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EVALUATION OF ALUMINUM AND
IRON ADDITION DURING
CONDITIONING AND DEWATERING
FOR ODOR CONTROL

PHASE IV

by:

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ABSTRACT AND BENEFITS

Abstract:

The objectives of this research were to investigate the factors impacting the effectiveness of metal salts in reducing the production of volatile organic sulfur compounds (VOSCs) in biosolids, with the goal of developing recommendations for applying metal salt addition in the field for odor reduction. The research examined a number of factors which could impact the effectiveness of metal salt addition which included chemical dosage, types of chemicals, location of the addition point, the shear applied to the solids, and different biosolids sources. The results showed that metal salt addition can reduce VOSC production, but their effectiveness is especially impacted by the shear applied to the biosolids. Greater amounts of shear resulted in greater dosages required to achieve VOSC reduction. Comparison of different metals including, alum, polyaluminum chloride, sodium aluminate, ferric chloride, ferrous chloride, ferric sulfate, ferrous sulfate, zero-valent iron and magnesium chloride showed that all could reduce VOSC production, and some worked slightly better than others, but none were clearly superior to the others. In special cases where a biosolids produced higher quantities of hydrogen sulfide, addition of iron based chemicals generally had lower hydrogen concentrations than aluminum based chemicals, likely due to iron-sulfide precipitation. However, addition of sodium aluminate also reduced hydrogen sulfide, mainly due to the increased pH above which hydrogen sulfide volatilizes. Little differences were found when comparing the chemical addition points during conditioning, either before, with, or after the polymer. Addition directly to the cake was also effective. The addition of metal salts can be applied to reduce the production of odorants, although it is difficult to predict the dosage that will be required without laboratory and possibly pilot testing.

Benefits:

- ◆ Provides a better understanding of the impact of shear on VOSC production.
- ◆ Provides an improved understanding of the interactions of metal salts, biosolids, and shear, and the effectiveness of metal salt addition for reducing odorant production.
- ◆ Demonstrates that the different forms of aluminum and iron such as alum, polyaluminum chloride, sodium aluminate, ferric chloride, ferrous chloride, etc., had similar effects on TVOSC control, some performing better than other under different conditions.
- ◆ Demonstrates the benefits of metal salt addition for reducing polymer demand and VOSC production.
- ◆ Provides recommendations and guidance for applying metal salts in the field for controlling odors.

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

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LIST OF ACRONYMS

CST	capillary suction time
DMS	dimethyl sulfide
DMDS	dimethyl disulfide
HSCSP	high solids centrifuge simulation procedure
MGD	million gallons per day
MT	methyl mercaptan or methanethiol
OPD	optimum polymer dose
PWD NE	Philadelphia Water Department – Northeast Plant
PWD SW	Philadelphia Water Department – Southwest Plant
SG	Selinsgrove Plant
TVOSC	total volatile organic sulfur compounds (mainly MT and DMS)
VOSC	volatile organic sulfur compounds
ZVI	zero valent iron

EXECUTIVE SUMMARY

A series of experiments were performed to examine the impact of metal salt addition on the production of a key group of odor causing compounds, the volatile organic sulfur compounds (VOSCs) which are mainly methyl mercaptan and dimethyl sulfide. Hydrogen sulfide was also investigated. The goal was to investigate the factors which impact the effectiveness of the metal salt addition in reducing odorant production, with an overall goal of developing recommendations for practitioners that would like to implement metal salt addition for odorant reduction. The project investigated the following factors:

- ◆ effect of shear
- ◆ effect of chemical dosage
- ◆ effect of chemical addition location
- ◆ effect of chemical types
- ◆ effect of different sludge types

The results showed that metal salts could reduce VOSC production when added to biosolids either during conditioning and dewatering or directly to the cake after dewatering. During conditioning and dewatering, addition either before, after, or simultaneously with the polymer had similar effects on reducing VOSCs. However, addition of the metals after the polymer caused a deterioration in dewaterability and increased the polymer demand, while addition prior to or with the polymer reduced the polymer demand. The results showed that the chemical dosage required for odorant reduction varied based on several factors, especially the shear applied to the solids. For example, the testing showed that as the shear applied to the solids increased, the production of VOSCs also increased. As a result, the dosage required to achieve the same level of VOSC reduction also increased. The results agree with and help explain some of the previously reported field results from the prior WERF biosolids odor project and other published field trials.

Different metal salts were examined and included aluminum sulfate, polyaluminum chloride, sodium aluminate, ferric chloride, ferric sulfate, ferrous chloride, ferrous sulfate, zero-valent iron, and magnesium chloride. All had the ability to reduce odorant production, but some variability was observed, although none was clearly better than the others. However, in circumstances when a biosolids produced hydrogen sulfide and was low in iron, addition of aluminum sulfate (alum) could increase the hydrogen sulfide released, while addition of iron would help keep hydrogen sulfide concentrations lower, presumably through iron-sulfide precipitation.

The complicated interactions between the metals, polymer, shear, and solids properties make it difficult to predict the best dosages and chemicals for a given scenario, but through laboratory and pilot testing, reduction in odorant production can be achieved.

Additional research is suggested to further explore chemical addition, and especially to examine mixtures of chemicals that could attack the odor problem from multiple mechanistic levels and field implementation.

CHAPTER 1.0

INTRODUCTION

1.1 Overview of Odors and Effect of Metals

1.1.1 Project Background

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). 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. In one part of the work, Dr. John Novak of Virginia Tech examined the impact of iron and aluminum addition either before or during digestion on both digestion processes and odors produced from dewatered cake. The Novak team examined three distinct locations for the iron and/or aluminum addition. 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.

In this portion of the study performed at Bucknell University, the researchers examined the impact of chemical addition after digestion, either as a chemical conditioning agent during dewatering or directly to the cake.

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 (Chen et al., 2006, Higgins et al., 2006, Kim et al., 2003, Novak et al., 2006). Research has shown that most of these compounds can be produced during microbial degradation of bioavailable protein (Chen et al., 2006, Higgins et al., 2006, Adams et al., 2004). 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 OCCs.

1.1.2.1 Effect of Alum

Preliminary research was performed by the WERF odor research team to investigate the efficacy of alum addition on odorant reduction. The experiments used a laboratory high solids centrifuge simulation procedure to produce cakes with similar odorant profiles as full scale centrifuge cakes. The addition of alum greatly reduced the odorant production in these laboratory trials. For example, the production of total volatile organic sulfur compounds (includes methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) for alum added samples are shown in

Figure 1-1. The results show that addition of alum can greatly reduce odorant production. Several other laboratory trials produced similar results.

Based on these laboratory results, a field trial was undertaken to verify the effect of alum addition at a full-scale facility. Alum was added prior to the polymer addition, and samples of cake and centrate were collected for each alum dosage. The TVOSC production profile for the different alum dosages for one of the trials is shown in Figure 1-2. The addition of alum reduced the TVOSC production, and at the highest dosage the reduction was greater than 50%. However, the results were not as good as the laboratory scale trial. There are several possibilities to explain the differences. First, in the lab trial the alum and polymer were added together, and mixed at a defined shear rate. In the field trial, alum was added upstream of the polymer, and allowed to mix into the sludge prior to the polymer addition. Although this may seem like a small difference, the mixing regime and addition points play an important role in the effects of alum coagulation. The field trial results also showed a larger impact on inhibiting the methanogenic activity as shown in Figure 1-3. Inhibition of methanogens has been shown to increase TVOSC production, in general, although in the case of alum or iron addition, methanogens can be inhibited and TVOSC production can be reduced through protein binding and inhibition of the TVOSC producers. The results indicated that the decrease in pH was likely important in the inhibition of the methanogens, which would counterbalance the beneficial impact of protein binding.

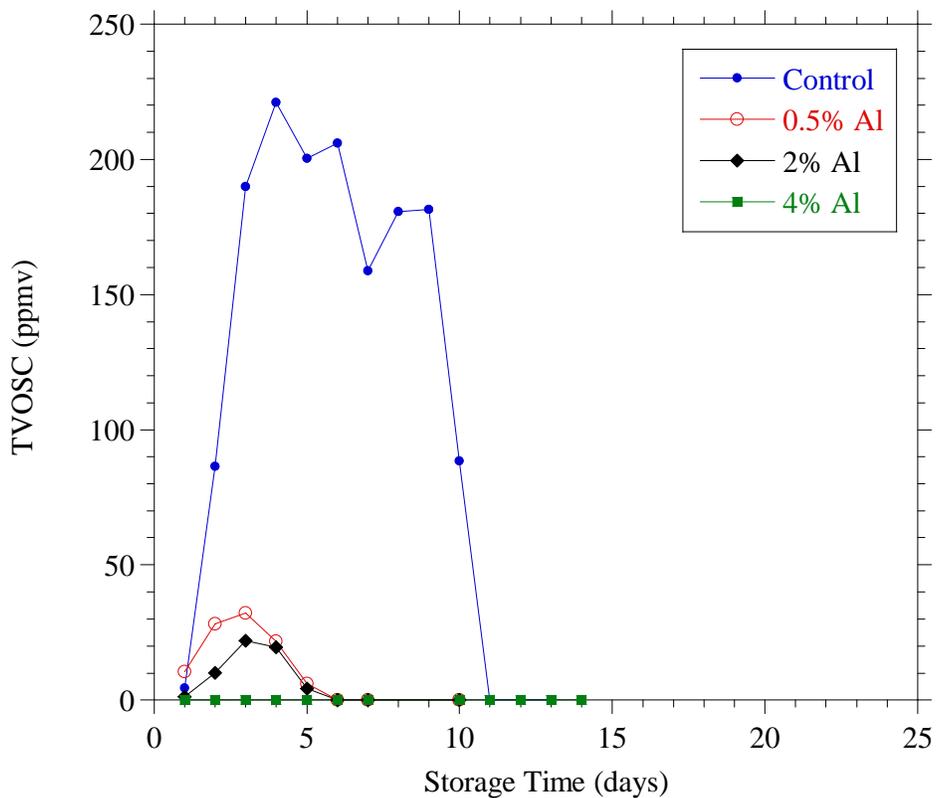


Figure 1-1. Effect of Alum Addition on TVOSC Production in Laboratory Trial.

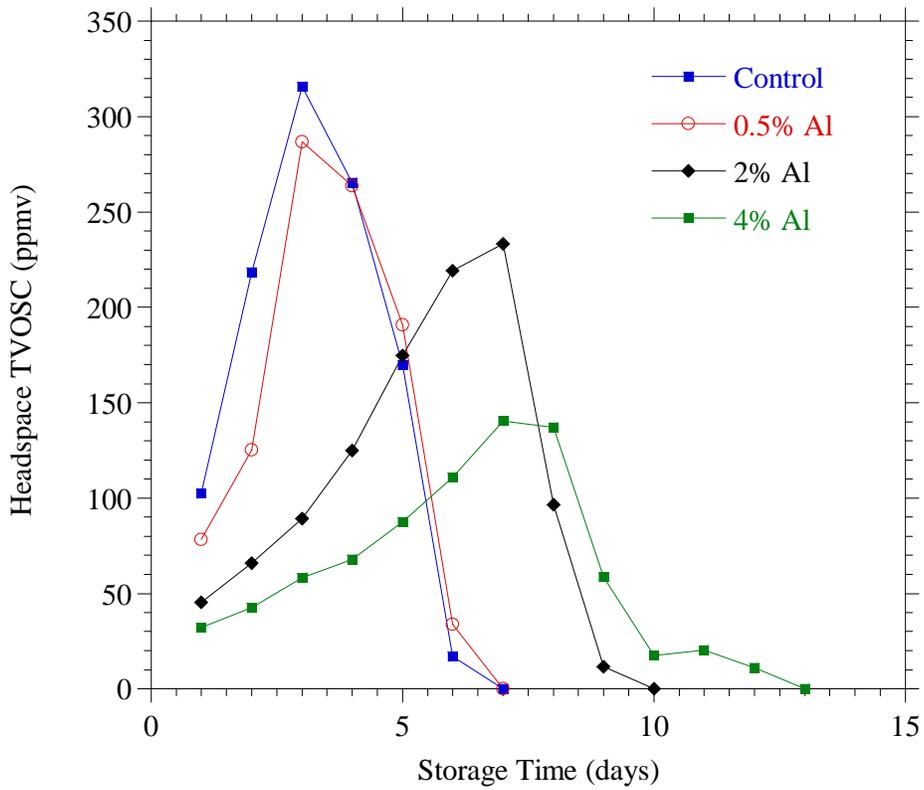


Figure 1-2. Effect of Alum Addition on TVOSC Production in a Field Trial at PWD.

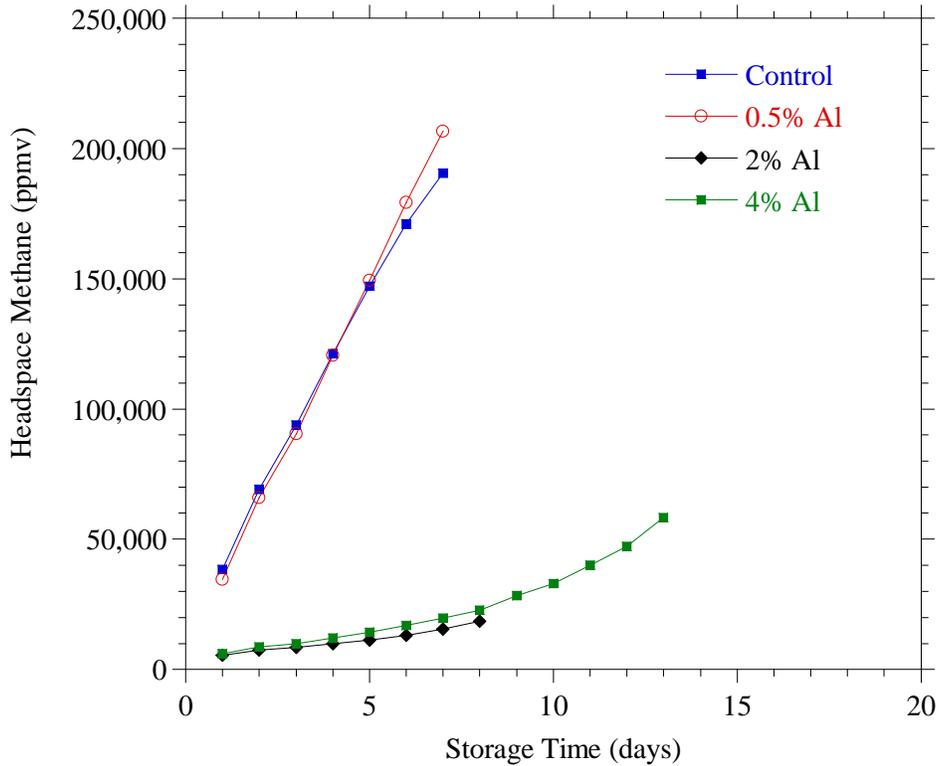


Figure 1-3. Effect of Alum Addition on Methane Production for Field Trial.

1.1.2.2 Effect of Iron

Similar to alum, iron addition has had mixed results. In a full-scale trial at the Philadelphia Biosolids Recycling Center, addition of ferric chloride prior to dewatering had a significant beneficial impact on the reduction of odorants from their Southwest (SW) Plant digested solids, namely DMS, and odor measured by an odor (Higgins et al., 2002). In contrast, the results from the NE plant did not show a similar effect. A follow up study to examine additional dosages on SW biosolids also showed relatively good reductions in MT. A similar comparison to San Francisco data collected as part of the WERF odor studies shows that iron addition potentially reduced odors. The results are separated by about two years, but the second sample set was after iron addition had been implemented, which shows a significantly lower concentration of TVOSCs being produced. In contrast, results from the WERF Phase III Odor Study (03-CTS-9T) did not show clear benefits to addition of iron at the Charlotte-Mecklenburg facility. The contradictory results from iron are likely related to the issues of sludge properties, location of iron addition, and polymer-iron interactions. It is critical to understand these factors in order to use these chemicals effectively for odor control

The mixed results from iron and alum addition indicate that metal addition holds promise for controlling odors, however, several important parameters need to be investigated in order to use these chemicals efficiently and effectively for odor control. Primarily, the effect and interactions between chemical addition point, mixing intensity, chemical species, sludge characteristics and polymer characteristics are not well understood for this application, and additional research is needed to clarify how these factors affect cake quality in terms of odor production, and potentially fecal coliform regrowth.

1.2 Research Objectives and Significance

The objectives of this research are to determine the impact of the following parameters on odorant production:

- ◆ Shear
- ◆ Chemical dosage
- ◆ Chemical addition location
- ◆ Chemical types
- ◆ Different biosolids samples from different locations

The research is critical to moving forward with potential solutions to the cake odors. Metal addition has shown promise for controlling odors in biosolids, however, several issues need to be investigated to optimize its use for this purpose. Metal addition could provide a cost effective, easy to implement method that could be used by utilities to control odors. This would reduce nuisance complaints for land application programs, and potentially increase beneficial reuse options for utilities.

CHAPTER 2.0

RESEARCH APPROACH AND METHODS

2.1 Research Approach

2.1.1 Overview

The research investigated the impacts of metal addition on the production of the key odorants, volatile organic sulfur compounds, which included methyl mercaptan (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). The total volatile organic sulfur compound (TVOSC) concentration was considered as the sum of these constituents (see Adams et al., 2008). A number of factors were evaluated which included:

- ◆ Effect of shear
- ◆ Effect of chemical dosage
- ◆ Effect of chemical addition location
- ◆ Effect of chemical type
- ◆ Effect of different sludge types

The laboratory trials that added metals during conditioning used the high solids centrifuge simulation process developed at Bucknell University which produces a cake with similar odorant production as full-scale centrifuges. This allowed complete control of the experimental regime. A detailed description of the method is available in Higgins et al. (2007). The following sections outline the different tests that will be performed, and the attached documents provide the suggested sample matrix for the four different sludge samples that will be tested.

In other tests, samples of cake were collected directly from centrifuges or belt filter presses and the chemicals were added directly to the cake as described below. Table 2-1 provides a summary of the relevant plant information where samples were obtained. Samples were collected from four different plants, all treatment mostly municipal wastewaters, although PWD NE had a higher industrial input. The plants all used mesophilic anaerobic digestion, one plant with pre-pasteurization before digestion and they dewatered with either belt filter press or centrifuges.

Table 2-1. Summary of Plant Data for Sampling Locations.

