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EFFECT OF ALUMINUM AND IRON ON ODORS, DIGESTION EFFICIENCY, AND DEWATERING PROPERTIES

PHASE IV

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ABSTRACT AND BENEFITS

Abstract:

This study was designed to be a follow up of the WERF Phase III odor study (*Biosolids Processing Modifications for Cake Odor Reductions*, 03-CTS-9T) odor study. The Phase III study found that iron and aluminum appeared to play important roles in odor generation so some additional data was sought to determine the role these play in determining odor generation from dewatered biosolids. In this portion of the study, the impact of iron and aluminum in sludges on both digestion and odors was investigated. Three distinct locations for the iron and/or aluminum were studied. First, the impact of iron and aluminum in the raw sludges on digestion and odors was evaluated. Second, the impact of the addition of iron or aluminum for chemical phosphorus removal in the activated sludge process was studied. Third, the direct addition of iron to the feed to an anaerobic digester was evaluated. All studies were conducted in the lab using a variety of sludges collected from seven wastewater utilities. In addition to digestion and odors, data were collected for sludge dewatering properties as indicated by the polymer conditioning dose requirements and dewatered cake solids.

The raw sludge iron content had a major impact on dewatering. As the concentration of iron increased, the polymer dose for anaerobically digested sludge increased. As suggested in the Phase III report, iron appeared to play a role in TVOSC production from dewatered biosolids. As the iron content increased, the TVOSC generation increased. As a result, iron increases both the volatile solids reduction and TVOSC generation. The implication of this is that sludges that digest better may also generate higher TVOSC. This has important implications for the regulations governing vector attraction based on volatile solids reduction. A reevaluation of regulations related to volatile solids reduction should be considered. Some of the data in this study shows results that are contradictory to conventional thought. Therefore, additional information concerning the impact of iron in raw sludge on odor generation, dewatering properties and volatile solids destruction characteristics would be useful. However, specifically funded research focused on this issue may not be justified. Rather, the iron and aluminum content in raw sludges should routinely be measured and field data used to further evaluate the role of iron and aluminum in anaerobic digestion and odor production.

With regard to iron and aluminum addition for phosphorus removal, little difference in volatile solids destruction by anaerobic digestion was seen for sludges that received iron while a slight decrease in volatile solids reduction was seen for aluminum addition. Both iron and aluminum addition to activated sludge produced lower TVOSC generation from digested sludges except for Plant F. In Plant F, iron is added to the primary and secondary systems for P removal.

Direct addition of iron to the combined primary and secondary sludges before anaerobic digestion resulted in greater volatile solids destruction, much lower TVOSC generation and higher dewatered cake solids. The benefits to TVOSC reduction were substantial enough that iron addition to digester feed should be considered as an odor reduction technology.

Benefits:

- ◆ Provides a determination that iron may play a role in determining odors from dewatered and anaerobically digested sludge cakes.
- ◆ Demonstrates that iron addition to the feed to a digester is an important tool for the reduction of volatile organic sulfur compounds from dewatered sludge cakes.
- ◆ Demonstrates that iron addition to the digester feed will also reduce polymer conditioning requirements and increase dewatered cake solids.
- ◆ Demonstrates that iron is preferred over aluminum for phosphorus removal based on volatile solids reduction in the digester, cakes solids and odor generation.

Keywords: Biosolids, odor, conditioning and dewatering, alum, iron.

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EXECUTIVE SUMMARY

ES.1 The Effect of Influent Iron and Aluminum on Digestion, Dewatering, and TVOSC Production

Both the iron and aluminum content in raw sludges being fed to anaerobic digesters were found to impact the digestibility, dewatering and TVOSC generation. A correlation between the iron content in the raw sludge and volatile solids reduction by anaerobic digestion was found. This has been seen by Park, et al. (2006) and was verified by this study. More iron resulted in higher volatile solids reduction except for the two plants that either received chemical sludge in the influent that contained iron and aluminum (Plant E) or had iron added in the treatment process for phosphorus removal (Plant F). This finding is important in that it provides for a method to predict volatile solids destruction by anaerobic digestion based on the influent iron content. Aluminum appeared to also influence digestion, reducing the volatile solids destruction of sludges by about 2%. However, in this study, it was difficult to separate both the effects of iron and aluminum.

Iron also had a major impact on dewatering. Although there was no correlation between the iron or aluminum content and cake solids, there was a distinct relationship between the iron content and polymer dose requirements. As the iron concentration in the raw sludge increased, the polymer dose increased following anaerobic digestion.

As suggested in the Phase III report, iron appeared to play a role in TVOSC production from dewatered sludge cakes. As the iron content increased, the TVOSC generation generally increased. As a result, iron increases both the volatile solids reduction and TVOSC generation. The data suggest that sludges that digest better may also generate higher TVOSC. This has important implications for the regulations governing vector attraction based on volatile solids reduction. Regulations regarding volatile solids reduction for vector attraction reduction (U S EPA, 1992) should be reconsidered since there is ample evidence from this study and prior WERF research (Adams, et al., 2007) that the percent volatile solids reduction does not correlate well with organic sulfur odor reduction.

Specific conclusions are:

- ◆ The volatile solids destruction by anaerobic digestion increases as the iron content of the feed sludge increases.
- ◆ The TVOSC increases from dewatered sludge cakes and the iron content in the feed sludge increases.
- ◆ Aluminum appears to decrease the volatile solids destruction by anaerobic digestion.
- ◆ Increased volatile solids destruction does not result in a decrease in TVOSC. Therefore, regulations that rely on volatile solids reduction criteria for control of vector attraction should be reconsidered.

ES.2 The Effect of Iron and Aluminum Added for Phosphorus Removal to Activated Sludge on Digestion, Dewatering, and TVOSC Production

When iron or aluminum was added to activated sludge to reduce soluble phosphorus, there were distinctly different impacts on volatile solids reduction by anaerobic digestion. The effect of iron addition on volatile solids reduction was minimal. The effect of aluminum was to decrease the volatile solids reduction by approximately 2%.

Both iron and aluminum addition to activated sludge generally reduced the generation of TVOSC from anaerobically digested, dewatered biosolids cakes. Iron reduced TVOSC more than aluminum in most cases. The amount of TVOSC reduction varied from a few percent to 90 percent. For the sludge that came from the plant where iron addition was being practiced, the benefits were minor.

Neither iron nor aluminum addition to activated sludge had a major impact on either polymer dose requirements or dewatered cake solids. There were modest effects but no consistent pattern.

Specific conclusions are:

- ◆ The volatile solids destruction by anaerobic digestion decreased by approximately 2% when aluminum was added to activated sludge for phosphorus control.
- ◆ The volatile solids destruction by anaerobic digestion was unchanged or increased slightly when iron was added to activated sludge for phosphorus control.
- ◆ The TVOSC generally decreased for both iron and aluminum addition, but iron resulted in the greatest decrease.
- ◆ Neither iron nor aluminum addition to activated sludge had much impact on polymer doses or cake solids.
- ◆ In general, considering volatile solids destruction, TVOSC and dewatering properties of the biosolids following anaerobic digestion, ferric chloride would be a better choice for phosphorus removal in the activated sludge process than alum.

ES.3 The Effect of Addition of Iron to the Digester Feed on Digestion, Dewatering, and TVOSC Production

Iron is frequently added to anaerobic digesters to control the hydrogen sulfide content of the gas. This portion of the study was to determine if there were other impacts.

Iron addition to the digester feed sludge was beneficial for volatile solids reduction for most of the sludges. For several of the plants, the gain in volatile solids reduction was 5%.

Iron addition resulted in a dramatic reduction in TVOSC for most of the sludges in this study. The TVOSC reduction for one of the sludges was in excess of 95% and TVOSC was reduced in the sludges that received iron in the plant or chemical sludges in the plant influent. Direct addition to the digester feed should be considered as a potentially useful tool to reduce the odors from dewatered biosolids cakes.

Iron addition also reduced cationic polymer doses for the sludges that did not receive iron in the plant or chemical sludges in the influent. The polymer dose reduction was greatest for sludges with the highest polymer dose requirements. Iron addition also increased the dewatered cake solids for five of the seven sludges by an average of 3%.

Specific conclusions are:

- ◆ The addition of iron to the digester feed had beneficial effects on cake solids, polymer dose requirements and volatile solids destruction for most of the sludges.
- ◆ The addition of iron to the digester feed had a dramatic effect on TVOSC production, decreasing TVOSC by 50 to over 95% for most of the sludges.
- ◆ Direct addition of iron to the digester feed should be considered one of the important tools for TVOSC reduction in treatment plants that practice anaerobic digestion.

CHAPTER 1.0

INTRODUCTION

1.1 Overview of Odor and Effect of Iron and Aluminum

1.1.1 Project Background

This study was designed to be a follow up of the Phase III (Adams, et al., 2007) odor study. The Phase III study found that iron and aluminum appeared to play important roles in odor generation so some additional data was sought to determine the role these play in determining odor. Dr. Matt Higgins conducted one portion of the study, the impact of aluminum used as a chemical conditioning agent during dewatering on odor reduction. In this portion of the study, the impact of iron and aluminum in sludges on both digestion and odors was investigated. Three distinct locations for the iron and/or aluminum were studied. First, the impact of iron and aluminum in the raw sludges on digestion and odors was evaluated. Second, the impact of the addition of iron or aluminum for chemical phosphorus removal in the activated sludge process was studied. Third, the direct addition of iron to the feed to an anaerobic digester was evaluated.

All studies were conducted in the lab using a variety of sludges collected from several utilities. In addition to digestion and odors, data were collected for sludge dewatering properties as indicated by the polymer conditioning requirements and dewatered cake solids.

1.1.2 Overview

Research has shown that odors produced by biosolids are due to several classes of chemicals, mainly organic sulfur compounds, volatile organic compounds, and nitrogen based compounds. The specific odorants include methyl mercaptan, dimethyl sulfide, dimethyl disulfide, p-cresol, indole, skatole, and trimethylamine (Higgins et al., 2006; Novak et al., 2006). Research has shown that most of these compounds can be produced during microbial degradation of bioavailable protein (Higgins et al., 2006). Therefore, reducing the bioavailable protein in dewatered biosolids would directly reduce the production of odor causing compounds (OCCs). Researchers have shown that addition of iron and alum reduced the bioavailability of several biomolecules, including proteins, through complexation (Dentel and Gossett, 1982). This suggests that addition of alum or iron to biosolids may reduce bioavailable protein and the associated odor causing compounds.

1.1.2.1 Effect of Iron

As part of a series of studies performed by the WERF odor research team, iron appeared to be important in predicting both odor generation and volatile solids reduction during anaerobic digestion. These data, for sludges from 12 plants, indicate that as iron increases in sludge, digestion efficiency increases. These data are shown in Figure 1-1. These sludges were batch digested, and two of the sludges rapidly generated volatile fatty acids and this resulted in inhibition of the digestion process. These data are consistent with results from Park, et al, (2006)

who showed that iron in waste activated sludge could determine the degree of volatile solids reduction by anaerobic digestion.

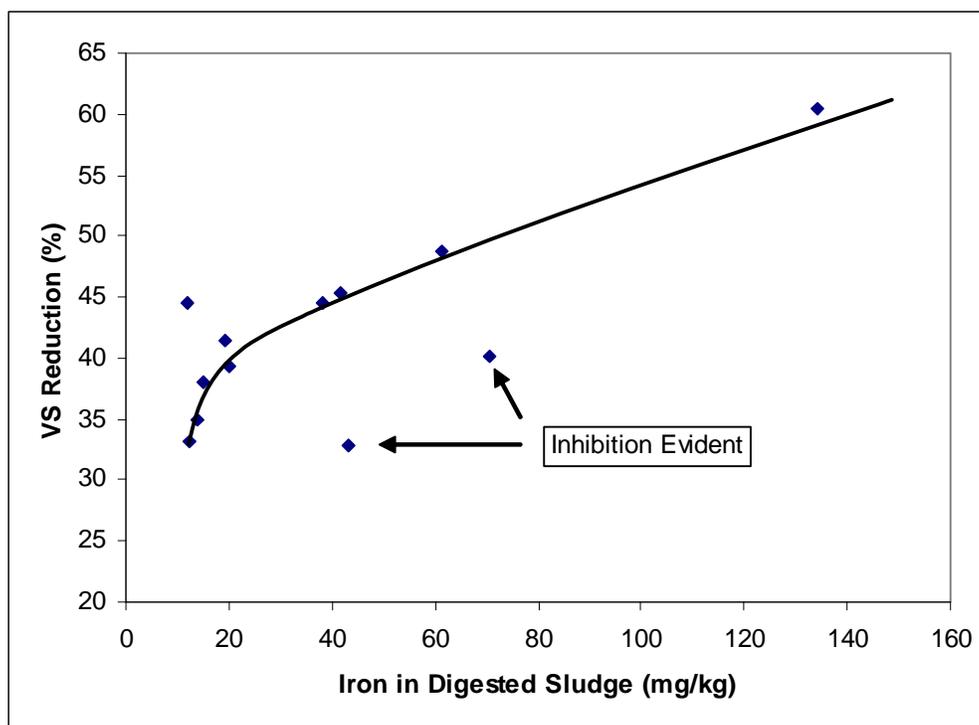


Figure 1-1. Effect of Alum Addition on TVOSC Production in Laboratory Trial.

The data from the Phase III study also showed that the total volatile organic sulfur concentration (TVOSC) was dependent on the iron content of the sludges. These data are shown in Figure 1-2. What these data suggest is that iron increases volatile solids destruction, but also increases the odor potential as measured by the TVOSC. This conflicts with EPA regulations that relate increased volatile solids with a reduction in vector attraction. Further, it contradicts some of the research conducted in the Phase III study showing that for sludge from Los Angeles County, increased detention time in the anaerobic digester reduces both volatile solids and TVOSC.

An explanation for this apparent discrepancy is that for a single sludge, a reduction in volatile solids will usually reduce TVOSC. However, when comparing sludge from one plant to one from another plant, the higher iron-containing sludge can be expected to have a higher odor potential. The sludge from Los Angeles County had very high iron content as a result of iron addition in the distribution system to control the generation of H_2S and also had the highest TVOSC of any of the sludges tested in both the Phase II and Phase III odor studies. So even though a high digester SRT reduced TVOSC, it still remained high compared to sludges from other plants. The field data shown in Figure 1-2 is from the Los Angeles County plant.

1.1.2.2 Effect of Aluminum

Data from the Phase III study shows that the presence of aluminum in raw sludge appears to result in reduced TVOSC generation, although the data are not as clear as for iron. The data in Figure 1-3 suggest that aluminum can bind to protein and reduce the generation of TVOSC. The

relationship between aluminum and TVOSC is explored further in the portion of the study conducted by Higgins.

