31] found that an optimum potassium concentration in the range of 0.25 – 0.50 meq/l is required for achieving optimal dewatering. They also observed that excessive potassium concentration (> 0.50 meq/l) can be detrimental to sludge dewatering. Bruus et al [30] studied the importance of calcium ion for the structure of activated sludge floc. They examined whether the removal of calcium ion would result in disintegration or deflocculation of sludge flocs. They found out that sludge deteriorates along with the removal of calcium ion.

Higgins and Novak [32] studied the relationship between exocellular biopolymer concentration and cation concentration using laboratory scale activated sludge reactors. An increase in the divalent cation concentration in the feed to the reactors was associated with an increase in the bound exocellular protein concentration and high sodium concentration resulted in a decrease in the bound protein concentration. They suggested changes in the bound biopolymer to the cation bridging model.

Novak et al [27] have shown that during aerobic digestion of sludge, calcium and magnesium ions are released into the solution. They attributed this to the degradation of that part of the floc that contains calcium and magnesium ions that are part of the floc biopolymer structural network. When this biopolymer degrades it releases the associated calcium and magnesium into solution.

Role of Iron and Aluminum

The stability of sludge flocs is important for the solid liquid separation (dewatering) process in wastewater treatment. Large amounts of iron are found in sludge either by the accumulation from influent or by its addition for phosphorus removal. In well aerated systems this iron is in the oxidized state. However Rasmussen et al [33] suggested that anaerobic degradation during anaerobic storage can lead to iron and sulfate reduction thereby disintegrating sludge flocs and deteriorating the dewaterability. When the ferric iron reduction takes place it would also release the chemically bound phosphate into solution. Rust et al [34] suggested that both ferrous iron and iron hydroxide promote bioflocculation by forming a bridge between the proteins and the floc. Novak et al [35] suggested that the conversion of Fe^{+3} to Fe^{+2} in anaerobic digestion resulted in the deterioration of sludge dewaterability. The iron reduction weakened the protein bonds and the floc structure resulting in the release of EPS in the solution.

Oxygen limitations are known to result in rapid deflocculation. Caccavo et al [36] showed that activity of Fe (III) reducing bacteria caused a decrease in the floc strength due to the change in floc properties by the conversion of Fe (III) to Fe (II). Other activities in sludge also lead to weaker floc strength. Sulfate reduction reduces the floc stability by the production of sulfide which reacts with Fe (III) and forms FeS and thereby removes the floc forming capacity from Fe (III). Wilen et al [37] studied the influence of microbial activity on the stability of activated sludge flocs. They observed the reduction of Fe (III) to Fe (II) whenever oxygen and nitrate were absent. Also deflocculation was observed when sulfate reducing bacteria were added to the sludge. Deflocculation was also observed when Fe (III) and Fe (II) were removed from the sludge.

Zeta Potential

Zeta potential measurement can help in understanding and controlling colloidal behavior and colloidal suspensions. In many cases, the performance of a suspension can be improved by understanding the effect of colloidal behavior on such properties as viscosity, settling and effective particle size [38]. Zeta potential is a tool that has been used for decades to optimize the dose of chemical coagulants for water and wastewater treatment. The magnitude of zeta potential gives an indication of the potential stability of the colloidal system. If all the particles have a large positive or negative charge, there will be dispersion stability [38]. In this case the particles will have no forces of interaction and will remain freely in suspension. If the particles have low zeta potential, then there is no force to prevent the particles from coming together and there will be dispersion instability [38]. The zeta potential of typical waste activated sludge has been found to be -30 mv (Bohm and Kulicke [39]; Chitikela and Dentel [40]). Particles with zeta potential greater than + 30 mv are considered stable. Particles with zeta potential more negative than – 30 mv are considered stable. Microbial cells, EPS and sludge foc consists of negative charge because of the ionization of groups such as the carboxylic and phosphate. The most difficult suspended solids to remove are the colloids. Because of their small size, they easily escape both sedimentation and filtration. The removal of such colloidal particles can be done easily by the reduction of their zeta potential by the addition of coagulants, such as alum, ferric chloride or cationic polymers. The addition of these coagulants reduces the net zeta potential and once the charge is reduced then no repulsive forces exist and the particles can easily come into contact with each other, form larger flocs and can then be settled out.

The most important factor that affects zeta potential is the pH. In general the zeta potential versus pH curve will be positive at low pH and lower or negative at higher pH. There may be a point where the curve passes through the zero potential. This is the point of least stability and is known as isoelectric point.

Hydrophobicity

Sludge flocculation is generally found to increase with the hydrophobicity of EPS, cells and flocs. The hydrophobicity of the flocculated sludge may be measured either for the sludge as is or for the sludge after disintegration. (Jorand et al [19], Bura et al [28]). Mozes and Rouxhet [41] found that the sludge hydrophobicity is affected by a number of operating parameters such as substrate, bacterial growth phase and conditions, oxygen, temperature, pH ionic strength and the presence of multivalent cations and phosphate. Hydrophobic interaction between microbial cells is crucial to the floc formation and sludge settling. Bacteria in activated sludge may be hydrophobic or hydrophilic. Jorand et al [19] found that hydrophobic bacteria produced lesser amounts of EPS than hydrophilic.

THERMOPHILIC DIGESTION

In the late 1960's Kambhu and Andrews [42] conducted the first study on ATAD technology. In the following decades a number of ATAD facilities came up in Europe and particularly in Germany due to higher pathogen destruction requirements. Over the past decade about 30 ATAD plants have been placed in service. Many of these plants have been plagued by problems such as erratic solid destruction levels, off gas odor etc (Staton et al [43]). The development of ATAD technology in the USA and Canada was because of is potential cost and space savings benefits over conventional aerobic and anaerobic digestion processes. When the EPA regulations for the management of biosolids came into effect in 1993, this technology became important as a Process to Further Reduce Pathogens. Some of the advantages of ATAD process over other digestion processes are its ability to meet class A biosolids, simplified control of foul odors because of enclosed digesters, no pretreatment of biosolids required, simple mechanical systems to start up, operate and shut down. However it also has some apparent disadvantages which include the need to pre thicken the sludge to about 5 % solids concentration, increased polymer demand for dewatering, the digested sludge needs to be cooled off to reduce odorous off gases and to improve the dewatering, a side stream requiring further treatment and foaming problems (Kelly et al [44]).

As the name suggests the process is self heat generating or autothermal, but this term is also a little misleading as about 30 % of the heat requirement for this process is supplied through mixing energy. The temperature in the first stage of digestion is lower than in the subsequent stages. This is because in the first stage of digestion, more heat energy is required to raise the temperature than to maintain it in the subsequent stages. Although the process is thought to be aerobic, it is not entirely aerobic, but is a combination of aerobic, anaerobic and facultative processes (Kelly et al [45]).

Research Related to ATAD

Even though the ATAD process has been in existence for almost four decades now, very little literature exists about its performance and efficiency, and other operational parameters. Most of the ATAD plants that exist were developed in the Republic of Germany and Europe were sludge dewatering was not carried out prior to land application, hence little research was done in that direction. Since its development in North America, some research has been conducted to understand this technology better.

Thermophilic digestion results in rapid deterioration in the dewaterability of secondary sludge, which has been attributed to increased EPS in the sludge (Burnett et al [46], Murthy et al [3]). These researchers have also found out that the polymer dosage to adequately condition ATAD biosolids are up to 10 times higher than mesophilicly digested biosolids. Zhou et al [47] studied the role of digestion temperatures and release of extracellular protein on the dewaterability of thermophilicly digested sludge. They found that higher digestion temperatures had a more significant impact on dewatering than lower digestion temperatures. Also they found a direct relation between the amount of protein in the solution and the dewatering of thermophilicly digested sludge. Murthy et al [2, 3] also found large amounts of protein and polysaccharide in the thermophilicly digested sludges from various plants. They also found that inorganic conditioners such as ferric chloride and alum were effective in reducing polymer requirement by removing the protein and polysaccharide over all size ranges.

Zhou et al [48] studied the role of various parameters in affecting the dewatering of sludge. They found that the composition of the feed sludge strongly affected the dewaterability of secondary sludge but did not have much effect on the dewaterability of primary and mixed sludge. The solids retention time for digestion was not found to have little impact on dewatering of thermophilically digested sludge though it did seem to affect the mesophilically digested sludge. Also there was a large increase in solution protein, polysaccharide and phosphate concentrations during the digestion. These researchers suggest that there are several variables that can affect the dewatering of ATAD sludge. While some of the mechanisms leading to the poor dewatering are now well-documented, not much success has been made in improving the dewatering of these sludges. Kelly et al [49] found that the addition of ferrous iron as pickle liquor reduced the polymer dose to one half. Murthy et al [2, 3] found that iron, aluminum and post digestion aeration could all substantially improve the dewatering of ATAD sludges and reduce the polymer conditioning demand. Abu-Orf et al. [50] found that electrical arc pretreatment enhances the ATAD dewaterability to some degree. Previous experience has shown that the cost of chemically conditioning the thermophilic sludge for dewatering has increased by a factor of 20 -30 times over mesophilic sludge. Murthy [2, 3] found that cost of dewatering ATAD sludge to be in excess of $ 150 / dry ton of solids whereas for mesophilicly digested sludge it was found to be $20- $ 30/ dry ton of solids.

Zhou et al [51] did a comparative study of the floc size distribution and its effect on dewatering for mesophilic and thermophilic digested sludge. They found that thermophilic digestion produced many small size particles after just one day of digestion and was accompanied by deterioration in dewatering. They also suggested that temperature rather than digestion time had more effect on dewatering. Murthy et al found that storage of ATAD biosolids in mesophilic aerated tanks was found to improve dewatering properties. Though several studies have been conducted that looked into the various aspects of thermophilic treatment of sludge, more research is needed for a better understanding of the process and in particular the factors leading to the poor dewatering.

References

[1] USEPA (1990). Environmental Regulations and Technology: Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge.

[2] Murthy, S. N., Novak, J. T., Holbrook, R. D. and Surovik, F. (2000 a). Mesophilic aeration of ATAD biosolids to improve plant operation. Water Environment Research, **72**, 476-483.

[3] Murthy, S. N., Novak, J. T. and Holbrook, R. D. (2000 b). Optimizing dewatering of biosolids from Autothermal Thermophilic Aerobic Digesters (ATAD) using inorganic conditioners. Water Environment Research, **72**, 714-721.

[4] Kyprianoff, J. (1958). Bound water in foods. Fundamental Aspects of the Dehydration of Foodstuffs. Society of Chemical Industry, Macmillan, New York.

[5] Vesilind, P. A. (1994). The role of water in sludge dewatering. Water Environment Research **66**, 4-11

[6] Katsiris, N. and Katsiri, A. K. (1987). Bound water content of biological sludges in relation to filtration and dewatering. Water Research, **21**, 1319 – 1327

[7] La Mer, V. K. and Healy, Y. W. (1966) Solid-liquid separation, H.M.S.O.

[8] Duan, J. and Gregory, J. (2003). Coagulation by hydrolyzing metal salts. Advances in Colloid and Interface Science, **100-102**, 475 – 502.

[9] Gregory, J (1996). Industrial Water Soluble Polymers., Royal Society of Chemistry, Cambridge, 62–75.

[10] Liu, Y and Fang, H.P. (2003). Influences of Extracellular polymeric substances (EPS) on flocculation, settling, and dewatering of activated sludge. Critical Reviews in Environmental Science and technology, **33**, 3, 237 – 273.

[11] Grady, C.P.L., Daigger, G.T., Lim, H.C. (1998). Biological Wastewater Treatment, 2nd edition, Marcell Dekker, Inc., New York, NY.

[12] Laspidou, C. S. and Rittmann B. E. (2002). A unified theory for extracellular polymeric substances, soluble microbial products, and active inert biomass. Water Research, **36**, 2711 – 2720

[13] Gehr, R. and Henry, J. G. (1983). Removal of extracellular material techniques and pitfalls. Water Research, **17**, 1743-1748

[14] Forster, C. F. and Lewin, D. C. (1972). Polymer interactions at activated sludge surfaces. Effluent Water Treatment. Journal. **12(10)**, 520–525.

[15] Novak, J. T., Becker, H., and Zurrow, A. (1977). Factors influencing activated sludge properties. Journal of Environmental Engineering. **103(5)**, 815–828.

[16] Houghton J. I., Quarmby, J. and Stephenson, T. (2001). Municipal wastewater sludge dewaterability and the presence of microbial extracellular polymer. Water Science and Technology. **44**, 373 – 379.

[17] Dignac, M. F., Urbain, V., Rybacki, D., Bruchet, A., Snidaro, D., and Scribe, P. (1998). Chemical description of extracellular polymers: implication on activated sludge floc structure. Water Science and Technology. **38(8/9)**, 45–53.

[18] Frølund, B., Palmgren, R., Keiding, K., and Nielsen, P. (1996). Extraction of extracellular polymers from activated sludge using a cation ion exchange resin. Water Research. **30(8)**, 1749–1758.

[19] Jorand, F., Guicherd, P., Urbain, V., Manem, J., and Block, J. C. (1994) Hydrophobicity of activated sludge flocs and laboratory-growth bacteria. Water Science and Technology. **30(11)**, 211–218.

[20] Nielsen, P. H., Frølund, B., and Keiding, K. (1996). Changes in the composition of extracellular polymeric substances in activated sludge during anaerobic storage. Applied Microbiology Biotechnology. **44**, 823–830.

[21] Higgins, M. and Novak, J.T. (1997a). The effect of cations on the settling and dewatering of activated sludges: laboratory results. Water Environment Research, **69**, 215- 224.

[22] Higgins, M. and Novak, J.T. (1997b). Dewatering and settling of activated sludges: the case for using cation analysis. Water Environment Research, **69** 225-232.

[23] Eriksson, L. and Hardin, A. M. (1984). Settling properties of activated sludge related to floc structure. Water Science and Technology. **16**, 55-68.

[24] Karr, P.R. and Keinath, T.M. (1978). Influence of particle size on sludge dewaterability. Journal of Water Pollution Control Federation. **50**, 1911–1930.

[25] Novak, J.T., Goodman, G.L., Pariroo, A. and Huang, J.C. (1988). The blinding of sludges during filtration. Journal of Water Pollution Control Federation. **60,** 206-214.

[26] Rasmussen, H., Bruus, J. H., Keiding, K. and Nielsen P. H. (1994). Observations on dewaterability and physical, chemical and microbiological changes in anaerobically stored activated sludge from a nutrient removal plant. Water Research. **28**, 417-425.

[27] Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003). Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. Water Research, **37**, 3136-3144.

[28] Bura, R., Cheung, M., Liao, B., Finlayson, J., Lee, B. C., Droppo, I. G., Leppard, G. G., and Liss, S. N. (1998). Composition of extracellular polymeric substances

in the activated sludge floc matrix. Water Science and Technology. **37(4/5)**, 325–333.

[29] Zita, A. and Hermansson, M. (1994). Effects of ionic strength on bacterial adhesion and stability of flocs in a wastewater activated sludge system. Applied Environmental Microbiology. **60(9)**, 3041–3048.