Plant Location	Digester Feed and Notes	Digestion Type	Dewatering Equipment
Selinsgrove (SG)	Primary and Secondary Mix	Conventional Mesophilic Anaerobic Digestion, Typical SRT = 30 days	Belt Filter Press
Philadelphia Water Dept. – South West (PWD SW)	Primary and Secondary Mix	Conventional Mesophilic Anaerobic Digestion, Typical SRT = 18 days	High and Low Solids Centrifuges
Philadelphia Water Dept. – North East (PWD NE)	Primary and Secondary Mix, greater industrial inputs	Conventional Mesophilic Anaerobic Digestion, Typical SRT around 20 days	High and Low Solids Centrifuges
Plant 4	Primary and Secondary Mix	Pre-pasteurization followed by Mesophilic Anaerobic Digestion with SRT = 15 days	High Solids Centrifuges

2.1.2 Metal Addition Point or Sequence

Previous research in the laboratory has used simultaneous alum and polymer addition which was proven to be effective in controlling odors. However, the field trial used alum addition prior to polymer addition, and was less effective. The interaction of polymer and alum/iron for binding of protein may be very important for controlling odors. Research has shown that cationic polymers used for conditioning of sludges prior to dewatering bind solution phase protein (Higgins et al., 2005, Novak et al., 2003). It is thought that polymer bound protein is bioavailable. Since alum and iron can also bind protein, the sequence of events that lead to binding of protein may greatly impact the bioavailability of the protein. Metals may play a role in forming a protein-polymer-metal matrix which reduces the bioavailability of the protein, and the timing of the metal addition could be important. A series of experiments will be performed to examine the effect of metal and polymer addition sequence. The experiments will examine the effect of adding alum or iron before, after, and simultaneously with the polymer. All other parameters will be held constant. The experiment will be performed on three different sludges for comparison.

2.1.3 Mixing or Shear Intensity

Mixing of metal coagulants is an important parameter which will impact its behavior as a coagulant and it may also be important for binding of protein and its bioavailability. A series of experiments will be performed to examine the effect of mixing intensity on the ability of alum or iron to bind protein and affect protein bioavailability. The mixing parameter G , known as the velocity gradient, was used to quantify mixing shear, and a value of about 30,000 was used for most of the testing, with additional shear applied to the cake for comparisons. WERF funded research that examined the effect of shear on polymer demand and dewatering was performed at Bucknell University, therefore, the setup and equipment was available to do these tests.

2.1.4 Chemical Forms of Al and Fe

The laboratory and field trials were performed using alum as the source of Al, and ferric chloride as a source of Fe. One disadvantage of alum is that it will decrease the pH of the solution, which was evident in the field trial. Several other forms such as polyaluminum chloride (PAC) and sodium aluminate are potential alternatives which could act to bind protein, but have less effect on the solution pH. This may reduce the inhibition of methanogens, and thereby result in better odor reductions. Similarly, other forms of iron such as iron sulfate will also be investigated. A series of trials will be performed using side-by-side comparisons of the different chemical forms.

2.2 Experimental and Analytical Methods

2.2.1 Conditioning and Dewatering Experiments

A protocol for conditioning, dewatering, and processing solids was developed that generates a cake with a similar odor production profile as a high solids centrifuge. This process is termed the high solids centrifuge simulation process (HSCSP), and was used in previous WERF odor related research. The step-by-step procedure for conditioning and dewatering is provided below.

Conditioning with Chemical Addition During conditioning, the chemical was added either before, after or simultaneously with the cationic polymer used for conditioning. Typically, the polymer was provided by the plant for which the study was being performed. One liter of solids is placed in a baffled reactor, and polymer is added to the solution. The sludge is mixed at a predefined mixing intensity and time, to achieve a given energy input or shear. After mixing, the capillary suction time (CST) is measured to determine the dewaterability of the solids (APHA, 1998). This process is repeated with varying polymer dosages until the optimum polymer dose is obtained, as measured by the polymer dose that produces the minimum CST.

When the chemical was added prior to polymer addition, the chemical was added and mixing was performed for 30 seconds at 200 rpm at which time the polymer was added to the solution and mixed for another 30 s at 200 rpm then 50 rpm for 90 s. The mixing regimes for each scenario are shown in Figure 2-1 to 2-3. In each case, the total shear imparted to the solids was the same and the Gt value for this mixing regime was approximately 30,000.

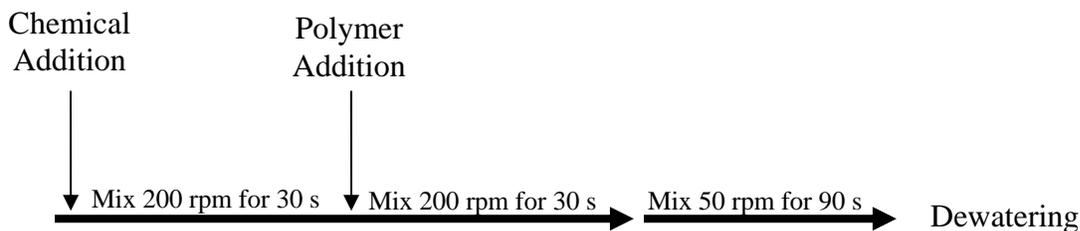


Figure 2-1. Mixing Regime for Chemical Addition Before Polymer.

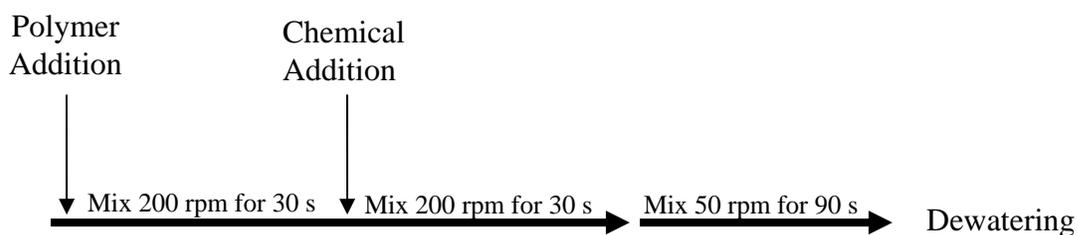


Figure 2-2. Mixing Regime for Chemical Addition After Polymer Addition.

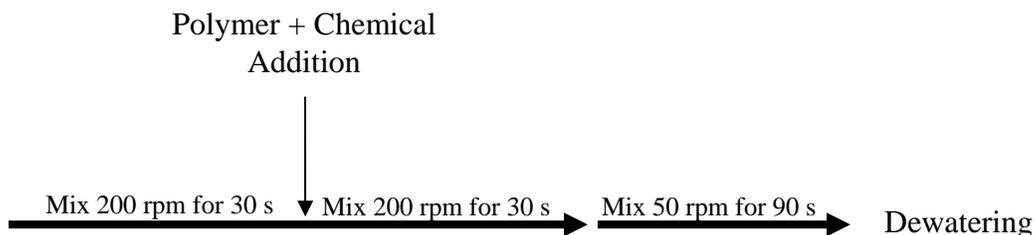


Figure 2-3. Mixing Regime for Chemical Addition Simultaneously with Polymer Addition.

Dewatering The sludge conditioned with the optimum polymer dose is then placed in 250 mL centrifuge bottles, and dewatered using a laboratory centrifuge at 3000 x g, for 10 minutes. After centrifuging, the supernatant is removed (this centrate can be analyzed for different constituents as well), and the cake is combined from the different tubes. Typically, about 200-300 g of wet cake is generated, with solids contents around 25%. Higher cake solids can also be obtained with additional dewatering using a belt filter press simulator.

Processing Next, the wet cake samples are processed to simulate the high shear experienced in the full scale centrifuge. To do this, the cake is processed through a meat-grinder apparatus that

pushes the cake forward using a scroll-conveyor, followed by extrusion through a small opening at the end of the conveyor.

Direct Addition to Cake In several experiments, the chemical was added directly to the cake. In this case, the chemical was added to the cake at the prescribe dosage and mixed for 40 s in a standard bench mixer as described by North et al., (2008) to assure complete mixing. A control sample was also mixed for 40 s without chemical addition to eliminate the mixing variable.

Headspace Serum Bottles For the study to investigate the effect of chemical addition location and chemical dose, cake storage experiments were performed to mimic the conditions present in a biosolids storage pile. In general, the inside of a storage pile has little gas transfer and can be considered anaerobic. To accomplish this, ten grams of wet cake were placed in 125 mL Wheaton serum bottles after the appropriate treatment. The serum bottles were sealed using 20 mm Teflon faced butyl rubber septa, tear-off aluminum caps and a crimper. The serum bottles were stored at a 25°C. Samples were withdrawn by a syringe each day for headspace analysis by gas chromatography as discussed below.

2.2.2 Headspace Gas Analysis

VOSCs and methane were measured in the headspace of the serum bottles on a regular basis during storage. Headspace gas chromatography was performed using a Hewlett Packard 5890A Gas Chromatograph equipped with a flame ionization detector (FID). A Restek RT-Sulfur packed column measuring 2 m long with an inside diameter of 32 mm was used. Both the injection port and detector temperatures were 200°C. Zero nitrogen was used as the carrier gas at a flow-rate of 20 mL per minute. Zero air and zero hydrogen were supplied to the FID at flow rates of 450 mL/min and 20 mL/min respectively. All gases were purchased from Airgas Inc. The duration of each sample run was 18 minutes. During the run, initially, the oven temperature is held at 100°C for 3 minutes followed by an increase to 220°C at a rate of 15°C per minute. This temperature was then maintained for 7 minutes, completing the run. Headspace samples were taken from the reactor vessels using a Hamilton 1 mL gas-tight locking syringe. One mL of headspace was manually injected into the gas chromatograph for VOSC analysis. Volatile sulfur compounds were identified and quantified by comparing the experimental chromatograms to those of pure standards.

Hydrogen sulfide was measured using GC with a flame photometric detector which is a sulfur specific detector.

CHAPTER 3.0

FIELD SAMPLING AND EFFECTS OF DIGESTION AND DEWATERING: RESULTS AND DISCUSSION

3.1 Research Results

3.1.1 Overview of Dosages and Experimental Plan

In practice, dosages of chemicals such as iron and aluminum are expressed as a percentage on a dry weight basis or sometimes in lbs/ton or similar convenient unit. For the purpose of this research, we report the dosages as the percentage of metal on a dry weight basis since this seems to be the most commonly used in practice. For example, a dosage of 2% Al, would be the same as 2 g of Al per 100 g of dry solids. An important note is that this convention does not take into consideration the molecular weight of the metals. Therefore, 2% as Fe and 2% as Al have different actual numbers of molecules of the metal added. Table 3-1 provides a direct comparison and conversion of Al and Fe from a percentage to a mole basis. Because Fe has about twice the atomic mass as Al (55.8 g for Fe vs 27 g for Al), a dosage of say 2% for both Fe and Al would result in twice as much actual Al molecules in solution or in the cake compared to Fe. When these differences are of importance, it will be noted in the text of the report.

Table 3-1. Comparison of Dosage Units and the Effect on Al and Fe Concentrations.

Dosage (% metal on a dry weight basis)	Al Effective Dose (millimoles of Al per gram dry solids)	Fe Effective Dose (millimoles of Fe per gram dry solids)
1%	0.37	0.18
2%	0.74	0.36
4%	1.48	0.72

A total of 18 different trials were performed to examine several different process variables that could impact the performance of chemical addition for controlling odors. These variables included:

- ◆ Effect of addition location
- ◆ Effect of dosage
- ◆ Effect of shear
- ◆ Effect of chemical type
- ◆ Effect of different sludge types

Although the researchers describe these as separate variables, some of these factors also interact to affect the other variables, so they are not all treated individually in the following discussions. In addition to these variables, the effect of the chemical addition on dewatering was

also investigated since this may impact the overall plant processing goals. The results from these trials are described in the following sections.

3.1.2 Effect of Addition Location

A number of trials were performed to examine the impact of the chemical addition location on the effect of the chemicals. A summary of the different locations is shown in Figure 3-1. Basically, the chemicals could be added during conditioning and dewatering or directly to the cake. During conditioning, they could be added either before, after or simultaneously with the polymer as shown in Figure 3-1.

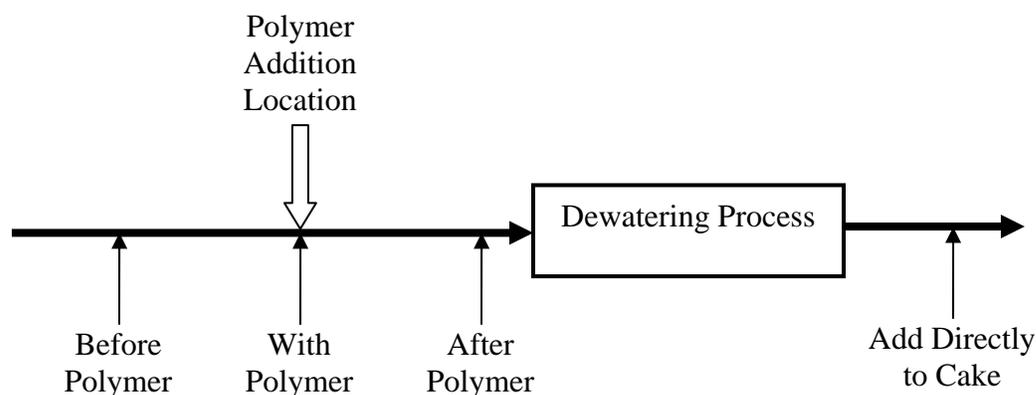


Figure 3-1. Different Chemical Addition Locations During the Conditioning and Dewatering Processes.

After addition of the chemicals, the cakes that were produced were stored in headspace serum bottles and the headspace was analyzed daily for the organic sulfur compounds and other gases as described in Chapter 2.0.

In comparing the different addition points prior to dewatering, most of the trials did not show an appreciable difference in the TVOSC profile for the different addition points. For example, Figures 3-2 and 3-3 show the TVOSC profiles for two different alum dosages. In each case the differences in the TVOSCs produced for the different addition point were minimal. It should be noted that these TVOSC profiles are fairly typical of most TVOSC profiles in that the TVOSC concentrations in the headspace increase, reach a peak concentration, and then decrease. Similar results were found in seven other trials with several different sludge sources as well as the use of ferric chloride and alum at different dosages. This data isn't shown for brevity and it shows very similar results each time. *From this testing, it appears that addition of alum or ferric chloride either before, during, or after polymer addition will provide similar effects on the TVOSC profile.*

However, differences were seen in the dewaterability of the sludges. When the chemicals were added either before or during the polymer addition the dewaterability was generally improved, and the polymer demand was reduced. For example, Figure 3-4 shows the CST profile as a function of polymer dose for a trial with ferric chloride addition. For the condition of adding ferric chloride either before or with the polymer, the optimum polymer dose (OPD) was reduced

by about 15-20%. However, adding the chemical after the polymer often resulted in worse dewaterability and an increase in the optimum polymer dose as shown in Figure 3-4. Also, when the chemical was added after the polymer, we often observed that slight changes in the polymer dose (added prior to the chemical) could result in very large variations in the CST measured after mixing. In other words, this addition point led to unstable flocculation during conditioning.

Since the differences related to the TVOSC profile were not meaningful, and the dewatering improved either before or during polymer addition and got worse when the chemicals were added after polymer addition, the best location for adding the chemicals appears to be either before or simultaneously with the polymer addition.

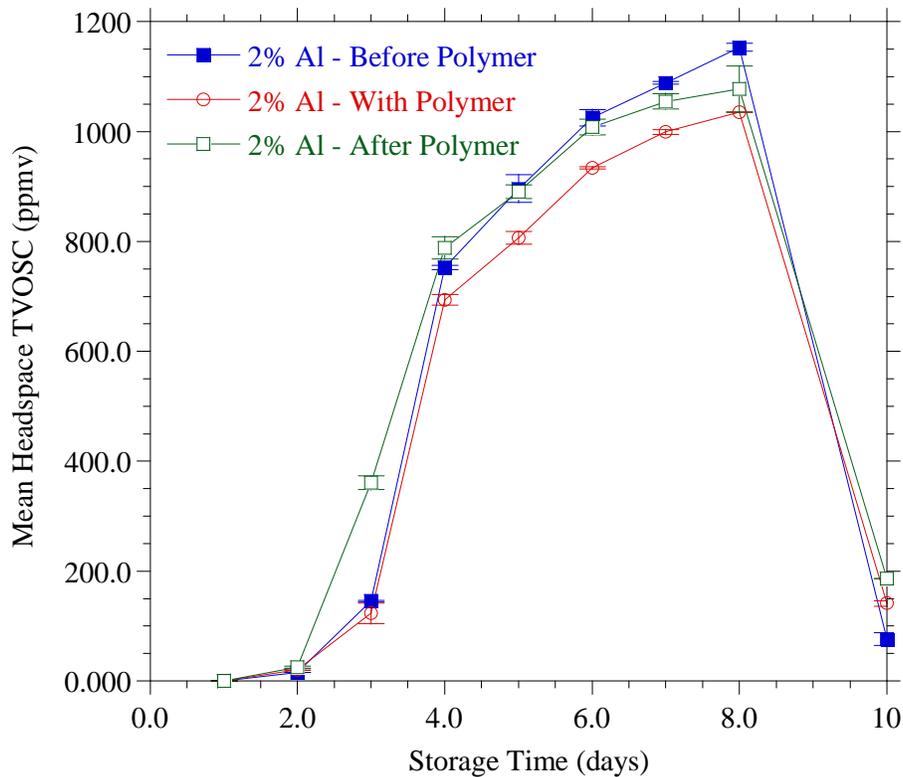


Figure 3-2. Effect of Chemical Addition Location on TVOSC Profile for SG Sample. Error Bars Represent One Standard Deviation.