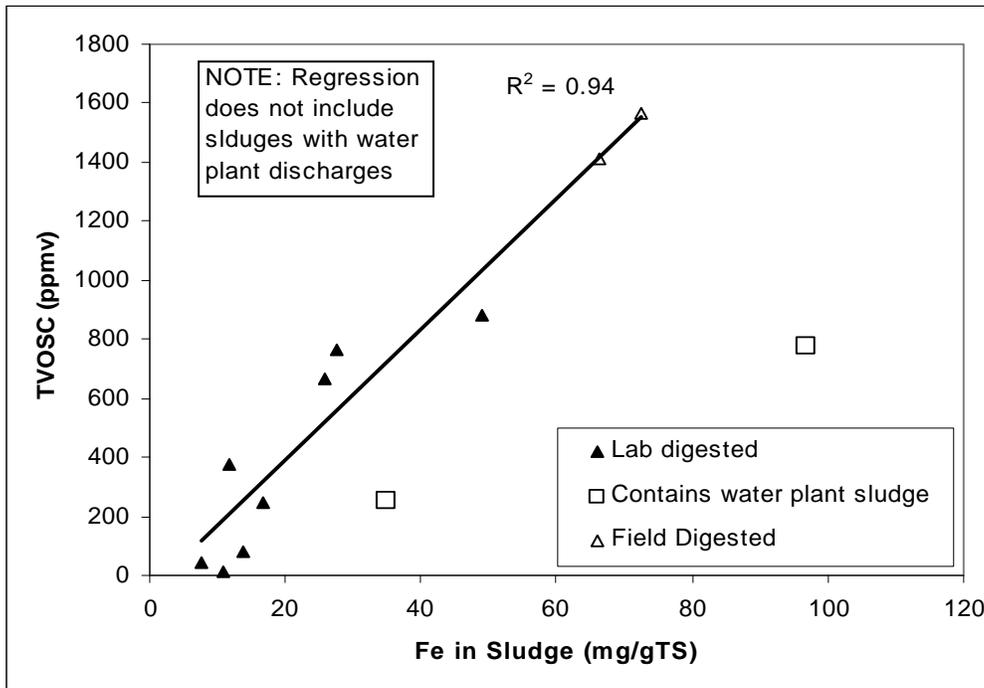


Figure 1-2 Relationship between Iron in Raw Sludge and TVOSC Production Following Batch Anaerobic Digestion.

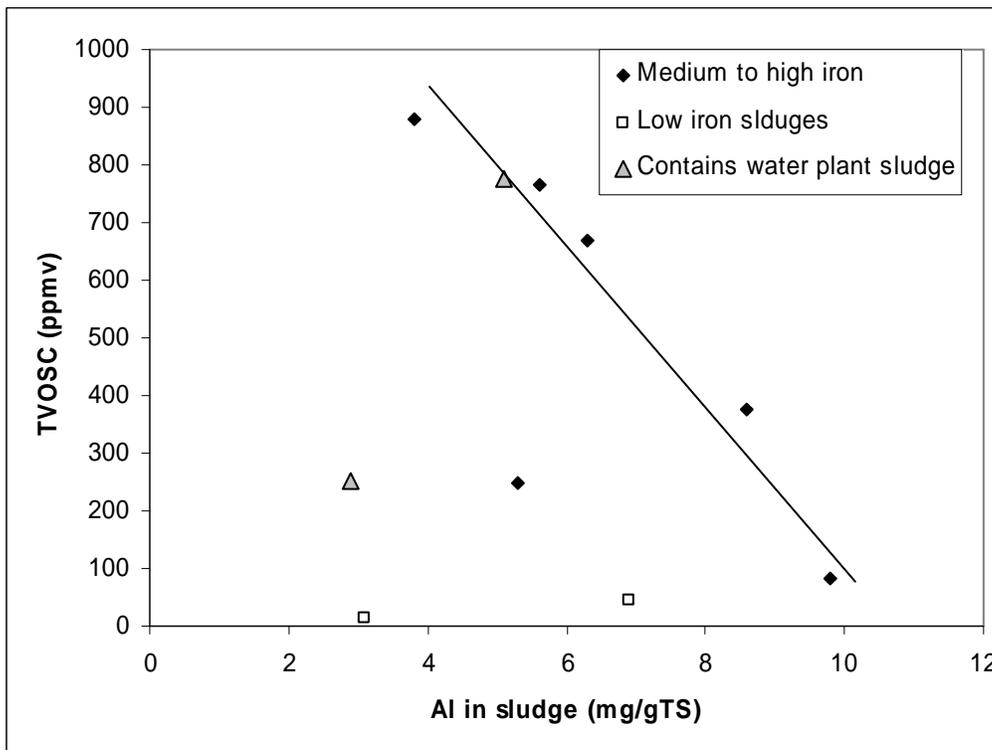


Figure 1-3. Relationship between Aluminum in Raw Sludge and TVOSC Production Following Batch Anaerobic Digestion.

Because the presence of both iron and aluminum in raw sludge influences both volatile solids reduction by anaerobic digestion and the odor potential as measured by the TVOSC, it was thought that addition of iron or aluminum within the treatment system could also impact digestion efficiency and odor potential. Iron and aluminum are often added within a treatment plant to chemically precipitate phosphorus. The effect of this addition on both digestion and especially TVOSC generation is not known. Knowledge of the potential benefits and detrimental effects would help plant operators to decide if iron or aluminum was best for their plant design and layout. Further, iron is often added directly to digesters to reduce the amount of H₂S in the digester gas. The impact on digestion and TVOSC generation from the dewatered biosolids is not known. Therefore this study was undertaken to determine the effect of iron and aluminum addition to activated sludge for phosphorus removal and the addition of iron to the digester feed for H₂S control.

All studies were conducted in the lab using a variety of sludges collected from several wastewater utilities. In addition to digestion and odors, data were collected for sludge dewatering properties as indicated by the polymer conditioning requirements and dewatered cake solids.

1.2 Research Objectives and Significance

Specific objectives of this study were:

- ◆ To determine the effect of background iron and aluminum in sludge on anaerobic digestion efficiency and total volatile organic sulfur compounds (TVOSC) generation.
- ◆ To determine the effect of the addition of iron or aluminum for phosphorus removal on anaerobic digestion efficiency and total volatile organic sulfur compounds (TVOSC) generation.
- ◆ To determine the effect of the direct addition of iron to digester feed on anaerobic digestion efficiency and total volatile organic sulfur compounds (TVOSC) generation.
- ◆ For all these conditions, evaluate the effects on sludge dewatering properties.

The research is critical to determining the role of iron in digestion and odor generation. Further, the impact of iron and aluminum addition for phosphorus removal on both digestion and odor generation will assist utilities in optimizing plant performance and reducing odors. Metals, especially iron can be added in several places in a wastewater plant. The effect on odors is not known. This study will help close that gap and will also determine if iron and aluminum addition to a wastewater plant is a worthy subject to continue to investigate.

CHAPTER 2.0

LITERATURE REVIEW

2.1 Introduction

This chapter includes a general review of the literature dealing with digestion of sewage sludge, the role of iron and aluminum in digestion, the production of organic sulfur odor compounds and dewatering. Recent findings from earlier WERF studies have shown that organic sulfur odors are produced primarily from shear in high solids centrifuges and even for well digested sludge, odors can be generated. The WERF report also showed that both iron and aluminum appeared to play a role in digestion and organic sulfur generation. Iron in the feed wastewater increased total volatile organic sulfur (TVOSC) of anaerobically digested sludges and aluminum appeared to reduce TVOSC. Based on these findings, a follow up study was conducted to determine the impact of iron and aluminum added in the plant for phosphorus precipitation in the activated sludge system and the impact of iron added to the anaerobic digester for H₂S control.

2.2 Overview of Anaerobic Digestion

Understanding the multistep nature of anaerobic biochemical operations is of importance since the interaction between the bacteria and the archaea occurs in both suspended and attached growth systems. The insoluble organic matter or complex biodegradable particulates are hydrolyzed to proteins, carbohydrates and lipids. Also, size reduction to facilitate transport across the cell membrane is considered as part of the hydrolysis process (Grady et al., 1998).

Amino acids and sugars are degraded to acetic acid by fermentative reactions under anaerobic condition. Volatile and long chain fatty acids from lipids are transformed to hydrogen through anaerobic oxidation. Both acetic acid and hydrogen are the direct methane precursors in anaerobic operations. In this acidogenesis system, the high partial pressure of hydrogen can be an inhibitor thermodynamically for anaerobic oxidation. Acetic acid, H₂, methanol, and methylamines can be used as substrates for methane production (Grady et al., 1998).

Methanogens utilize the products of acidogenesis such as acetic acid and H₂ to produce methane gas. Acetoclastic methanogens which are involved in splitting acetic acid into methane and carbon dioxide and H₂-oxidizing methanogens which reduce carbon dioxide to methane participate in these methanogenesis reactions. Generally, two-thirds of methane formation in anaerobic digestion results from the acetic acid and the remaining portion is derived from H₂ and carbon dioxide (Grady et al., 1998). These methanogens have relatively low maximum growth rates, so they are rate-limiting in the overall anaerobic digestion process (Metcalf and Eddy, 1991).

2.3 The Role of Cations in Anaerobic Digestion

Chemical coagulants such as alum and ferric chloride are commonly used for phosphorus removal in wastewater treatment. In addition, suspended solids removal can be achieved

simultaneously when coagulants are applied to the primary or secondary treatment processes (U.S. EPA, 1975). However, that practice also has adverse effects on anaerobic digestion of the sludge bound to coagulants (Rudolfs et al., 1932, Derrington et al., 1973, Brown and Little, 1977, Baillod et al., 1977). Gossett et al. (1978) studied the adverse effects on both plant-scale and bench-scale digesters receiving metal ion coagulants. They observed a significant decrease in volatile solids destruction, COD removal, organic nitrogen catabolism, alkalinity production, methane production, and total gas production. The mechanisms causing those problems had been thought to be due to coagulants “locking up” substrates such as proteins (Rudolfs and Setter, 1931) or phosphate limitation caused by aluminum and iron precipitation of phosphorus (Pfeffer and White, 1964).

Cations may be important for prediction of digester performance such as solids destruction and odor generation. Basically, it is difficult to predict digestability and effluent sludge characteristics based on the type of process used or the solids detention time. Such prediction is of importance and cost-effective when the design of wastewater treatment is made (Novak et al., 2007). In order to understand the effect of cations on anaerobic digestion, the role of cations in floc structure needs to be better understood. Park and Novak (2007) proposed that there are iron bound organics that could be degraded by anaerobic digestion and an aluminum bound fraction that resists biological degradation under aerobic and anaerobic condition, and a divalent cation-bound fraction that is degraded primarily under aerobic conditions. Novak *et al.* (2003) also showed that the floc fraction associated with iron degrades differently from the Ca^{++} and Mg^{++} associated fraction. Higgins and Novak (1997a) showed that cations such as Ca^{++} and Mg^{++} can affect the characteristics of sludge settling and dewatering and effluent quality from the activated sludge process. The effect of calcium and magnesium on solid/liquid separation for anaerobically digested sludges has not been investigated.

2.4 The Effect of Iron and Aluminum on Digestion and Odors

Recently, Park et al. (2006) showed that volatile solids destruction of waste activated sludge under anaerobic conditions is dependent on the iron content in the sludge. Murthy et al. (2000) suggested that iron in sludge has an affinity for protein. Park, et al. proposed that iron in the sludge is reduced when it enters an anaerobic digester and the organics associated with iron are released in combination with sulfide. These released organics are degraded in the digester, resulting in the volatile solids destruction. As the iron in sludge increases, volatile solids destruction also increases (Novak et al., 2007).

It was observed in the Phase III odor study (Adams, et al., 2007) that as iron in the feed sludge to an anaerobic digester increases, TVOSCs from the dewatered cake also increases in spite of increase in volatile solids destruction. It is thought that odors are generated by further release of protein that remain undegraded in the digester. This remaining iron-bound organic matter is released for degradation due to the shear in a centrifuge.

This result conflicts with the volatile solids destruction and stability regulation in the U.S. EPA regulation which specify a level of volatile solids destruction to reduce vector attraction (Novak et al., 2007). However, Novak et al. (2002) suggested that Ca^{++} and Mg^{++} associated organics are not related to odor generation from the dewatered biosolids since Ca^{++} and Mg^{++} do not increased after centrifugation. It was found that TVOSC and the aluminum content in the

sludge have an inverse correlation. As the aluminum content increases, the TVOSC from centrifugally dewatered anaerobically digested biosolids decreases. It is speculated that this is because the aluminum-bound organics are bound more tightly to the floc and are not released under high shear. These results are controversial and that is the reason this study was undertaken. These results could be the foundation for predicting odor generation in the anaerobic digestion based on the characteristics of the raw wastewater. However, further study should be needed to support and clarify the role of iron and aluminum in odor production and digestion (Novak et al., 2007).

2.5 VOSC Production and Degradation

The balance between the production and degradation of VOSCs has been shown to occur in fresh water sediments resulting in low VOSC emissions. This shows that the production rate of VOSCs is basically equal to the degradation rate of VOSCs under steady-state condition (Lomans et al., 2001). However, if toxic compounds such as chloroform, toluene, or sodium are added to the anaerobic systems, the balance will be disturbed, resulting in inhibition of methanogenic activity. A reduction in methanogenic activity has been associated with the production of MT and odors (Zitomer and Speece, 1995, Zitomer et al., 2000). Thus, MT accumulation in anaerobic digesters could be an indicator of toxicity or inhibition of the methanogenic community (Zitomer et al., 2000).

Higgins et al. (2006) studied the mechanisms of production, degradation, and transformation of volatile organic sulfur compounds and described the pathways followed during cake storage. The production of odor-causing VOSCs, H₂S and MT result from degradation of protein. In addition, the free sulfate and sulfonate-based surfactants present in wastewaters contribute to another source of hydrogen sulfide even though the quantities are quite small (Field et al., 1995). A strong correlation between the peak MT concentration measured during incubation and the mass of bound methionine extracted from biosolids cake has been shown with 10 different mesophilic anaerobically digested sludges. The peak concentration of MT increased linearly as the mass of bound methionine increased (Higgins et al., 2004).

The generation of MT and DMS appears to be from methylation of H₂S and MT in which methyl groups are added (Higgins et al., 2006). The degradation of methionine or cysteine, common amino acids, can result in the formation of dimethyl sulfide (Persson et al., 1990).

Dimethyl disulfide is readily formed from oxidation of methanethiol when oxygen is present in the environment (Chin and Lindsay, 1994, Fritz and Bachofen, 2000, Kelly and Smith, 1990, Parliament et al., 1982, Tulio et al., 2002). Lehninger et al. (1993) has suggested that the thiol groups in cysteine are readily converted to disulfide bonds through oxidation in the protein which can be catalyzed by agents such as iron and copper (Chin and Lindsay, 1994, Prentice and Bryce, 1998). This fact corresponds with the results of Higgins et al. (2006) that suggested that methanethiol was produced only after DMDS reached its peak and started to decrease. Also, additional research data support the fact that the formation of DMDS from MT only occurs when oxygen is present in the system. It was observed that the concentration of MT increased and DMDS formation stopped when oxygen was exhausted in the serum bottles.