[30] Bruus, J.H., Nielsen, P.H. and Keiding, K. (1992). On the stability of activated sludge flocs with implications to dewatering. Water Research, **26**, 1597- 1604

[31] Murthy, S.N. and Novak, J.T. (1998). Effects of potassium ion on sludge settling, dewatering and effluent properties. Water Science Technology. **37**(4-5), 317-324.

[32] Higgins, M. and Novak, J.T. (1997c). Characterization of exocellular protein and its role in bioflocculation. Journal of Environmental Engineering, **123(5)**, 479-485.

[33] Rasmussen H., Nielsen P. H. (1996). Iron reduction in activated sludge measured with different extraction techniques. Water Research. **30**, 551 – 558.

[34] Rust, M.E. (1998). Biopolymer and cationic release in aerobic and anaerobic digestion and the consequent impact on sludge dewatering and conditioning properties. M.S. Thesis, VPI & SU, Blacksburg, VA.

[35] Novak, J. T., Muller, C. D., and Murthy, S. N (2001). Floc structure and the role of cations, Proc. Sludge Management Entering the 3rd Millenium — Industrial, Combined, Water and Wastewater Residues, Taipei, Taiwan,354–359, 2001.

[36] Caccavo, F., Blakemore, R.P. and Lovely, D.R. (1992). Applied Environmental. Microbiology. **58**, 3203- 3211.

[37] Wile´n, B.M., Nielsen, J.L., Keiding K. and Nielsen P.H. (2000). Influence of microbial activity on the stability of activated sludge flocs. Colloids and Surfaces, **18** , 145 – 156.

[38] Zeta Meter Inc, USA. http://www.balancedforhealth.com/zetafiveminute.pdf

[39] Bohm, N., Kulicke, W.-M. (1997). Optimization of the use of polyelectrolytes for dewatering industrial sludge of various origins. Colloid Polymer Science. **275**, 73_81.

[40] Chitikela, S., Dentel, S. (1998). Dual chemical conditioning and dewatering of anaerobically digested biosolids: laboratory evaluations. Water Environment Research, **70**, 1062 - 1069.

[41] Mozes, N. and Rouxhet, P. G. (1987). Methods for measuring hydrophobicity of microorganisms. Journal of Microbiol. Methodology, **6(2)**, 99–112.

[42] Kambhu, K., and Andrews, J. F. (1969). Aerobic Thermophilic Process for the Biological Treatment of Wastes - Simulation Studies. Journal of Water Pollution Control Federation, **41**: R127.

[43] Staton K L. and Alleman J. E (2001). "2nd Generation Autothermal Thermophilic Aerobic Digestion: Conceptual Issues and Process Advancements". WEF/AWWA/CWEA Joint Residuals and Biosolids Management Conference, Biosolids 2001: "Building Public Support"

[44] Kelly, H.G., Donald S. M, et al. (2003). Autothermal Thermophilic Aerobic Digestion Research, Application and Operational Experience, WEFTEC 2003 Los Angeles, CA.

[45] Kelly, H.G. and Roger, W. (1997). Autothermal Thermophilic Aerobic Digestion Design.

[46] Burnett, C., Woelke, A. and Dentel, S. K. (1997) Dewaterability of ATAD sludges. WEFTEC '97. **2,** 299 - 309.

[47] Zhou, J., Kelly H. G., Mavinic D.S. and Ramey W.D. (2001). Digestion Effects on Dewaterability of Thermophilic and Mesophilic Aerobically Digested Biosolids WEFTEC 2001, Atlanta, Georgia

[48] Zhou, J., Donald S. M., Harlan G. K., and William D. R. (2002). Effects of Temperatures and Extracellular Proteins on Dewaterability of Thermophilically Digested Biosolids. Journal of Environmental Engineering and Science, **1**, 6.

[49] Kelly, H.G., Hart, F., Allan G. and Jianpeng Z. (2000). Dewatering Improvements of Thermophilically Digested Biosolids through Addition of Metal Salts at the Salmon Arm Water Pollution Control Centre. Canadian Society for Civil Engineering, 6th Environmental Engineering Specialty Conference, London, Ont.

[50] Abu-Orf, M.M., Griffin, P. and Dentel, S.K. (2001). Chemical and Physical pretreatment of ATAD For dewatering. Water Science and Technology.**44**, 309-314.

[51] Zhou, J., Mavinic, D. S. and Kelly, H. G. Floc size profiling to characterize dewatering properties of thermophilic and mesophilic aerobically digested biosolids.

CHAPTER III

(The following manuscript was submitted to Water Research for publication)

Sequential Polymer Dosing for Effective Dewatering of ATAD Sludges

Saurabh Agarwal[a], Mohammad M. Abu-Orf [b], John T. Novak [a,*]

[a] Virginia Polytechnic Institute & State University, 419 Durham Hall, Blacksburg, VA 24061, USA
[b] USFilter/Veolia, 1901 West Garden Road, Vineland, NJ 08360, USA
* corresponding author TELE 540-231-6132, FAX 540-231-7916, jtnov@vt.edu

Sequential Polymer Dosing for Effective Dewatering of ATAD Sludges

Saurabh Agarwal[a], Mohammad M. Abu-Orf [b], John T. Novak [a,*]

[a] Virginia Polytechnic Institute & State University, 419 Durham Hall, Blacksburg, VA 24061, USA
[b] USFilter/Veolia, 1901 West Garden Road, Vineland, NJ 08360, USA

ABSTRACT

The dewatering problems associated with the sludge from autothermal thermophilic aerobic digestion (ATAD) of sludge result in large chemical conditioning costs for effective dewatering. Different chemical coagulants were used to improve the dewatering of the sludge, but none of them were able to dewater the sludge as desired and at acceptable conditioning doses. It was found that during the digestion process chemical precipitation of divalent cations occurred. ATAD sludge colloids were also found to have a positive zeta potential. Sequential polymer dosing using iron or cationic polymer followed by anionic polymer was found to improve the dewatering. It is suggested that the high pH developed during the digestion of sludge resulted in the precipitation of calcium and magnesium solids and this resulted in formation of chemical solids that were positively charged. As a result, conditioning with either iron salts or cationic polymer alone may not properly flocculate these solids. The use of anionic polymer is essential and allows the use of smaller amounts of iron or cationic polymer for effective dewatering. The use of the cheaper anionic polymer along with cationic polymers has the potential to make the use of ATAD process more economical.

Key words: Aerobic thermophilic digestion, conditioning, dewatering, cations, anionic polymer, chemical precipitation

INTRODUCTION

Sludge digestion is often an integral part of the overall wastewater treatment scheme. Digestion is used to produce sludges suitable for land application and may be conducted aerobically or anaerobically. The USEPA 40 CFR Part 503, regulations that came into effect in 1993, and similar regulations in other countries have resulted in stricter standards for the pathogen content of sludges. This has forced many municipalities to look for more effective methods of sludge digestion in order to meet these requirements. Among the more effective methods is the autothermal thermophilic aerobic digestion (ATAD) process, which has been in existence for several decades. This process has increasingly found favor for small plants because the higher temperatures result in effective pathogen destruction.

To reduce the amount of final sludge to be hauled, municipalities choose to dewater the sludge prior to their final disposal. The digested sludge from ATADs has been found to dewater very poorly, resulting in excessive chemical conditioning costs. Thus the benefits achieved by the digestion of sludge through ATAD process are somewhat offset by the large dewatering costs. Murthy et al. [1, 2] found the cost of chemically conditioning ATAD sludge to be ten or more times higher than that processed through mesophilic aerobic digestion. Burnett et al. [3] found the cost of dewatering ATAD processed sludge to range from $63 to $121/ dry ton of solids as compared $ 20 - $ 30 / dry ton of solids for mesophilically digested sludge [1].

Several researchers have tried to find the reasons for the poor dewatering of these sludges. Zhou et al. [4] investigated the role of higher digestion temperatures and extracellular proteins on dewatering of ATAD sludge and found a direct correlation between the dewatering rate as measured by CST and the extracellular protein present in the liquid phase. Zhou et al. [5] studied the role of various parameters in affecting the dewatering of sludge. They found that the composition of the feed sludge strongly affected the dewaterability of secondary sludge but did not have much effect on the dewaterability of primary and mixed sludge. The solids retention time for digestion was not found to have little impact on dewatering of thermophilically digested sludge though it did seem to affect the mesophilically digested sludge. Also there was a large increase in solution protein, polysaccharide and phosphate concentrations during the digestion.

These researchers suggest that there are several variables that can affect the dewatering of ATAD sludge. While some of the mechanisms leading to the poor dewatering are now well-documented, not much success has been made in improving the dewatering of these sludges. Kelly et al. [6] found that the addition of ferrous iron as pickle liquor reduced the polymer dose to one half. Murthy et al. [1] found that iron, aluminum and post digestion aeration could all substantially improve the dewatering of ATAD sludges and reduce the polymer conditioning demand. Abu-Orf et al. [7] found that electrical arc pretreatment enhances the ATAD dewaterability to some degree, but the observed benefit does not justify the use of this technology without further optimization of the arc treatment process.

Novak et al. [8] have shown that during aerobic digestion of sludge, calcium and magnesium ions are released into the solution. They attributed this to the degradation of the part of the floc that contains calcium and magnesium ions that are part of the floc biopolymer structural network. When this biopolymer degrades it releases the associated calcium and magnesium into solution. Higgins and Novak [9, 10] suggested that divalent cations are important for holding the floc together and that for good dewatering the ratio of monovalent to divalent cations in wastewater should be around 2. Thus the role played by the divalent cations released during thermophilic aerobic digestion may influence dewatering behavior. It appears that a suitable and economic method for dewatering ATAD sludges is required to make this technology more favorable.

Objectives

The objectives of this study were to investigate the reasons for the poor dewatering and excessive chemical conditioning requirements for ATAD sludges and the role that chemical precipitants might have on dewatering. Sludges from four ATAD plants were used for the studies. The goal of this study was to better understand the changes that occur in sludges as they aerobically digest under high temperatures and find better approaches for conditioning and dewatering of ATAD sludges.

Methods and Materials

Experimental Approach

Waste Activated sludge was obtained from ATAD processing facilities in Ephrata, PA, Cranberry, PA, College Station, TX and Titusville, FL. The Ephrata treatment plant consists of two autothermal digesters in series and a post ATAD holding tank. During the course of this study, only one of the two ATAD reactors was operational due to maintenance. The Cranberry and Titusville ATAD plants had two autothermal digesters in series and a post ATAD holding tank. The College Station ATAD plant consisted of 3 ATAD digesters and two holding tanks. The samples were obtained from each unit of the process train, including pre ATAD, ATAD reactors and the holding tank(s).

Sample collection

Samples were obtained by treatment plant personnel, packed in ice and shipped to Virginia Tech overnight. The samples were stored at 4^0C until used.

Analysis

Samples for solution cation analysis were centrifuged at 9000g for 30 minutes. The centrate was filtered through 1.5 µm glass fiber filter. Dissolved calcium, magnesium were measured using a Dionex ion chromatograph (IC). Methane sulfonic acid (30 mM) was used as the eluent at a flow rate of 1.0 ml/min. Total calcium and magnesium were measured using an atomic absorption spectrophotometer (AAS). For zeta potential measurement, samples were centrifuged for 30 minutes at 14,300 G and the centrate was analyzed with a zeta meter (Zeta Meter 3.0+, Zeta Meter, Inc.). The cation analysis and zeta potential measurements were conducted for the pre ATAD, the ATAD reactors, and the holding tank.

Dewatering tests were conducted by measuring the Capillary Suction Time (CST) using Standard Method 2710 G [11]. Several conditioning polymers were screened for optimum conditioning and a high charge cationic polymer, BC 650 (Stockhausen) at 2 % (w/v), ferric chloride at 25 % (w/v) and superfloc A 1820 (1 % v/v) anionic polyacrylamide were selected for use in this study.

Results and Discussions

Dewatering Properties and Conditioning Requirements

This study focused on the ATAD sludge from Ephrata, PA, but once the Ephrata data were evaluated, additional ATADs were studied in order to determine the general applicability of the Ephrata results. Therefore, the Ephrata data is more complete.

The CST of the four ATAD sludges was measured for the raw feed sludges and digested sludges to get an indication of the variation in dewatering properties and the changes that occur through the ATAD system. These are listed in Table 1. As expected, all the sludges deteriorated after digestion, but some became extremely difficult to dewater. The CST for the feed sludge was found to be relatively low except for the Cranberry sludge. The digested sludges had CST values exceeding 50,000 seconds, with the exception of Cranberry, which had a CST of 2500 seconds. In the holding tank, the dewatering properties of two of the sludges improved. The CST for Cranberry decreased from 3600 to 2500 seconds and the Ephrata sludge decreased from over 50,000 to 8000 seconds. These results show that autothermal aerobic digestion results in deterioration of the sludge dewatering properties, but the extent of the deterioration varies. Also, it appears that the extent of deterioration is unrelated to the dewatering properties of the sludge prior to digestion.

To improve the dewatering of the sludges, several chemical conditioning agents were tested. These included cationic polymer (Stockhausen 650 BC), alum and ferric chloride. Figure 1 shows a typical response to conditioning by iron salts for the sludge from Cranberry, PA. A ferric chloride dose of ~0.1 g/gDS is required to achieve the minimum CST. This is a similar ferric chloride dose to those reported by others for ATAD sludges [1, 7].

A summary of the conditioning results for the sludge from Ephrata during various stages of treatment is shown in Table 2. From the data in Table 2, it can be seen that the minimum CST that could be attained was 54 seconds, a CST which is higher than that desired (< 20 sec) for satisfactory dewatering. The data in Table 2 show that ferric chloride works best, followed by cationic polymer. Alum did not work as well as iron or polymer so it was not tested further as a sole conditioner. What the data show is that it is was not possible to reduce the CST of any of the sludges to values less than 54 seconds, and this was also true for the feed sludges except for Cranberry. This suggests that there is something in the thickened sludge that makes conditioning difficult, even before it enters the ATAD system.

In Table 3, the dewatering properties of the conditioned sludges from the holding tanks of all four ATAD plants are shown. In general, ferric chloride reduced the CST to lower values than cationic polymer. As can be seen in Table 3, the minimum CST for both Titusville and College Station using cationic polymer remained above 300 seconds and the doses were in excess of 0.13 g/g DS. Basically these data indicate that neither Titusville nor College Station could be effectively conditioned using the cationic polymer chosen, because of the high dose requirements and poor dewatering rate at optimum dose. Sludge from the Ephrata plant was also difficult to dewater, especially using cationic polymer but was not as poor as the Titusville or College Station.

Sludge from the Cranberry plant dewatered better than the other plants (see Table 1) and the optimum cationic polymer dose was much less than that for the other three plants, 0.02 g/g TS versus 0.077 g/g TS, 0.134 g/g TS and 0.132 g/g TS for Ephrata, Titusville and College Station, respectively. The CST was also reduced below 20 seconds, the only conditioner to do so for the holding tank sludges. The CST for the Cranberry holding tank sludge was also the lowest of the four plants so the low polymer dose requirement is consistent with the low CST prior to conditioning. Unlike the other plants, cationic polymer worked better than iron for the Cranberry holding tank sludge. As shown in Table 3, the minimum CST that was achieved with the holding tank sludge from Ephrata, Titusville and College Station was almost the same when using ferric chloride for conditioning.