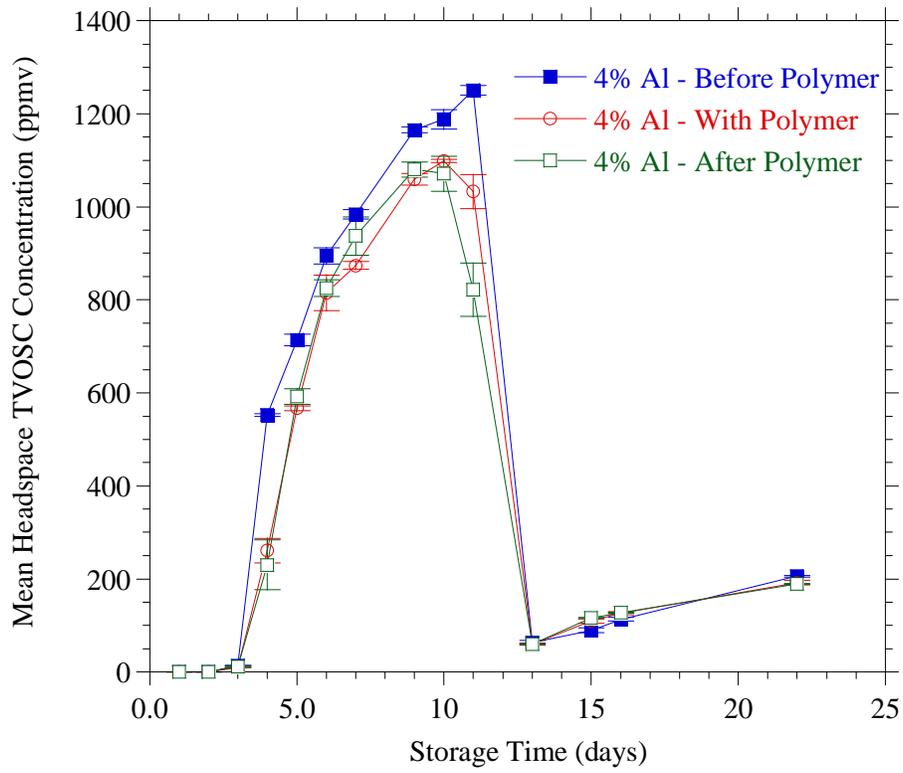


Figure 3-3. Effect of Chemical Addition Location on TVOSC Profile for SG Sample. Error Bars Represent One Standard Deviation.

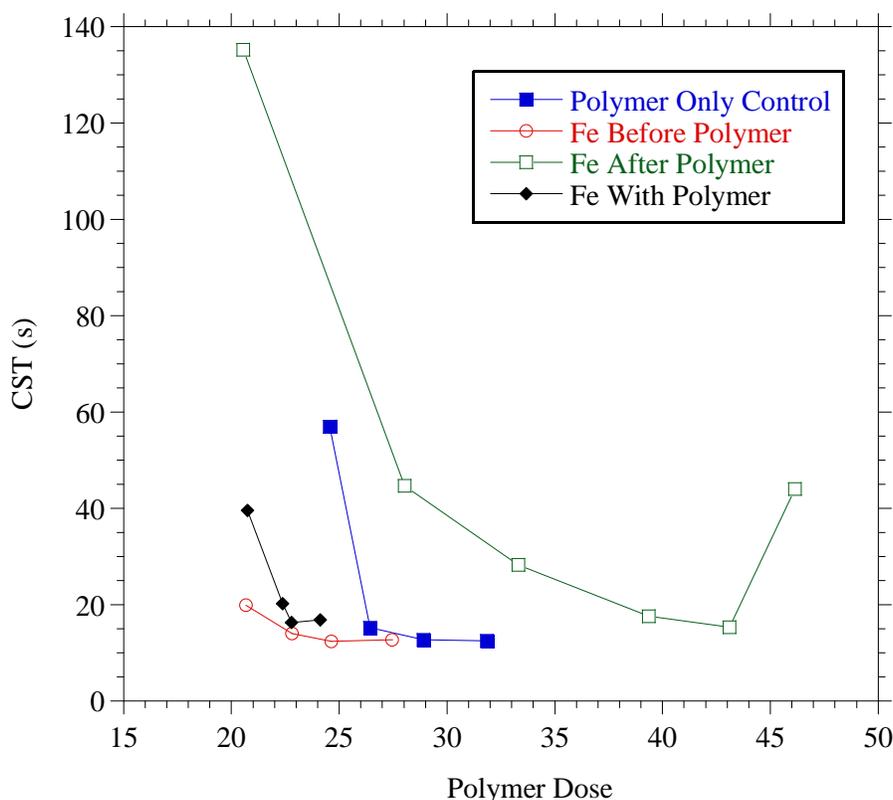


Figure 3-4. Effect of Chemical Addition Location on CST and Polymer Demand During Conditioning with Ferric Chloride and/or Polymer.

A set of tests were also performed in which the chemicals were added directly to the cake. In most of these cases, addition directly to the cake resulted in better performance in terms of consistently reducing TVOSCs compared to the addition prior to dewatering. The results from the cake additions are presented below in Section 3.1.3.3.

3.1.3 Effect and Interactions of Shear and Chemical Dosage.

The effect of chemical dosage was investigated by adding different dosages either during conditioning or directly to the cake. Typical dosages ranged from about 0.5% up to 4%. Dosages beyond 4% were not investigated because these are fairly impractical in the field. In addition, the effect of shear was simultaneously investigated to determine the inter-relation of shear and chemical dosage on the TVOSC production pattern. The results are presented in the following two sections. The first section presents results related to the effect of shear, the second section presents results for addition of the chemicals prior to dewatering, while the second section examines the addition of the chemicals directly to the cake.

3.1.3.1 Effect of Shear on TVOSC Production

A set of tests were performed to examine the effect of shear on the TVOSC profile. A sample of PWD SW biosolids was collected and dewatered using the HSCSP and then the cakes that were generated were put through scroll/shear mixer for different numbers of passes through the device. The TVOSC profile for each test is shown in Figure 3-5. As more shear is imparted to the cake, a greater amount of TVOSCs are produced. Interestingly, no shear resulted in no net

TVOSC production. The increase in shear can impact TVOSC production in two ways. First, it can release more bioavailable protein which is the substrate for TVOSC production (Higgins et al., 2006a). Secondly, it can result in greater inhibition of methanogens which have been shown to degrade VOSCs (Chen et al., 2005 and Higgins et al., 2006a). In this set of experiments, the production of methane was inhibited to a greater extent as the shear increased as shown in Figure 3-6. As a result, it is likely that as shear increases in dewatering processes, greater amounts of chemical will be needed to realize the same TVOSC reduction. Interestingly, for this particular sample (PWD SW), the 1-Pass condition was closest to the full scale cake in terms of TVOSC and methane production as shown in Figures 3-7 and 3-8.

Another confounding factor is cake solids. As cake solids increases, the production of odorants can increase as shown by others (Dentel and Novak, 2001). In addition, the solids are more susceptible to shear. In other words, for a cake solids of 20% versus 25%, the increase in TVOSC production would be greater for the same amount of shear imparted to the 25% cake compared to the 20% cake. For example, TVOSC production for cakes solids in the range of 17-22% all sheared the same amount of five passes is shown in Figure 3-9. As a result, depending on the particular full-scale dewatering process and the resultant solids, we have found that anywhere from 1-5 passes are needed to closely replicate the TVOSC profile from the full-scale cake.

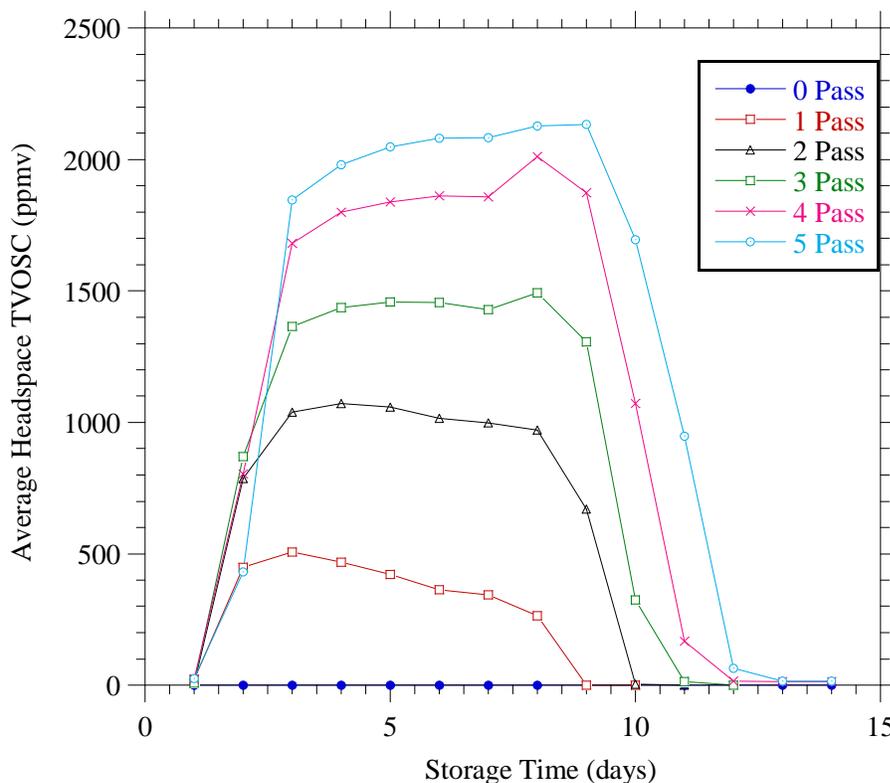


Figure 3-5. Effect of Shear Imparted to the Cake on the TVOSC Profile.

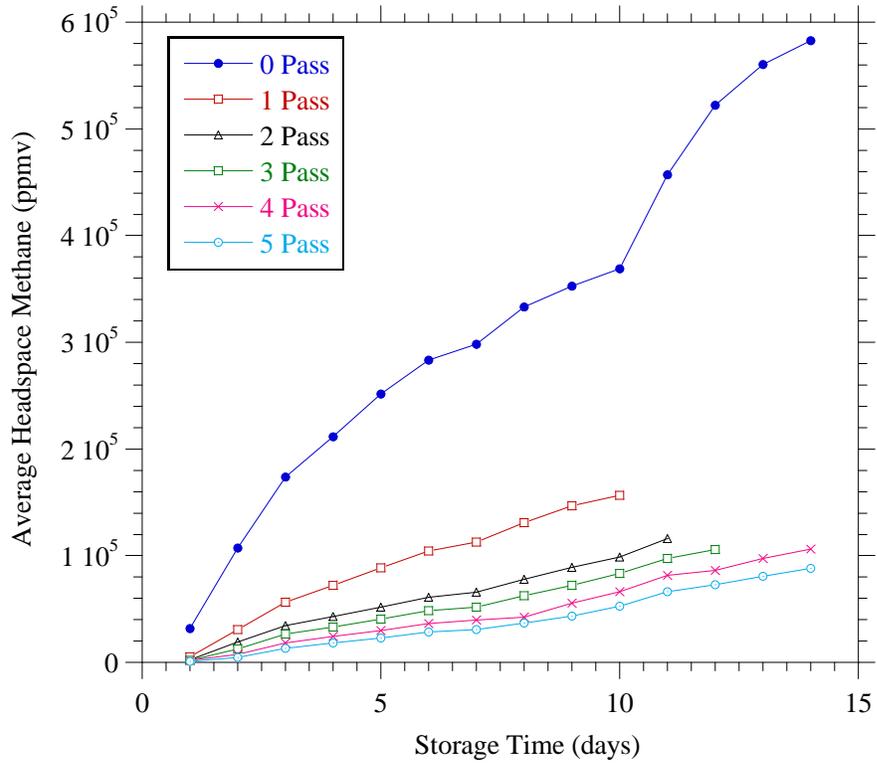


Figure 3-6. Effect of Shear Imparted to the Cake on the Methane Production.

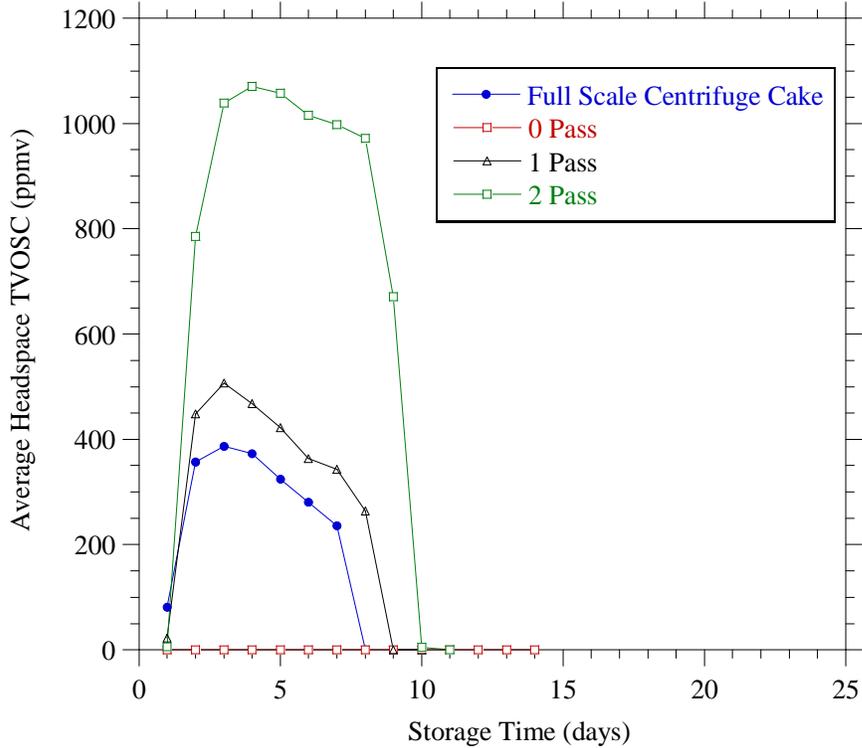


Figure 3-7. Comparison of TVOSC Production from Lab Scale Cakes Produced with Full Scale Centrifuge Cake.

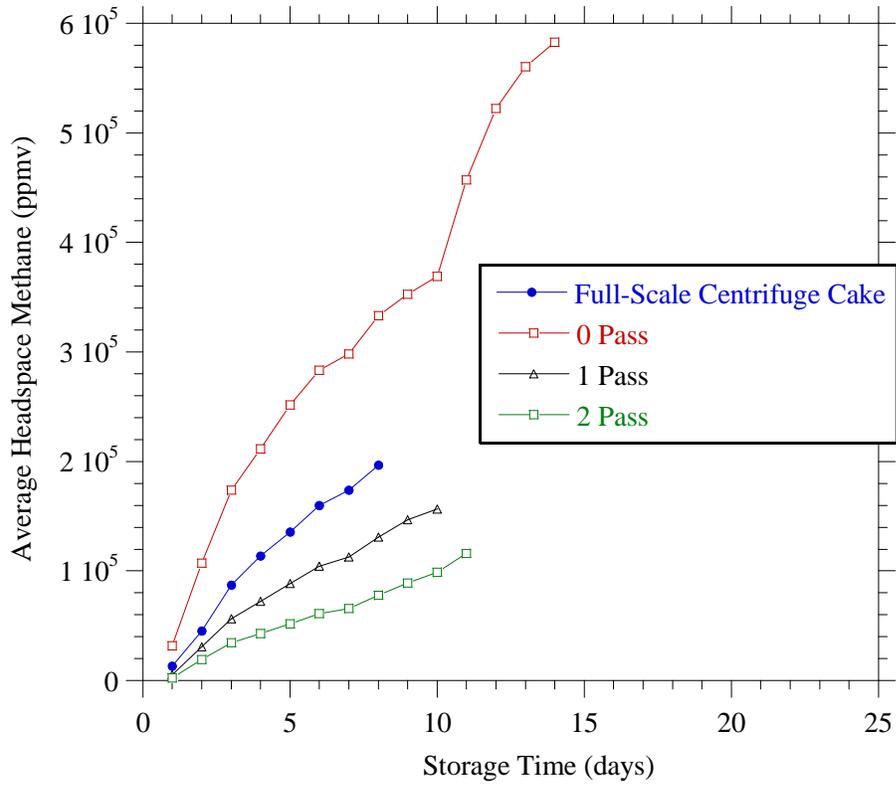


Figure 3-8. Comparison of TVOSC Production from Lab Scale Cakes Produced with Different Shear and a Cake Sample from a Full-Scale Centrifuge.

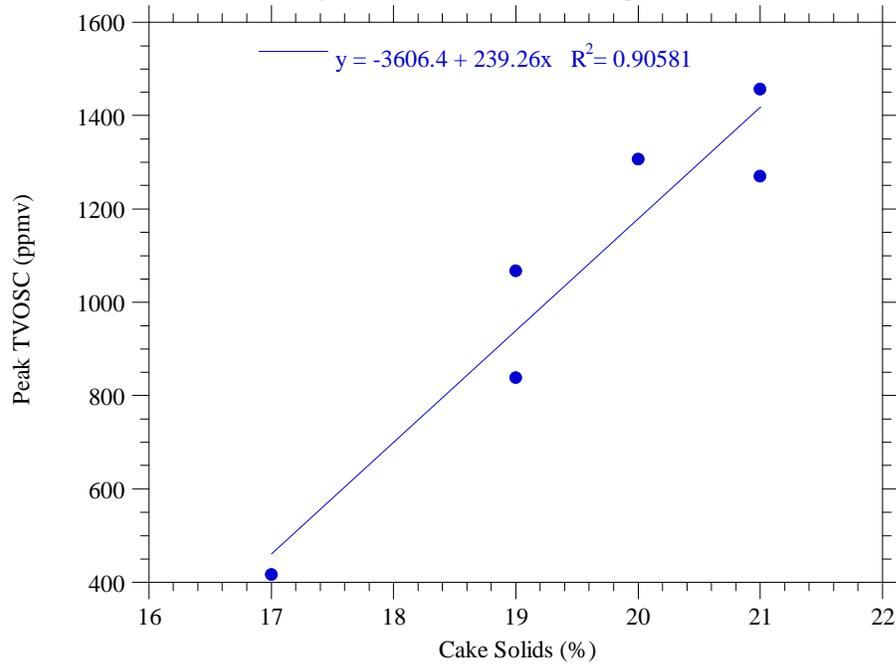


Figure 3-9. Peak TVOSC Concentrations Measured from SG Cake All Sheared Five Passes but at Different Starting Cake Solids Concentrations.

3.1.3.2 Effect of Shear and Al Dosage Prior to Dewatering on TVOSC Production

A series of tests were performed to examine the impact of alum and iron dosages on TVOSC production as well as the interaction of shear. In these cases the chemical addition occurred before the polymer addition to eliminate addition sequence as a variable. In the first set, alum was added at 2% and 4% as Al, for a low-shear condition. Low shear was achieved by simply generating a cake using the conditioning and dewatering procedure described in Chapter 2.0, but the cake was not passed through the scroll device. Therefore, shear was only imparted to the solids during the mixing of the chemicals and polymer during the conditioning step. The results are shown in Figure 3-10. As shown in the figure, addition of increasing amounts of Al resulted in a reduction in the TVOSC production. For example, 2% Al resulted in about a 20% reduction in the TVOSC concentration, while 4% reduced the TVOSC concentration by about 55%. Under moderate shear conditions using 1 pass through the scroll system, however, the 2% Al dosage was only slightly lower than the control, and the 4% Al dosage was about 30% less than the control, see Figure 3-11a. At the highest shear of three passes through the scroll system, neither the 2% or 4% improved the TVOSC production compared to the control. Similar results were found when Al was added to the cake as shown in Figure 3-11b.