2.6 Control Strategies for VOSCs

Recent surveys have shown that nuisance odors associated with biosolids are highly ranked as a top concern and main restriction of land application programs, thereby indicating the need for further research (Adams et al., 2003, Dixon and Field, 2004). Thus, a reduction in odors associated with biosolids has a significant impact on land application programs (Higgins et al., 2006). Higgins et al. (2006) suggested two major strategies in order to control volatile organic sulfur compounds. The first method could be removal of precursors of VOSCs which contain the sulfur-containing amino acids, cysteine and methionine. Proteins are the parent material for cysteine and methionine. Also, intermediate reactions such as demethylation would aid in decreasing VOSC-related odors. Removal of hydrogen sulfide that is the final product of demethylation would help prevent production and degradation cycle of VOSC from proceeding further. Changes in digestion operations, dewatering processes, storage and land application methods, and chemical addition to biosolids before and after dewatering practice may be control method for reducing odors. When better digestion performance is achieved, the more available protein concentration could be reduced, thereby decreasing in the amount of substrate for production of odorous VOSCs. Secondly, an increase in methanogenic activity, which could be obtained by minimizing the shear forces during dewatering or eliminating inhibition of methanogens could increase the conversion of organic sulfur compounds to sulfide.

2.7 Relationship between Dewatering and Biosolids Odors

Odors associated with anaerobically digested biosolids are important for dewatering, transport, and land application in the aspect of esthetic effects and potential health risks (Novak et al., 2006). Anaerobic digestion for land application is commonly used in order to reduce odors and vector attraction. However, reactions that occur in dewatering processes with anaerobically digested sludge may be a major cause of unacceptable odors (Murthy et al., 2002).

Anaerobically digested sludge that does not inhibit VOSC degradation has relatively low odors. However, dewatering processes can disturb the balance between the production and degradation rate of VOSC, thereby significantly increasing odors. Factors that influence dewatering effects on odors are the type of dewatering equipment, polymer dose, and cake handling and transport (Higgins et al., 2006).

First, high-solids centrifuges trigger inhibition of the activity of methanogens in degrading VOSC and impart more shear, causing cell lysis and damage or greater floc breakup to occur, resulting in an increase in bioavailable protein. Odors associated with biosolids resulting from high-solids centrifuges are usually more produced than medium-solids centrifuges which are greater than belt-filter presses (Murthy et al., 2003).

Second, an increase in polymer dose promotes isolation of soluble protein present in liquid sludge, depositing the protein into the cake sludge. This polymer-associated protein appears to remain bioavailable, even after being reincorporated into the dewatered biosolids. Thus, the increased amount of protein which is bioavailable as a substrate for the production of VOSC could result in more odor production during storage (Higgins et al., 2002, Murthy et al., 2003).

Last, transport of cake through high-shear conveyance such as cake pumps and screw conveyors can raise the odor production (Murthy et al., 2002). It appears that when a modest amount of shear is applied to a dewatered biosolids, odor production increases.

2.8 Chemical Conditioning and Dewatering of Sludges

Dewatering is one of the important solids processes, since a drier sludge can reduce the volume of solids for disposal or land application. Chemicals are usually added to improve the efficiency of dewatering processes and the quality of the filtrate or centrate. In municipal wastewater plants, high-solids centrifuges or belt filter presses are commonly used (Novak, 2006). Dentel (2001) studied the selection of the conditioning chemicals to achieve good dewatering using synthetic organic polymers or metal ions, usually iron salts. These chemicals are normally used for coagulation and removal of the colloidal fractions, aggregating them within the sludge. When the optimal conditioner is used in sludge, water in it separates faster (Novak, 2006).

The structure and role of floc have a relation with the dewatering and conditioning requirements of biological sludges (Novak et al., 2001). Higgins and Novak (1997a) proposed that the integral structure of floc contains cations and poor effluent quality and dewaterability were shown to occur when monovalent cations were much greater than divalent cations in wastewater influent. In addition, Higgins and Novak (1997b) showed that the protein component in the biopolymer is important in determining the characteristics of floc.

Novak et al. (2003) suggested that two types of biopolymers exist in floc, lectin-like proteins and a mix of proteins, polysaccharides, and humic acids. The lectin-like proteins are linked by Ca^{++} and Mg^{++} to polysaccharides. Higgins and Novak (1997a) showed that settling and dewatering properties were improved as Ca^{++} and Mg^{++} concentrations increased in the digester. In addition, the sodium content in the sludge improved the settling and dewatering characteristics until the M/D ratio based on equivalents exceeded 1:1. However, when the ratio of mono to divalent cations was above 2:1, sludge dewatering properties deteriorated. This problem could be overcome by addition of Ca^{++} and Mg^{++} to the activated sludge feed.

The mix of proteins, polysaccharides, and humic acids in solution can be agglomerated by aluminum and iron. The aluminum associated fractions have been poorly studied. However, it is thought that iron-associated proteins, polysaccharides and humic acids are released into solution when iron is reduced under anaerobic conditions, resulting in biocolloids in solution with a size range between 1.5 μm and 30,000 daltons. As more of the protein fraction is degraded, more colloidal materials accumulate in the solution. The biopolymer fraction that is released to solution is not completely degraded, resulting in the need for higher polymer conditioning doses and poor dewatering (Bivins and Novak, 2001). Thus, the polymer conditioning dose in the sludge is determined by these colloidal proteins that remain and interrupt dewatering under anaerobic condition. The accumulation of colloidal materials increases as volatile solids destruction increases. Thus, dewatering properties often get poorer as the efficiency of anaerobic digestion increases. According to a related study by Park (2002), conditioning and dewatering properties could be predicted based on the cation content of the wastewater, providing a tool for estimating sludge handling costs prior to construction of a digestion facility.

CHAPTER 3.0

RESEARCH APPROACH AND METHODS

3.1 Research Approach

In order to reduce the effect of experimental variables, sludge storage and organic loading of the digesters were consistent for each sample (Smith, 2006). Seven different primary and secondary sludges (except for Sludge D) were obtained from municipal wastewater treatment plants (WWTPs) and shipped to Virginia Tech using coolers with cold packs. They were stored in a refrigerator immediately upon arrival. The plants are designated by letters from A to G. The primary and secondary sludges were thickened by a low speed centrifuge to maintain a consistent total solids concentration in the digester feed. The target TS of the predigested sludge was 2.5% for both the primary and secondary sludge.

The iron and aluminum concentrations in the primary sludge and secondary sludges, shown in Table 1, were measured before digestion. Anaerobic digestion was carried out in the laboratory using the same batch digestion approach that was used in the Phase III odor study (Adams, et al., 2007). Batch digestion was necessary because of the number of sludges and the budget and time constraints. The raw sludge feed consisted of one liter each of primary and secondary sludge. The sludge was combined and fed to a batch digester containing a half liter of digested seed sludge and was then anaerobically digested in a batch digester for 30 days at 37°C in a constant temperature room. The sludge was hand mixed once per day. The seed sludge was obtained from the anaerobic digester of each of the plants that had anaerobic digesters. For those without an anaerobic digester, digested sludge from a local treatment plant was used.

Plant D did not have primary sludge so only secondary sludge (2L) was used. Plants E and F received iron or both iron and aluminum within the plant and as can be seen in Table 3-1, these had high iron or aluminum or both.

Table 3-1. Total Aluminum and Iron Content in Influent from Seven Municipal WWTPs.

| WWTP | Fe and Al in Primary Sludge (mg/g TS) | | Fe and Al in Activated Sludge (mg/g TS) | | Fe and Al in Combined Sludge (mg/g TS) | |
|------|--|-------|--|------|---|-------|
| | Fe | Al | Fe | Al | Fe | Al |
| A | 3.90 | 2.48 | 5.53 | 3.64 | 4.71 | 3.06 |
| B | 3.83 | 2.44 | 10.40 | 1.05 | 7.12 | 1.74 |
| C | 5.09 | 0.51 | 6.27 | 4.86 | 5.68 | 2.69 |
| D | NA | NA | 1.87 | 3.77 | 1.87 | 3.76 |
| E | 9.20 | 15.95 | 8.97 | 8.77 | 9.09 | 12.36 |
| F | 10.50 | 0.94 | 20.34 | 1.70 | 15.42 | 1.32 |
| G | 3.77 | 2.41 | 7.83 | 1.79 | 5.80 | 2.10 |

NA = no primary sludge at this plant so not applicable

The chemical coagulant dosage of aluminum and iron used to remove phosphorus was determined based on jar test using waste activated sludge from plant A as shown in Figure 3-1. Based on these results, three moles of either iron or aluminum per mole of phosphorus in the activated sludge was added at which more than 90% of phosphorus removal was achieved. The concentration of iron and aluminum added in mg/g is shown in Table 3.2. It can be seen that the lowest amount was for the sludge from Plant F that received iron for P removal.

Table 3-2. Aluminum and Iron Content Added for P Removal.

| Plant | TS in WAS (%) | Addition of Cations in WAS (gm/kg TS) | |
|-------|------------------|--|-----|
| | | Fe | Al |
| A | 2.269 | 71 | 58 |
| B | 1.519 | 106 | 86 |
| C | 1.206 | 134 | 109 |
| D | 3.000 | 64 | 52 |
| E | 2.288 | 70 | 57 |
| F | 4.610 | 35 | 28 |
| G | 2.274 | 71 | 58 |

Also, in a separate set of experiments, iron at a dose of 1.25% of dry sludge solids as Fe was added to a separate sample of combined primary and secondary sludge prior to digestion. This

addition of iron was to simulate the addition of iron to an anaerobic digester for hydrogen sulfide control. The additions are summarized below in Table 3-3.

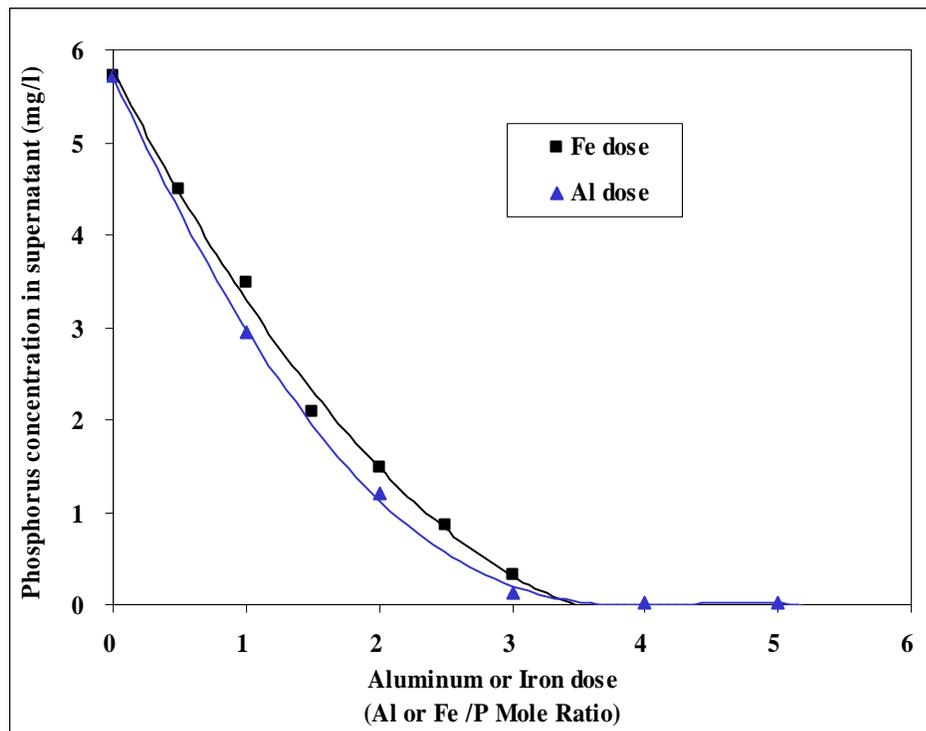


Figure 3-1. Iron and Aluminum Doses for Phosphorus Precipitation in Activated Sludge.

Table 3-3. Iron and Aluminum Additions to Sludges Prior to Anaerobic Digestion.

| Control – nothing added | Fe addition to activated sludge | Al addition to activated sludge | Fe addition to anaerobic digester feed |
|-------------------------|---------------------------------|---------------------------------|--|
| | 3:1 Fe to P molar ratio | 3:1 Fe to P molar ratio | FE at 1.25% of dry solids |

Using data obtained before and after digestion, the effect of influent cation concentrations and iron and/or aluminum addition on total solids destruction, volatile solids destruction, COD removal, gas volume production, and organic nitrogen catabolism was assessed. In addition, organic sulfur compounds were measured from dewatered solids cakes following anaerobic digestion for sludge from both field (where available) and laboratory samples.

3.2 Centrifuge Simulation, Dewatering, TVOSC

3.2.1 High Solids Centrifuge Simulation

For simulating centrifugal dewatering, the method of Muller, et al. (2004) was used. This method performs chemical conditioning under high shear conditions in the laboratory. The optimum dose of cationic polymer is determined by shearing in a Waring blender using thirty seconds of blending at a G of approximately $10,000s^{-1}$. The polymer dose is varied and the capillary suction time (CST) is measured for each dose. The polymer dose which provides the minimum CST is defined as the optimum dose. The cationic polymer conditioned samples are dewatered in a laboratory centrifuge and then the pellet further dewatered using a laboratory press to achieve a dewatered cake solids concentration similar to a high solids centrifuge (Novak et al., 2007). This method provides for a comparison of the optimum polymer dose and dewatered cake solids among various samples. For this study, these data could be used to determine the effect of iron and aluminum additions on polymer doses and cakes solids concentrations.

3.2.2 Measurement of Headspace Gases (TVOSC)

The dewatered pellets are then placed in 250mL serum bottles with Teflon[™] coated septa and the volatile organic sulfur compounds are measured in the headspace every one or two days during incubation. One hundred ul of headspace gas is manually injected to the gas chromatograph and quantified by comparing the experimental chromatograms to those of gas standards (Higgins et al., 2006; Glindemann, et al., 2006). The concentration of hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide was measured and total volatile organic sulfur compounds (TVOSCs) in ppmv are calculated from the measurements.

3.3 Analytical Methods

Liquid samples were analyzed for total solids (TS), volatile solids (VS), pH, soluble total Kjeldahl nitrogen (TKN), ammonium (NH_3 -N), and soluble COD according to Standard Methods (APHA et al., 1995).

