

Impacts of the Use of Magnesia Versus Iron on Mesophilic Anaerobic Digestion and Odors in Wastewater

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science

In

Civil Engineering

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September 15, 2011

Blacksburg, VA

Keywords: mesophilic anaerobic digestion, iron, magnesium, dewatering, odors,
biosolids, struvite, nutrient removal

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ABSTRACT

Addition of iron to sewer lines for chemical phosphorus removal is widely practiced around the world. However, high dosage of iron may prove detrimental to the anaerobic digestion process and also lead to higher organic sulfur odors and deteriorating biosolids quality. The following research focuses on finding an alternative to the use of iron in wastewater systems by comparing the roles of iron and magnesium on mesophilic anaerobic digestion, the digested effluent characteristics and odors in biosolids. Three anaerobic digesters were operated, one serving as a control with no additives, and the other two having known doses of iron and magnesium added. Comparison of the effluent characteristics revealed an improvement in the overall performance of the magnesium amended digester (in terms of pH, solids and COD reduction, alkalinity and gas production) over the other two reactors, suggesting the benefits of magnesium addition. Both iron and magnesium were found to be effective in achieving high levels of phosphate removals and reducing nuisance odors in dewatered sludge cakes.

ACKNOWLEDGEMENTS

I express my heartfelt gratitude to my advisor and mentor, Dr. John T. Novak for his continuous guidance and support. He is primarily responsible for the success of this work, and I am highly indebted to him for his benevolence, his timely advice and the faith he reposed in me throughout. Likewise, I wish to extend my gratitude to my committee members Dr. William R. Knocke and Dr. John C. Little for their support and guidance.

I acknowledge the monetary support that I received from Premier Magnesia, LLC. for this research. I thank Tampa (FL) and Dallas (TX) utilities for providing me with the sludge samples for this study. Special thanks go to Mr. Matthew P. Madolora, Senior Technical Business Unit Manager, Premier Magnesia, LLC. His enthusiasm and keen insights into this study were really helpful for me.

I would also like to acknowledge and thank the timely help and advice I have had regarding lab practices and experimental methods from Julie Petruska and Jody Smiley. I cannot forget the numerous occasions that Jody has calmly helped me with different instruments. Betty Wingate and Beth Lucas have been most co-operative and supportive in administrative issues and I duly acknowledge their help. Special thanks to Beth for reserving vehicle from fleet services every time I had to do a sludge run to the Town of Christiansburg Wastewater Treatment Plant. I would also like to thank Dottie, Daniel, Dennis, Jackie and everyone else from the Town of Christiansburg Wastewater Treatment Plant for their cooperation.

I thank my fellow researchers and friends Ana Arango, Andrew Jones, Cheng Qian, Evan Bowles, Gargi Singh, Jennifer Miller, Katherine Young, Laurel Ackinson, Nevin Yagci, Nirupa Maharajh, Pallavi Bishnoi, Renzun Zhao, Ritika Kacker, Sheldon Masters, Vidula Bhadkamkar to name a few, for having innumerable valuable discussions with me throughout the span of this study and maintaining a friendly environment in the laboratory. Special mention goes to Jongmin Kim for his timely guidance and advice, to Jennifer Miller and Katherine Young for sharing the work load and data for the control

reactor and to Pallavi Bishnoi for taking care of my reactors in my absence. I thank Anuj Mistry, my friend and colleague from Industrial Systems Engineering department for helping me with statistical analyses of my data. I also thank all my friends and well-wishers who made my stay in Blacksburg pleasant. Finally, I sincerely thank my family for being with me as my support and strength and inculcating values in me throughout my life. I dedicate this work to them, whose support and blessings have been instrumental for me in pursuing my goals. Lastly, my hands join in the praise of the almighty Lord for ushering me into this beautiful world.

TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iii
TABLE OF CONTENTS.....	v
LIST OF TABLES AND FIGURES.....	vii
CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: LITERATURE REVIEW.....	3
2.1 Overview of Anaerobic Digestion (AD).....	3
2.2 Role of Cations, especially Iron, Magnesium and Aluminum.....	7
2.3 Odors from Dewatered Sludge Cakes.....	12
2.4 Phosphorus Removal and Recycling as Struvite.....	15
2.4.1 Phosphorus Removal from Wastewater.....	15
2.4.2 Struvite Precipitation Issues in Anaerobic Digestion.....	16
2.4.3 Interests in Controlling and Recovering Phosphorus as Struvite (Corre et al., 2009).....	18
2.5 Iron Addition for Phosphorus Removal.....	20
2.6 THIOGUARD® in Sanitary Treatment Plants and Collection Systems (THIOGUARD® White paper).....	22
CHAPTER 3: MATERIALS AND METHODS.....	24
3.1 Production and Dosing of Primary Sludge and Waste Activated Sludge Blend... ..	24
3.2 Anaerobic Digester Setup and Operation.....	25
3.3 Analytical Methods.....	27