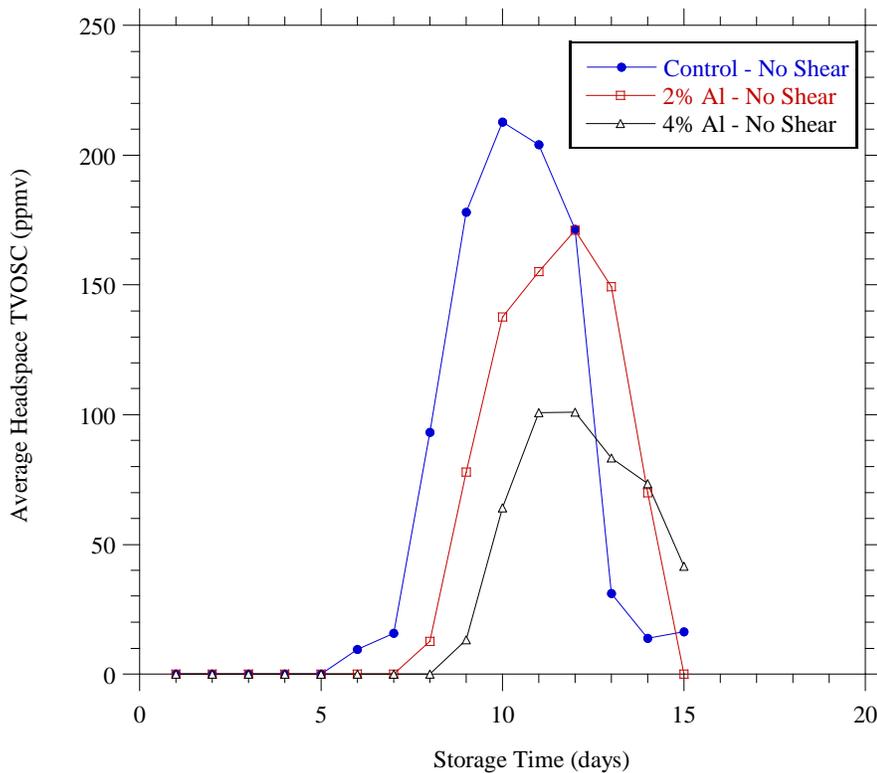


Figure 3-10. SG BFP Cake with No Shear at 2% and 4% Al Dosages Added Before Polymer.

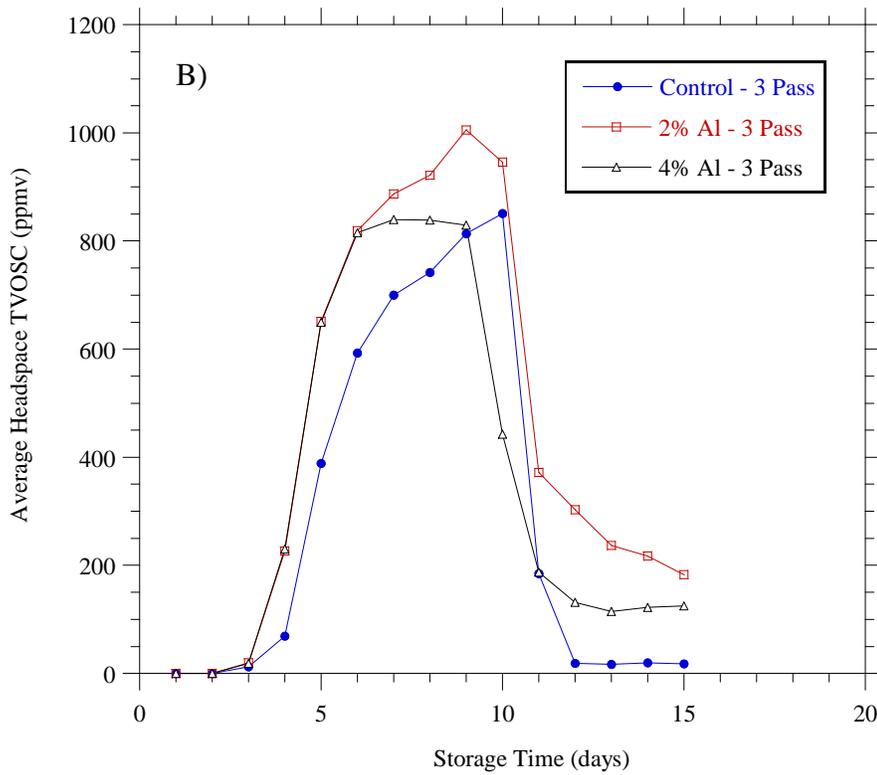
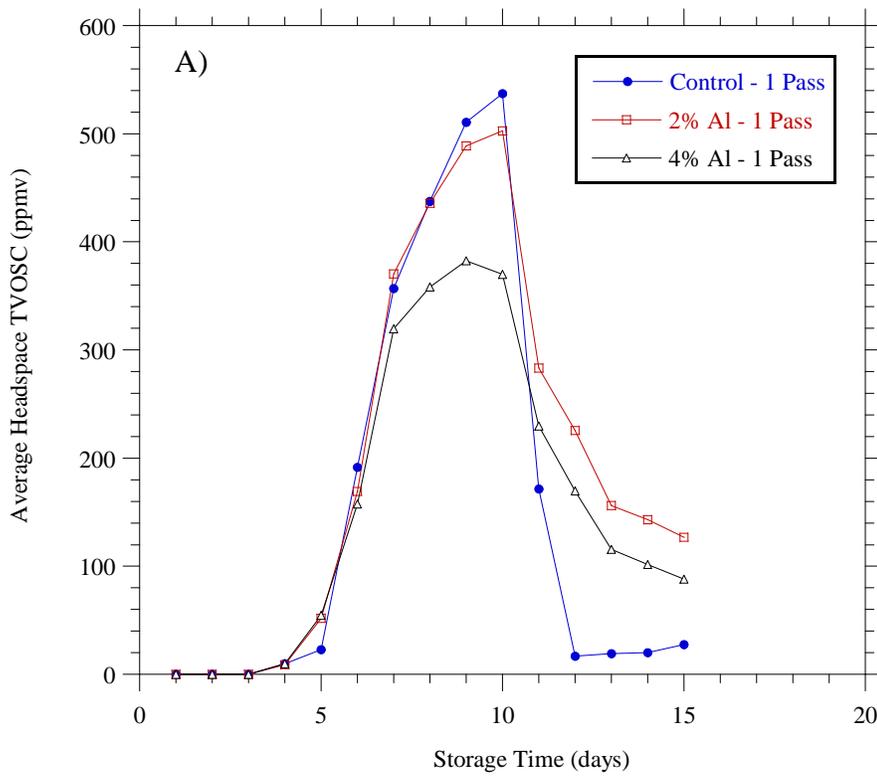


Figure 3-11. Effect of 2% and 4% Al Dosages Added Before Polymer for a) Low Shear Conditions and b) Medium Shear.

Similar results were found for the PWD SW samples. For example, Figure 3-12 shows the production of TVOSCs for a moderate shear of 3 passes and dosages of 0, 2 and 4% Al. The 2% Al had greater TVOSC production while the 4% Al was able to inhibit TVOSC production completely. In comparison, imparting five passes result in the 4% dosage having substantial TVOSC production, although the peak concentration was about 50% of the control cake as shown in Figure 3-13.

The results highlight the complex interactions between cake solids, shear, and dosage. As the shear increases, it is likely that more protein could become available to produce odors and it also can cause greater inhibition of methanogens, these two factors would result in greater odorant production. As a result, greater amounts of alum (or other protein binding chemical) would be needed to offset these effects.

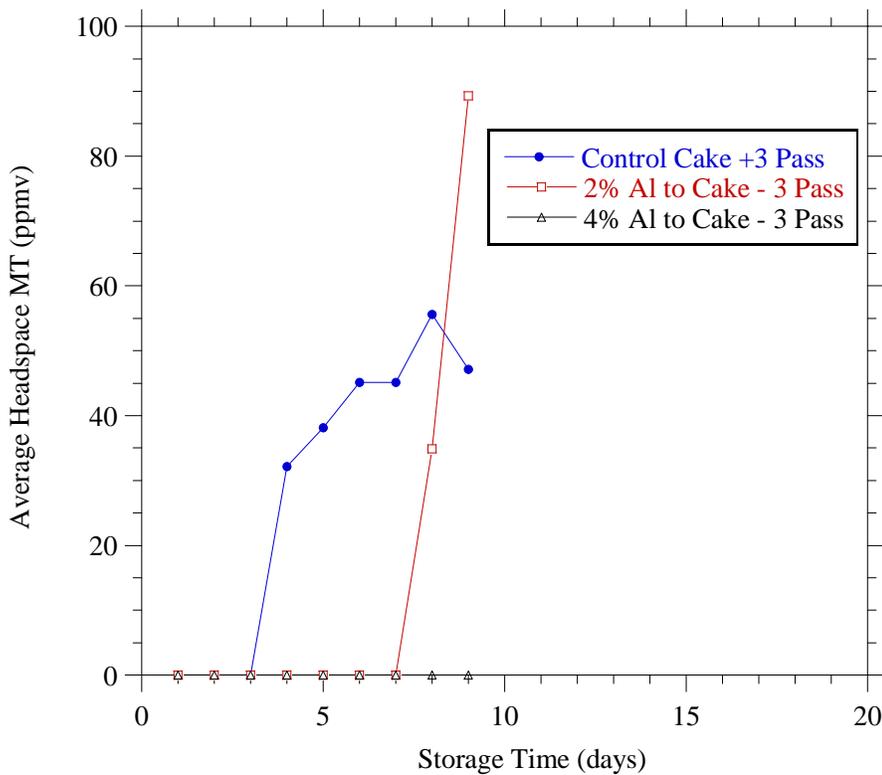


Figure 3-12. PWD SW Moderate Shear at 2% and 4% Al Dosages Added Before Polymer.

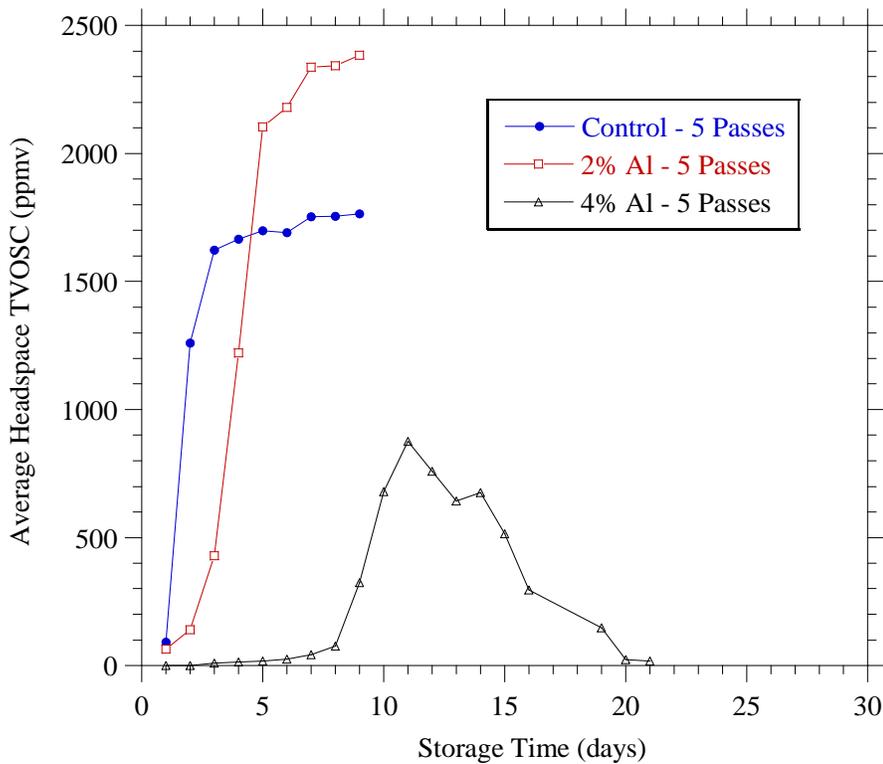


Figure 3-13. PWD SW High Shear at 2% and 4% Al Dosages Added Before Polymer.

Addition of alum to the sludge during the conditioning step resulted in a reduction in the pH of the sludge after conditioning as shown in Figure 3-14. However, the cake pH did not decrease and was actually slightly greater than the control. Therefore, at these dosages, the pH is not negatively impacted in the cake. Also, the alum dosages did inhibit the methane production as shown in Figure 3-15. As the alum dose increased, the methane production decreased.

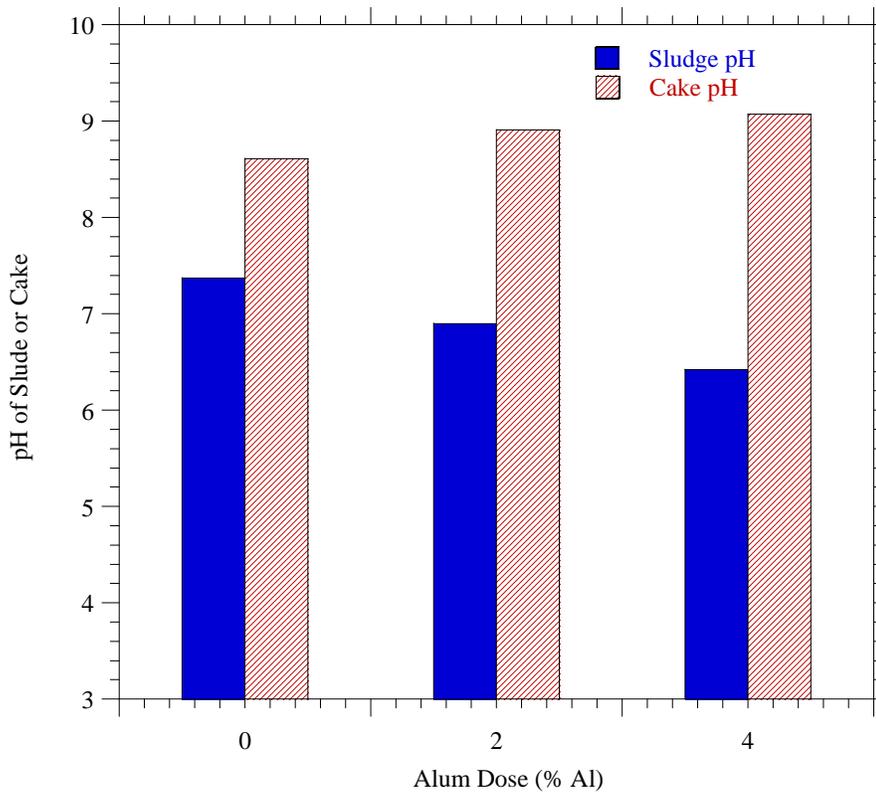


Figure 3-14. PWD SW High Shear at 2% and 4% Al Dosages Added Before Polymer.

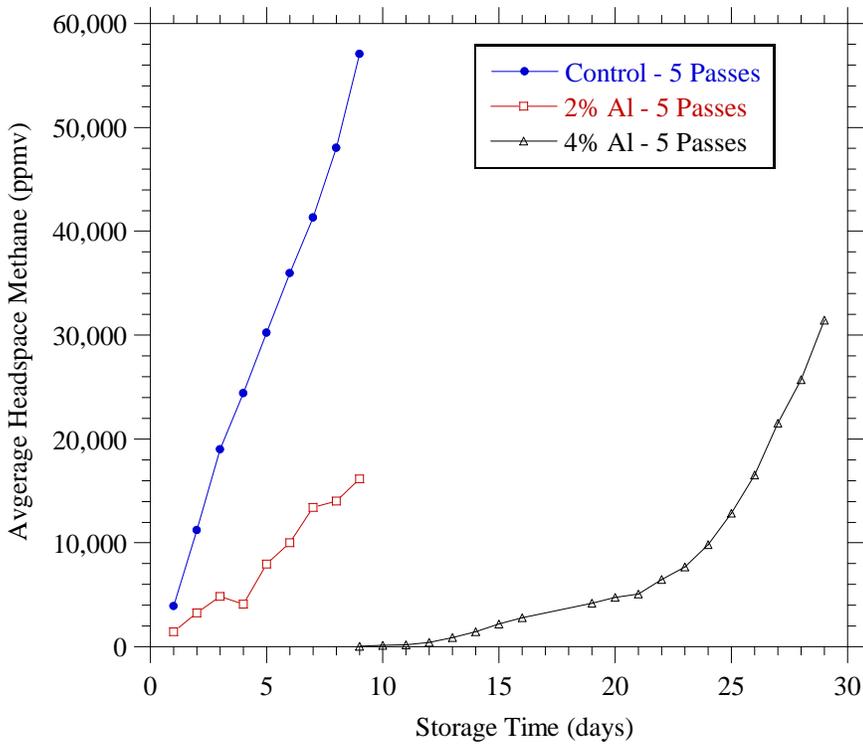


Figure 3-15. PWD SW High Shear at 2% and 4% Al Dosages Added Before Polymer.

The results show that as the shear increases, more Al is needed to overcome the release of bioavailable materials that cause odors. This finding may help explain some of the field results and discrepancies between the lab and full-scale trials. To accurately estimate the effect of the different chemicals during dewatering, it is important to simulate the actual shear in the full-scale system.

3.1.3.3 Effect of Shear and Al Dosage Added Directly to the Cake

For comparative purposes, a set of trials was also performed to examine the impact of adding the chemicals directly to the cake. This approach could provide the benefit of an easier to implement solution, with all of the chemical ending up in the cake. However, the improvements in conditioning and dewatering would not be realized.

The effect of Al addition to the PWD NE cake resulted in reductions in the TVOSC when the dosage was 2% or greater as shown in Figure 3-16. Both the 2 and 3% Al dosage resulted in TVOSC concentrations below the detection limits while the 1% Al had about twice the peak TVOSC concentration than the control. Results from the PWD SW sample are shown in Figure 3-17. In this trial, the 1% Al dosage was lower than the control, and the 2 and 4% dosages did not completely eliminate the TVOSC production. These results highlight the differences that can occur between sludges and the difficulty in predicting the effect of alum or iron addition on TVOSC production. The controls for the NE and SW samples were also different with the peak TVOSC for the SW sample being about five times the NE sample.