The concentration of iron and aluminum in influent wastewater was measured using EPA method 3050B (acid digestion for metal analysis of soils, sediments, and sludges). Metals in the samples were quantified using an AA. Metal concentrations were expressed as mg/g TS.

A liquid cationic polymer, Clarifloc 3275, high molecular weight polymer, at 1% (w/w) was used as sludge conditioner in this study. Optimum dosages of each conditioner were determined using a capillary suction time (CST) test by reading the lowest value. CST was an indicator of the sludge dewatering rate according to the method described by Method 2710G (APHA et al., 1995). Waring Blender which has 1/5 H.P. was used with a 100 ml standard sample size.

Analysis of orthophosphorus ions was performed by an ion-chromatograph from DIONEX.

Gas was collected in a tedlar bag and the gas volume was measured with peristaltic pump that has been characterized with a flow rate of 0.913 L/min and standard deviation of 4.84% for 10 replicates.

CHAPTER 4.0

RESULTS AND DISCUSSION

4.1 Volatile Solids Reduction by Anaerobic Digestion

4.1.1 Volatile Solids Reduction with No Iron or Aluminum Added

A mixture of primary and secondary sludge in the ratio of 1 to 1 by solids was anaerobically digested in a constant temperature room at 37°C to determine the volatile solids reduction and TVOSC production. Volatile solids destruction in plants A, B, C, E, and G were in the range of 36 to 44 percent as shown in Table 4-1. However, VS destruction in the plant D sludge was relatively low (26.6%). Plant D did not use primary treatment and also had the lowest iron content. Plant F had the highest volatile solids removal (47.2%) and also the highest iron content.

These results show that VS destruction is dependent on influent aluminum or iron content since plant D had 1.87 mg/g TS of iron and plant F had 15.42 mg/g TS of iron in raw sludge. The data show that VS destruction increases as the iron content in the raw sludge increases. It is thought that one major mechanism for degradation of organics in an anaerobic digester is through the release of Iron-associated organics which are then degraded (Novak et al., 2007). Thus, it is expected that plant E would have high VS destruction since it had high concentration of iron in the feed sludge.

In Figure 4-1, the relationship between the iron content of the raw sludge and volatile solids reduction is shown. These data are consistent with the data of Park, et al. (2006) and show that the iron content of the sludge appears to have an important influence on volatile solids reduction. Sludges E and F have very high iron contents. In plant F, iron is added in both the primary and secondary systems for phosphorus removal. In plant E, the utility has one large treatment plant and several smaller plants. Sludge, containing aluminum used for phosphorus removal is hauled to the main plant where it is anaerobically digested with the sludge from the main plant. It can be seen from Table 3-1 that plant F has high Fe and plant E has both high iron and aluminum. The plant with the lowest iron content, Plant D was also the only plant that did not have primary treatment so the low VS reduction could be associated with the lack of easily degradable primary sludge.

The relationship between aluminum in the feed sludge and volatile solids reduction is shown in Figure 4-2. It appears that the effect of aluminum in the raw sludge is to decrease volatile solids reduction except for sludge E which receives aluminum in the form of alum sludge. Because it is difficult to separate the effects of iron and aluminum from each other because both change, it appears that both iron and aluminum influence the volatile solids reduction. Because the differences in volatile solids reduction appear to be dramatic, further investigation of these effects is warranted. The plant with the highest aluminum content was Plant D with no primary sludge and this could have influenced the degradation results.

Table 4-1. Characteristics of Lab Digested Sludge from Seven Municipal WWTPs Without Chemical Addition.

| WWTP | TS Removal (%) | VS Removal (%) | COD Removal (%) | Organic N Removal (%) | Optimum Polymer Dose (g/kg TS) |
|------|----------------|----------------|-----------------|-----------------------|--------------------------------|
| A | 30.4 | 39.4 | 52.0 | 26.1 | 3.38 |
| B | 29.7 | 36.7 | 45.4 | 12.6 | 3.84 |
| C | 27.1 | 42.5 | 62.7 | 44.3 | 3.78 |
| D | 19.9 | 26.6 | 68.0 | 32.1 | 2.63 |
| E | 32.5 | 43.9 | 65.3 | 41.2 | 4.03 |
| F | 39.4 | 47.2 | 35.9 | 42.4 | 3.82 |
| G | 31.2 | 37.8 | 49.8 | 50.4 | 3.99 |

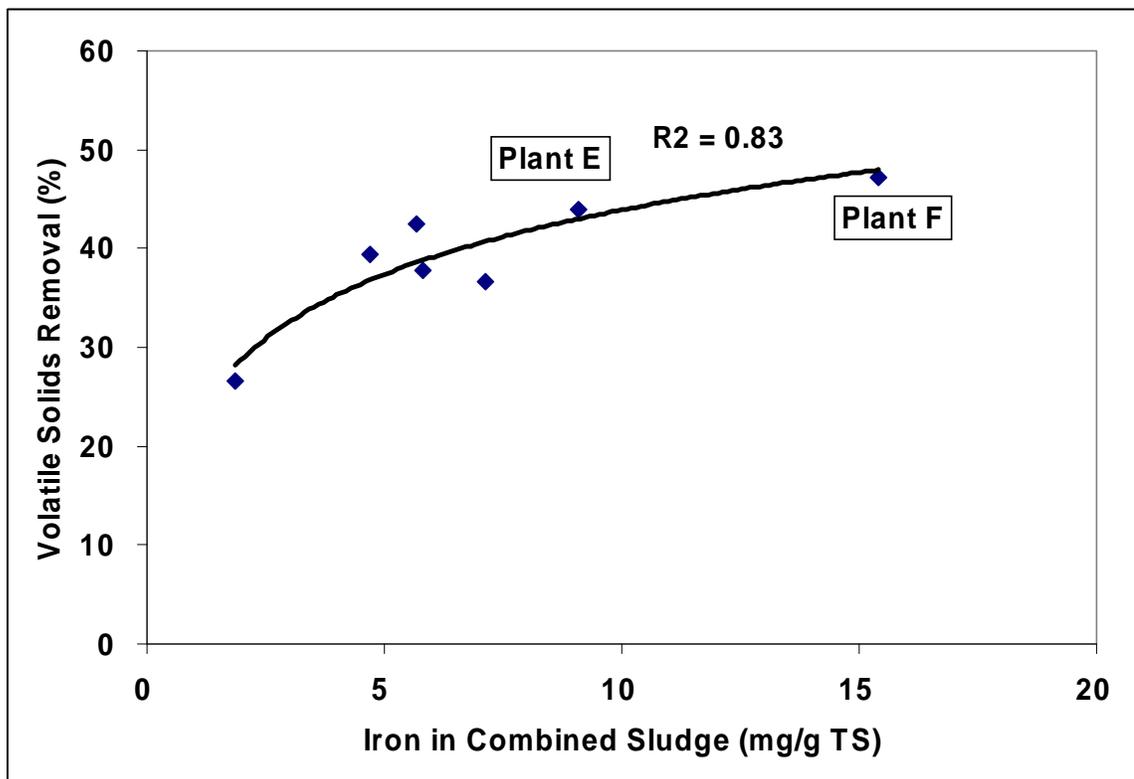


Figure 4-1. Relationship Between Influent Iron and Volatile Solids Reduction Without Chemical Addition.

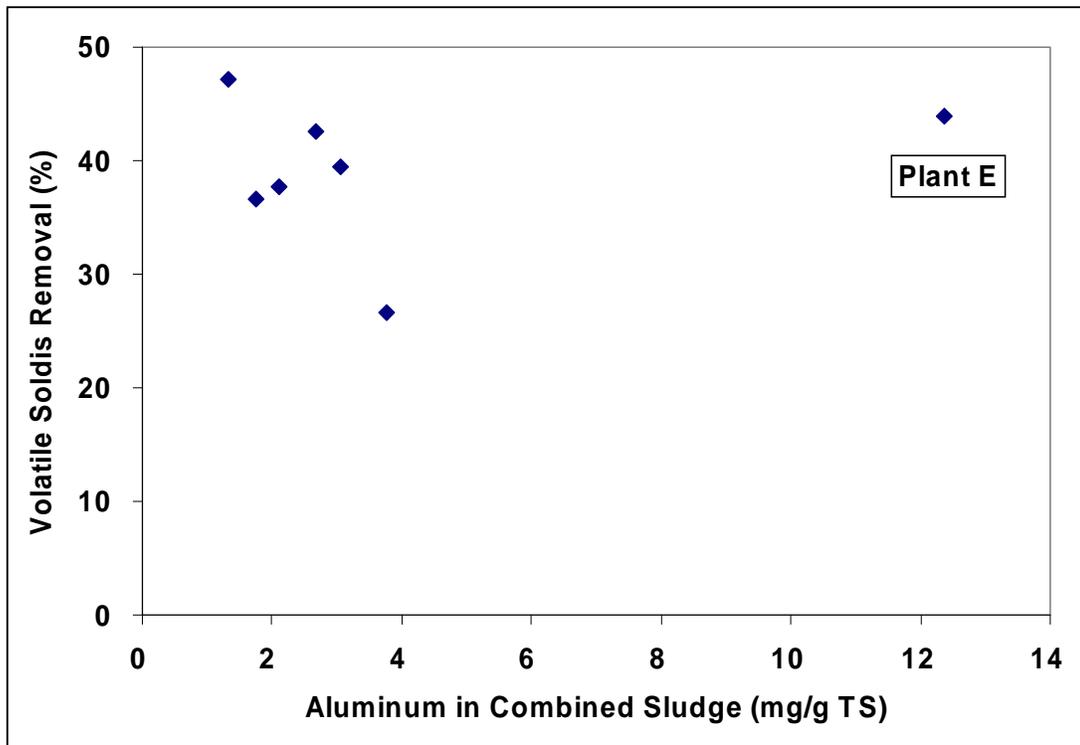


Figure 4-2. Relationship Between Influent Aluminum and Volatile Solids Reduction Without Chemical Addition.

4.1.2 Volatile Solids Reduction with Iron or Aluminum Added to Remove Phosphorus

The addition of aluminum and iron to WAS was carried out to simulate phosphorus removal prior to anaerobic digestion. The chemical addition of iron to WAS showed about a 2% increase in volatile solids destruction for five or the seven sludges. These data are presented in Figure 4-3. Smith and Carliell-Marquet (2008) showed similar results in that iron-dosed RAS generated more VS destruction than undosed sludge. However, Gossett, et al. (1978) found that both iron and aluminum addition reduced VS destruction. The authors attributed the effect on VS reduction to be due to reduced bioavailability of iron or aluminum-associated organics, particularly proteins. Park, et al. (2006) concluded that the mechanism for reduced VS destruction with aluminum addition was similar to that proposed by Gossett, et al. but for iron, Park, et al. proposed that iron would likely be reduced, releasing bound proteins which could then be biodegraded.

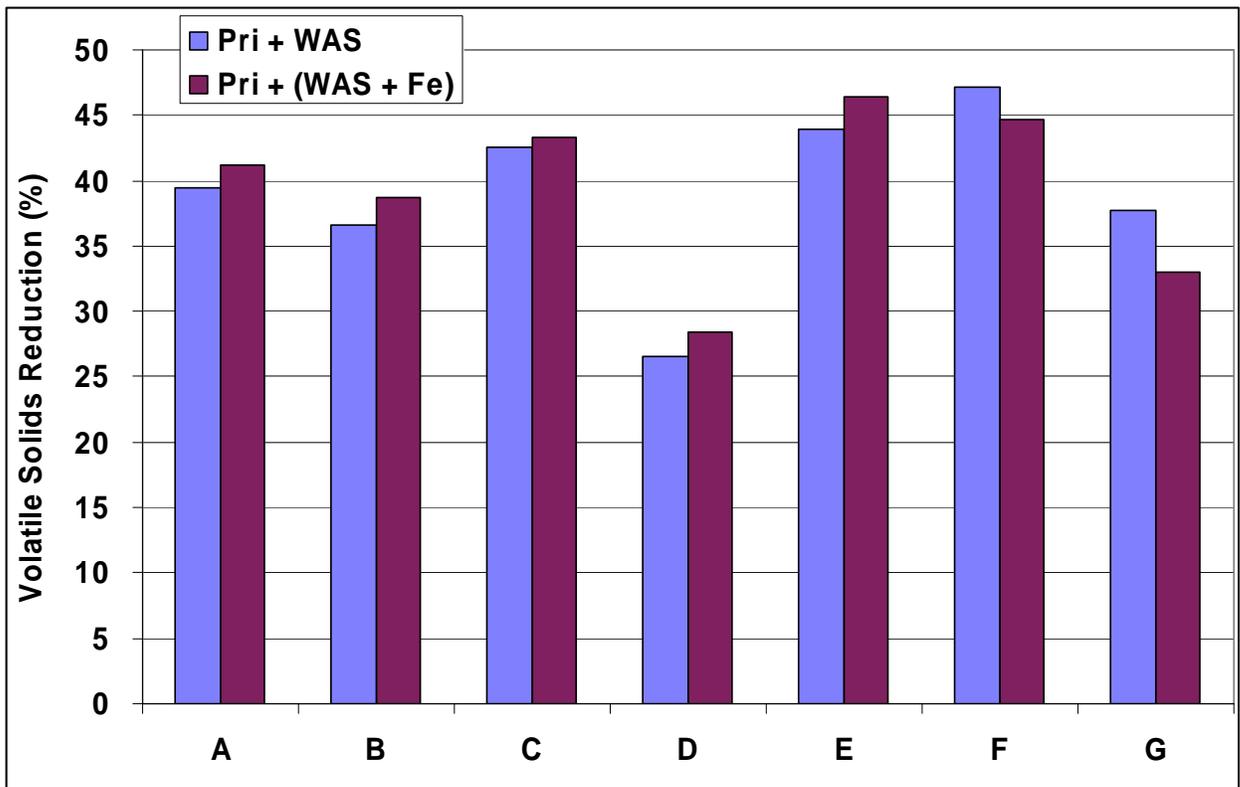


Figure 4-3. Effect of Iron Addition to WAS on Volatile Solids Reduction.

As shown in the Figure 4-4, when aluminum was added to WAS, a lower percentage of volatile solids destruction was observed in all plants. This result is consistent with the findings of Dentel and Gossett (1982) that the chemical coagulation of organic materials with aluminum in the activated sludge led to decrease in volatile solids destruction by anaerobic digestion. It is also in accord with the suggestion by Park and Novak (2007) that aluminum associated organics under anaerobic condition are not readily biodegradable. The decrease in volatile solids reduction is approximately 2 percent. This may not be important if other benefits of aluminum addition offset the loss of volatile solids reduction.