Accordingly, ATAD sludges are generally difficult to condition and dewater very poorly. However, there are some ATAD sludges that can be dewatered more easily and at lower conditioning doses. Ferric chloride usually works better than cationic polymer but not in all cases. It also appears that some of the difficulty in conditioning, especially the ability to achieve a low CST, is already contained in the feed sludge. As shown in Table 2, the CST of the feed sludge from Ephrata could not be reduced to less than 54 seconds, a level similar to holding tank sludge. The only ATAD sludge that could achieve the desired CST of less than 20 seconds was the Cranberry sludge and this was achieved only with cationic polymer, not ferric chloride.

Zeta Potential (ζ) Measurements

Because of the difficulty in achieving a low CST following conditioning, it was thought that colloidal particles remained that could not be coagulated with cationic polymer or ferric chloride. Since the zeta potential of sludge particles has been found to be at or near zero at optimum dose, especially when conditioning with cationic polymer [12, 13], the zeta potential was measured to determine if charged particles remained. It was thought that this might lead to an indication of the nature of the uncoagulated colloids.

The digested sludge from the Ephrata plant was dosed with different amounts of iron, the resulting mixture was centrifuged and the zeta potential of the centrate was measured. The ζ for centrate from the unconditioned sludge was found to be positive and was also positive at all iron doses. Typical results are shown in Figure 2 and indicate that the charge initially increased slightly with addition of ferric chloride and then declined, but remained positive. The fact that positively charged colloids for unconditioned sludge were observed is surprising since previous reported results showed negatively charged values for similar sludges as measured by a streaming current detector [7].

To determine if all the ATAD sludges contained colloids that had positive surface charges, sludges from each of the plants were analyzed for their ζ values. The zeta potential was measured for the pre digested sludge, the sludge from the ATAD reactors and the post ATAD sludges (holding tank). The data in Table 4 shows the ζ values across each stage of the process. All were positive except for the feed to the College Station ATAD. The positive charge for the undigested sludges was unexpected.

It has been shown that during digestion, protein and polysaccharide are released into solution [2, 14] and since these proteins and polysaccharides have a negative charge, it was expected that the ATAD sludges would have negative ζ values. The ζ values tend to become more positive through each stage of the ATAD system. Although the particles measured using the Zeta meter were positive, it was thought that the bulk of the sludge biopolymer matrix remained negatively charged. However, the centrate particles that were visible in the Zeta meter were positive.

The observed positive ζ is consistent with the inability to achieve a low CST upon conditioning. The conditioning chemicals, being positively charged, are unable to coagulate the positive colloids and as a result, their presence results in a high CST following conditioning with ferric chloride or cationic polymer. The sludge from College Station had the only negative zeta potential and also had the lowest CST prior to conditioning, 11.2 seconds (Table 1). However, once the sludge was digested, the zeta potential for the College Station sludge became strongly positive, indicating that positive colloids were generated in the ATAD system. The sludge from Cranberry had the lowest positive ζ compared to the other plants and a lower CST could be achieved following conditioning. The high, positive colloidal charge in the digested sludges from Ephrata, Titusville and College Station can clearly be related to the poor dewatering and the inability of conditioners, especially cationic polymer, to reduce the CST to a satisfactory level.

Calcium and Magnesium Precipitation

One explanation for the positive zeta potential values in the ATADs is the formation of chemical colloids resulting from the precipitation of inorganic chemical species in the digesters. Calcium and magnesium concentrations in solution were measured across the plants and were generally found to decrease, especially in the first ATAD unit (Figure 3). For College Station (Figure 3 d), the calcium concentration did not change much during digestion and the magnesium concentration was found to be below the detection limit.

Calcium and magnesium can precipitate to form a number of solid species depending on their concentration, the pH, and the presence of other ions, so they were candidates for forming positively charged chemical species. Measurement of pH across each stage of the ATAD systems showed increased pHs, reaching a range where chemical precipitation of calcium as $CaCO_3$ could occur. The pH data is shown in Table 4. The pH increase in ATAD systems has been attributed to the stripping of carbon dioxide and ammonia at higher temperatures [15]. The pH in the Cranberry sludge after digestion was much lower than for the other plants and this sludge dewatered better and had lower conditioning requirements than the other sludges.

Magnesium also decreased in the ATADs and was likely also being precipitated. Magnesium may precipitate as $Mg(OH)_2$ or struvite ($MgNH_4PO_4 \cdot 6H_2O$). However, the pH was too low to result in $Mg(OH)_2$ but struvite precipitation is likely due to the high ammonium and phosphorus produced by degradation of sludge solids. It can be seen in Figure 3 that the ammonium concentration always exceeded 200 mg/L and approached 800 mg/L and the phosphorus concentration was also frequently above 100 mg/L in the

ATADs (Table 5). The precipitated species would have a positive charge and would explain the positive ζ values.

The presence of positively charged species in the feed sludges was likely due to the formation of struvite. As can be seen in Figure 3, the ammonium concentration exceeded 100 mg/L in all the feed sludges except for College Station. College Station, had a low magnesium concentration so no chemical precipitation was likely, and, as a result, the ς value was negative. The feed sludges are thickened and stored prior to being fed to the ATADs and during this period it is likely that some degradation of protein occurs, generating enough ammonium, and also phosphorus (Table 5), to form struvite. Continued precipitation of chemical solids in the first ATAD reactor results in further deterioration of the sludges as can be seen in Table 2 for the Ephrata sludge.

Release of Calcium and Magnesium when conditioning with ferric chloride

Because the zeta potential for the Ephrata sludge increased initially when ferric chloride was added for conditioning, it was of interest to determine the changes in calcium and magnesium during conditioning. The holding tank sludges from Ephrata, Cranberry and Titusville were dosed with ferric chloride and the resulting mixture was centrifuged at 9000*g* for 30 minutes and the centrate analyzed for calcium and magnesium. Data for Ephrata is shown in Figure 4. Cranberry and Titusville followed the same pattern

Data in Figure 4 shows that the calcium and magnesium concentrations in solution increased linearly with increasing iron doses and the increases were considerable. It is believed that when iron is added to the sludge, an ion exchange mechanism takes place between iron and calcium and magnesium in the floc. For Ephrata and Titusville the release of calcium was much greater than for Cranberry. It is believed that iron does not solubilize the precipitated calcium and magnesium by lowering the pH, because the zeta potential does decline in direct response to iron addition. To investigate this, the pH of the solutions was lowered by addition of acid and compared to a similar pH level that resulted from iron addition. When the pH was adjusted to pH 3 with acid, the calcium increased from 68.7 to 71.2 mg/L. However, when the pH dropped to 4.2 due to iron addition, the calcium increased from 71.2 mg/L to 2250 mg/L. Magnesium also responded in a similar manner. Therefore, it was concluded that the role of iron was likely to be ion exchange rather than solubilization of precipitated chemical species due to a reduction in pH. It is hypothesized that calcium and magnesium in the biopolymer is being exchanged for iron.

Sequential polymer dosing for improving the dewatering

The presence of positively charged particles and the likely precipitation of calcium and magnesium suggested the use of anionic polymers for dewatering improvement. Several anionic polymers were tested but none improved the sludge dewatering rate when used as the sole conditioning agent. However, when used in conjunction with either a cationic polymer or ferric chloride, conditioning was dramatically improved. The sludges were first dosed with either cationic polymer or ferric chloride while being stirred and then anionic polymer (Superfloc A 1820 1% v/v, in water in oil emulsion) was added to the mixture and the sludge again stirred.

Dual conditioning data for one conditioning test using the Titusville sludge is shown in Figure 5. When iron alone was used as the coagulant, a dose of 0.117 g/g TS, was needed to reach the lowest CST of 68 seconds. The iron dose was reduced to 0.093 and a small amount of anionic polymer was added, the CST was reduced to 12 seconds. The improved dewatering rate using iron with anionic polymer contrasts with that achieved with iron alone. By combining the two conditioners, the amount of iron required decreased by 20%, and much better dewatering was obtained. For some of the ATAD sludges, the iron dose could be cut in half and the CST could still be reduced to less than 20 seconds with a small addition of anionic polymer.

For sludge from College Station, effective conditioning could also be obtained with a combination of ferric chloride and anionic polymer. As can be seen in Figure 6, anionic polymer was more effective when the ferric chloride dose was less than the optimum for ferric chloride alone. As can also be seen in Figure 6, conditioning was more easily accomplished and the CST lower when the ferric chloride dose was 0.057 g/g than when the ferric chloride dose was 0.68 g/g. These data indicate that additional ferric chloride results in an increased demand for anionic polymer. That is consistent with the release of divalent cations that occurs when ferric is added to the sludge. As more ferric chloride is added, more calcium and magnesium are released and this leads to more chemical solids being formed and therefore, a higher anionic polymer dose requirement.

In Figure 7, data are shown for combined cationic and anionic polymer conditioning. As can be seen in Figure 7, the dual polymer combination was not as effective and the ferric chloride/anionic polymer combination. For the data in Figure 7, the minimum CST achieved was 29 seconds. The iron/anionic polymer combinations could generally reduce the CST to less than 20 seconds.

It is believed that in the ATAD process, calcium and magnesium are precipitated and then get incorporated in the biopolymer floc structure. The biopolymer then acts like a dipole, with a negatively charged protein/polysaccharide fraction and a positively charged mineral fraction. The negatively charged fraction probably is the more dominant fraction. For this dipole-like system, cationic polymer or ferric chloride is required for binding the negatively charged biopolymer and the anionic polymer is used for binding the positively charged mineral species. When anionic polymer is added first, the negatively charged biopolymer fraction of the sludge gets surrounded by more negatively charged particles causing repulsion between the two. When cationic polymer or ferric chloride is added first, they bind to the negative charges on the biopolymer, and when anionic polymer is then added it binds to the positively charged chemical particles, leading to coagulation of the chemical solids and improved dewatering.

The results from this paper showed that dual conditioning of cationic coagulant (iron or polymer) with anionic polymer is able to decrease the dewatering rate as measured by CST tests to acceptable levels. However, other factors must be considered to apply these findings to full-scale levels. It is recommended that treatment plant trials be conducted to determine if this conditioning regime creates flocculated sludges able to withstand the shear during dewatering via different devices in order to achieve the desirable dewatering performance. The strength of the flocs generated by this dual conditioning must be able to withstand the shear within the dewatering devices. Ultimately, the choice of either cationic polymer or ferric chloride as the cationic component is plant specific and depends on the cost effectiveness of chemicals added once the desired dewaterability is achieved.

CONCLUSIONS

1. ATAD sludges generally dewater poorly.
2. Cationic polymers, iron or alum are, by themselves, unable to improve the dewatering of ATAD sludge to the generally desired level for effective sludge dewatering (CST < 20 seconds).
3. Elevated pH that occurs during thermophilic sludge digestion leads to precipitation of calcium and magnesium species, which interferes with dewatering.
4. Addition of iron releases calcium and magnesium into solution, thereby increasing the formation of insoluble calcium and magnesium particles.
5. Sequential dosing of ATAD digested sludge with iron/anionic polymer or cationic/anionic polymer improves the dewatering of the sludge to desired level. It also offers economic solution to improve the dewatering, by reducing the dose of the expensive iron or cationic polymer with the less expensive anionic polymer.
6. The requirement for anionic polymer results from the formation of chemical precipitates of Ca and Mg, which because of their colloidal nature interfere with the dewatering.

REFERENCES

[1] Murthy, S. N., Novak, J. T., Holbrook, R. D. and Surovik, F. (2000 a). Mesophilic aeration of ATAD biosolids to improve plant operation. Water Environment Research, **72**, 476-483.

[2] Murthy, S. N., Novak, J. T. and Holbrook, R. D. (2000 b). Optimizing dewatering of biosolids from Autothermal Thermophilic Aerobic Digesters (ATAD) using inorganic conditioners. Water Environment Research, **72**, 714-721.

[3] Burnett, C., Woelke, A. and Dentel, S (1997). Dewaterability of ATAD sludges. Proceedings, WEFTEC '97. Volume 2, 299-309.

[4] Zhou, J., Mavinic, D. S., Kelly, H. G. and Ramey, W. D (2002). Effects of temperatures and extracellular proteins on dewaterability of thermophilically digested biosolids. Journal of Environmental Engineering and Science, Volume 1, No 6.

[5] Zhou, J., Kelly, H. G., Mavinic, D. S. and Ramey, W. D (2001). Digestion effects on dewaterability of thermophilic and mesophilic aerobically digested biosolids. WEFTEC 2001, Water Environment Federation 74th Annual Conference & Exposition, Oct. 13-17, 2001, Atlanta, Georgia.

[6] Kelly, H.G., Hart, F., Gibb, A. and Zhou, J (2001). Dewatering improvements of thermophilically digested biosolids through addition of metal salts at the Salmon Arm Water Pollution Control Centre. Canadian Society for Civil Engineering, 6th Environmental Engineering Specialty Conference, June 7-10, 2000, London, Ont.

[7] Abu-Orf, M.M., Griffin, P. and Dentel, S.K. (2001). Chemical and Physical pretreatment of ATAD For dewatering. Water Science and Technology.**44**, 309-314.

[8] Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003). Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. Water Research, **37**, 3136-3144.

[9] Higgins, M.J. and Novak, J.T. (1997a). The effect of cations on the settling and dewatering of activated sludges: Laboratory results. Water Environment Research, **69**, 215- 224.

[10] Higgins, M.J. and Novak, J.T. (1997b). Dewatering and settling of activated sludges the case for using cation analysis. Water Environment Research, **69**, 225-232.

[11] American Public Health Association (1998) Standard Methods for the Examination of Water and Wastewater, 19th Ed., Washington, D.C.

[12] Novak, J. T. and Haugan, B. E. (1979). Chemical conditioning of activated sludge. Journal Environmental Engineering Division American Society of Civil Engineers, **105**, No. EE5, 993-1008.

[13] Abu-Orf, M.M. and Dentel, S.K. (1997). Polymer dose assessment using the streaming current detector. Water Environment Research. **69**, 1075-1085.

[14] Bivins, J.L. and Novak, J.T. (2001). Changes in dewatering properties between thermophilic and mesophilic stages in Temperature-Phased Anaerobic Digestion Systems. Water Environment Research. **73**, 4, 444-449.

[15] Lapara, T. M. and Alleman, J. E. (1999). Thermophilic aerobic biological wastewater treatment. Water Research, **33**, 895-908.