Results from the SG sample were similar, but the 4% dosage was able to reduce TVOSC production below the detection limit for both the one and three pass conditions as shown in Figure 3-18 and 3-19. When using Fe based chemicals, similar results were generally found as shown in Figure 3-20. More data on comparison of different chemicals is discussed in more detail in Section 3.1.4.

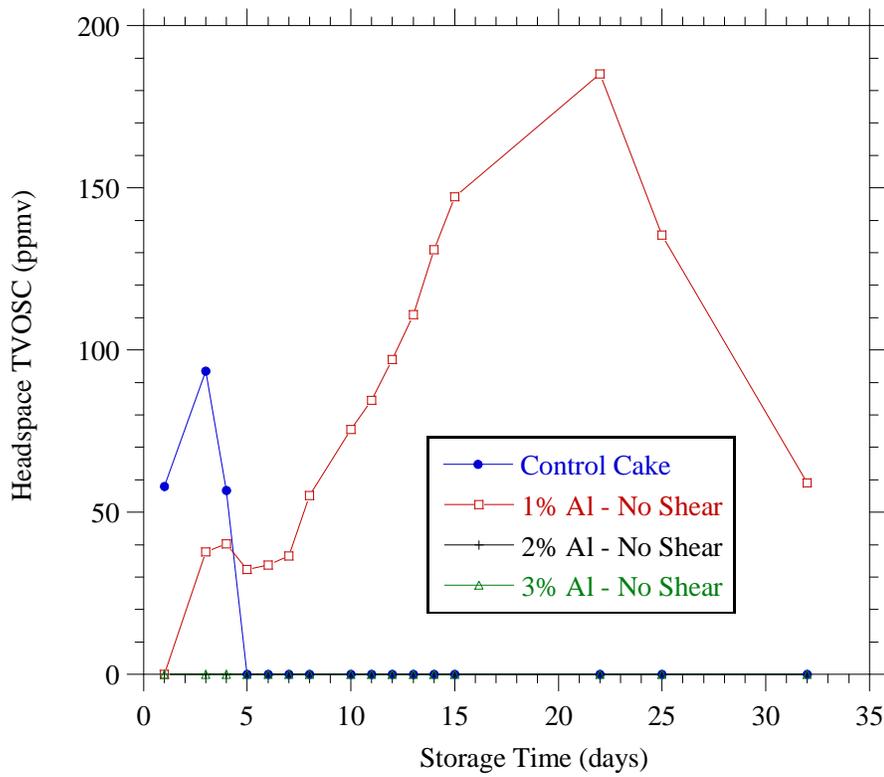


Figure 3-16. PWD NE Effect of Al Added Directly to the Cake on TVOSC Profile.

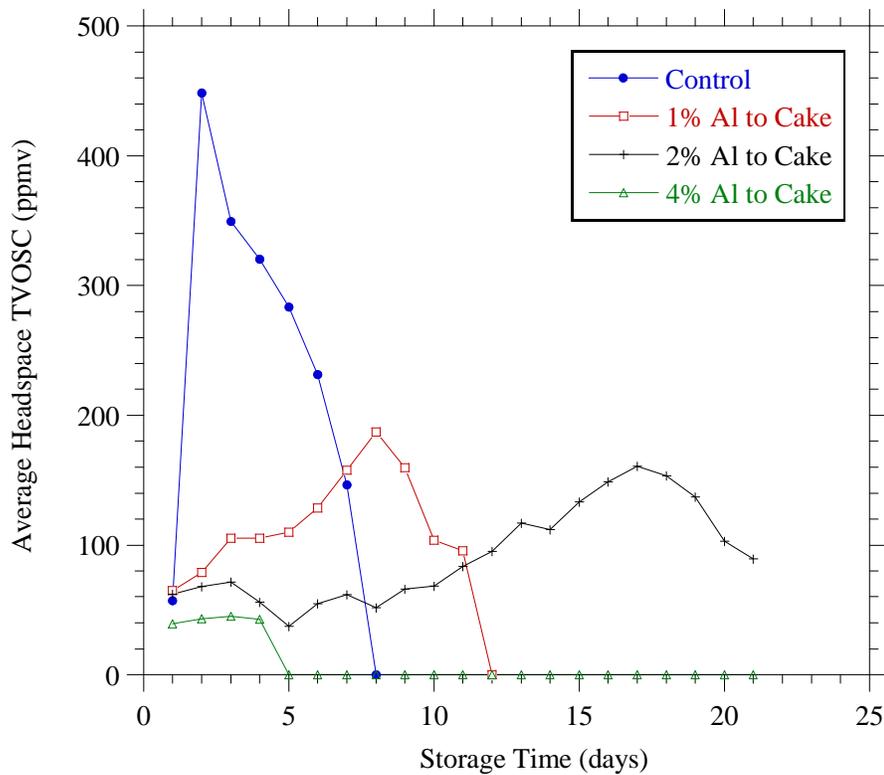


Figure 3-17. Effect of Al Addition Directly to Full-Scale Centrifuged Cake from PWD SW Plant.

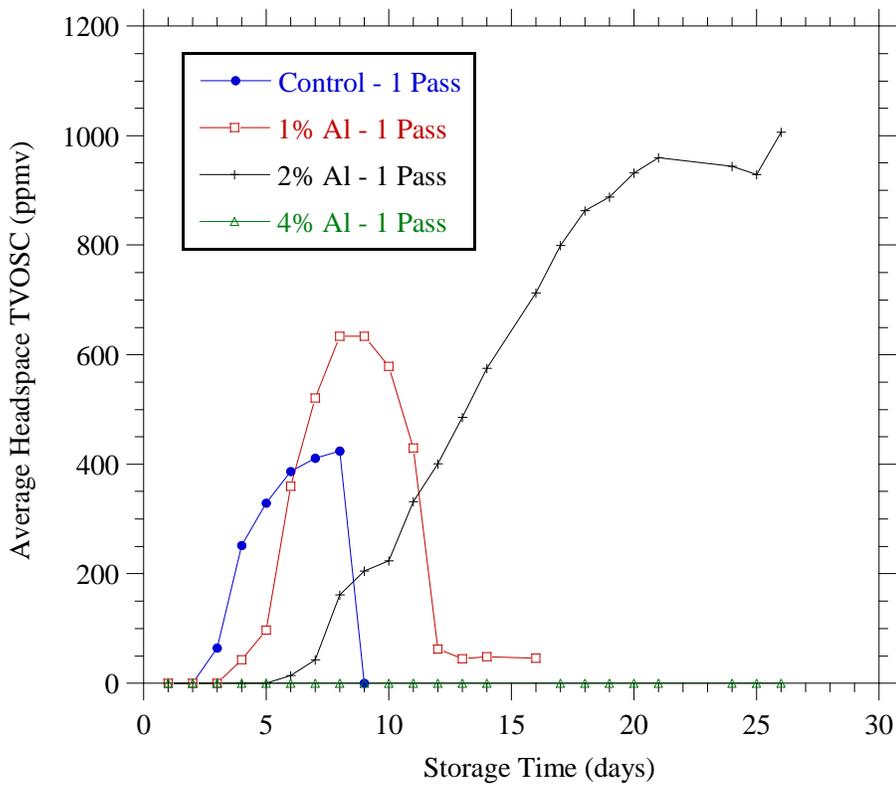


Figure 3-18. Effect of Al Addition Directly to BFP Cake from the SG Plant and Sheared One Pass.

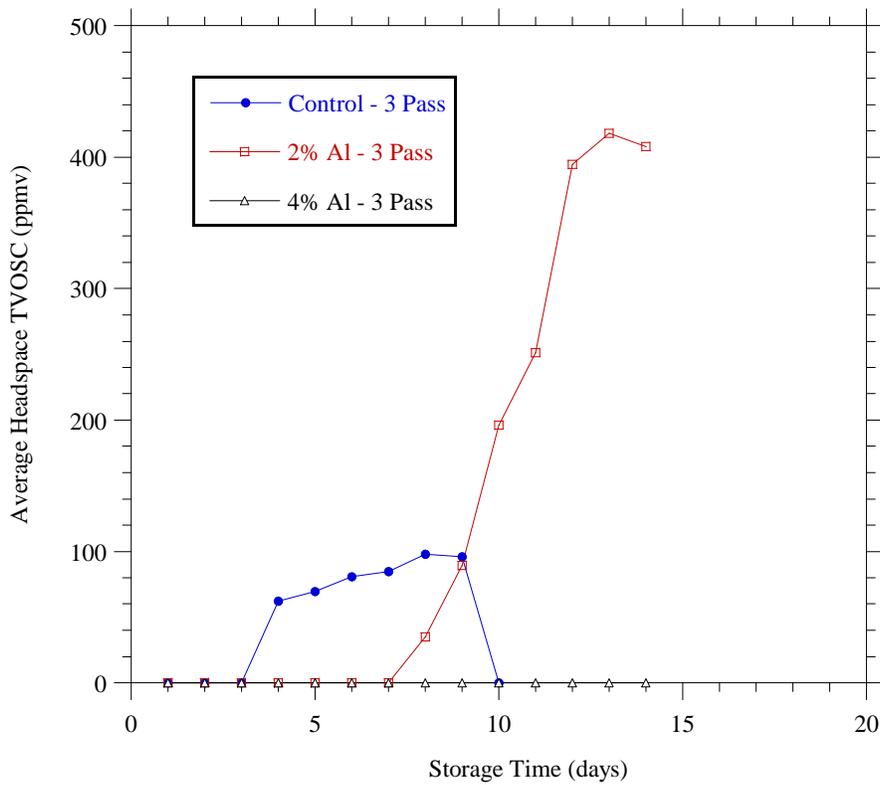


Figure 3-19. Effect of Al Addition Directly to BFP Cake from the SG Plant and Sheared Three Passes.

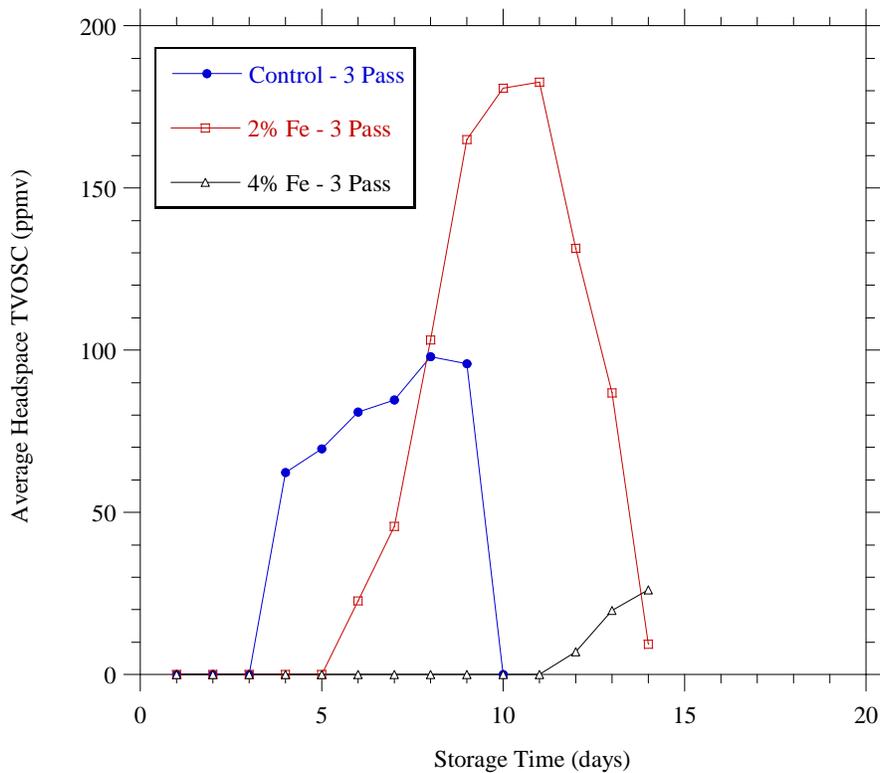


Figure 3-20. Effect of Fe Addition Directly to BFP Cake from the SG Plant and Sheared Three Passes.

Interestingly, the addition of the alum directly to the cake leads to a greater decrease in the pH of the cake compared to adding to during conditioning. As shown in Figure 3-21, the pH of the cake was 3.9 at the highest dosage of 4% Al. This is a very low pH, and would potentially become problematic for land application programs. Addition to the cake also has a greater impact on the methane production as would be expected from the very low cake pH environment. Figure 3-22 shows the methane production for three conditions, a control, 2% and 4% Al dosages. The addition of alum at these dosages almost completely inhibited the methane production. Similar results were found in other trials with direct cake addition for both alum and ferric chloride and

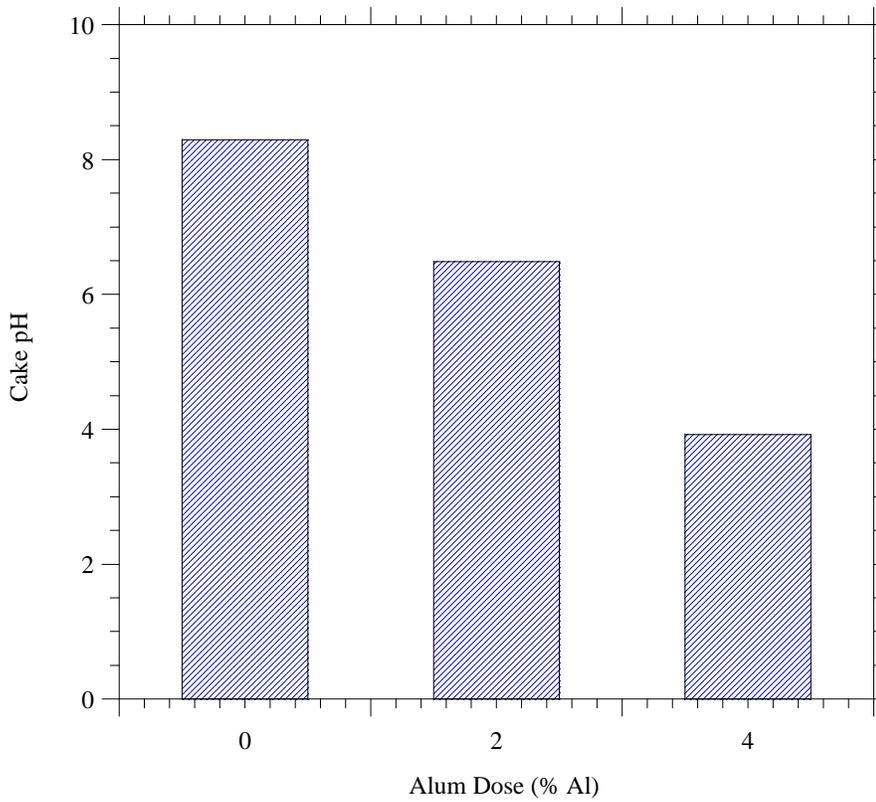


Figure 3-21. Effect of Al Addition Directly to BFP Cake from the SG Plant on Cake pH.

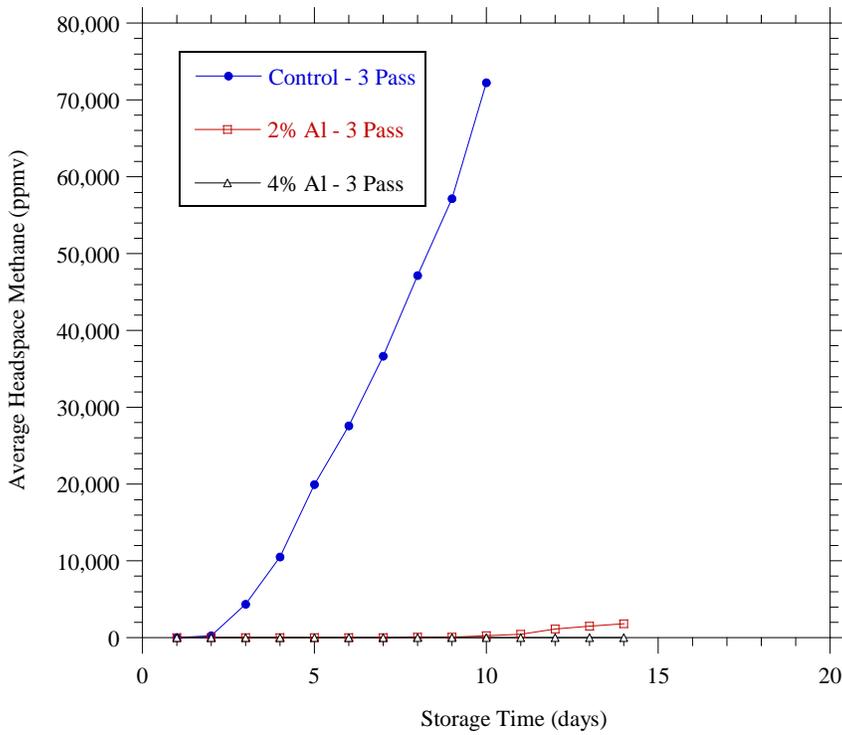


Figure 3-22. Effect of Al Addition Directly to BFP Cake from the SG Plant and Sheared Three Passes on Methane Production.

3.1.4 Effect of Different Chemical Types

A series of tests were performed to compare the different chemicals, mainly different forms of Al and Fe, but Mg salts were also tested since Mg has been shown to have a high affinity for protein. The chemicals that were tested included:

- ◆ Aluminum Sulfate (alum)
- ◆ Polyaluminum Chloride (PAC)
- ◆ Sodium Aluminate
- ◆ Ferric Chloride
- ◆ Ferrous Chloride
- ◆ Ferric Sulfate
- ◆ Ferrous Sulfate
- ◆ Zero Valent Iron (ZVI)
- ◆ Magnesium Chloride
- ◆ Magnesium Hydroxide

When possible, the chemicals were tested in a side-by-side trial, but since the number of samples that can be analyzed at one time is limited, multiple trials were also performed. The results are discussed in the following two sections.