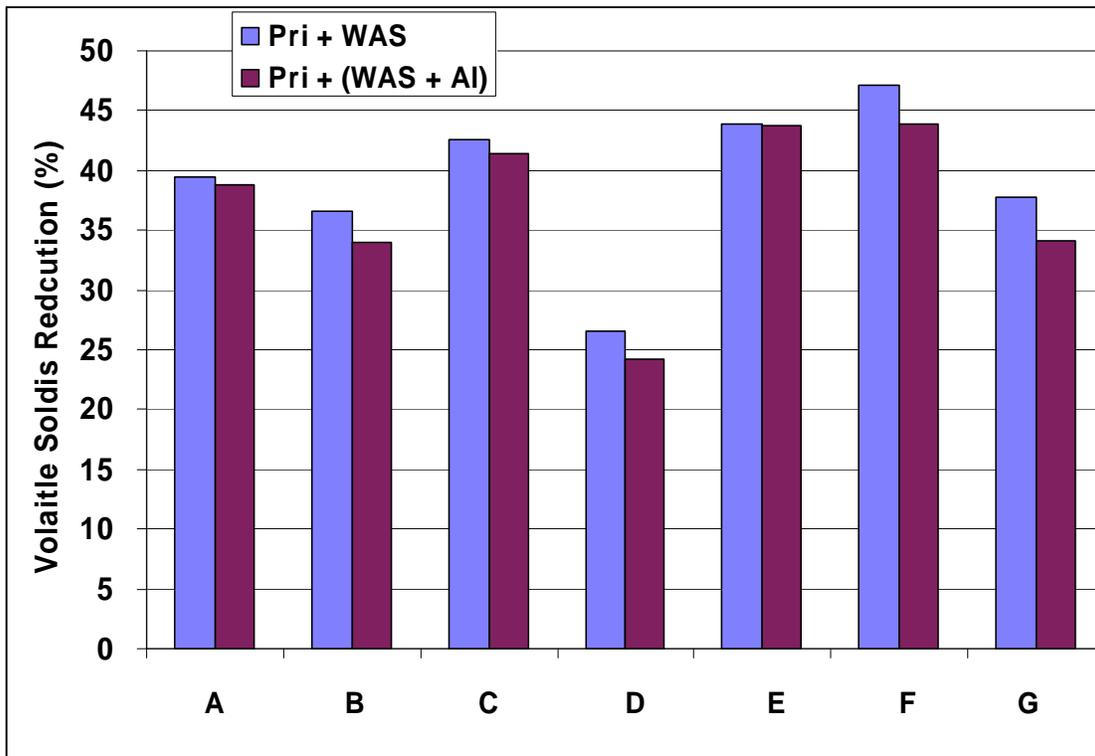


Figure 4-4. Effect of Aluminum Addition to WAS on Volatile Solids Reduction.

4.1.3 Volatile Solids Reduction with Iron Added to the Sludge Prior to Digestion

When iron was added to the combined primary and secondary feed to the digester (Figure 4-5), the volatile solid destruction increased for the sludges except sludges F and G. For the sludges that had a high iron content (sludge E and F) due to either the addition of iron for phosphorus removal or when iron entered as a chemical sludge, the added iron had little effect. It might be expected that a very high iron addition could remove bioavailable phosphorus and this might retard digestion. For the lower iron sludges, iron addition was generally beneficial. The greatest increase in volatile solids reduction, 6%, was for the sludge that had the lowest iron content in the feed sludge.

Overall, it appears that iron addition to sludges either as direct addition to the digester feed or for phosphorus removal has a small but positive influence on digestion. For the sludge that had the highest iron content due to iron addition in the plant, additional iron had a minor effect. Therefore, with regard to volatile solids destruction, there appears to be little harm and potential benefit to adding iron to sludges that are to be anaerobically digested.

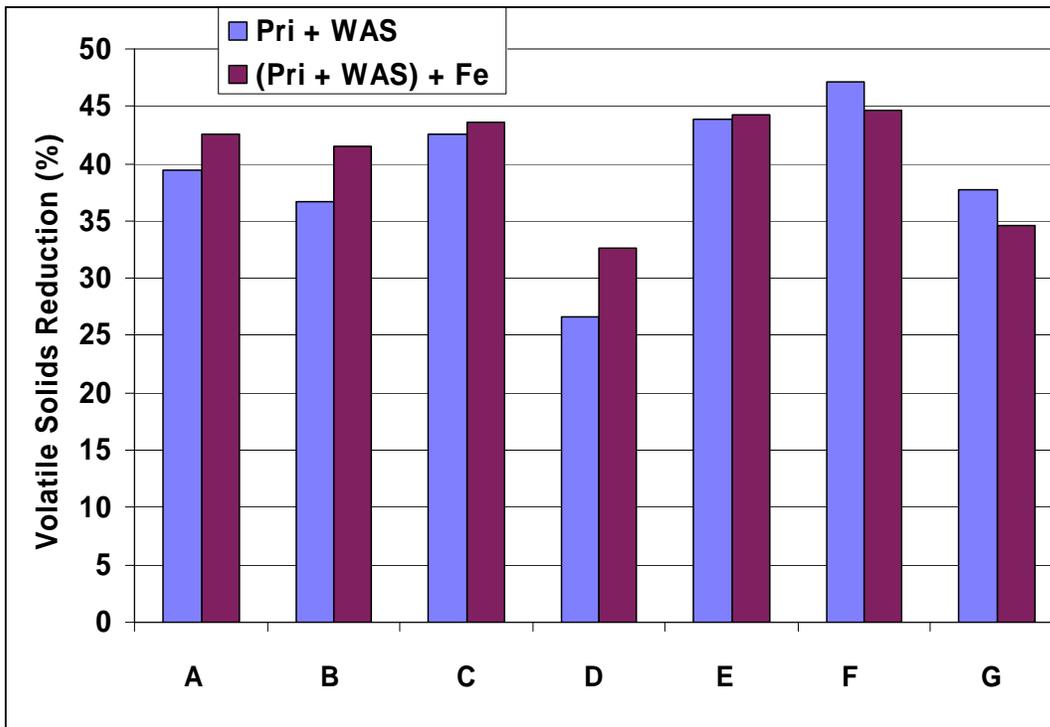


Figure 4-5 Effect of Iron Addition to Sludge Prior to Digestion on Volatile Solids Reduction.

4.2 Effect of Iron and Aluminum Addition on TVOSC

The digested sludges from the chemical additions described above were tested for volatile sulfur compounds using the techniques described in the Methods section. Data for sludge A is shown in Figures 4-6 and 4-7 for TVOSC and methanethiol, respectively. As was found in the Phase III study, most of the TVOSC is contributed by methanethiol. It can also be seen for sludge A that the highest TVOSC and methanethiol were for the sludge that did not receive any chemical addition. It can also be seen that the sludge obtained from the digester at the plant had a TVOSC that was not very different from the sludge that was lab digested. This suggests that the lab approach to digestion and centrifuge simulation used in this study provides a reasonable estimate of the digestion and odor generation capacity of the field digested sludges.

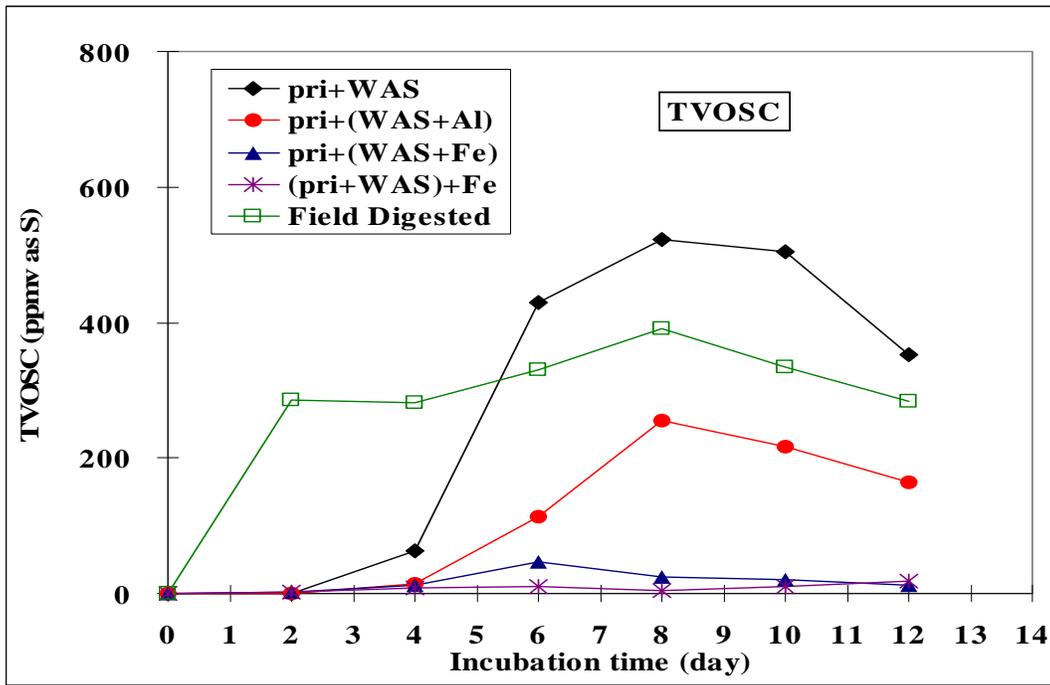


Figure 4-6. Effect of Chemical Addition on the TVOSC of Sludge A.

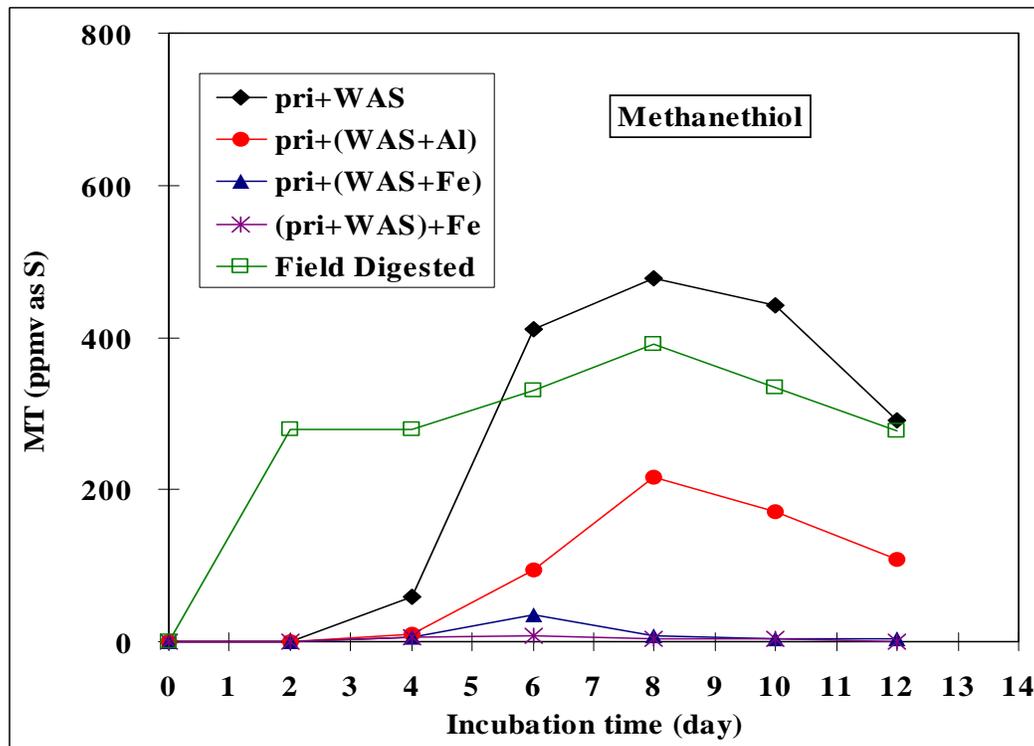
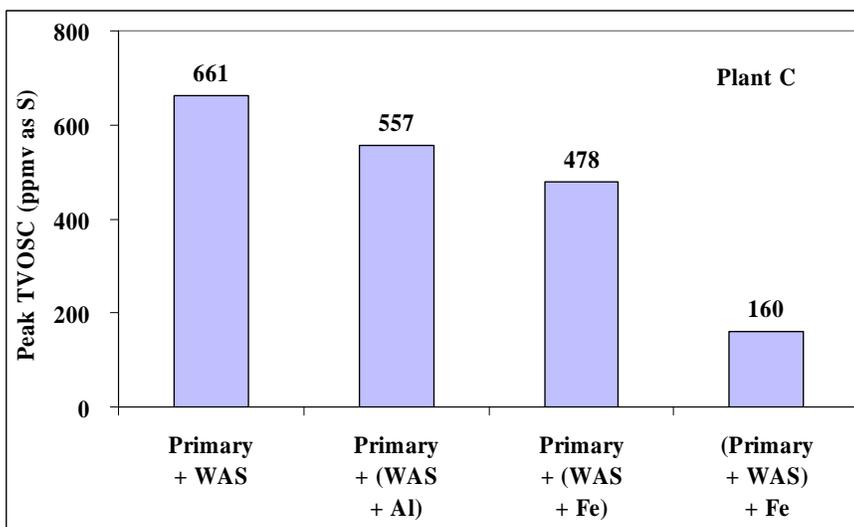
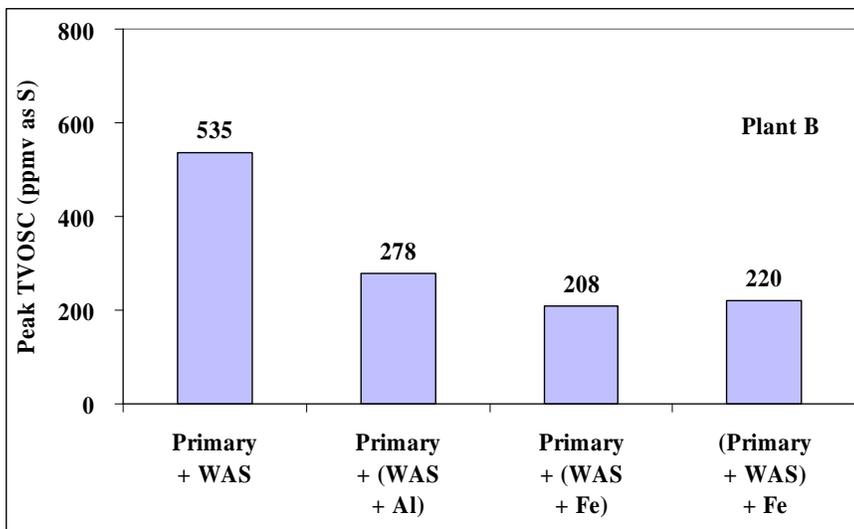
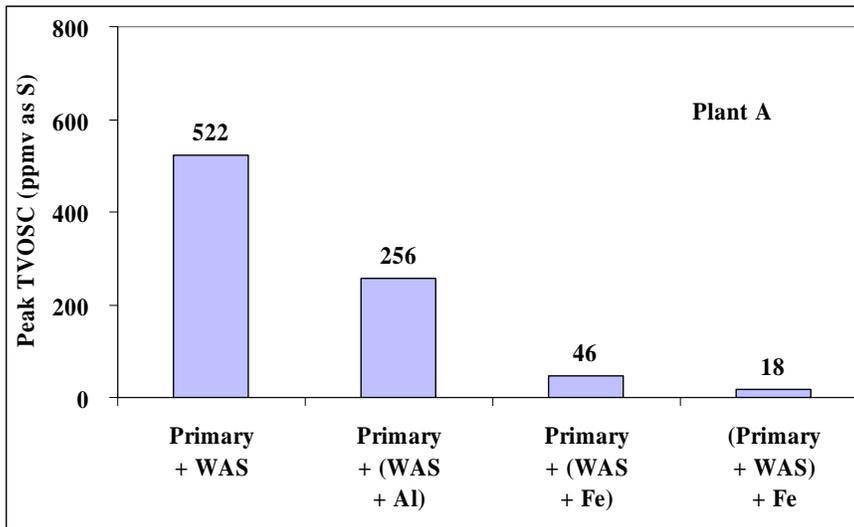
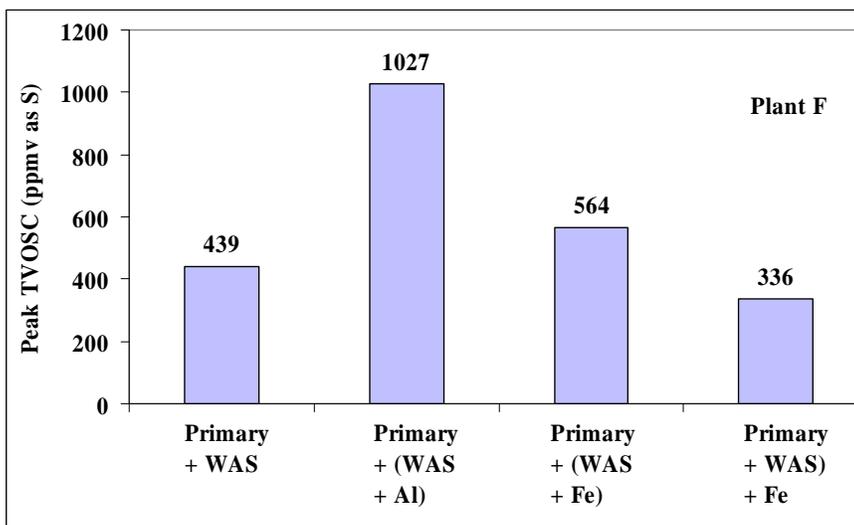
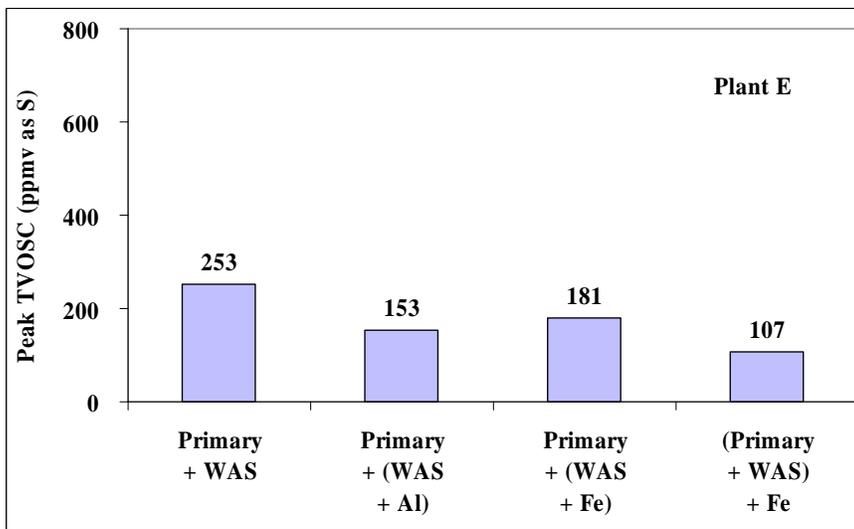
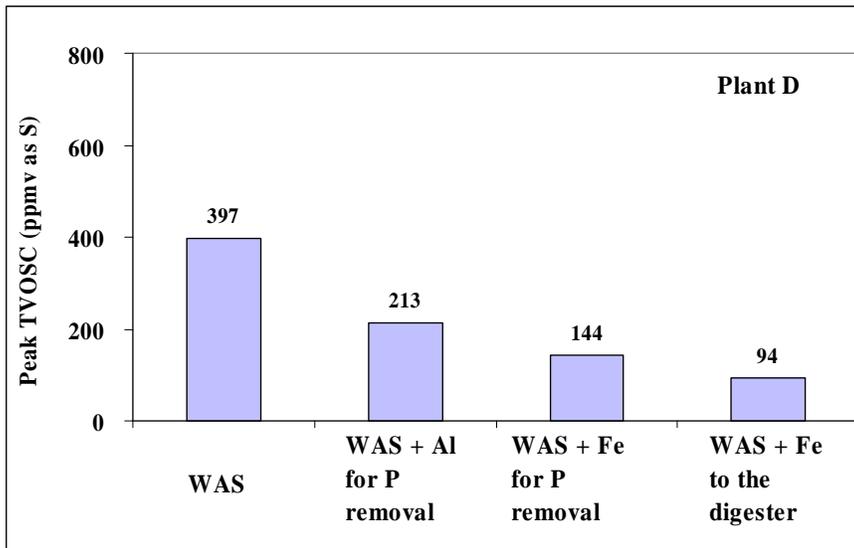