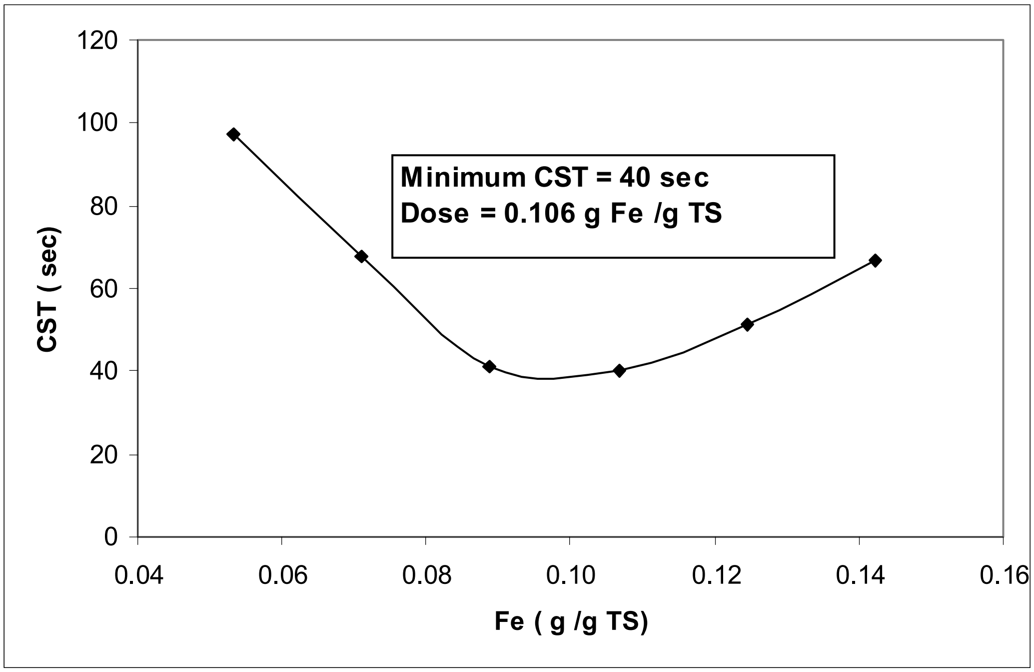

Figure 1: Dewatering using Ferric Chloride (Sludge from Cranberry, PA)

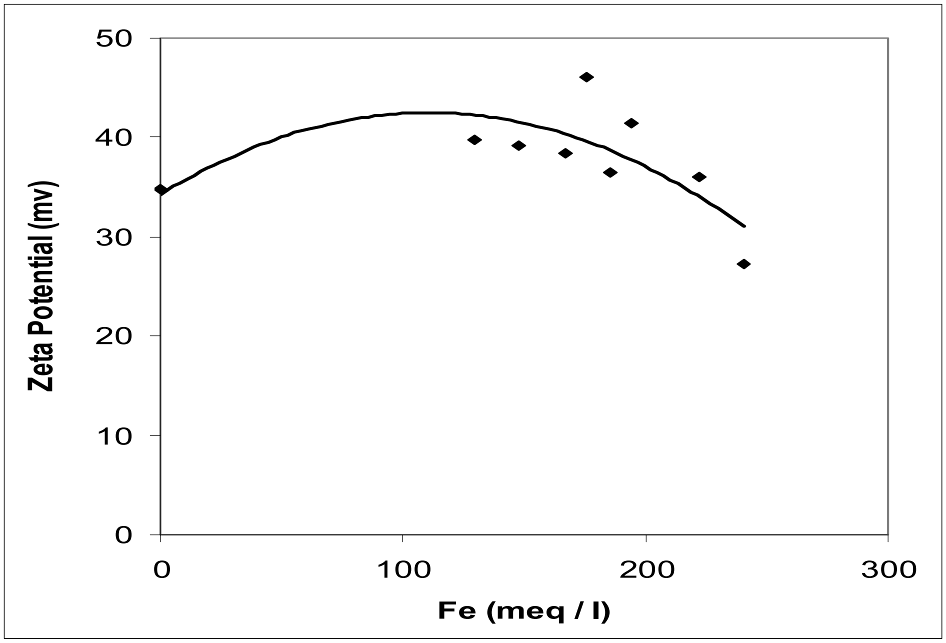

Figure 2: Variation in Zeta Potential for the sludge from Holding Tank of Ephrata dosed with Ferric Chloride

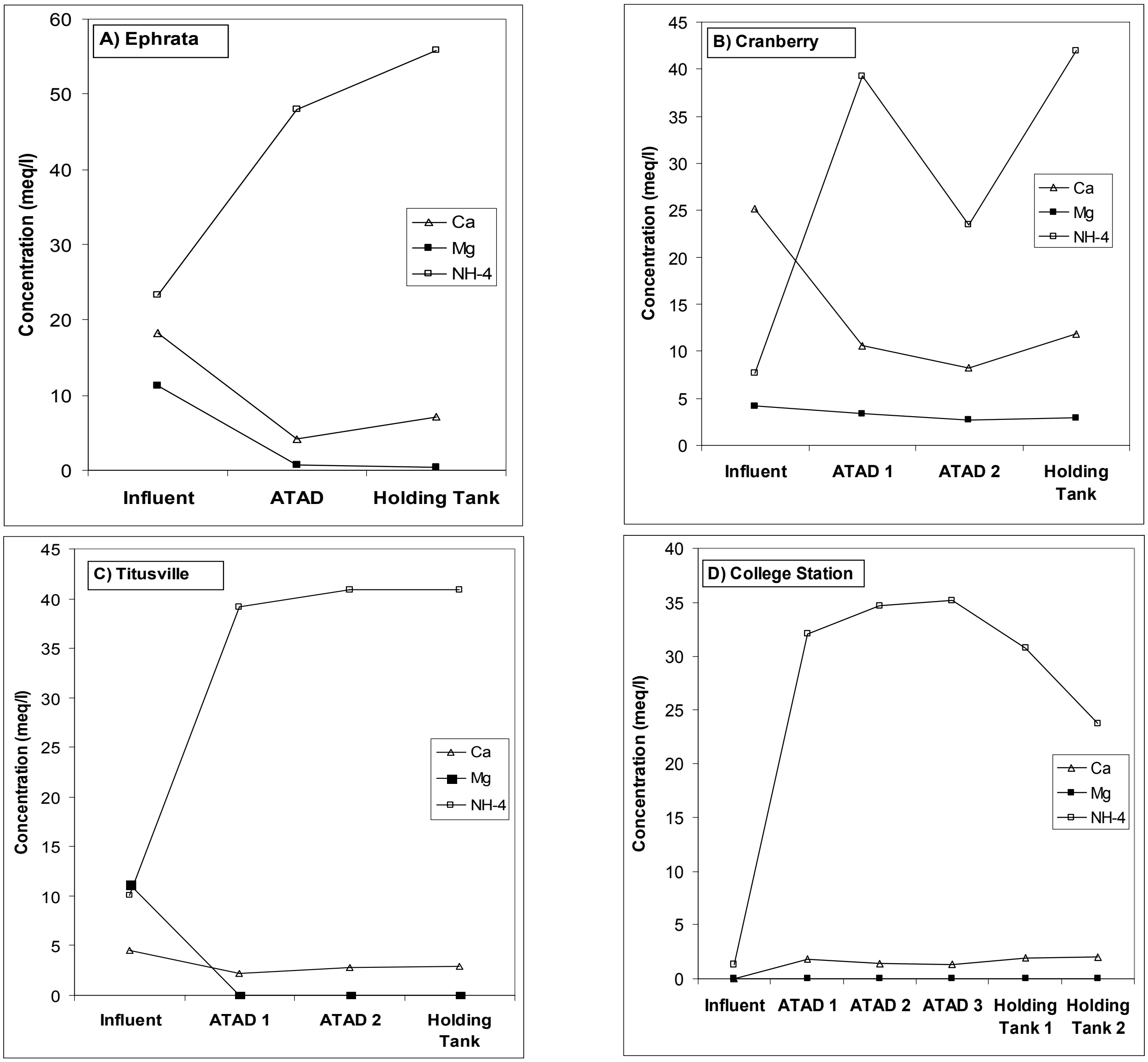

Figure 3: Changes in selected cations across the ATAD systems for the four treatment plants

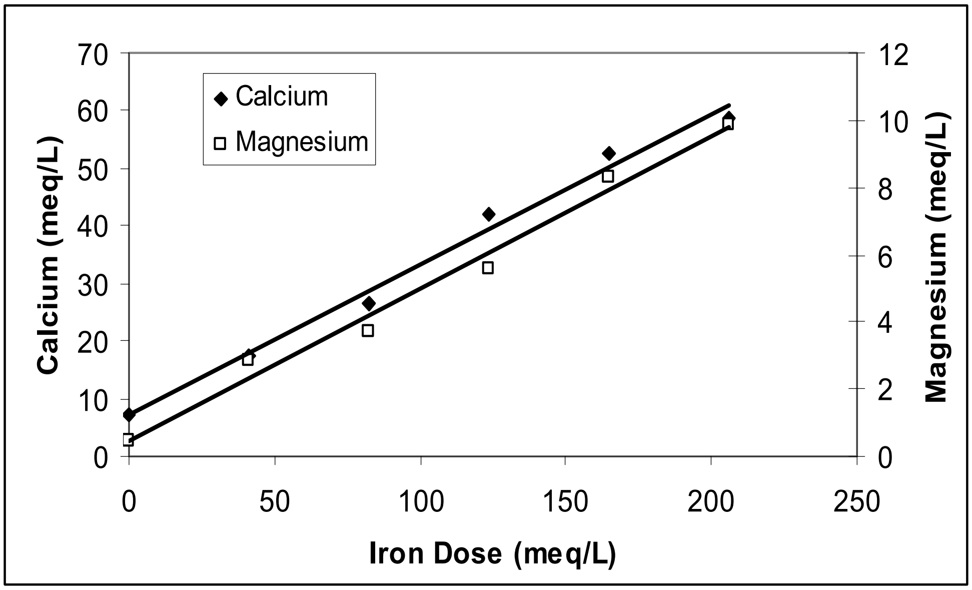

Figure 4: Calcium and Magnesium concentration in solution after dosing with iron (Ephrata)

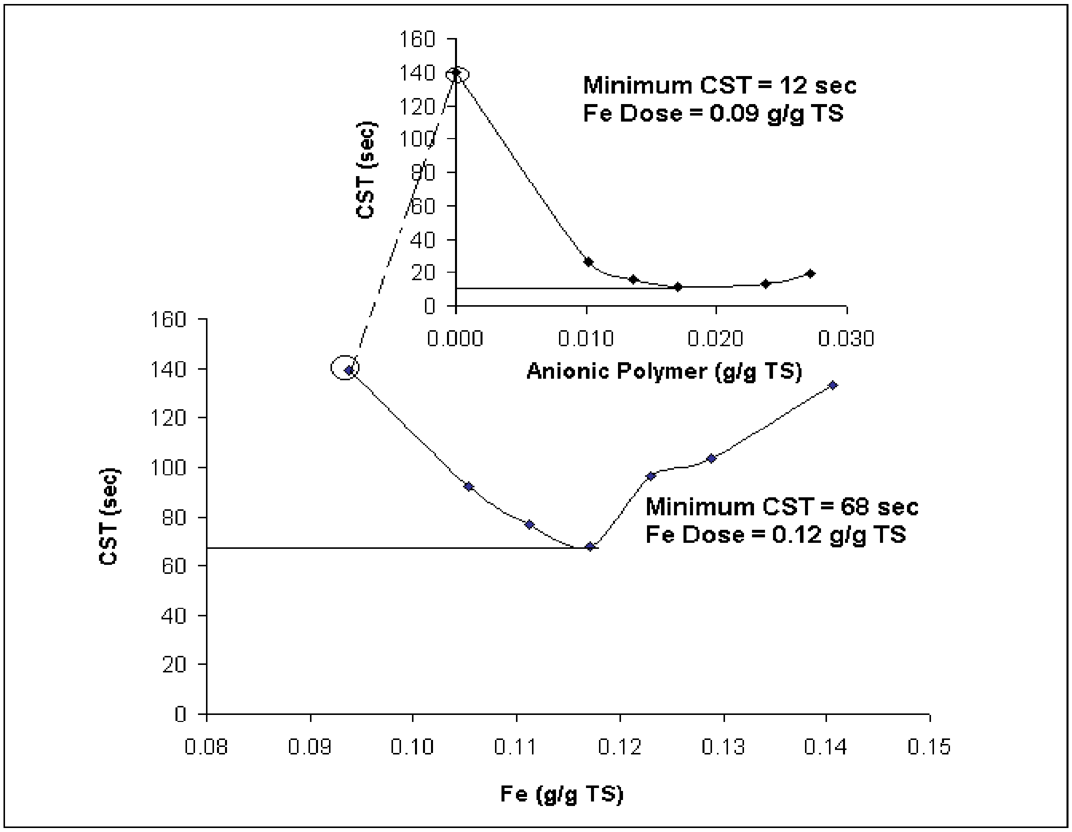

Figure 5: Conditioning of the sludge from the holding tank at Titusville using iron and anionic polymer

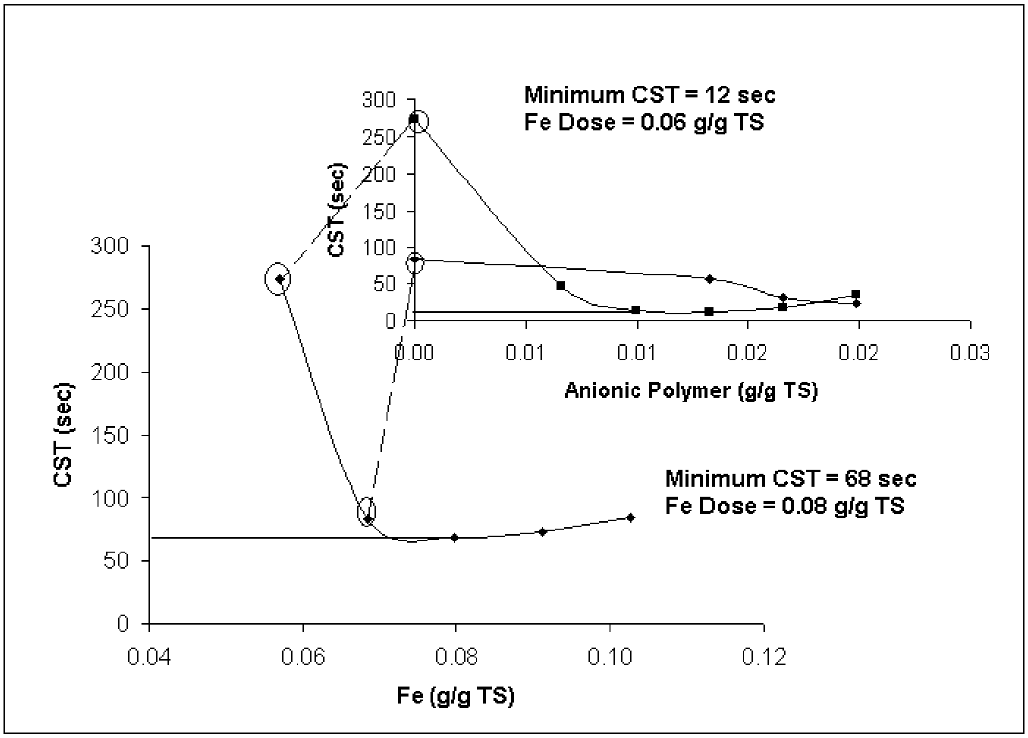

Figure 6: Conditioning of the sludge from holding tank using iron and anionic polymer for College Station