3.1.4.1 Different forms of Al and Fe

In one of the more extensive trials, three forms of aluminum based chemicals and two forms of iron based chemicals were added to the SG cake at 0, 2 and 4% dosages. The chemicals used were:

- ◆ Aluminum Sulfate (alum)
- ◆ Polyaluminum Chloride
- ◆ Sodium Aluminate
- ◆ Ferric Chloride
- ◆ Ferrous Chloride

The cakes were first passed through the scroll three times and the chemicals were then added to the cake. The results from the 2% and 4% dosages are shown in Figures 3-23 and 3-24, respectively. At the 2% dosage, the chemicals did behave differently, and only one, sodium aluminate, had a TVOSC concentration lower than the control. The PAC performed better than alum while the ferric chloride and ferrous chloride performed better than the PAC. Sodium aluminate provided the best treatment for reducing TVOSCs at this dosage. Interestingly, the addition of 2% sodium aluminate resulted in a cake pH of 10.3, which greatly inhibited methanogenesis, yet some TVOSCs were still produced.

At a 4% dosage, the chemicals generally performed better except ferrous chloride was nearly unchanged and the sodium aluminate was only slightly better. The PAC, alum and ferric

chloride all reduced the TVOSC concentrations below the control, and were all non-detect for the first 10 days. The TVOSC began to increase for the ferric chloride on day 12. Interestingly, ferric chloride performed better than ferrous chloride at the 4% dosage. It is possible that the ferric ion, with a +3 charge, had a greater affinity for binding protein, and it may play a role through acting as an electron acceptor.

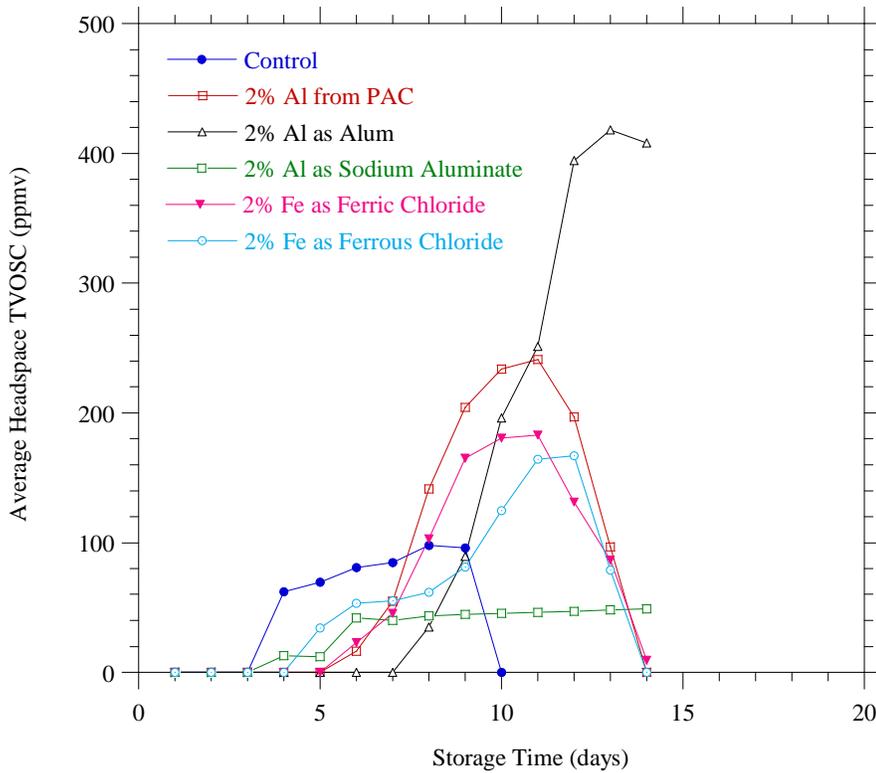


Figure 3-23. Effect of Different Forms of Al and Fe Added Directly to Cake on TVOSC Production.

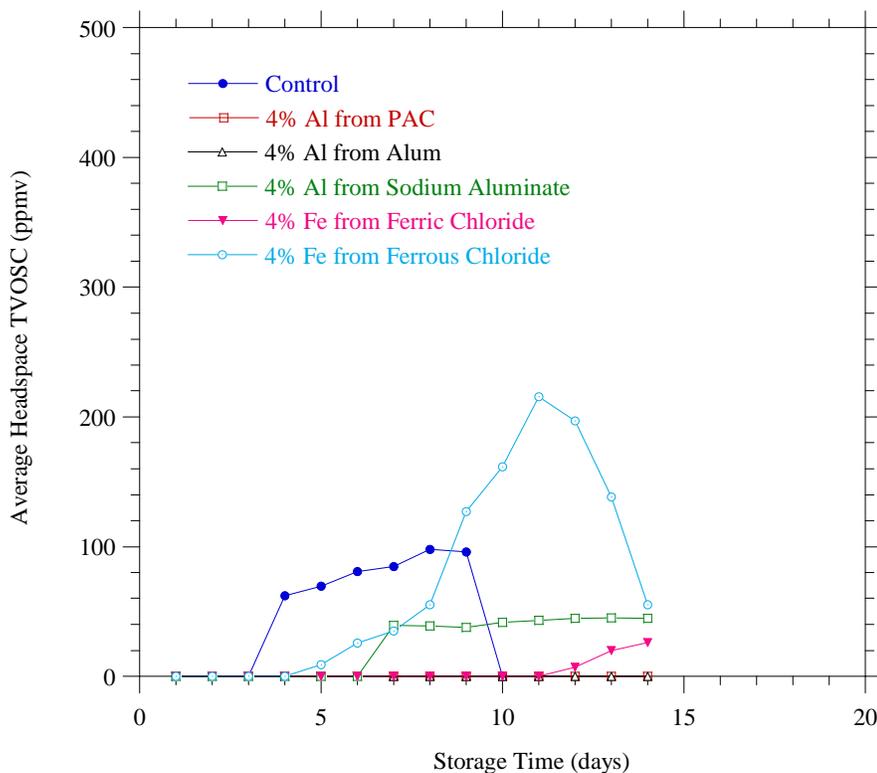


Figure 3-24. Effect of Different Forms of Al and Fe Added Directly to Cake on TVOSC Production.

A second experiment was performed in which three chemicals were added directly to the SG cake as described before, at dosages of 0, 1, 3, and 4%. These chemicals were:

1. alum
2. ferric chloride and
3. zero-valent iron (ZVI)

The TVOSC profile for the different alum, ferric chloride and ZVI additions are shown in Figures 3-25, 26, and 27, respectively. As seen in previous trials, the lower dosages of alum resulted in an increase in the TVOSC production, but at the higher dosages the TVOSC concentration were all below the detection limit. Ferric chloride addition at 1% as Fe did not appreciable impact the TVOSC production compared to the control. At a 2% Fe dosage, the peak TVOSC was very similar to the control, however the peak was delayed by about 15 days. At the 4% Fe dosages, no measurable TVOSCs were produced during the time-frame of the experiment. The addition of ZVI to the cake resulted in slight decreases in the TVOSC production for each dose as shown in Figure 3-27, and the decrease was approximately proportional to the dosage. The ZVI that was added had a relatively large particle size, and this may have limited its effectiveness. ZVI may help reduce odors by providing an alternative electron acceptor and acting also as a reducing agent. Additional tests using a nano-scale ZVI may prove more effective since the smaller particle size may lend itself to better utilization by microbes.

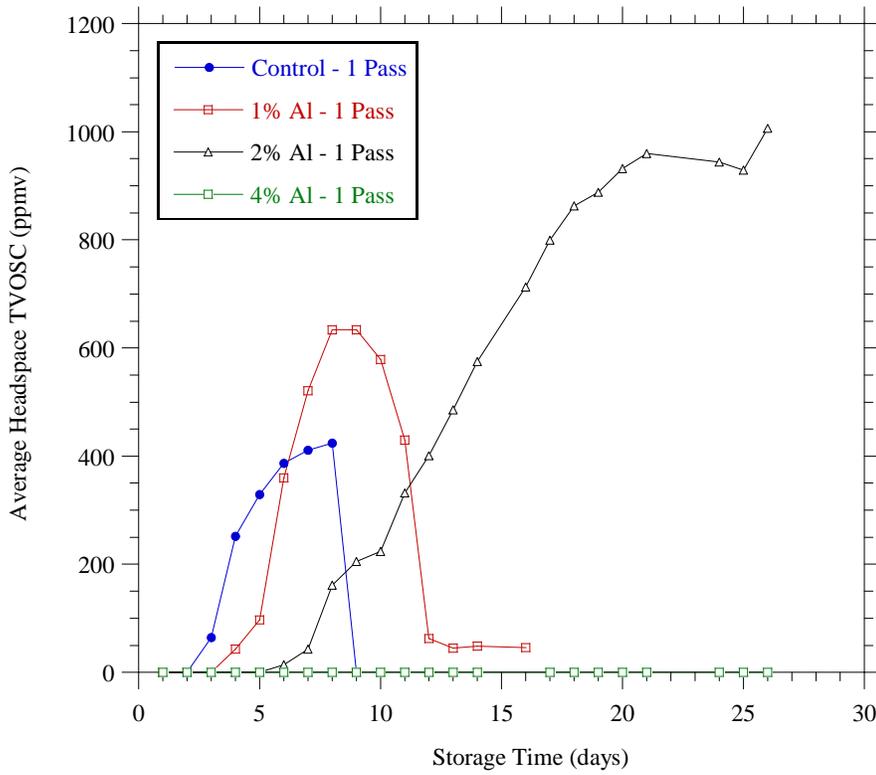


Figure 3-25. Effect of Alum Added Directly to Cake on TVOSC Production.

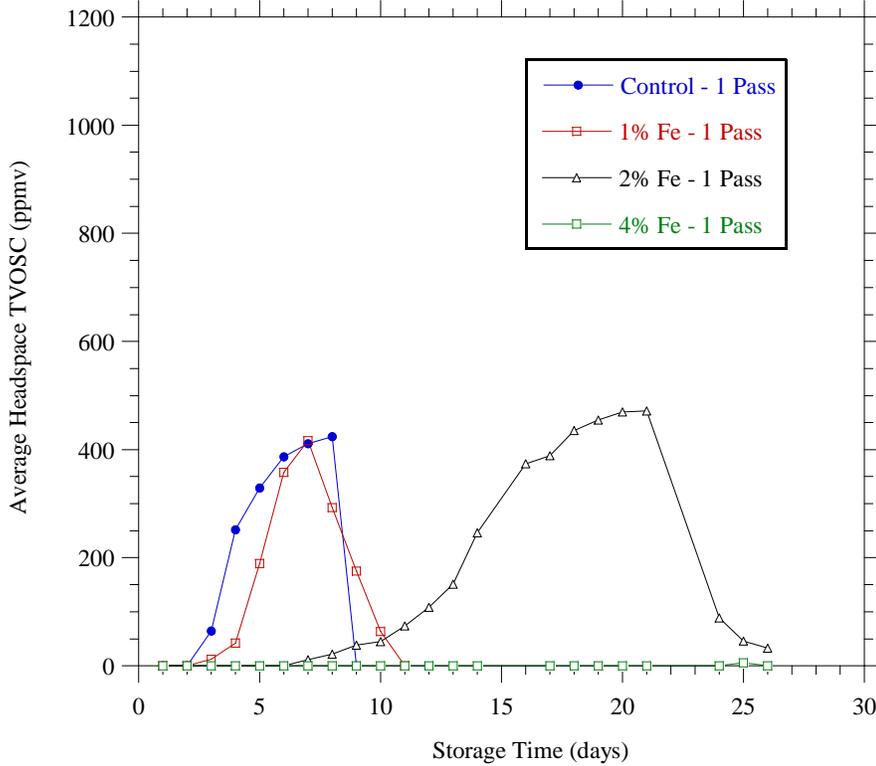


Figure 3-26. Effect of Ferric Chloride Added Directly to Cake on TVOSC Production.

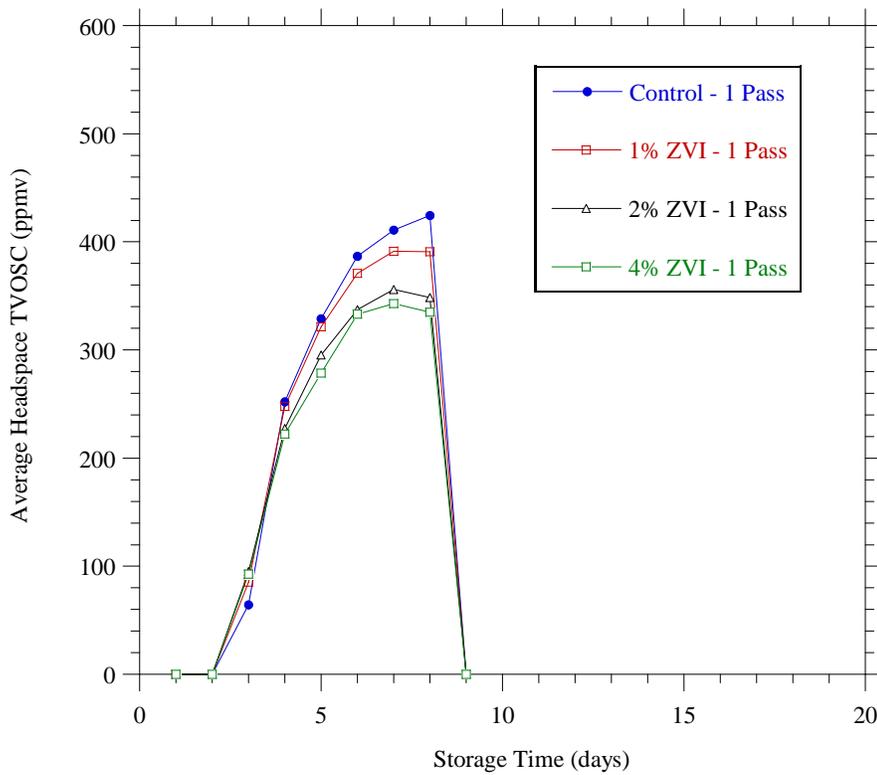


Figure 3-27. Effect of Zero Valent Iron Added Directly to Cake on TVOSC Production.

The addition of the alum and ferric chloride had a significant inhibitory effect on methane production, while the ZVI did not appreciably impact the methane production as shown in Figure 3-28.

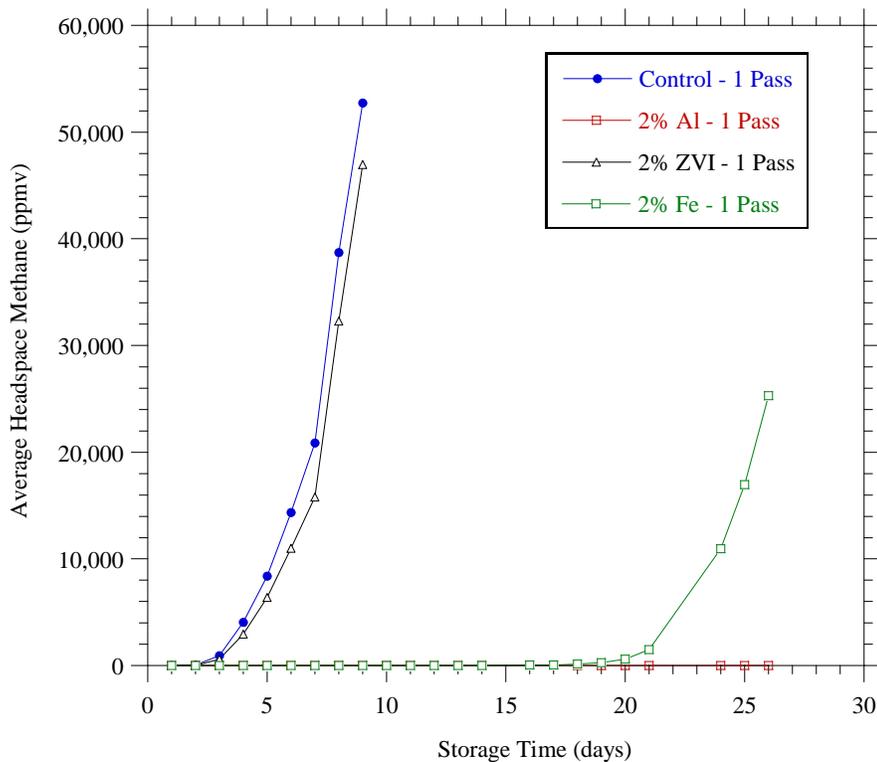


Figure 3-28. Effect of Chemical Added Directly to Cake on Methane Production.

Another set of trials were performed to compare other sources of iron as well as examine lower dose scenarios. The concept to use a lower dose was determine if the lower dose would be effective in the range where the benefit is derived from the metal addition, but the dosage is low enough such that the negative impacts do not occur. In this trial, the following chemicals were added directly to the cake at dosages between 0.3-0.4% as Fe:

- ◆ ferric chloride
- ◆ ferric sulfate
- ◆ ferrous chloride
- ◆ ferrous sulfate

The effect of the chemical addition on the TVOSC production is shown in Figure 3-29. The different chemicals all had a positive effect in reducing the TVOSC production, even at the relatively low dose. The highest dosage of 0.4% resulted in a greater than 50% reduction in the TVOSCs. Interestingly, these low dosages did not appreciably impact the methane production as was observed for higher dosages, see Figure 3-30.

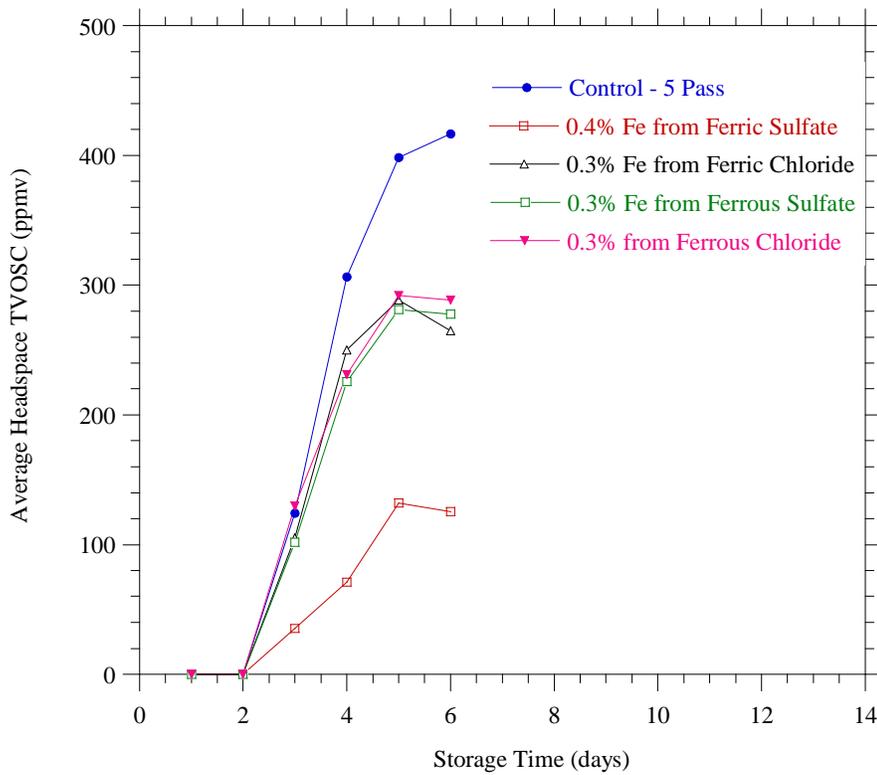


Figure 3-29. Effect of Different Fe Sources Added Directly to Cake on TVOSC Production.