Figure 4-7. Effect of Chemical Addition on the Methanethiol Content of Sludge A.

Summary data for all the sludges tested are shown in Figure 4-8.





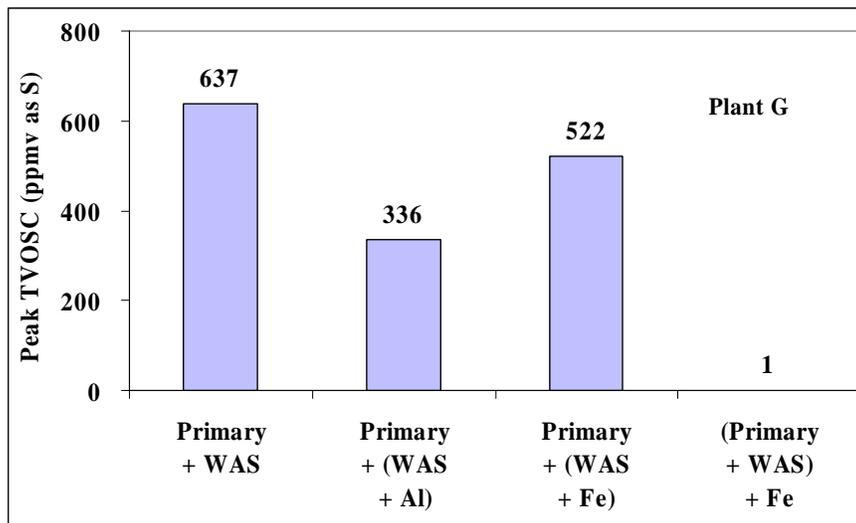


Figure 4-8. Effect of Chemical Addition on the TVOSC of All Sludges in the Study.

Lomans et al. (1999 a); Lomans (1999 b); and Lomans et al. (1999 c) showed that precipitation of sulfide as FeS is caused by addition of ferric chloride to a pure culture of *Methanococcoides hollandica*. Iron addition to the feed to a digester is frequently used for hydrogen sulfide control. Since TVOSC can be caused by microbial conversion of H₂S to methanethiol (Higgins, et al., 2007), iron addition can also be expected to reduce TVOSCs somewhat. However, the extent of removal found in this study was surprisingly large.

It can be seen that for all sludges except F, addition of iron and aluminum reduced TVOSC. In general, the lowest TVOSC was for sludges that received direct addition of iron to the digester feed. Sludge F used iron for phosphorus removal so the results for TVOSC are not unexpected. Even with the large addition of iron at this plant, addition of iron to the digester feed did reduce TVOSC somewhat. Plant E contains a high level of both iron and aluminum in the feed sludge and had the lowest TVOSC for the sludge that was not chemically treated.

When the TVOSC was compared to the influent iron and aluminum contents of the sludges, no clear trend is apparent. In Figure 4-8, the two plants, E and F, get additional iron into the plants. By replotting the data without Plants E and F (Figure 4-9), the data appear to show a weak correlation between iron and TVOSC. However, the lowest TVOSC is from Plant D with no primary and that may have influenced the data. Data from the Phase III report indicated that iron in the wastewater can influence TVOSC generation. The data in Figure 4-9 neither confirm or refute that observation. More data is needed to better clarify the role of iron in organic sulfur emissions.

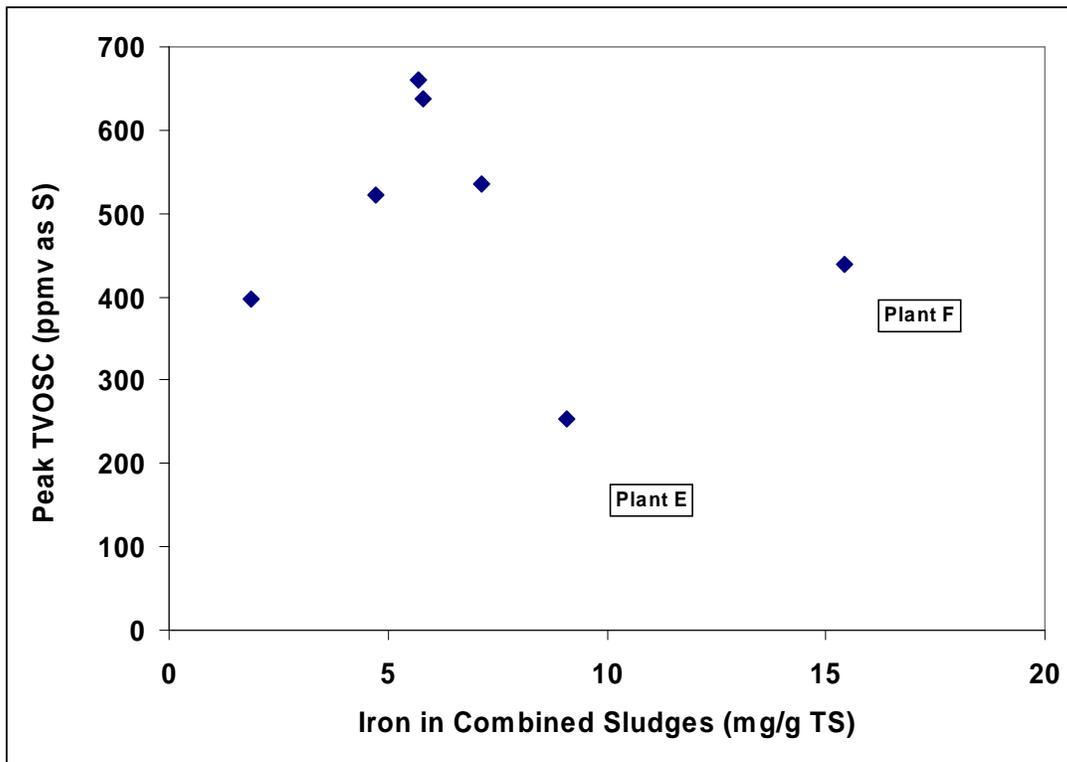


Figure 4-9. Relationship Between the Influent Iron Content and TVOSC.

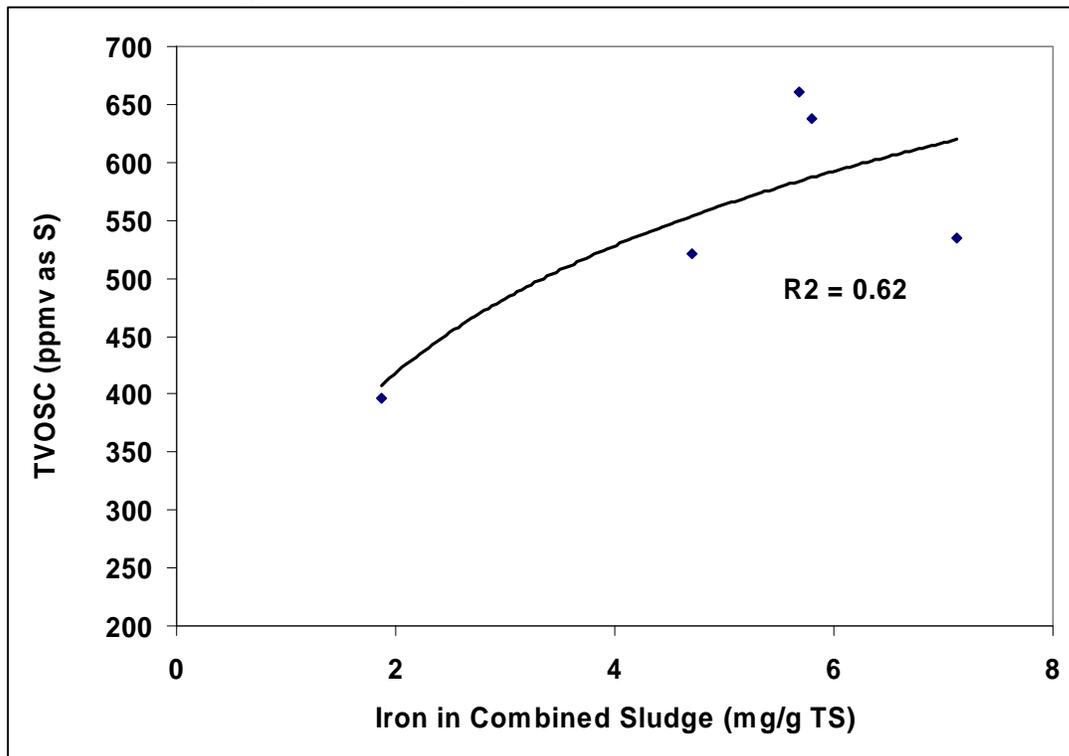


Figure 4-10. Relationship Between the Influent Iron Content and TVOSC Without Plants E and F.

These data are important because when the data from Figure 4-1 is combined with data in Figure 4-10, this suggests that a sludge that has a high volatile solids reduction cannot be expected to have a low TVOSC. This is more clearly shown for the five sludges that did not receive additional iron in the plant were plotted versus volatile solids destruction. It can be seen that as the volatile solids destruction increase, the TVOSC increases. These data are contrary to what is generally thought and also conflict with a provision in the EPA 503 regulations where a 38% volatile solids reduction by anaerobic digestion is considered to meet the requirements for vector traction. Since a major factor in vector attraction is odors, it is clear that the regulations regarding volatile solids reduction may need to be reconsidered.