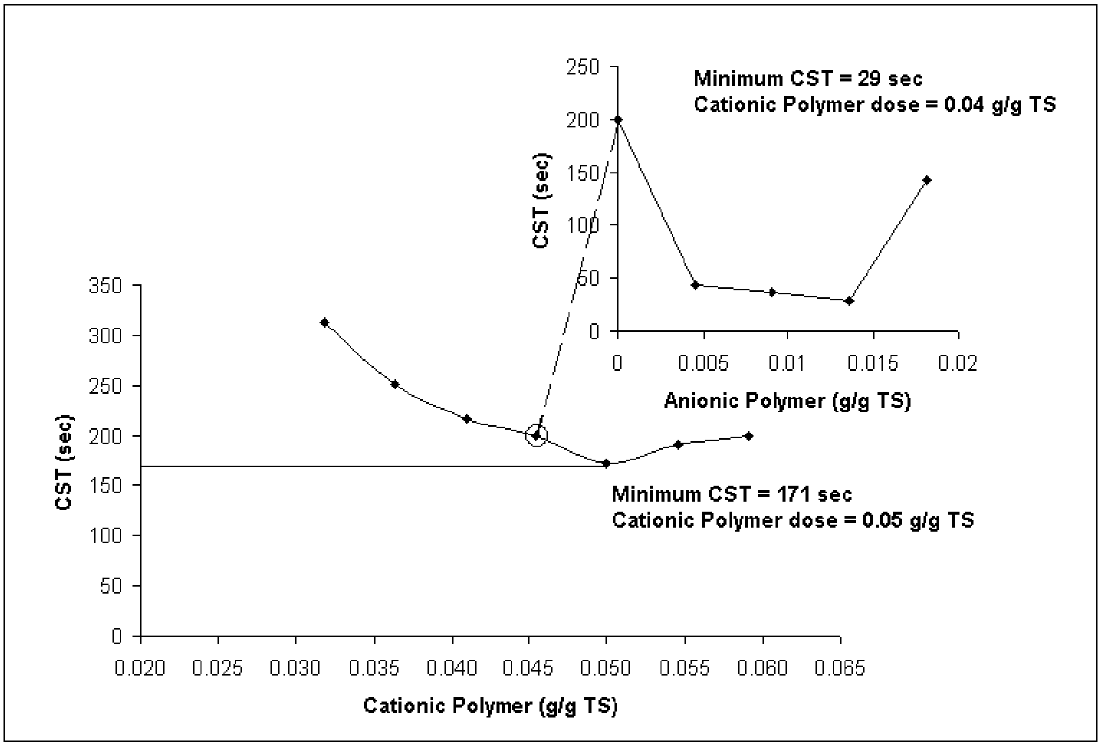

Figure 7: Conditioning of sludge from holding tank using cationic and anionic polymer for Ephrata

Table 1: Dewatering Rates for the Four ATAD plants

ATAD Plant	***CST for ATAD Influent Sludge (sec)***	***CST for last ATAD in series (sec)***	***CST for Holding Tank (sec)***
Cranberry	1200	3600	2500
Ephrata	105	>50,000	8,000
Titusville	340	>50,000	>50,000
College Station	11.2	>50,000	>50,000

Table 2: Optimum conditioning using different chemical coagulants for sludge from different stages of treatment (Ephrata)

		Cationic Polymer		*Ferric Chloride*		*Alum*	
	Initial CST (sec)	***Final CST (sec)***	***Dose (g/g TS)***	***Final CST (sec)***	***Dose (g/g TS)***	***Final CST (sec)***	***Dose (g/g TS)***
Influent	104	54	0.004	54	0.036	-	-
ATAD 1	18,500	540	0.17	57	0.1	213	0.85
ATAD 2	99,000	230	0.13	69	0.11	163	0.65
Holding Tank	8100	102	0.077	54	0.15	197	1.1

Table 3: Minimum CST for Sludge from Holding Tank Following Conditioning and Dose required

Plant	*Ferric Chloride*		*Cationic Polymer*		*Alum*	
	Minimum CST (Sec)	*Fe Dose (g/g TS)*	*Minimum CST (Sec)*	*Polymer Dose (g/g TS)*	*Minimum CST (Sec)*	*Alum Dose (g/g TS)*
Cranberry	40	0.106	11.4	0.02		
Ephrata	54	0.15	102	0.077	197	1.1
Titusville	68	0.177	>300*	0.134	-	
College Station	68	0.08	>300*	0.132	-	

* Is not the minimum CST, but at the given doses of polymer, the CST was found to be greater than 300 seconds

Table 4: Changes in Zeta Potential (ζ) and pH across the ATAD system for the various plants

	Cranberry		*Ephrata*		*Titusville*		*College Station*	
	ζ (mv)	**pH**	**ζ (mv)**	**pH**	**ζ (mv)**	**pH**	**ζ (mv)**	**pH**
Pre ATAD	+ 12.3	5.32	+ 34.9	6.11	+10.6	6.35	-22.0	7.06
ATAD 1	+ 43.5	7.29	+ 68.2	8.74	+55.1	8.98	+ 80.6	7.35
ATAD 2	+ 20.3	7.8	-	-	+ 41.4	9	+ 75.4	7.89
ATAD 3	-	-	-		-		+63.8	8.87
Holding Tank 1	+43.5	7.41	+ 111.4	7.42	+65.4	8.79	+ 69.9	8.15
Holding Tank 2	-	-	-	-	-	-	+ 65.9	7.82

Table 5: Phosphorus concentrations across the ATAD systems

	Ephrata (mg/l)	***Cranberry (mg/l)***	***Titusville (mg/l)***	***College Station (mg/l)***
Influent	54	20	629	12
ATAD 1	107	14	653	98
ATAD 2	-	9	696	110
ATAD 3	-	-	-	101
Holding Tank 1	226	12	813	115
Holding Tank 2	-	-	-	116

CHAPTER IV

(The following manuscript was submitted to Water Environment Research for publication)

The Effect of Biopolymers on the Dewatering Characteristics of ATAD Sludges

Saurabh Agarwal[a], Mohammad M. Abu-Orf [b], John T. Novak [a,*]

[a] Virginia Polytechnic Institute & State University, 419 Durham Hall, Blacksburg, VA 24061, USA
[b] USFilter/Veolia, 1901 West Garden Road, Vineland, NJ 08360, USA

The Effect of Biopolymers on the Dewatering Characteristics of ATAD Sludges

Saurabh Agarwal[a], Mohammad M. Abu-Orf [b], John T. Novak [a,*]

[a] Virginia Polytechnic Institute & State University, 419 Durham Hall, Blacksburg, VA 24061, USA
[b] USFilter/Veolia, 1901 West Garden Road, Vineland, NJ 08360, USA

ABSTRACT

Autothermal thermophilic digestion of sludge is known to produce poorly dewatering sludges. Laboratory studies were conducted to investigate the reasons for the poor dewatering. It was found that during digestion, protein and polysaccharide were released into solution and these could be linked to the deterioration in dewatering. It was also found that the biopolymer release was related to the increase in the monovalent to divalent (M/D) cation ratio that occurs in the systems. The degree to which the M/D caused deterioration of the sludges depended on the presence of iron in sludge. When the iron content was high, the release of protein and polysaccharides was low. When iron was low, the release of protein and polysaccharides increased linearly with the M/D ratio. Protein and polysaccharide removal was observed when the sludge was conditioned. The dose of conditioning chemicals, cationic polymer or ferric chloride, was related to the amount of colloidal biopolymer present in the solution.

Key words: autothermal digestion, biopolymer release, monovalent divalent cation ratio, optimum conditioning, high iron, low iron.

INTRODUCTION

Autothermal thermophilic aerobic digestion of sludge was developed in the mid 1960's in the Republic of Germany. Since then it has been successfully implemented in many countries in Europe including Great Britain, France, and Italy (USEPA, 1990). ATAD processing facilities have also been successfully applied in the United States and Canada. The ATAD process is unique because its operation came into existence without the benefit of prior research. The lack of research during the development of this process has resulted in many questions, about its efficiency, cost effectiveness, and processes that occur through the system.

Under current US Federal regulations (USEPA, 1990) the ATAD process is recognized as a process to further reduce pathogens. The two most significant features of the current regulation regarding disposal of sewage sludge include pathogen reduction and vector attraction reduction. Some of the advantages of the ATAD process are its ability to attain class A biosolids, no pre treatment of biosolids feed is required, a high sludge volume treatment rate can be achieved, it has a small footprint, and achieves destruction of approximately 50 % of the organic matter (Lapara et al., 1997; Csikor et al., 2003; Kelly et al., 2003).

The ATAD process is classified as a high temperature aerobic digestion process. Generally, 2 ATAD reactors are operated in the series, with partially digested sludge being fed from first ATAD to the second ATAD. The ATAD reactors are followed by one or two holding tanks. In the two ATAD reactors, aeration and complete mixing are provided, while in the holding tank only mixing is provided. The SRT for the whole ATAD process ranges from 10 - 25 days. Typically for ATAD operation the incoming sludge is thickened to about 4-6 % TS level. The VS destruction provides the heat or energy to sustain the process and make it autothermal (Staton et al., 2001). Sometimes an outside source of heat is required when the solids content in the sludge is not high enough to produce the necessary heat.

Over the last few years extensive research has been conducted on the ATAD process. Previous research has focused on production of VFA during aerobic thermophilic pre treatment of primary sludge (McIntosh et al., 1997) and the effects of temperatures and extra-cellular proteins on the dewaterability of thermophilically digested biosolids (Zhou et al., 2002).

Some of the recent research was designed to address the poor dewatering properties associated with the ATAD sludges that have reduced some of the benefits of this process. Both aerobic and anaerobic digestion are known to cause deterioration of the dewatering characteristics of sludge (Novak et al., 2003). To improve the dewatering, polymer conditioners are frequently used. The importance of dewatering of sludge can be gauged from the fact that polymer costs are a major expense for the operation of a wastewater treatment facility.

Zhou et al. (2002) studied the role of digestion temperatures and release of extracellular protein on the dewaterability of thermophilically digested sludge. They found that higher digestion temperatures had a more significant impact on dewatering than lower digestion temperatures. Also they found a direct relation between the amount of protein in the solution and the dewatering of thermophilically digested sludge. Murthy et al., (2000b) also found large amounts of protein and polysaccharide in thermophilically digested sludges. They also found that inorganic conditioners such as ferric chloride and alum were effective in reducing polymer requirement by removing the protein and polysaccharide over all size ranges.

Objectives

The objectives of this study were to evaluate the changes in dewatering properties during the ATAD digestion of sludge and to determine the factors that may be responsible for the poor dewatering of sludge.

METHODS AND MATERIALS

Approach

For this study waste activated sludge was first collected from ATAD processing facility in Ephrata (PA). After the samples from this plant had been analyzed for various parameters, similar tests were conducted using sludges from ATAD facilities in Cranberry (PA), Titusville (FL) and College Station (TX). The sludge samples were preserved on ice and shipped to Virginia Tech and the samples were frozen till they could be analyzed. The Ephrata facility consists of two ATAD reactors in series followed by a holding tank (also called post ATAD). Waste activated sludge from a settling clarifier is thickened to 3 – 4 % solids concentration before it is fed to the first ATAD reactor. In the treatment plant, ferrous chloride is used for phosphorus control. The total detention time averages 55. 5 hours. The temperature in the digesters averages 55^0C and ranges from 39^0 C to 61^0C. The digested sludge from the first ATAD reactor is fed into the second ATAD reactor. The sludge from the holding tank is dewatered using a belt filter press and land applied. Sludge samples were collected from the influent to the first ATAD reactor, from the two ATAD reactors and from the final holding tank. During the course of this study the plant had to shut down one of the digesters for maintenance, in this case the samples were collected from the influent, the single operational ATAD reactor and the holding tank.

The Titusville plant consists of 2 ATAD reactors followed by a holding tank. In the Titusville plant, the sludge from the clarifier is pumped to a drum thickener and mixed with polymer for dewatering prior to being fed to the ATAD. It is thickened to about 6 - 8 % solids and is stored in a holding tank (pre ATAD). The average hold time in the ATAD reactors is between 20- 25 days. The average temperature in tank 1 is 55^o C with a peak value of 72^o C. Tank 2 has a steady temperature of about 68^o C. The samples were collected from the pre ATAD, the two ATAD digesters and the holding tank. The Cranberry plant consists of 3 ATAD reactors and a holding tank. Samples were collected from the pre ATAD, the first two ATAD reactors and the holding tank. In the Cranberry plant, ferric chloride and caustic soda are fed to the primary clarifiers for phosphorus removal. Primary and secondary sludge is pumped to gravity thickeners, where they are thickened to about 3 % solids. The total hydraulic retention time is 8 days. The temperature in the first digester is 38 – 42^0 C, and that in the second digester is 40 -44 ^{0} C.

The College Station facility consists of three ATAD digesters in series followed by two post ATAD holding tanks. Waste activated sludge is first collected in a holding tank (pre ATAD). Polymer is then added to this sludge and fed into a Rotary drum thickener where the free water is removed and a solids concentration of 4- 5 % is attained. The thickened sludge then goes into a holding tank where it is mixed and then fed into the ATAD. Sludge samples were collected from the pre ATAD, the three ATAD reactors and the two sludge holding tanks (post ATAD).

Sludge Characterization

Capillary Suction Time (CST) was used as a measure of the sludge dewatering rate according to Method 2710 G (APHA, 1998). For protein and polysaccharide measurements sludge samples were centrifuged at 9000g for 30 minutes. The centrate was divided into two parts. One part was filtered through 0.45 µm Whatman filter paper, and the other part was ultrafiltered with molecular separation of 30,000 Dalton (30K). The filtrates were analyzed for solution protein and polysaccharide. The solution protein and polysaccharide fraction in the size range from 0.45 µm to 30,000 Dalton is considered to be the colloidal fraction and the material passing the 30,000 Dalton membrane is classified as subcolloidal.

The Frølund et al., (1996), modification of Lowry method was used for the determination of protein concentration, and Dubois et al., (1956) method was used for the measurement of polysaccharide. Bovine Serum Albumin (BSA) was used for preparation of the protein standards. Dextrose was used as the standard for polysaccharide. The cation concentration was measured using Dionex Ion Chromatogram (IC). Methane sulfonic acid was used as the eluent. The cations that were measured included ammonium, potassium, calcium, magnesium, and sodium. For measuring cations, the sludge samples were centrifuged at 9000g for 30 minutes, filtered using a 1.5 µm glass micro fiber filter and the filtrate was used for cation analysis. Iron and aluminum concentrations in sludge were measured after acid digesting the sludge using EPA method 3050B. The acid digested sludge samples were analyzed for iron and aluminum using Atomic Absorption Spectrophotometer (AAS).

RESULTS AND DISCUSSIONS

Dewatering Rates

The dewatering rate of sludge from each stage of treatment was measured for the four ATAD plants. The results from these tests are presented in Table 1.