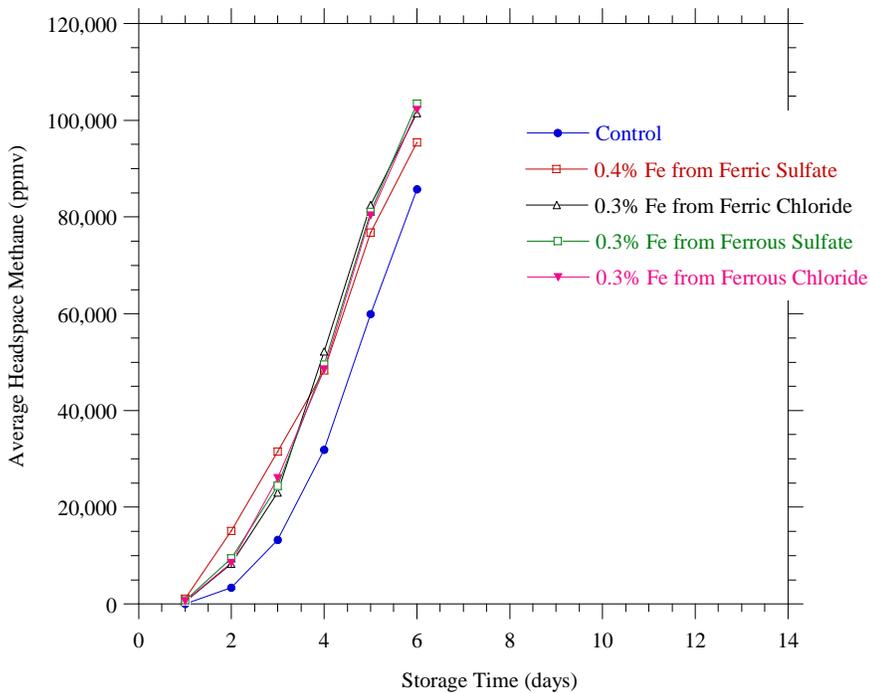


Figure 3-30. Effect of Fe Sources Added Directly to Cake on Methane Production.

A similar trial at low dosages of Fe and Al was performed using a sample from a full-scale high solids centrifuge from Plant 4. The TVOSC production is shown in Figure 3-31. The low dosages for this system again reduced the TVOSCs by about 50%. The addition of the ferrous sulfate actually had a slight beneficial effect on the methane production while the alum addition was slightly less than the control, as shown in Figure 3-32.

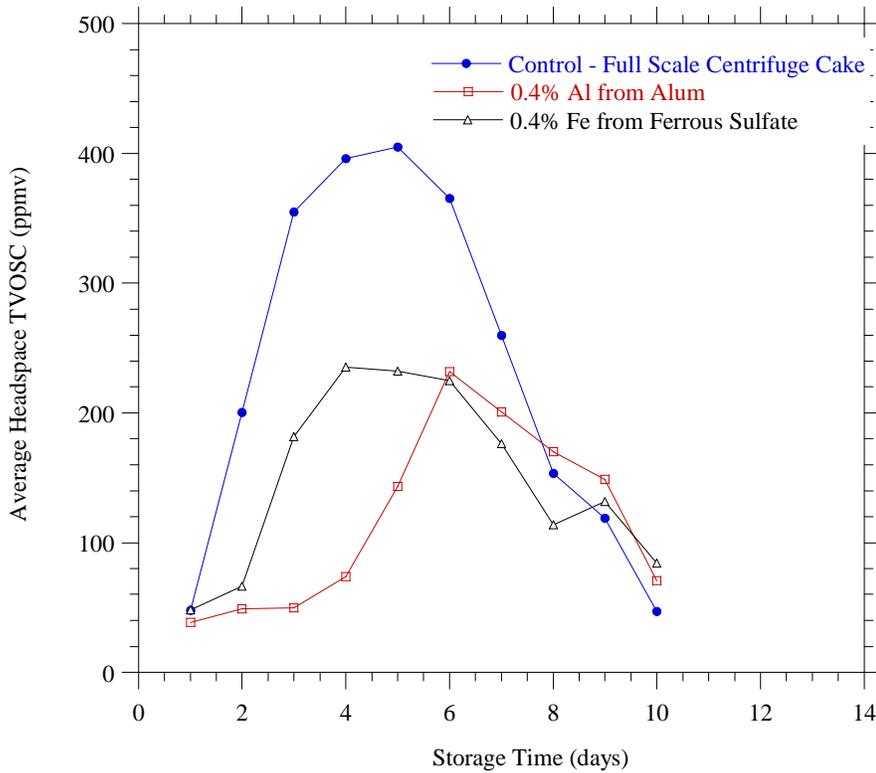


Figure 3-31. Effect of Fe Sources Added Directly to Cake on Methane Production.

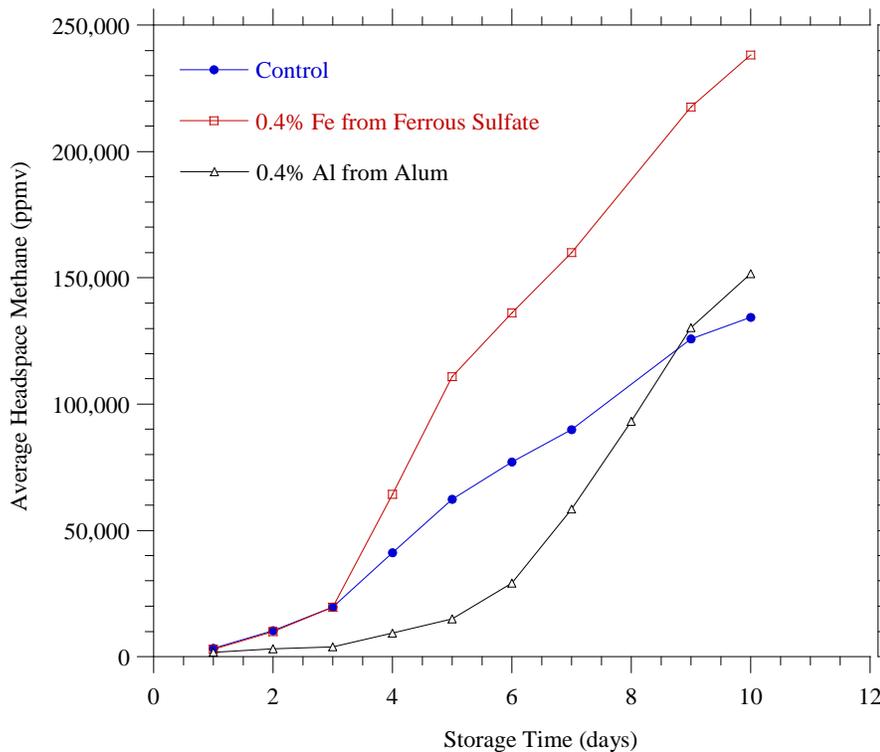


Figure 3-32. Effect of Fe and Al Added Directly to Cake on Methane Production for Plant 4.

A trial was performed to investigate the addition Mg^{2+} on TVOSC production. Previous research has shown that calcium and magnesium ions have a strong affinity for biopolymer, and magnesium, in particular, has a strong affinity for protein (Higgins and Novak, 1997a,b and Sobeck and Higgins, 2001). To test the effect of Mg addition, $MgCl_2$ was added to liquid sludge prior to conditioning and dewatering and slow mixed for 2 hours. The dosages were to 0.5% and 2% as Mg. After incorporation of the Mg, the solids were conditioned and dewatered as described previously. The effect of the Mg addition on TVOSC production is shown in Figure 3-33. The addition of the Mg reduced the TVOSC production by over 50% at the lower dosage of 0.5% and the higher dosage of 2% had a slightly greater beneficial effect. The Mg addition also did not negatively impact the methane production (data not shown).

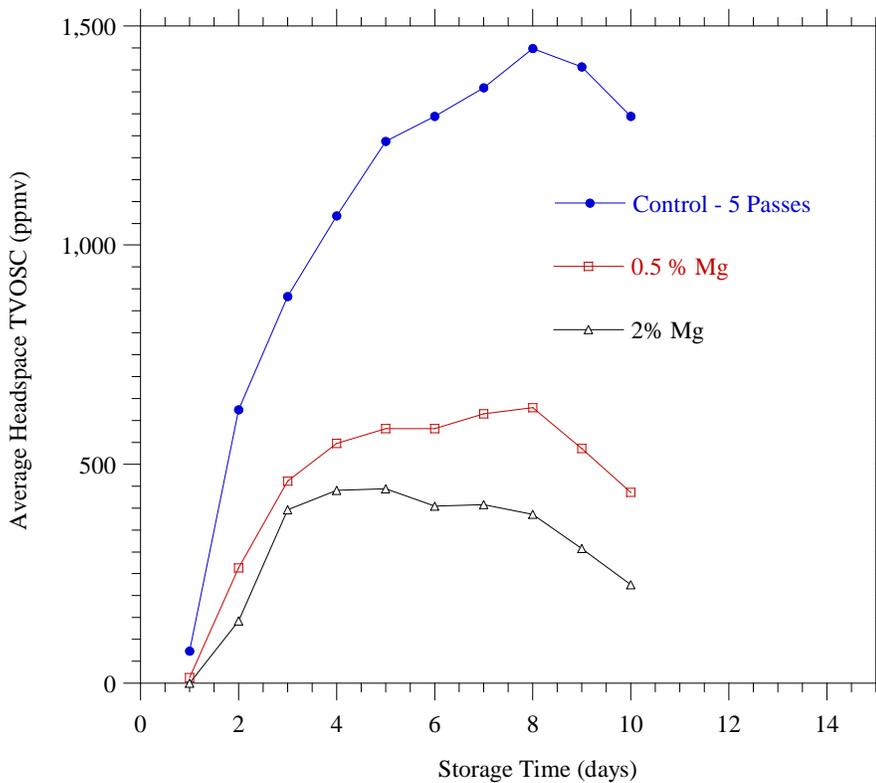


Figure 3-33. Effect of Mg Addition During Conditioning and Dewatering on TVOSC Profile at SG.

3.2 Discussion and Implications

The results show that addition of metal salts, mainly Al, Fe and Mg can reduce the production of TVOSCs when applied appropriately. The results suggest that the different chemicals generally behave similarly, although some differences were found. The challenge of applying these chemicals is that they can also increase TVOSC production at certain dosages, and this appears to be due to the inhibition of methanogens which are important in degrading TVOSCs. For example, Figure 3-34 shows this concept graphically. Initially, a low dose of chemical can have a positive impact in which bioavailable protein is bound such that it is less available for producing TVOSCs. In addition, the dosage is low enough to not cause inhibition of methanogens which can increase TVOSCs. As the dosage increases, the chemical addition begins to inhibit methanogens, and this negative impact is greater than the benefits of protein binding. As the dosage is increased further, the beneficial impacts become greater than the negative impacts of methanogens inhibition, resulting in a net reduction in TVOSCs.

The range at which these impacts occur is also variable and is a factor of the shear imparted during the dewatering process and the solids properties. In general, as the shear increases, greater dosages of chemicals are needed to achieve the same level of treatment. Therefore, in developing an odor reduction plan, the plant should first try to reduce shear imparted to the solids. This will also help reduce the polymer demand since greater shear has been shown to increase the polymer demand (Novak and Lynch, 1990, Novak and Bandak, 1989, Higgins et al., 2006b). For example, Higgins et al. (2005) performed an extensive trial with the Western Lake Superior Sanitation District (WLSSD) to examine the impact of shear on odors

and to develop strategies to reduce shear. They showed that as polymer dosage increased, odors as measured by an odor panel and TVOSC measurements also increased. Also, steps to reduce shear also reduced the polymer demand and odors. For example, adding the polymer directly into the centrifuge compared to adding it even 1 ft upstream of the centrifuge reduced the odors by half and the equivalent shear was also reduced by greater than 50%. Therefore, by taking steps to reduce shear first, the benefits that are derived will reduce odors (and polymer requirements), and the dosages of chemicals needed to control odors should also be reduced.

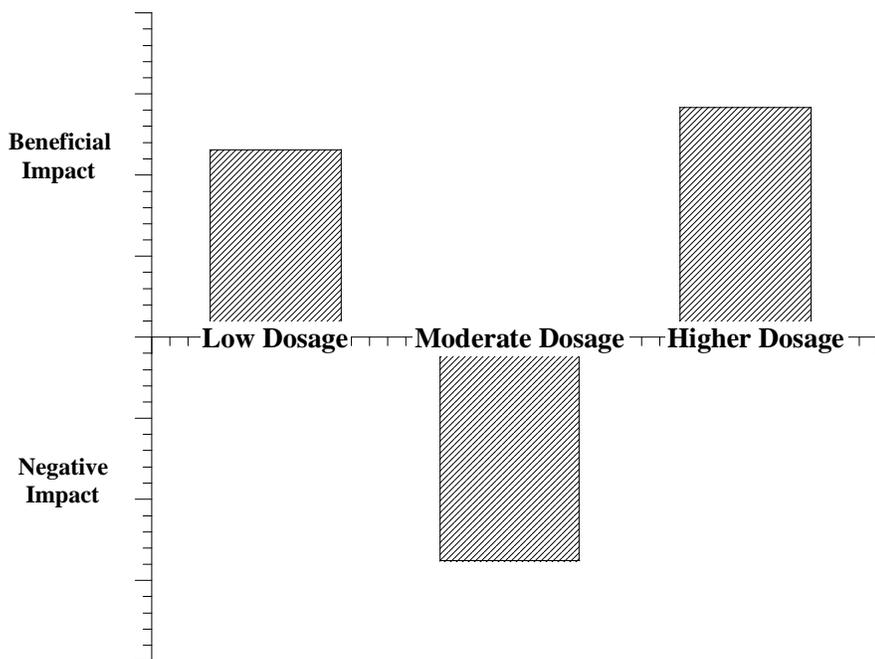


Figure 3-34. Schematic of Chemical Addition Effects on TVOSC Production.

The results from this study also showed that the addition sequence of adding the chemicals relative to the polymer did not have a large impact on the odorant production. Adding either before or with the polymer appears to be the best choice because these locations provided a benefit in terms of odorant reduction, and also resulted in a decrease in the polymer demand. Adding the chemicals after the polymer (and before dewatering) created some dewaterability issues and also increased the polymer demand and is therefore not recommended. The chemicals can also be added directly to the cake, however, they have a large effect on the cake pH while adding the chemicals during dewatering did not depress the cake pH nearly as much as direct cake addition.

Overall, the results generally fit well with results from the field. For example, Figure 3-35 shows the results from a field trial at the PWD SW plant that was performed as part of the WERF Phase II Project. At a 0.5% dosage, no appreciable effect was measured. The addition of 1% Al resulted in greater TVOSC production compared to the control, but addition at higher dosages decreased the TVOSC production. Unfortunately in this trial, a dosage wasn't reached in which the TVOSC production was prevented. The methane production was not impacted at the lowest dosage of 0.5%, but was reduced substantially at 1% as shown in Figure 3-36. Similar to

the lab results in this trial, the inhibition of the methanogens could increase the TVOSC production, and the dosage of 1% was not enough to overcome this negative impact. At the higher dosages of 2 and 4%, the methanogens were inhibited to a greater extent, and had the same level of inhibition, yet, the TVOSC production was reduced. These dosages were enough to overcome the negative impacts of the methanogenic inhibition.

For the PWD NE plant, the addition of alum did not have an impact on the TVOSC production, see Figure 3-37. It is likely that the dosages were not enough to overcome the effects of shear and inhibition of methanogens to reduce TVOSC production. The reason for the difference between the SW and NE plants is still not clear, but is likely due to the difference in shear susceptibility of the sludges and the sludge chemistry. The NE solids required a 62% greater polymer dose for conditioning, which suggests the solids are more susceptible to shear (Higgins et al., 2006b). From this study and others, greater polymer demand and greater susceptibility to shear is linked to greater TVOSC production.