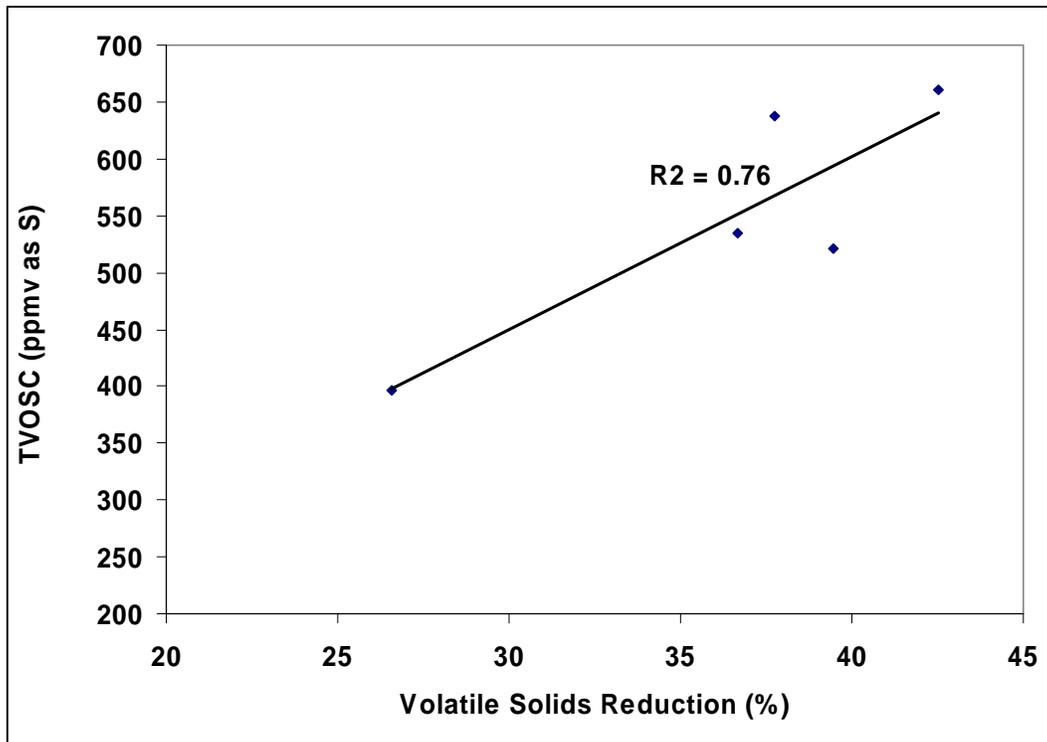


Figure 4-11. Relationship Between Volatile Solids Destruction and TVOSC without Plants E and F.

4.3 Effect of Iron and Aluminum Addition on Dewatering Properties

As part of the of the TVOSC testing, both polymer dose data and dewatered cakes solids data were obtained. The polymer used in this study, Clarifloc 3275, was a high molecular weight cationic polymer and was supplied by one of the treatment plants.

The data for the cake solids and optimal polymer dose are shown in Figures 4-11 and 4-12. It can be seen that the cake solids increase for five of the seven sludges when iron was added to the digester feed. Generally, the gain was 3% but in some cases, it was as much as 5%. For iron or aluminum added for phosphorus removal, the benefits were mixed, some cake solids

increased and some did not. Similarly, the polymer dose requirements generally decreased for sludge that received iron as part of the digester feed but did not change much when iron or

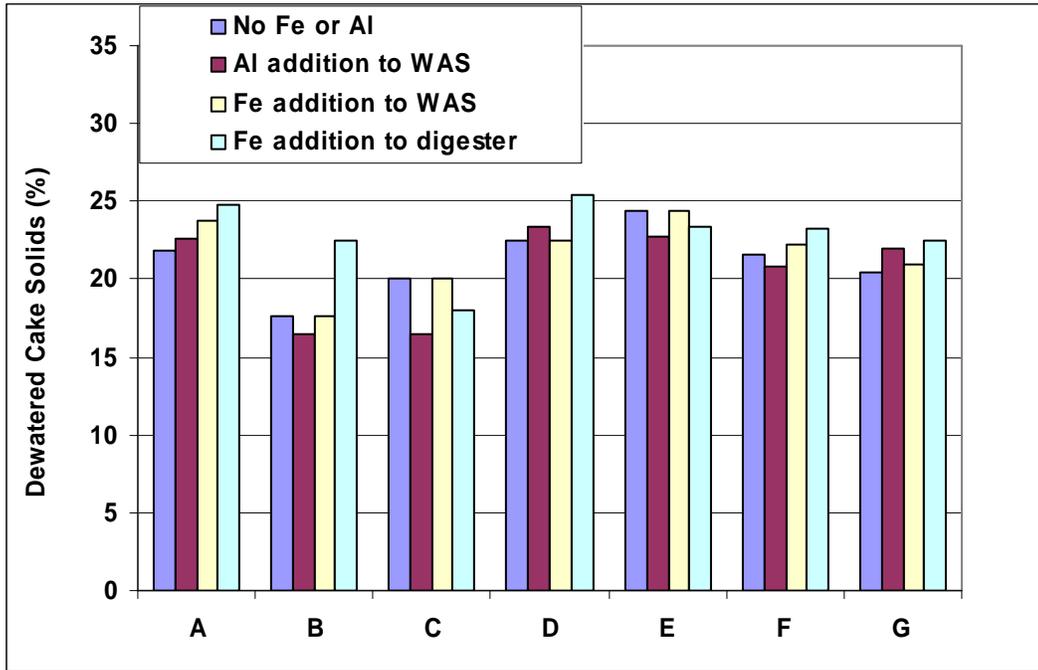


Figure 4-12. Bar Charts for Cake Solids Comparing Seven Municipal WWTPs.

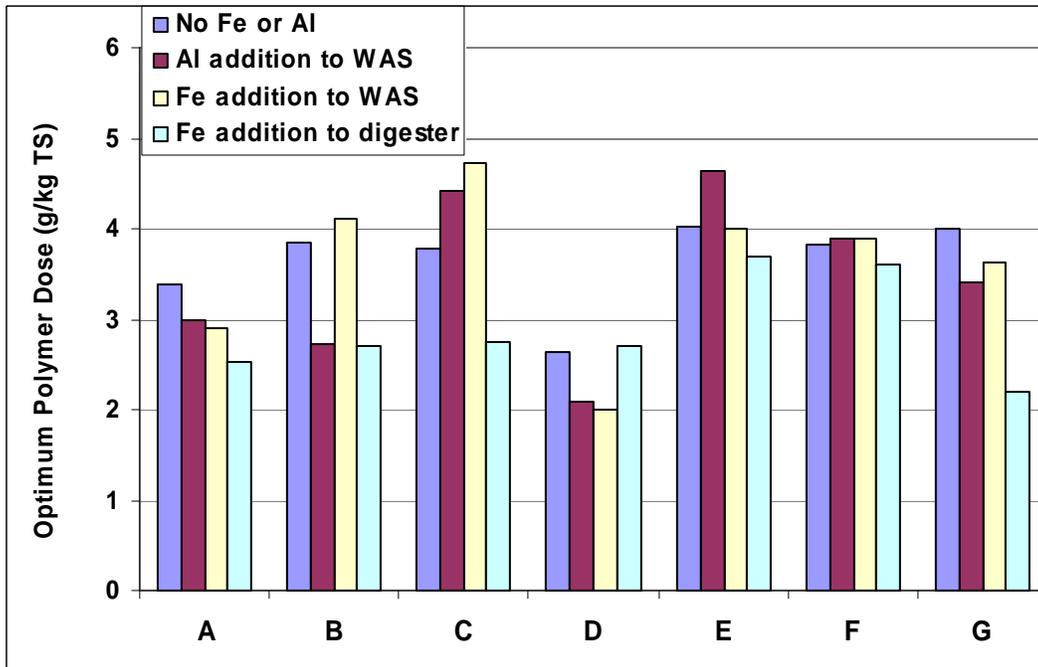


Figure 4-13. Bar Charts for Optimal Polymer Dose Seven Municipal WWTPs.

aluminum were used for phosphorus removal. In some cases, the reduction in polymer dose was dramatic, with doses decreasing by 30-40%.

The data were plotted as a function of the iron in the feed sludge, an interesting pattern emerges as shown in Figure 4-13. For the five plants that did not receive any iron in the plant, the optimum polymer dose increased as the amount of iron in the feed increased. This is consistent with data

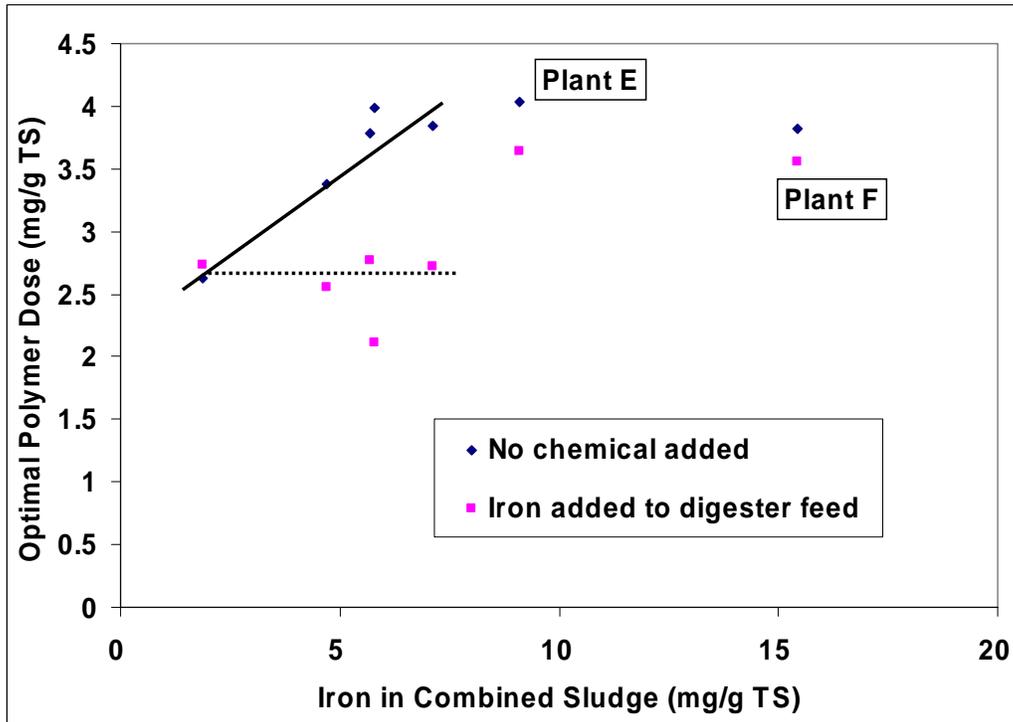


Figure 4-14. Relationship Between Influent Iron, Iron Added to the Digester Feed and Optimal Polymer Dose.

from Novak and Park. (2004) who showed that as the digestion efficiency increased, more non-degradable proteins would accumulate in solution, increasing the demand for polymer conditioning chemicals. When iron was added prior to digestion, the polymer dose decreased for all plants including plants E and F. However, the benefits for plants E and F were smaller than for the other plants. The addition of iron was most beneficial for those plants, excluding plant E and F, with the higher polymer requirement.

No relationship was found between polymer dose and the aluminum content of the raw sludges or with the additional of iron or aluminum for phosphorus removal. However, as noted in Figure 4-12, the polymer dose generally decreased when iron was added for phosphorus removal. Some of the differences in the response to iron between iron added to the digester feed and iron added for phosphorus removal is that the iron dose varied when added for phosphorus removal but was constant when added to the digester feed.

4.4 Implications for Digestion, Odors, and Dewatering

The addition of iron and aluminum in treatment plants for phosphorus removal have modest effects on digestion and dewatering. Aluminum addition reduced digestability by about 2% and iron increased volatile solids reduction for five of the seven plants. The addition of iron to the digester feed resulted in an increase in volatile solids reduction, especially for sludges A, B, C and D. For plants F and G, iron addition, either for phosphorus control or as a direct feed to the digester, resulted in lower VS destruction. Because plant F receives iron in the plant, iron addition was not expected to be beneficial. The reason for the reduced volatile solids reduction for sludge G is not known.

With regard to TVOSC impacts, all of the metal additions tended to reduce TVOSC. However, the most beneficial was direct addition of iron to the digester feed. Of the odor mitigation methods investigated in the Phase III study, direct addition of iron to the digester feed appears to be equal to or superior to these. These methods included various advanced digestion methods and the use of alum for sludge conditioning during centrifugation. For plants B, C and D, TVOSC reductions of 75-95% were seen. This finding should have major benefits for plants with high TVOSC concentrations from anaerobically digested sludge being centrifugally dewatered.

It was also seen that direct addition of iron to the digester would reduce polymer dose requirements and increased cake solids. The reductions in polymer dose were dramatic in some cases.

CHAPTER 5.0

SUMMARY AND CONCLUSIONS

5.1 Summary

In this study, the impact of iron and aluminum on volatile solids reduction by batch anaerobic digestion, on TVOSC generation from the dewatered biosolids using a simulation of centrifugal dewatering and on sludge dewatering properties was measured. This study can be considered a screening study in that it will provide a useful direction for further study of the effects of iron and aluminum on digestion, TVOSC and dewatering.

Iron and aluminum were added to WAS to simulate the addition of iron and aluminum for chemical phosphorus removal in the activated sludge system. Iron was also added directly to the combined primary and secondary sludge prior to anaerobic digestion. The iron and aluminum doses to the WAS were set at a molar ratio 3 times the molar ratio of phosphorus.

Iron and aluminum addition for phosphorus removal effected digestion, dewatering and TVOSC generation. Iron was usually generally beneficial. The major effect of aluminum was to reduce volatile solids destruction in the digestion process by about 2% for all the sludges tested. Aluminum in the feed sludge also appeared to reduce volatile solids destruction by digestion.

Direct addition of iron to the digester feed was uniformly beneficial. Iron addition increased dewatered cake solids, decreased the polymer conditioning dose and improved volatile solids reduction for most sludges, several by 5%. However, the major benefit was to reduce TVOSC generation dramatically. Iron addition to anaerobic digesters needs further study to insure that the results for these studies are also confirmed by full-scale digestion studies. However, it appears that iron addition to the digester feed could be an important tool for odor reduction from anaerobically digested, centrifugally dewatered biosolids.

5.2 Conclusions

5.2.1 The Effect of Influent Iron and Aluminum on Digestion, Dewatering, and TVOSC Production

- ◆ There was a small increase in volatile solids destruction by anaerobic digestion as the iron content of the feed sludge increased.
- ◆ Increased volatile solids destruction does not result in a decrease in TVOSC. Therefore, regulations that rely on volatile solids reduction criteria for control of vector attraction should be dropped from the EPA 503 regulations.