The pre ATAD sludges were highly variable with regard to the CST, ranging from 11.2 seconds, an excellent sludge, to 1200 seconds, a poorly dewatering sludge However, all sludges worsened during digestion and CST for some of them was in excess of 50,000 seconds. For effective dewatering, a CST of < 20 seconds is desired. In the Ephrata and Cranberry plants, dewatering was found to improve in the holding tank as compared to the last ATAD reactor. The CST for the last ATAD in series was found to be greater than 50,000 seconds for every plant except Cranberry. The dewatering properties of the ATAD sludges were unrelated to the pre ATAD dewatering rates. While Cranberry had a much higher CST in the feed sludge than the other plants, after digestion it dewatered much better than sludges from the other plants.

Biopolymer in solution

Biopolymer or extracellular polymeric substances (EPS) in activated sludge are known to be essential for forming a good floc (Li and Ganzarczyk, 1990; Rudd et al., 1983). However, when it is released into solution, the colloidal biopolymeric material interferes with dewatering and increases chemical conditioning requirements (Novak, et al., 2003). The bulk of the biopolymer released from floc during digestion has been found to be protein and polysaccharides, with more protein than polysaccharides being released during anaerobic digestion and equal amounts of protein and polysaccharides being released during mesophilic aerobic digestion (Novak, et al., 2003).

It was of interest to determine the release of biopolymer from the ATAD process so the protein and polysaccharide concentrations in solution were measured for all the sludges. The sum of protein and polysaccharide concentrations has been represented as the total biopolymer. Solution biopolymer data for Titusville is shown in Figure 1, and for the other three plants in Table 2.

The protein and polysaccharide concentrations shown are those that passed 0.45 µm and 30 K filters. The protein and polysaccharide concentration between 0.45 µm and 30 K is considered to be “colloidal”. This material has been shown to be important for determining sludge dewatering properties (Novak et al., 2003).

Protein and polysaccharide concentrations in the pre ATAD sludge was low for all the plants, typically between 200 and 270 mg/l for protein and 25 – 70 mg/l for polysaccharide. Ephrata, Cranberry and Titusville had almost the same protein and polysaccharide concentrations in the pre ATAD sludges. The protein and polysaccharide concentrations were found to increase dramatically after digestion for all the sludges (Figures 1 (a, b); Table 2 (a, b)). After digestion, Cranberry and Ephrata had similar protein concentration which was less than 1000 mg/L, while those for Titusville and College Station increased to over 2000 mg/L. Previous research has shown that high temperature during ATAD digestion contributes to the release of protein and polysaccharide in solution (Zhou et al., 2002).

Except for College Station, most of the protein released in the first and second digesters was in the colloidal range. For College Station, there was not much colloidal protein in the first digester, but in the subsequent digesters and holding tank, the colloidal fraction increased while the total protein less than 30 K decreased. The increase in the colloidal fraction and decrease in the subcolloidal fraction across the College Station ATAD system suggests polymerization of protein is occurring. For College Station and Titusville the total polysaccharide and colloidal polysaccharide is much higher than for Ephrata and Cranberry. In the Cranberry and Ephrata plant, there is much less protein and polysaccharide in the colloidal range and these sludges dewater better than the other sludges. The large release of protein and polysaccharide during digestion coincides with the increase in the CST for all the sludges (Table 1).

For all the plants except Titusville, the protein concentration in the holding tank was less than that in the preceding ATAD reactors. The protein concentration less than 0.45 µm in the last ATAD digester for Cranberry, College Station and Ephrata was 930 mg/l, 2606 mg/l, and 840 mg/l respectively, while that for the holding tank was 710 mg/l, 1875 mg/l, and 716 mg/l respectively (Table 2).

For Ephrata, polysaccharide is released in the first stage of digestion and then there is no change in its concentration in the second digester or the holding tank. There is an almost equal amount of polysaccharide in the colloidal and the sub colloidal range. In Cranberry, the polysaccharide concentration increases steadily from the influent through the first and second digesters. Unlike Ephrata this concentration decreases in the holding tank. With this decrease in biopolymer, the dewatering was also found to improve. For each of the stages of the sludge treatment (the 2 ATAD digesters and the holding tank), the amount of colloidal polysaccharide in Cranberry is less than that in Ephrata and the Cranberry sludges dewater better than the corresponding sludges from Ephrata. It was found that for Cranberry and Ephrata, the protein concentration decreased in the holding tank and dewatering improved, while for Titusville (figure 1a) and College Station (Table 2b) the protein content changed little and dewatering remained poor.

Iron and aluminum

Iron and aluminum have been shown to influence floc properties by increasing the binding of biopolymer to floc (Park et al., 2003). The iron and aluminum concentrations in the sludge were measured in the different stages of treatment from the four plants. Since the concentrations of total iron and aluminum differed little across the reactors, only the data for the first ATAD reactor from each plant is shown in figure 2.

The aluminum concentrations in the sludges ranged from a low for the Ephrata sludge of 7 mg/g TS to a high of 14 mg/g TS for Titusville. The range of aluminum concentrations was much less than for iron. The iron concentrations in sludges from Ephrata and Cranberry were found to be much higher 52 and 56 mg/g) than those for Titusville or College Station (11 and 8 mg/g). The high iron concentrations in the sludges from Ephrata and Cranberry occured because iron salts are added to the activated sludge system for phosphorous control. Soluble iron and aluminum (Figure 2b) was measured for three plants and is less than 20 mg/L for all systems. The soluble iron and aluminum generally account for about 1-2 percent of the total iron or aluminum in the digesters.

It was also seen that the total protein concentration less than 0.45 µm for both Cranberry and Ephrata decreased in the holding tank (Table 2). For Cranberry and Ephrata, the dewatering was found to improve in the holding tank, while this was not the case with College Station and Titusville, both of which had low iron concentrations. The high iron concentration in the sludge appears to contribute to the improved dewatering in the holding tanks. Murthy et al., (2000a) also observed a reduction in biopolymer in the ATAD holding tanks and suggested the role of iron in removing them from the solution by flocculation.

The presence of a higher amount of iron in the sludge also seems to decrease the cationic polymer dose that is required to condition the sludge. For Titusville and College Station, a dose in excess of 0.13 g Fe/g TS resulted in a CST which could not be reduced to less than 300 seconds, while for Ephrata and Cranberry the dose requirements were 0.08 g Fe/g TS and 0.02 g Fe/g TS respectively and resulted in CSTs of 100 and 40 seconds, respectively.

Figure 3 shows the variation in the solution biopolymer concentration with iron for all the plant samples including feed sludge and holding tank sludge. Both the protein and polysaccharide concentrations appear to respond to the concentration of iron, decreasing as the iron concentration increases, indicating that iron is helping to bind biopolymer to floc. These results show the importance of iron in floc formation and prevention of biopolymer release during digestion. The addition of iron in the feed sludge could improve the floc by reducing the release of biopolymer and also help in phosphorus control, thereby decreasing struvite (($MgNH_4PO_4 \bullet 6H_2O$) formation, which is thought to interfere with dewatering (Agarwal et al., under review). The variation in solution biopolymer with aluminum was also evaluated, but no trends were evident.

Monovalent to Divalent (M/D) ratio

Novak et al., (2003) showed that during aerobic digestion of sludge, calcium and magnesium are released into solution. When calcium and magnesium are released, this results in the release of proteins and polysaccharides associated with these cations. The cation concentrations were measured for each of these sludges. The cations that were measured included the monovalent cations, ammonium, sodium and potassium and the divalent cations, calcium and magnesium

Figure 4 shows the changes in the cation concentration across the ATAD system for the sludge from Titusville. The data in Figure 4 is typical of the other plants. It can be seen that while the sodium concentration remains almost constant, the potassium and ammonium concentrations increase considerably after digestion. The increase in ammonium results from degradation of protein. The increase in potassium is likely due to cell lysis (Bott and Love, 2001). Along with the increase in the monovalent cations is a decrease in divalent cations. It was found that the divalent cations precipitate during the digestion, forming additional inorganic colloids that interfere with dewatering (Agarwal et al., under review).

The increase in monovalent cations and decrease in divalent cation across the ATADs increases the monovalent to divalent cation ratio. As the M/D ratio increases, flocs begin to disintegrate, releasing protein and polysaccharides and this contributes to deterioration in dewatering (Higgins and Novak, 1997. The M/D ratio increased considerably across all the plants during digestion (Table 3), but declined somewhat in the holding tanks.

Higgins and Novak (1997) suggested an optimum monovalent to divalent cation ratio of 2 for good sludge dewatering. As this ratio increases the floc starts to deteriorate and the dewatering becomes poorer. For all the plants, the monovalent to divalent cation ratio (M/D) increased markedly after digestion. Cranberry had the lowest M/D ratio for the sludge from the holding tank, and it dewaters the most easily of all the holding tank sludges. It can be seen that the even though the M/D ratio in the influent for all the plants is low, the influent sludge to the Cranberry plant does not dewater as easily as the influent to the other plants.

Figure 5 shows the effect of M/D ratio on dewatering as measured by CST for M/D values less of 20 or less. When the M/D exceeded 20, the CST was usually above 50,000 seconds and the specific CST was not determined. It can be seen that the trend is for the CST to increase as the M/D increases. A number of factors such as the increase in temperature and shear in the process can affect the dewatering behavior, clearly the M/D is important. It is difficult to control the M/D for these systems because the high monovalent ion concentration is due to degradation of the sludge and the release of ammonium and potassium, coupled with the decline in divalent cations. Addition of calcium or magnesium to reduce the M/D is impractical because this could lead to chemical precipitation and further deterioration of sludge dewatering (Agarwal et al., under review).

It was also found that the M/D ratio had a strong effect on the total biopolymer content in solution. As the M/D ratio increased, the biopolymer present in solution also increased. Figures 6 shows the variation in the biopolymer concentration in sludge with the M/D ratio. The sludge from the different plants was separated into two categories, those that had high iron in the sludge (Ephrata and Cranberry) and those that had low iron (Titusville and College Station) in the sludge. For the plants that had a low iron content in the sludge, an increase in the M/D ratio increased the solution biopolymer concentration much more significantly than for the plants with a high iron content. As the M/D ratio increased for the low iron plants, the solution biopolymer increased in direct response to the M/D. For the high iron plants, the M/D had little impact on biopolymer. Therefore the combined M/D and iron appear to determine the sludge properties in ATADs. High iron results in much less biopolymer release and less deterioration of dewatering in the ATADs.

Conditioning of the sludge using cationic polymer and iron

The sludge from Ephrata and Titusville were conditioned with cationic polymer and ferric chloride and the protein and polysaccharide concentration in the solution was measured following conditioning and compared to protein and polysaccharide in the unconditioned sludge. Some of the data for protein is shown in Figure 7 and the complete set of biopolymer data is contained in Table 4.

It was found that upon conditioning with iron (ferric chloride) or cationic polymer, nearly all of the colloidal protein was removed. Removal of subcolloidal material was much lower, varying from none to nearly 50%. There was very little colloidal polysaccharide removal from the Ephrata sludge, but removal of colloidal polysaccharide from the Titusville sludge was nearly 80%. In the subcolloidal range, removals were poor for both protein and polysaccharides and for both sludges.

It appears that the primary role of conditioners is to remove colloidal material from solution. Removal of subcolloidal material may occur, but has little impact on the dewatering properties. Figure 8 (a, b) shows the relationship between the required conditioning dose and the colloidal biopolymer in solution. As the protein and polysaccharide concentration in solution increased, the optimum iron or cationic polymer dose required for conditioning the sludge also increased. Although the dose could be related to the combined colloidal protein and polysaccharide content, the colloidal protein appeared to be the most important factor in determining the conditioning dose and this is reflected in the nearly complete removal of colloidal protein at optimal dose.

Summary

From these results it can be seen that during digestion colloidal protein and polysaccharide are released into solution and these colloids result in poor dewatering. The release can be related to M/D ratio and the iron and aluminum concentrations. As the amount of colloidal protein and polysaccharide in solution increase, the optimum conditioning dose also increases. Control of the M/D ratio is difficult because the monovalent cation increase is associated with the degradation of the sludge and the addition of divalent cations would likely result in chemical precipitation. The addition of iron to the ATAD feed appears to be a potentially useful approach for sludges that have a low iron content.

CONCLUSIONS

1. Colloidal protein and polysaccharide concentrations were found to increase for the ATAD sludges after digestion.
2. The monovalent to divalent cation ratio increases during the course of digestion. The increase in the M/D ratio was accompanied by an increase in the solution protein or polysaccharide for the different plants. The increase in the M/D ratio was found to relate directly to the deterioration in dewatering.
3. The protein concentration in solution was also found to increase with a decrease in the iron concentration.
4. Upon chemically conditioning the sludge with iron or cationic polymer the protein and polysaccharide concentrations were found to decrease, but after the optimum dose, they were again found to increase, which means deflocculation takes place after that. Conditioning of the sludge seems to remove protein more than polysaccharide and thus the polysaccharide that remains in solution after conditioning contributes to the poor dewatering.
5. The iron or polymer dose required to condition the sludge increases as the amount of protein in solution increases. The dose requirement does not increase as much for the polysaccharide. Thus most of the dose requirement is used to remove the protein from the solution.

ACKNOWLEDGEMENTS

Credits

Financial support was provided by US Filter.

Authors

Saurabh Agarwal is a graduate student and John T. Novak a Professor in the Department of Civil and Environmental Engineering at Virginia Polytechnic Institute and State University. Mohammad M. Abu-Orf is Director-Biosolids Processing, Veolia Water North America, Vineland, New Jersey. Correspondence should be addressed to John T. Novak, Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA 24061.

REFERENCES

Agarwal, S., Abu-Orf, M.M. and Novak, J.T. (2004) "Sequential Polymer Dosing for Effective Dewatering of ATAD Sludges" *Water Research*, under review.

American Public Health Association (1998) *Standard Methods for the Examination of Water and Wastewater*, 19th Ed., Washington, D.C.

Bott, C. B., Love, N.G. (2001). "The immunochemical detection of stress proteins in Activated sludge exposed to toxic chemicals". *Water Research*, **35**, 91 – 100

Csikor, Zs., Miháltz, P., Hanifa, A., Kovács, R. and Dahab, M.F.(2003) "Identification of factors contributing to degradation in autothermal thermophilic sludge digestion". *Water Science and Technology*, **46**, 10, 131–138.

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.

Frølund, B., Palmgren, R., Keiding, K. and Nielsen, P.H. (1996). "Extraction of extracellular polymers from activated sludge using a cation exchange Resin". *Water Research*, **30**, 1749 – 1758.

Higgins, M.J. and Novak, J.T. (1997a). "The effect of cations on the settling and dewatering of activated sludges: Laboratory results". *Water Environment Research*, **69**, 215- 224.

Higgins, M.J. and Novak, J.T. (1997b). “Dewatering and settling of activated sludges the case for using cation analysis”. *Water Environment Research*, **69**, 225-232.

Houghton, J. I., Quarmby, J. and Stephenson, T. (2001). “Municipal wastewater sludge dewaterability and the presence of microbial extracellular polymer”. *Water Science and Technology*, **44**, 2-3, 373 – 379.

Kelly, H.G. and Mavinic, D.S. (2003). “Authothermal Thermophilic Aerobic Digestion Research, Application and Operational Experience”. *Proceedings, WEFTEC 2003*, Los Angeles, CA.