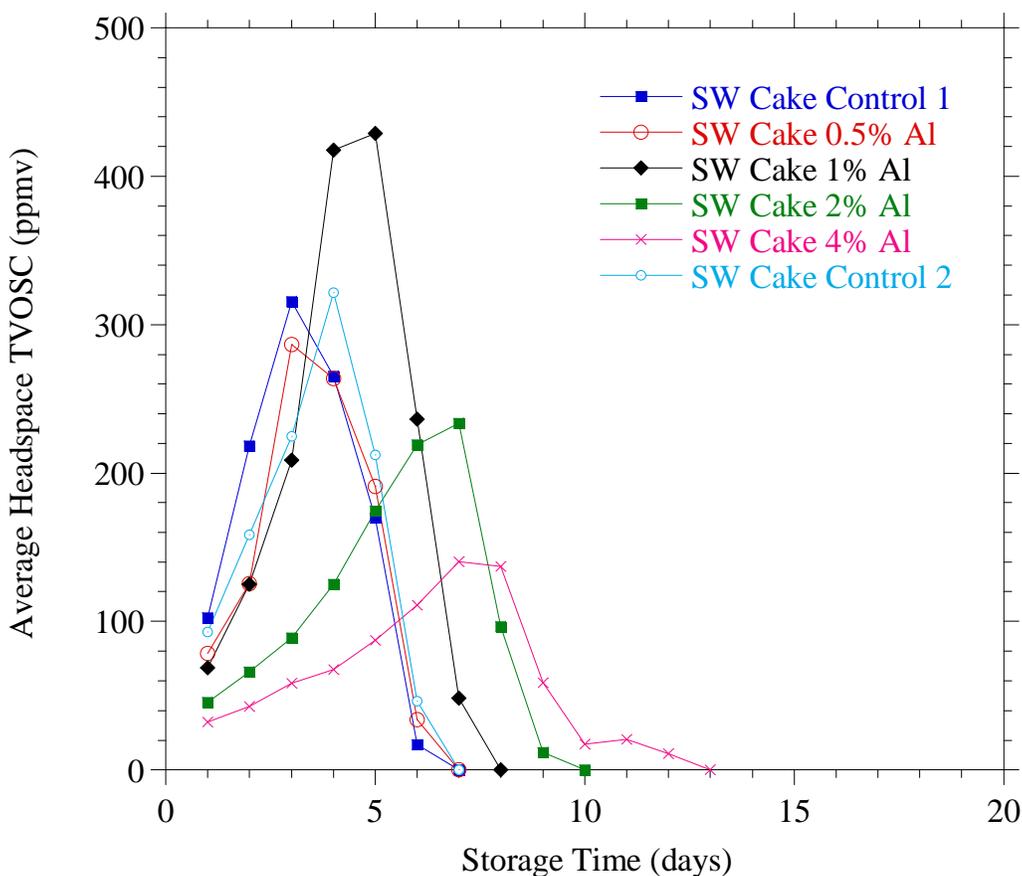


Figure 3-35. Field Trial Results of TVOSC Production with Alum Addition at the PWD SW Plant. (From Adams et al., 2008)

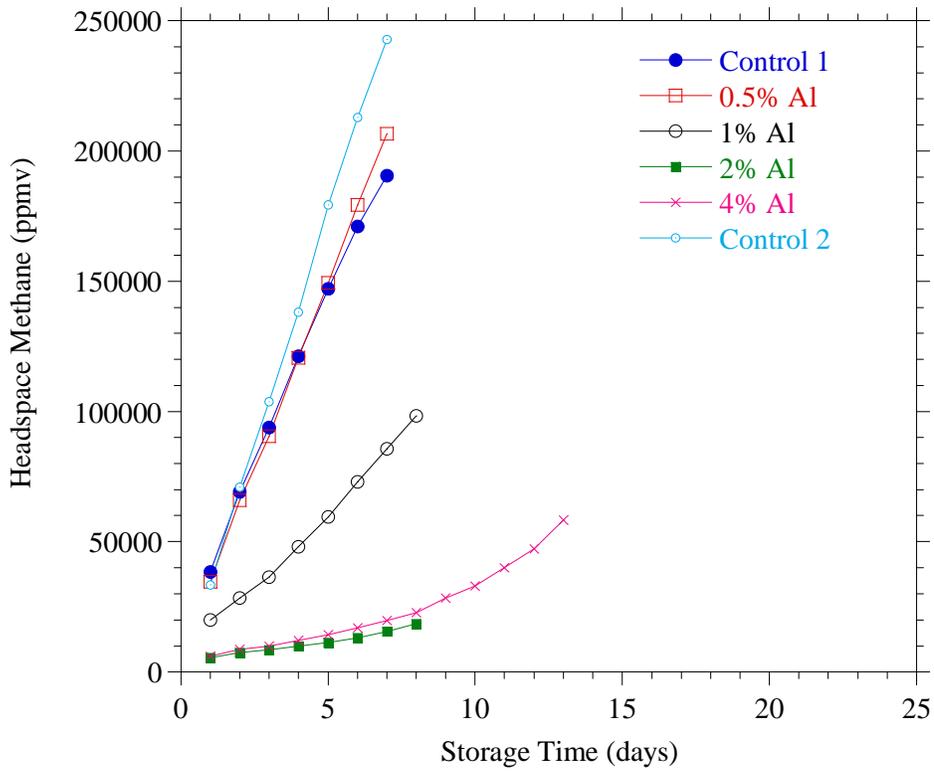


Figure 3-36. Field Trial Results of Methane Production with Alum Addition at the PWD SW Plant. (From Adams et al., 2008)

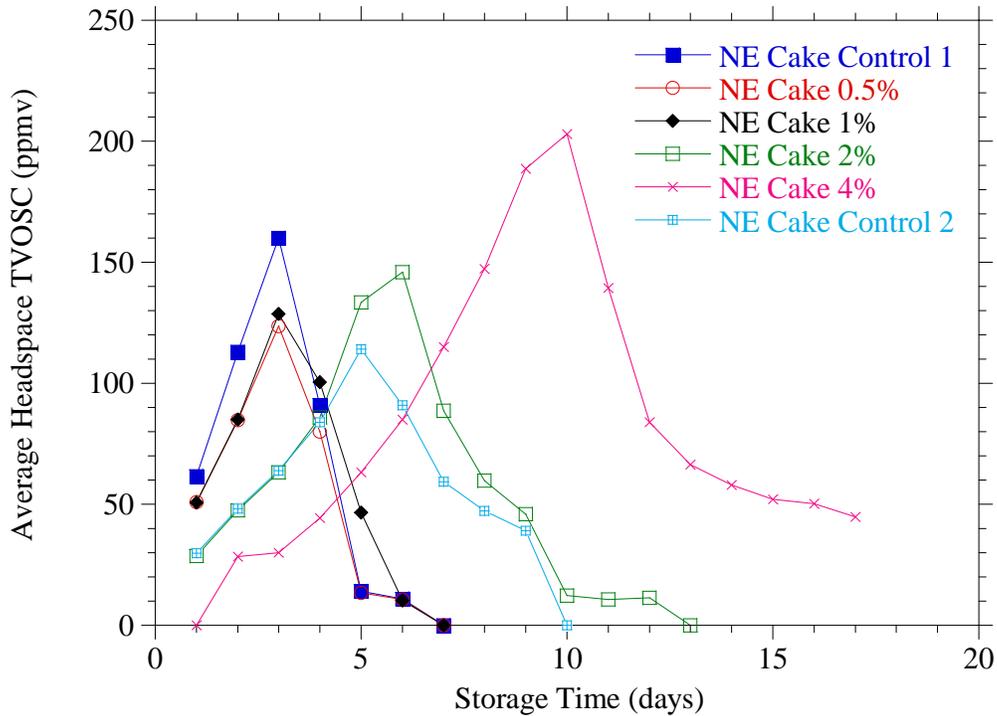


Figure 3-37. Field Trial Results of TVOSC Production with Alum Addition at the PWD NE Plant. (From Adams et al., 2008)

In a separate field trial with ferric chloride addition reported by Higgins et al. (2003, unpublished data) the addition of iron reduced the production of TVOSCs proportionally as shown in Figure 3-38. The peak hedonic tone (HT), which is the most negative or worst value, was also improved with the iron addition as shown in Figure 3-39.

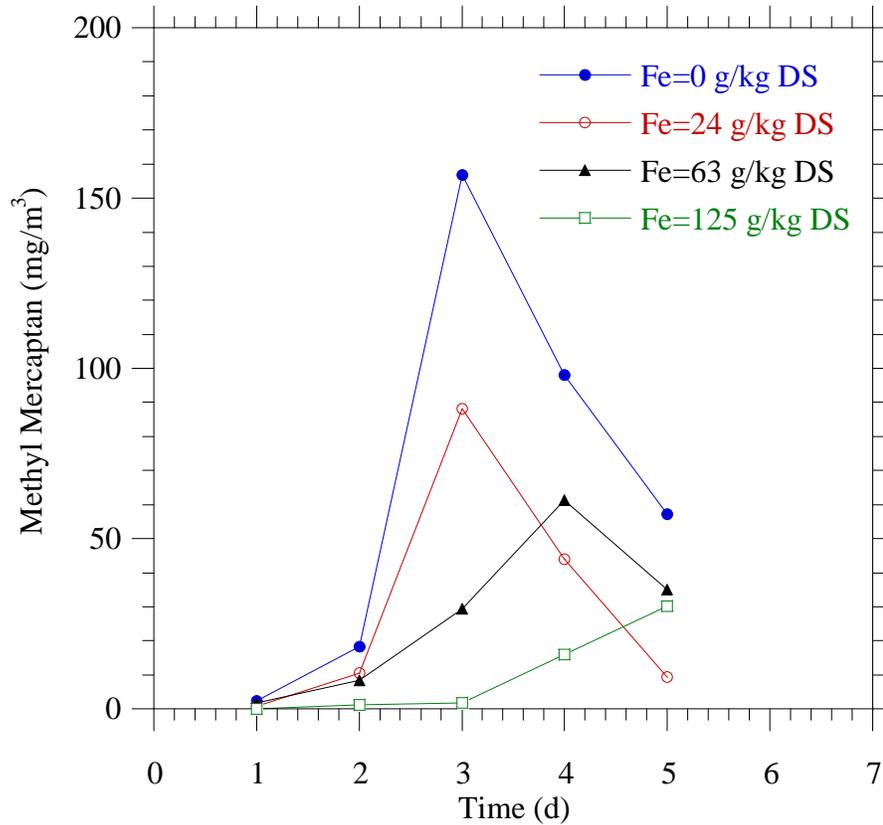


Figure 3-38. Field Trial Results of MT Production with Ferric Chloride Addition at the PWD SW Plant. (Adapted from Higgins et al., 2003 unpublished data)

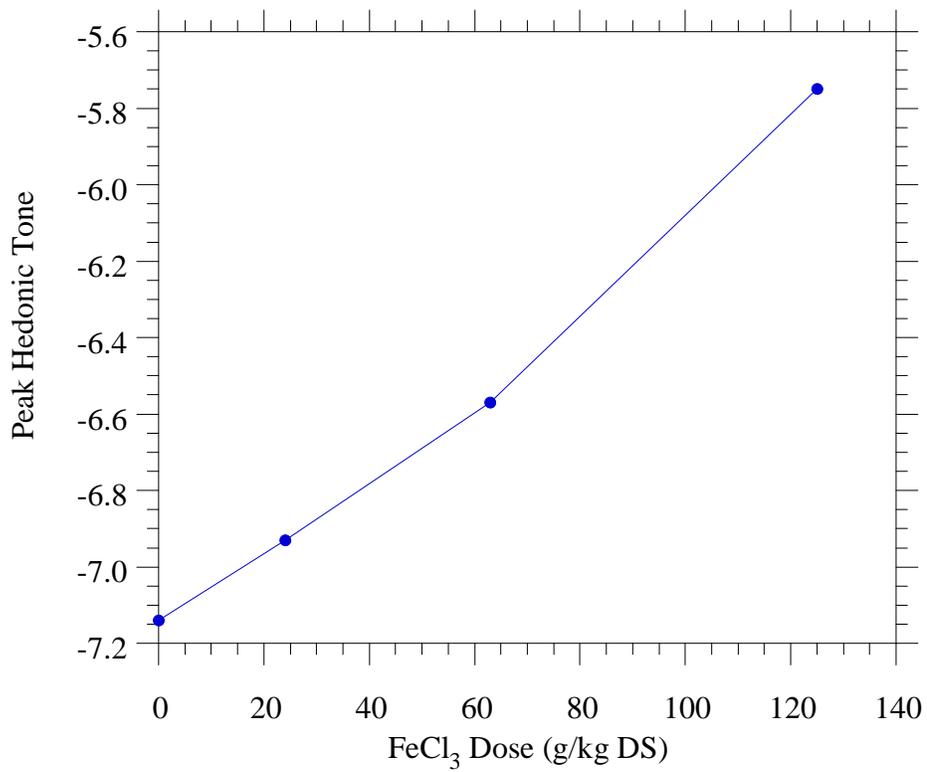


Figure 3-39. Field Trial Results of Hedonic Tone with Ferric Chloride Addition at the PWD SW Plant.
(Adapted from Higgins et al., 2003)

CHAPTER 4.0

SUMMARY AND RECOMMENDATIONS

4.1 Summary

- ◆ Metal salts addition can reduce TVOSC production at the appropriate dosages, but can also increase TVOSC production at lower dosages.
- ◆ The sequence of addition of the metal salts either before, with, or after the polymer addition during conditioning does not have a big impact on the production of TVOSCs in the resultant cake. However, adding the metal salts either before or with the polymer reduces the polymer demand while adding it after increases polymer demand.
- ◆ Addition of the metal salts directly to the cake provided better TVOSC reduction compared to adding the salts during the conditioning and dewatering step, however, addition to the cake also resulted in a greater reduction in the pH of the cake to levels probably below those desirable for land application.
- ◆ Greater amounts of shear applied to the cake leads to greater TVOSC production. Similarly, higher cake solids increases odorant production. In addition, as cake solids increase, the effect of shear is also increased and odorant production increases.
- ◆ The dosages of metal salts needed to reduce TVOSC production is impacted by the shear imparted to the solids. Greater amounts of shear require greater dosage levels to achieve the same reduction in TVOSC.

4.2 Recommendations

- ◆ Prior to undertaking a metal salts addition approach to controlling odorants, utilities should first consider the role of shear in their process and take steps to minimize shear. This could include changing the addition point of the polymer addition, reducing shear in piping systems, and reducing shear in centrifuge operations. All have been shown to reduce polymer demand as well as reduce odors. Since the efficacy of chemical addition is impacted by shear, this should improve the impact of the metal salts on reducing odorant production. At the least, it should reduce polymer demand which will reduce costs.
- ◆ Due to the complex interactions between the biosolids, dewatering equipment, and metal solids, laboratory and pilot testing is recommended as a preliminary step to estimate the potential for reducing the production of odor causing compounds. The testing should evaluate different shear and dosages of the chemicals in the lab as well as addition before dewatering and directly to the cake.

- ◆ A reasonable range of metal salt addition to examine during trials is between 0.1 and 4% on a dry weight basis. The lower dosages can be effective in some cases.
- ◆ The sequence of addition of the metal salts either before, with, or after the polymer addition during conditioning does not have a big impact on the production of TVOSCs in the resultant cake. However, adding the metal salts either before or with the polymer reduces the polymer demand while adding it after increases polymer demand and appeared to create some instability in dewaterability.
- ◆ When choosing between iron and aluminum, both produced similar results. However, in systems low in iron, addition of iron based chemicals can provide additional benefits in reducing hydrogen sulfide, another important odorant. Several trials in this study showed aluminum addition resulted in higher hydrogen sulfide than the addition of iron.
- ◆ Addition of most of these metal salts will depress the pH, especially when adding the metals directly to the cake. Adding it during dewatering has less of an impact on the cake pH. The effect on pH should be considered in a testing program.
- ◆ Iron and aluminum and other metals such as magnesium may play different but specific roles in reducing the odorant production. Therefore, research is needed to examine the potential of using multiple chemical additions which may be more effective than single chemical additions. Similarly, nano-scale versions of some of these chemicals such as zero-valent iron may be more effective than their larger sized alternatives due to the greater surface area and potential reactivity.
- ◆ Additional research is also needed to investigate the impact of metal salt addition on longer term odors that persist after VOSCs have dissipated.

REFERENCES

Adams, G.M., J.R. Witherspoon, Z.K Erdal, R.H. Forbes, R.H., J.R. Hargreaves, M.J. Higgins, D.W. McEwen, and J.T. Novak (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.

Adams, G.M., J. Witherspoon, T. Card, Z. Erdal, B. Forbes, J. Geselbracht, D. Glindemann, R. Hargreaves, L. Hentz, M.J. Higgins, D. McEwen, and S. Murthy. (2004) Identifying and Controlling Odor in the Municipal Wastewater Environment Phase 2: Impacts of In-Plant Operational Parameters on Biosolids Odor Quality. Water Environment Research Foundation Report No. 00HHE5T, Alexandria, VA.

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.

Chen, Y.C., M.J. Higgins, N.A Maas, S.N. Murthy, and W.E. Toffey (2005) Roles of Methanogens on Volatile Organic Sulfur Compound Production in Anaerobically Digested Wastewater Biosolids. *Water Sci. and Technology*, 52, 67-72.

Chen, Y.C., M.J. Higgins, N.A. Maas, and S.N. Murthy (2006) DNA extraction and Escherichia coli quantification of anaerobically digested biosolids using the competitive touchdown PCR method. *Water Research*, 40(16): 3037-3044.

Chen, Y.C., M.J. Higgins, S.M. Beightol, G.G. Araujo, S.N. Murthy, E.J. Barben, and W.E. Toffey. (2007) Odour Generation and Pathogen Indicator Regrowth after Dewatering: Are They Related? *Proceedings of Int. Wat. Assoc. Specialist Conference-Wastewater Biosolids Sustainability*, Moncton, Canada.

Higgins, M.J. and J.T. Novak. (1997a) Characterization of Exocellular Protein and Its Role in Bioflocculation. *Journal of Environmental Engineering*, **123**, 479-485.

Higgins, M.J. and J.T. Novak. (1997b) The Effect of Cations on the Settling and Dewatering of Activated Sludges: Laboratory Results. *Water Environment Research*, **69**, 215-224.

Higgins, M.J., K. Hamel, Y.C. Chen, S.N. Murthy, E.J. Barben, A. Livadaros, M. Travis, and N.A. Maas. (2005) Part II of Field Research: Impact of Centrifuge Torque and Polymer Dose on Odor Production from Anaerobically Digested Biosolids. *Proceedings of WEF/AWWA Joint Residuals and Biosolids Management Conference*. Nashville, TN.

Higgins, M.J., D.P. Yarosz, Y.C. Chen, S.N. Murthy, N. Maas, J. Cooney, D. Glindemann, and J.T. Novak. (2006a) Cycling of volatile organic sulfur compounds in anaerobically digested biosolids and its implications for odors. *Water Env. Research*, 78, 243-252.

Higgins, M.J., S.N. Murthy, and Y.C. Chen. (2006b) Understanding Factors Affecting Conditioning and Dewatering. Water Environment Research Foundation Report No. 01-CTS-1, Alexandria, VA.

North, J.M., J.G. Becker, E.A. Seagren, M. Seagren, M. Ramirez, and C. Peot (2008) Methods for Quantifying Lime Incorporation into Dewatered Sludge. I: Bench-Scale Evaluation. *J. Envir. Engrg.* **134**, p. 750.

Novak, J.T. and N. Bandak (1989) Chemical conditioning and the resistance of sludges to shear. *Water Environ. Res.*, **61**, 327-332.

Novak, J.T. and D.P. Lynch (1990) The Effect of Shear on Conditioning: Chemical Requirements During Mechanical Sludge Dewatering. *Wat. Sci. Tech.* **22**, 117-124.

Sobeck, D.C. and M.J. Higgins (2002) Examination of three theories for mechanisms of cation-induced bioflocculation. *Water Research*, **36**, 41-52.