5.2.2 The Effect of Iron and Aluminum Added for Phosphorus Removal to Activated Sludge on Digestion, Dewatering, and TVOSC Production

- ◆ The volatile solids destruction by anaerobic digestion decreased by approximately 2% when aluminum was added to the WAS for phosphorus control.

- ◆ The volatile solids destruction by anaerobic digestion was unchanged or increased slightly when iron was added to the WAS for phosphorus control.
- ◆ The TVOSC generally decreased for both iron and aluminum addition, but iron resulted in the greatest decrease.
- ◆ Neither iron or aluminum addition to the WAS had much impact on polymer doses or cake solids.
- ◆ In general, considering volatile solids destruction, TVOSC and dewatering properties of the sludges following anaerobic digestion, ferric chloride would be a better choice for phosphorus removal in the activated sludge process than alum.

5.2.3 The Effect of Addition of Iron to the Digester Feed on Digestion, Dewatering, and TVOSC Production

- ◆ The addition of iron to the digester feed had beneficial effects on cake solids, polymer dose requirements and volatile solids destruction for most of the sludges.
- ◆ The addition of iron to the digester feed had a dramatic effect on TVOSC production, decreasing TVOSCV by 50 to over 95% for most of the sludges.
- ◆ Direct addition to the digester feed should be considered one of the important tools for TVOSC reduction in treatment plants that practice anaerobic digestion.

5.3 Recommendations for Further Study

- ◆ This research has shown that iron can play an important role in all aspects of biosolids processing and handling from odor generation to dewatering properties. Additional studies are warranted to determine if iron addition to anaerobic digesters should become more widely adopted, especially for odor control.
- ◆ The role of iron addition to primary clarifiers for enhanced primary clarification can also have additional benefits. Iron addition to primary wastewater was not included in this study but based on the data generated, it is expected to be beneficial for digestion efficiency, odor control and dewatering. This should be investigated full scale.
- ◆ The doses of iron and aluminum were not varied. Some of the results from this study, especially when iron was added to the sludge from plant F that already received iron as part of the plant operation indicates that too much iron can reduce volatile solids reduction (although it did benefit dewatering and TVOSC generation). The specific dose of iron to maximize benefits should be investigated.
- ◆ Finally, the importance of iron the raw sludges being fed to digesters should be more thoroughly investigated. Iron impacted volatile solids reduction, TVOSC generation and most surprisingly, the polymer conditioning dose and cake solids. This, if supported by additional research, would provide an important tool for designers to incorporate into their designs. This should be investigated further using full-scale plant data.

REFERENCES

- American Public Health Association. 1998. Standard Methods for Examination of Water and Wastewater; 20th Edition. Eds. L.S. Clesceri, A.E. Greenberg, and A.D. Eaton. American Public Health Association, Washington, D.C.
- Adams, G.M., Witherspoon, J., Card, T., Erdal, Z., Forbes, B., Geselbracht, J., Glindemann, D., Hargreaves, R., Hentz, L., Higgins, M. J., McEwen, and D., Murthy S. (2003) Identifying and Controlling the Municipal Wastewater Odor Environment Phase 2: *Impacts of In-Plant Operational Parameters on Biosolids Odor Quality*. Water Environment Research Foundation Report 00-HHE-5, Water Environment Research Foundation, Alexandria, VA.
- Adams, G.M., Witherspoon, J.R., Erdal, Z.K., Forbes, R.H., Hargreaves, J.R., Higgins, M.J., McEwen, D.W., and Novak, J.T. (2007) Identifying and Controlling the Municipal Wastewater Odor Environment Phase 3: Biosolids Processing Modifications for Cake Odor Reduction. *Water Environment Research Foundation, Report No.03-CTS-9T*, Alexandria, VA.
- Baillo, C.R., Cressey, G. M., and Beaupre, R.T. (1977) Influence of phosphorus removal on solids budget. *J. Wat. Pollut. Control Fed.* **49**, 131-145.
- Bivins, J.L. and Novak, J.T. (2001). Changes in Dewatering Properties Between Thermophilic and Mesophilic States in Temperature-Phased Anaerobic Digestion Systems. *Water Environ Res.*, **73**, 444–449.
- Brown J.C. and Little, L.W. (1977) Methods for improvement of trickling filter plant performance – Part II. Chemical addition. North Carolina University at Chapel Hill, National Technical Information Service, Accession No. PB 266-424, Springfield, VA.
- Chin, H.W. and Lindsay, R.C. (1994) Ascorbate and Transition – Metal Mediation of Methanethiol Oxidation to Dimethyl Disulfide and Dimethyl Trisulfide. *Food Chem.*, **49**, 387-392.
- Dentel, S.K. Conditioning. In *Sludge into Biosolids, Processing, Disposal and Utilization*, Vesilind, P.A., Spinosa, L., Eds., IWA Publishing: London, 2001, 191-205.
- Derrington, R.E., Stevens, D.H., and Laughlin, J.E. (1973) Enhancing trickling filter plant performance by chemical precipitation. U.S. EPA 670/273060.
- Dixon, L.G. and Field, P. (2004) Proceedings from the Biosolids Research Summit. Water Environment Research Foundation Project Report 03-HHE-1, Water Environment Foundation Project Report: Alexandria, VA.

Field, J.A., Field, T.M., Poiger, T., Siegrist, H., and Giger, W. (1995) Fate of Secondary Alkane Sulfonate Surfactants During Municipal Wastewater Treatment. *Water Environ. Res.*, **29**, 1301-1307.

Fritz, M. and Bachofen, R. (2000) Volatile Organic Sulfur Compounds in a Meromictic Alpine Lake. *Acta Hydrochim. Hydrobiol.*, **28**, 185-192.

Gossett J.M., Wilson J.C., Evans D.S., and McCarty P.L. (1978) Anaerobic digestion of sludge from chemical treatment. *J. Wat. Pollut. Control Fed.* **50**, 533-542.

Grady, C.P.L., Daigger, G.T., and Lim, H.C. (1998) Biological Wastewater Treatment. 2nd Ed., Marcel Dekker, Inc. New York, N.Y.

Higgins, M.J. and Novak, J.T. (1997a). The effect of cations on the settling and dewatering on activated sludges – laboratory results. *Water Environ. Res.*, **69**(2), 215-224.

Higgins, M.J. and Novak, J.T. (1997b). Dewatering and settling of activated sludges: the case for using cation analysis. *Water Environ. Res.*, **69**(2), 225-232.

Higgins, M.J., Adams, G., Card, T., Chen, Y. C., Erdal, Z., Forbes, R.H. Jr., Glindemann, D., Hargreaves, J.R., Hentz, L., McEwen, D., Murthy, S.N., Novak, J.T., and Witherspoon, J. (2004) Relationship between Biochemical Constituents and Production of Odor Causing Compounds from Anaerobically Digested Biosolids. *Proceedings of Water Environment Federation and American Water Works Association Odors and Air Emissions Conference*, Bellevue, Washington, April 18-21.

Higgins, M.J., Chen, Y.-C., Yarosz, D.P., Murthy, S.N., Maas, N.A., Cooney, J.R., Glindermann, D., and Novak, J.T. (2006) Cycling of volatile organic sulfur compounds in biosolids and its implications for odors. *Water Environ. Res.*, **78**(3), 243-252.

Higgins, M.J., Murthy, S.N., Striebig, B., Hepner, S., Yamani, S., Yarosz, D.P., and Toffey, W. (2002) Factors Affecting Odor Production in Philadelphia Water Department Biosolids. *Proceedings of Water Environment Federation Odors and Toxic Air Emissions 2002 Specialty Conference*, Albuquerque, NM, April 28-May 1.

Kelly, D.P. and Smith, N.A. (1990) Organic Sulfur Compounds in the Environment: Biogeochemistry, Microbiology, and Ecological Aspects. In *Advances in Microbial Ecology 11*, Marshall, K. C. (Ed.); Plenum Press: New York.

Lehninger, A.L., Nelson, D.L., and Cox, M.M. (1993) *Principles of Biochemistry*. Worth Publishers: New York.

Lomans, B.P., Maas, R., Luderer, R., Op den Camp, H.J.M., Pol, A., Van Der Drift, C., and Vogels, G.D. (1999 a) Isolation and Characterization of *Methanomethylovorans hollandica* gen.nov., sp.nov., Isolated from Freshwater Sediments. *Appl. Environ. Microbiol.*, **65**, 3641-3650.

Lomans, B.P., Op den Camp, H.J.M., Smolders, A.J.P., Pol, A., Van Der Drift, C., and Vogels, G.D. (1999 b) Role of Methanogens and Other Bacteria in Degradation of Dimethyl Sulfide and Methanethiol in Anoxic Freshwater Sediments. *Appl. Environ. Microbiol.*, **65**, 2116-2121.

Lomans, B.P., Op den Camp, H.J.M.; Pol, A., and Vogels, G.D. (1999 c) Anaerobic versus Aerobic Degradation of Dimethyl Sulfide and Methanethiol in Anoxic Freshwater Sediments. *Appl. Environ. Microbiol.*, **65**, 438-443.

Lomans, B.P., Luderer, R., Steenbakkens, P., Pol, A., Van Der Drift, C., Vogels, G.D., and Op Den Camp, H.J.M. (2001) Microbial Populations Involved in Cycling of Dimethyl Sulfide and Methanethiol in Freshwater Sediments. *Appl. Environ. Microbiol.*, **67**, 1044-1051.

Metcalf and Eddy, Inc. (1991) Wastewater Engineering: Treatment, Disposal, and Reuse. 3rd Ed., McGraw Hill Inc., New York, NY.

Murthy, S.N., Forbes, B., Burrowes, P., Esqueda, T., Glindemann, D., Novak, J., Higgins, M.J., Mendenhall, T., Toffey, W., and Peot, C. (2002) Impact of High Shear Solids Processing on Odor Production from Anaerobically Digested Biosolids. *Proceedings of the 75th Annual Water Environment Federation Technical Exposition and Conference*, Chicago, Illinois, September 28-October 2, Water Environment Federation: Alexandria, VA.

Murthy, S.N., Higgins, M.J., Chen, Y.C., Toffey, W., and Golembeski, J. (2003) Influence of Solids Characteristics and Dewatering Process on VSC Production from Anaerobically Digested Biosolids. *Proceedings of the Water Environment Federation and American Water Works Association Annual Biosolids and Residuals Conference*, Baltimore, Maryland, February 19-22; Water Environment Federation: Alexandria, VA.

Murthy, S.N., Novak, J.T., and Holbrook, R.D. (2000) Optimizing Dewatering of Biosolids from Autothermal Thermophilic Aerobic Digesters (ATAD) Using Inorganic Conditioners. *Water Environ. Res.*, **72**, 714.

Novak, J.T. (2006) Dewatering of Sewage Sludge, *Drying Technology*, **24**, 1257-1262.

Novak, J.T., Muller, C.D., and S. N. Murthy (2001) Floc structure and the role of cations, *Water Sci. Tech*, **44**(10), 209-213.

Novak, J.T., Adams, G., Chen, Y.-C., Erdal, Z., Forbes, R.H. Jr., Glindemann, D., Hargreaves, J.R., Hentz, L., Higgins, M.J., Murthy, S.N., and Witherspoon, J. (2006) Generation pattern of sulfur containing gases from anaerobically digested sludge cakes, *Water Environment Res.*, **78**(8), 821-827.

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.

Novak, J.T., Murthy, S.N., and Higgins, M.J. (2002). Floc structure and its impact on conditioning, dewatering and digestion. *Proceedings WEFTEC 2002, Chicago, IL Sept. 30-Oct. 3*.

- Novak, J.T., Verma, N., and Muller, C.D. (2007) The role of iron and aluminum in digestion and odor formation, *Water Science & Technology*, **56**(9), 59-65.
- Park, C. (2002). MS Thesis, Virginia Polytechnic Inst & State University, Blacksburg, VA.
- Park, C., Abu-Orf, M.M., and Novak, J.T. (2006) “Predicting the Digestability of Waste Activated Sludges” *Wat Envr Res*, **78**, 1, 59-68.
- Park, C. and Novak, J.T. (2007). Characterization of activated sludge exocellular polymers using several cation-associated extraction methods. *Water Res.*, **41**(8), 1679-1688.
- Park, C., Abu-Orf, M.M., Muller, C., and Novak, J.T. (2006). The effect of cations on activated sludge characteristics: analysis and effects of iron and aluminum in floc. *Water Environ. Res.*, **78**(1), 31-40.
- Parliament, T.H., Kolor, M.G., and Rizzo, D.J. (1982) Volatile Components of Limburger Cheese, *J. Agric. Food Chem.*, **30**, 1006-1008.
- Persson, S., Edlund, M-B., Claesson, R., and Carlsson, J. (1990) The Formation of Hydrogen Sulfide and Methyl Mercaptan by Oral Bacteria. *Oral Microbiol. Immunol.*, **5**, 52.
- Pfeffer J.T. and White J.E. (1964) The role of iron in anaerobic digestion. *Proc. Nineteenth Ind. Waste Conf., Purdue Univ.* 887-901.
- Prentice, R.D.M. and Bryce, J.H. (1998) A Source of Dimethyl Disulfide and Dimethyl Trisulfide in Grain Spirit Produced with a Coffey Still. *J. Am. Soc. Brew. Chem.*, **56**, 99-103.
- Rudolfs, W. and Setter, L.R. (1931) After-effect of ferric chloride on sludge digestion. *Sewage Works J.* **3**, 352-361.
- Rudolfs, W., Baumgartner, W.H., and Setter L.R. (1932) Effect of coagulants on sludge digestion. *Sewage Wks J.* **4**, 628-636.
- Smith, J., 2006. An investigation into the anaerobic digestibility of iron-dosed activated sludge. Ph.D. thesis, University of Birmingham.
- Smith, J.A. and Carliell-Marquet, C.M., The digestibility of iron-dosed activated sludge, *Bioresour. Technol.* (2008), doi: 10.1016/j.biortech.2008.04.005.
- Tulio, A.Z., Yamanaka, J., Ueda, Y., and Imahori, Y. (2002) Formation of Methanethiol and Dimethyl Disulfide in Crushed Tissues of Broccoli Florets and their Inhibition Freeze – Thawing. *J. Agric. Food Chem.*, **50**, 1502-1507.

U.S. EPA (1975) Process design manual for suspended solids removal. U.S. Environmental Protection Agency Technology Transfer Series, *EPA 625/175003a*.

Zitomer, D.H., Owens, D., and Speece, R.E. (2000) Methanethiol Production as an Indicator of Toxicity in Anaerobic Treatment. *Water Sci. Technol.*, **42**, 231-235.

Zitomer, D.H. and Speece, R.E. (1995) Methanethiol in Nonacclimated Sewage Sludge after Addition of Chloroform and Other Toxicants. *Environ. Sci. Technol.*, **29**, 762-768.