La Para, T.M. and Alleman, J.E. (1997). “Autothermal aerobic waste treatment systems: A state of the art review”. *Proc. 52nd Purdue Waste Conference*, West Lafayette, Indiana USA, (May 5–7). Ann Arbor Press, USA.

Li, D.H. and Ganzarczyk, J. J. (1990) “Structure of activated sludge flocs”. *Biotechnology Bioengineering.* **35**, 57-65.

McIntosh K B, Oleszkiewicz J A. (1997).”Volatile Fatty Acid Production in Aerobic Thermophilic Pretreatment of Primary Sludge”. *Water Science and Technology*, **36,** 11, 189-196.

Murthy, S. N., Novak, J. T., Holbrook, R. D. and Surovik, F. (2000 a). “Mesophilic aeration of ATAD biosolids to improve plant operation”. *Water Environment Research*, **72**, 476-483.

Murthy, S. N., Novak, J. T. and Holbrook, R. D. (2000b). “Optimizing Dewatering of Biosolids From Autothermal Thermophilic Aerobic Digesters (ATAD) Using Inorganic Conditioners”. *Water Environment Research*, **72**, 714-721.

Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003). “Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids”. *Water Research*, **37**, 3136-3144.

Park, C., Abu-Orf, M.M. and Novak, J.T. (2003). “Predicting the digestibility of waste activated sludges using cation analysis”. *Proceedings, WEFTEC 2003*, Los Angeles, CA

Rudd, T., Sterrit, R. M. and Lester, J. W. (1983) “Extraction of extracellular polymers from activated sludge”. *Biotechnol. Lett.* **5**, 327 - 332.

Staton, K.L. and Alleman, J.E. (2001). “2nd Generation Autothermal Thermophilic Aerobic Digestion: Conceptual Issues and Process Advancements”. *WEF/AWWA/CWEA Joint Residuals and Biosolids Management Conference, Biosolids 2001*: "Building Public Support"

USEPA (1990). Environmental Regulations and Technology: Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge.

Zhou, J., Donald S. M., Harlan, G. K. and William, D. R. (2002). “Effects of Temperatures and Extracellular Proteins on Dewaterability of Thermophilically Digested Biosolids”. *Journal of Environmental Engineering and Science*, **1**, Number 6.

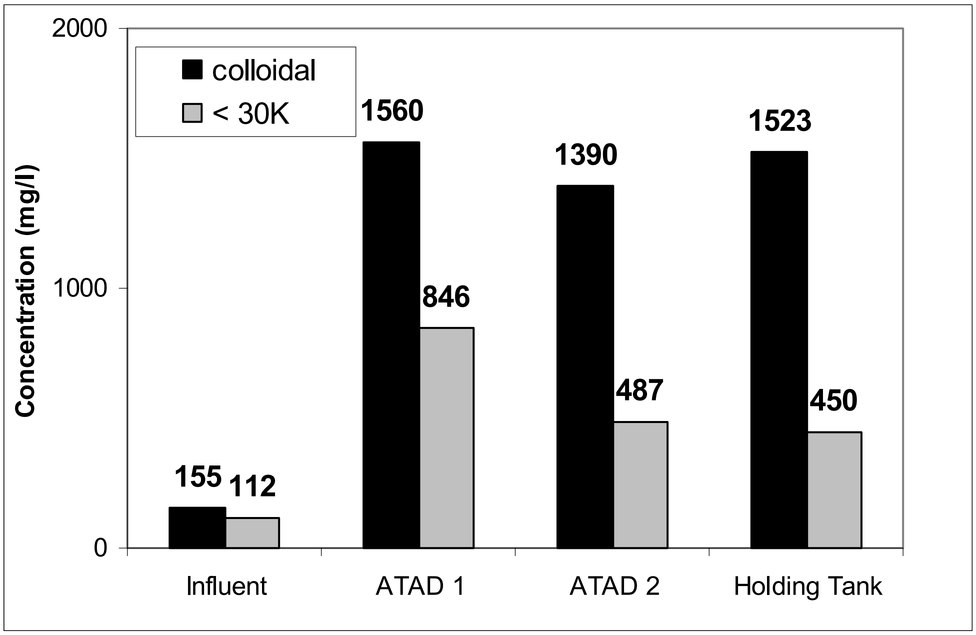

Figure 1a: Protein concentration in solution Across the ATAD System in different size fractions (Titusville)

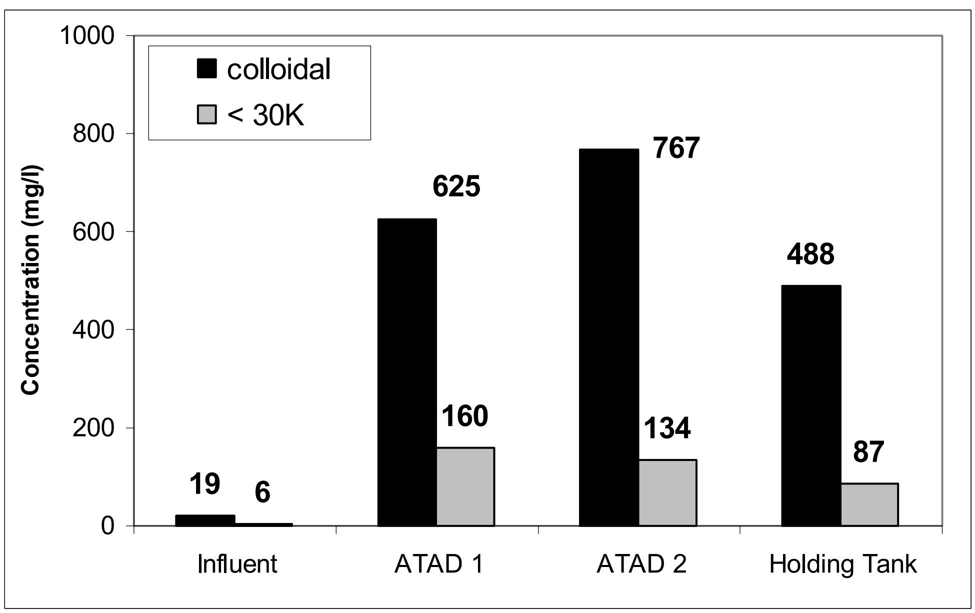

Figure 1b: Polysaccharide concentration in solution Across the ATAD System in different size fractions (Titusville)

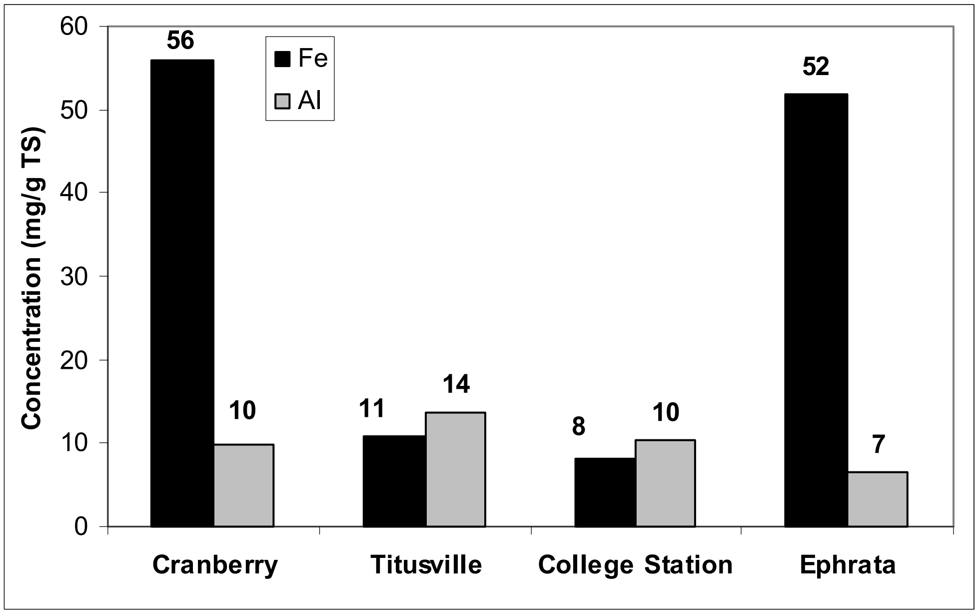

Figure 2a: Iron and Aluminum concentration in the sludge in first ATAD Digester for the different plants

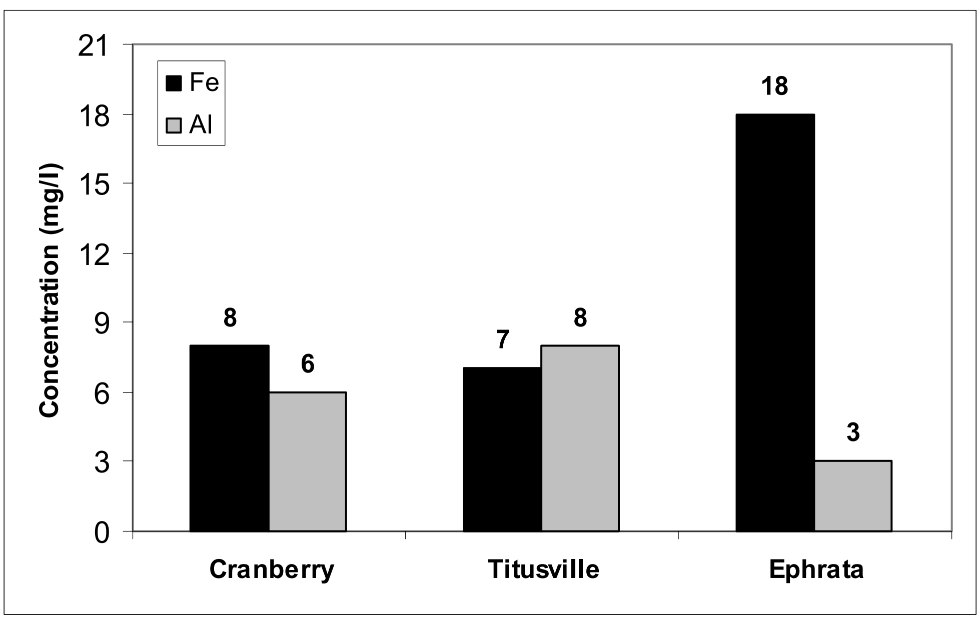

Figure 2b: Soluble iron and aluminum concentrations in the first ATAD Digester for three plants

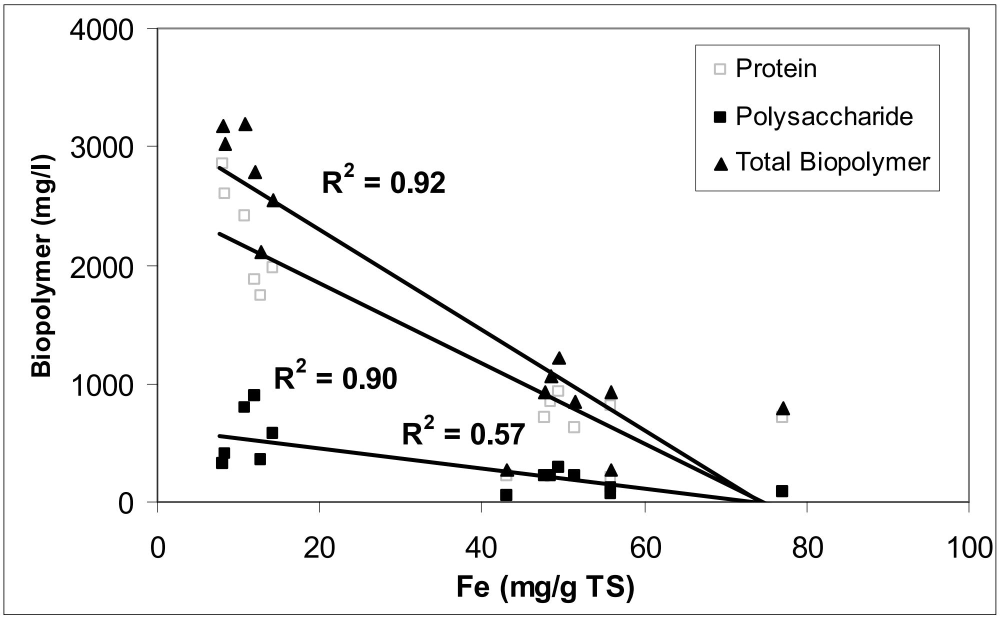

Figure 3: Variation in biopolymer with the total iron concentration

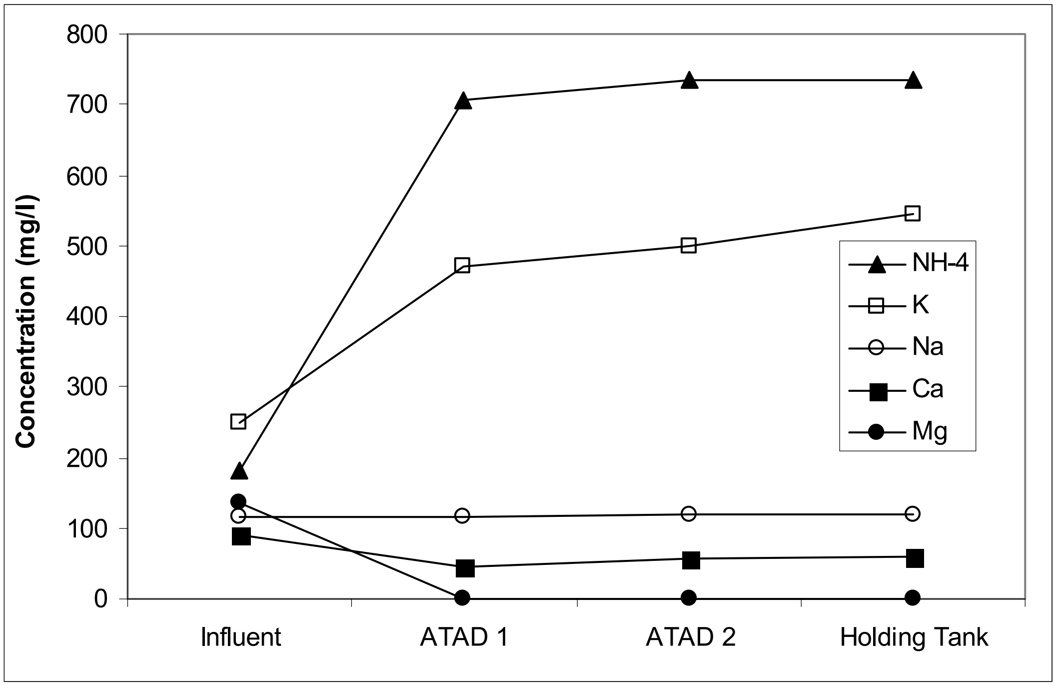

Figure 4: Changes in Cation Concentration in Solution Across the ATAD system (Titusville)

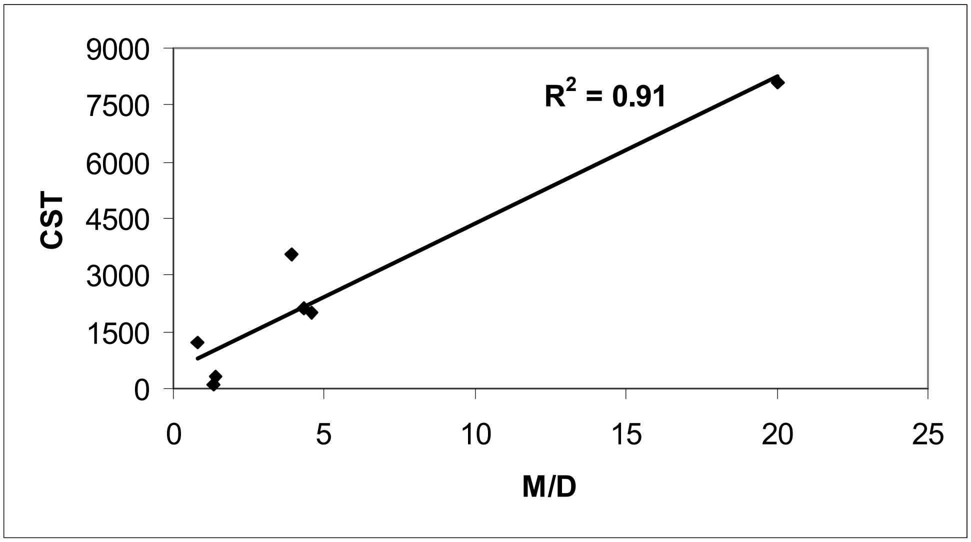

Figure 5: Dewatering as measured by CST and M/D ratio

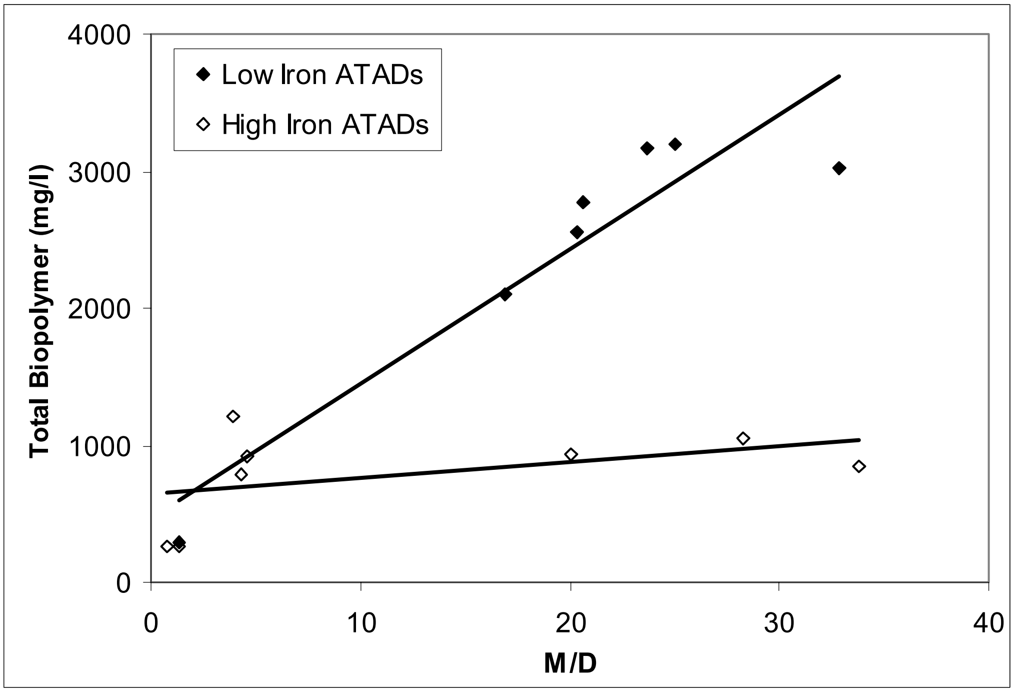

Figure 6: Effect of M/D ratio on solution biopolymer concentration

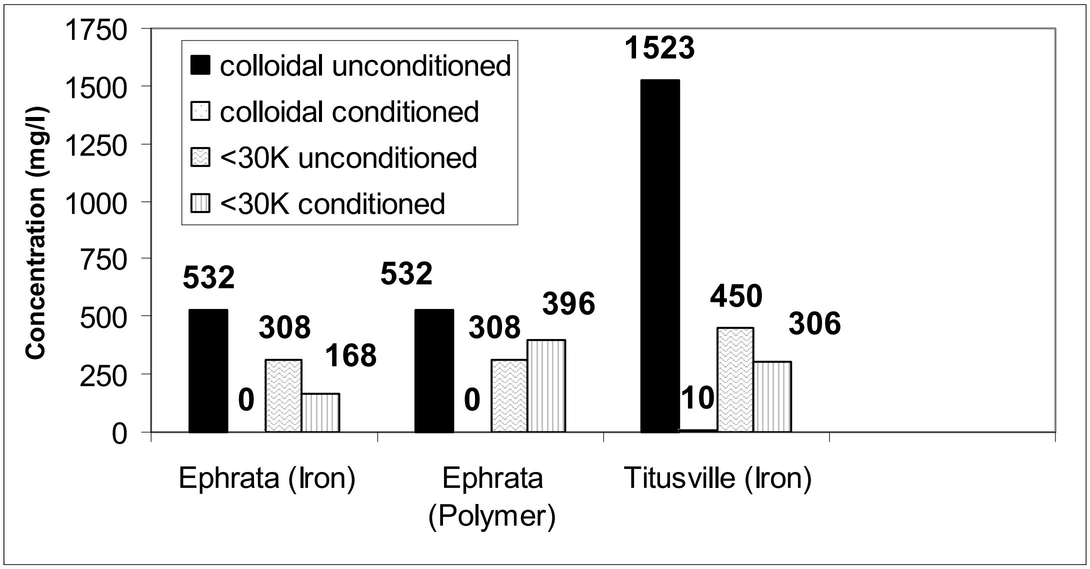

Figure 7: Protein in conditioned and unconditioned sludge for Ephrata and Titusville

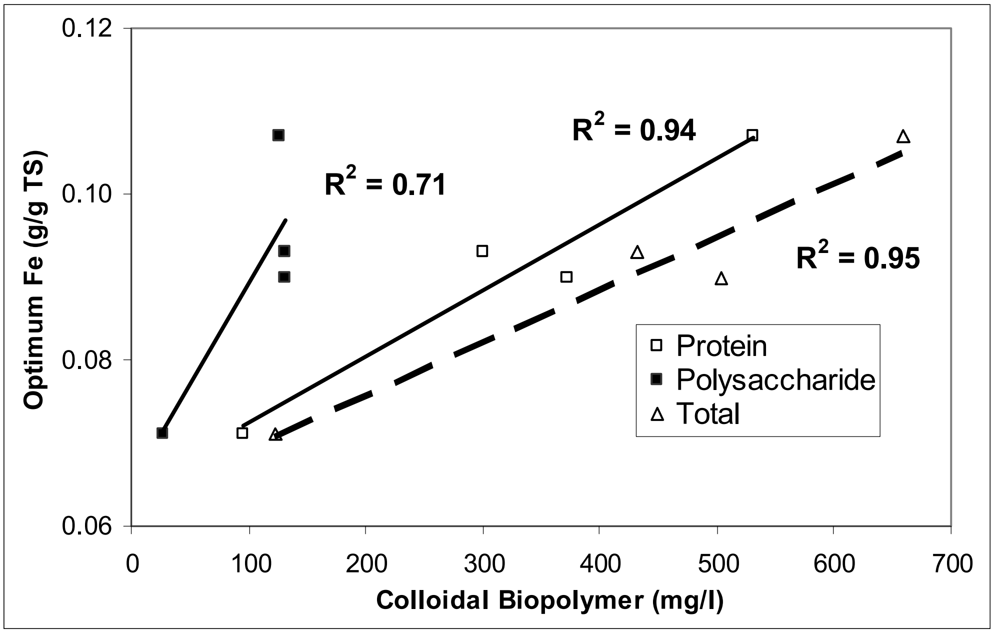

Figure 8a: Optimum iron dose vs Colloidal Biopolymer (Ephrata)

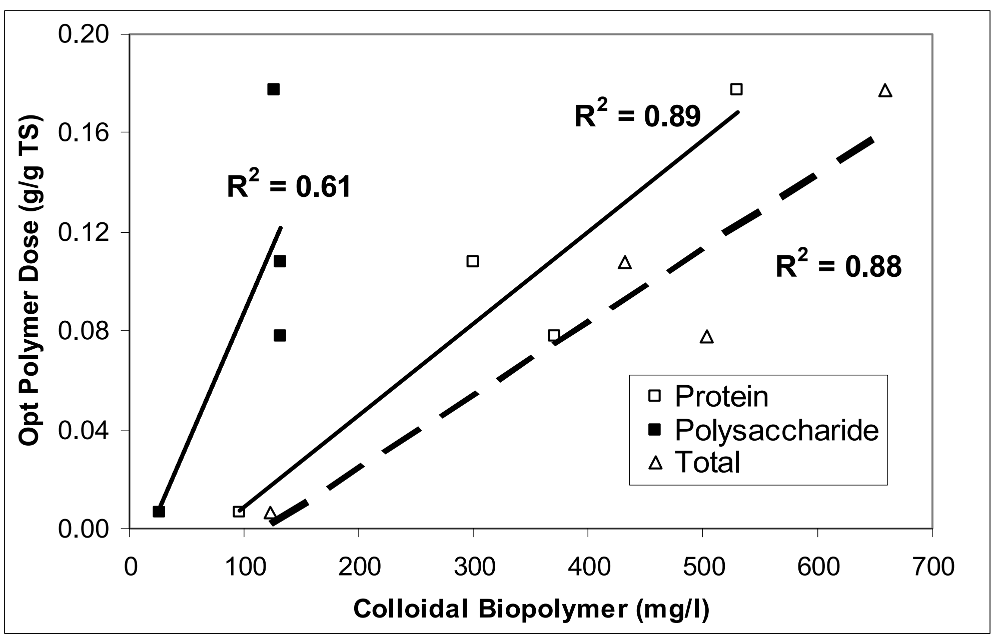

Figure 8b: Optimum polymer dose vs Colloidal Biopolymer (Ephrata)

Table 1: Dewatering Rates (CST) for the Four ATAD plants

ATAD Plant	***CST for ATAD Influent Sludge (sec)***	***CST for last ATAD in series (sec)***	***CST for Holding Tank (sec)***
Cranberry	1200	3600	2500
Ephrata	105	>50,000	8,000
Titusville	340	>50,000	>50,000
College Station	11.2	>50,000	>50,000

Table 2a: Protein concentration in solution for Cranberry, College Station and Ephrata

	Cranberry		**College Station**		**Ephrata**	
	colloidal	*<30K*	*colloidal*	*<30K*	*colloidal*	*<30K*
Influent	53	147	-	-	96	120
ATAD 1	375	430	498	2357	300	328
ATAD 2	178	752	751	1855	532	308
ATAD 3	-	-	1054	1284	-	-
Holding Tank 1	448	262	1337	538	371	345
Holding Tank 2	-	-	1018	727	-	-

Table 2b: Polysaccharide concentration in solution for Cranberry, College Station and Ephrata

	Cranberry		**College Station**		**Ephrata**	
	colloidal	*<30K*	*colloidal*	*<30K*	*colloidal*	*<30K*
Influent	26	41	-	-	28	22
ATAD 1	72	47	229	84	132	90
ATAD 2	49	236	383	29	128	88
ATAD 3	-	-	453	122	-	-
Holding Tank 1	38	45	374	31	132	85
Holding Tank 2	-	-	304	54	-	-

Table 3: Monovalent to Divalent (M/D) Cation ratio for the sludge from various treatment plants

	Ephrata (eq/eq)	*Cranberry (eq/eq)*	*Titusville (eq/eq)*	*College Station (eq/eq)*
Influent	1.3	0.81	1.4	-
ATAD 1	33.8	4.61	25.0	23.7
ATAD 2	28.3	3.94	20.6	32.8
ATAD 3	-	-	-	34.5
Holding Tank 1	20	4.28	20.3	21.7
Holding Tank 2	-	-	-	16.9

Table 4: Solution Protein and Polysaccharide Distribution For Unconditioned and Conditioned ATAD Sludges.

Biopolymer Fraction	*Ephrata*			*Titusville*	
	Unconditioned (mg/l)	*Iron conditioned (mg/l)*	*Polymer conditioned (mg/l)*	*Unconditioned (mg/l)*	*Iron conditioned (mg/l)*
Total Biopolymer	1056	339	621	2548	440
Total Protein	840	168	396	1973	316
Total Polysaccharide	216	171	225	575	124
Colloidal* Protein	532	0	0	1523	10
Colloidal* Polysaccharide	128	128	27	488	29
Sub Colloidal** Protein	308	168	396	450	306
Sub Colloidal** Polysaccharide	88	43	198	87	95

* Colloidal biopolymer is material passing a 0.45µm membrane filter and retained by a 30k ultrafiltration membrane
** Subcolloidal biopolymer is the material passing a 30k ultrafiltration membrane.

ENGINEERING SIGNIFICANCE

With the growing concern for sludge born pathogens, USEPA and other regulatory agencies are promulgating stricter standards for pathogen destruction in sewage sludges that are to be land applied. Several new technologies for sludge digestion have been developed as a result of this requirement. Of these, autothermal thermophilic aerobic digestion of sludge has gained interest because of its ability to produce Class A biosolids economically. However, the dewatering problems associated with the sludge produced from the ATAD process has resulted in large conditioning costs. This research aimed at analyzing the reason for the poor dewatering of sludge and to find an economical solution to this problem.

It was found that during ATAD digestion of sludge, a large release of biopolymer into solution occurs. The biopolymer release was found to be related to the M/D ratio and the iron content of the sludge. Also, during digestion the pH increases, causing precipitation of divalent cations, which not only interfered with the dewatering but also led to an increase in the M/D ratio. Though a large amount of biopolymer was released with an increase in the M/D ratio, high iron in sludge helped to keep this release low. An effective control of M/D ratio in the sludge is generally not feasible, but iron addition in the feed sludge could help to keep the biopolymer concentration low and improve dewatering. It also was found that even before the digestion process, changes take place in the sludge during thickening and holding in pre digestion storage tanks that contributes to poor dewatering. Further research is needed to evaluate the role of pre digestion thickening and holding. The use of sequential polymer dosing of iron or cation polymer followed by anionic polymer was found to improve the dewatering to the desired level. The use of anionic polymer also decreased the dose requirement of the expensive cationic polymer or iron. This sequential combination of dosing has the potential of making the ATAD process more economical and a more preferred form of sludge digestion.

VITA

Saurabh Agarwal was born on August 24th 1979, in New Delhi (India). He graduated from General Raj's School in June 1997. He received the B.E degree in Environmental Engineering from Delhi College of Engineering in June 2002. He undertook two stints of internships during this period at Tata Energy Research Institute (TERI), and Hospital Services Consultancy Corporation (HSCC). He started work on his M.S degree in Environmental Engineering in August 2002 at Virginia Polytechnic Institute and State University. After the completion of this degree he plans to work as a consultant and subsequently for a developmental agency.