CHAPTER 4: RESULTS AND DISCUSSION.....	31
4.1 Results.....	31
4.1.1 Phase I.....	31
(a) pH.....	32
(b) Solids.....	33
(c) Alkalinity.....	34
(d) Odors.....	35
(e) Ions.....	36
4.1.2 Phase II.....	38
(a) pH.....	39
(b) Solids.....	40
(c) COD.....	42
(d) Interactions Between the Above Parameters.....	43
(e) Alkalinity.....	46
(f) VFA.....	47
(g) Specific Gas Production.....	48
(h) Solution Ions.....	49
(i) Odors, Dewatering and Cake Solids.....	57
(j) Chemical Precipitation Experiment.....	61
4.2 Discussion.....	63
4.3 Proposed Mechanisms of Mg(OH) ₂ Functioning.....	66
4.3.1 Dissolved Mg(OH) ₂ Can Neutralize the Volatile Fatty Acids Produced by the Acidogens, Resulting in a Better pH Environment for the Methanogens.....	66

(a) Increase in pH Leads to Enhanced Digestion Operability.....	66
(b) Reduced Long Chain Fatty Acid Inhibition.....	68
4.3.2 Stimulatory Effects of Light Metal Cation Mg ⁺⁺	69
4.3.3 Phosphate Removal Efficiency and Struvite Formation Potential.....	71
 CHAPTER 5: CONCLUSIONS.....	 72
 CHAPTER 6: ENGINEERING SIGNIFICANCE AND FUTURE RECOMMENDATIONS.....	 73
 REFERENCES.....	 75

LIST OF TABLES AND FIGURES

TABLES

Table 4-1: Solution Ions data for Phase I.....	36
Table 4-2: Total Ions data for Fe and Mg influent feeds in mg of cations/ g TS.....	37
Table 4-3: Optimum Polymer Dose and Cake Solids data for Odor Run 1.....	59
Table 4-4: Optimum Polymer Dose and Cake Solids data for Odor Run 2.....	59
Table 4-5: Stimulatory and Inhibitory Concentrations of Light Metal Cations (Grady et al., 1999).....	70
Table 4-6: Antagonistic Responses for Light Metal Cations and Ammonia (Grady et al., 1999).....	70

FIGURES

Figure 2-1: Multistep nature of anaerobic operations.....	4
Figure 2-2: Proposed distribution of organics in sludge associated with specific metals (Novak et al., 2007).....	8
Figure 2-3: Effect of ferric chloride dose on solution protein, polysaccharide and CST.....	10
Figure 2-4: TVOSC generation from dewatered sludge cakes (Novak et al., 2010).....	14
Figure 4-1: pH data for Phase I.....	32
Figure 4-2: Solids reduction profiles for phase I.....	33
Figure 4-3: Average influent and effluent alkalinity values for phase.....	34
Figure 4-4: TVOSC Odors comparison for Phase I.....	35
Figure 4-5: pH data for phase II.....	39
Figure 4-6: TSR and VSR data for Phase II.....	40
Figure 4-7: COD reduction data for Phase II.....	42
Figure 4-8: Relation between VSR & pH for each reactor during Phase II.....	43
Figure 4-9: Relation between VSR & pH for all reactors combined during Phase II.....	43
Figure 4-10: Relation between VSR & CODR for each reactor during Phase II.....	44
Figure 4-11: Relation between VSR & pH for all reactors together during Phase II.....	44
Figure 4-12: Alkalinity data for Phase II.....	46
Figure 4-13: VFA data for Phase II.....	47
Figure 4-14: Specific gas production data for Phase II.....	48
Figure 4-15: Average cations concentration during Phase II.....	51
Figure 4-16: Average gain in cations concentration during Phase II.....	52
Figure 4-17: Average anions concentration during Phase II.....	54

Figure 4-18: Average gain in anions concentration for Phase II.....	55
Figure 4-19: H ₂ S Odor data for Phase II.....	57
Figure 4-20: TVOSC Odor data for Run 1 (6-7-11) during Phase II.....	58
Figure 4-21: TVOSC Odor data for Run 2 (7-8-11) during Phase II.....	58
Figure 4-22: Relation between soluble phosphate and Mg(OH) ₂ dose for precipitation experiment.....	61
Figure 4-23: Effects of pH and temperature on the total ammonia-N concentration necessary to give a free ammonia concentration of 100 mg/L as N. (Grady et al., 1999).....	67

Chapter 1: Introduction

The addition of iron to collection systems is a common practice in many municipal wastewater utilities to reduce corrosion. However, recent research at Virginia Tech (Novak et al., 2007) suggests that excessive iron addition leads to increased organic sulfur odors (resulting from methane thiol, dimethyl sulfide and dimethyl disulfide) from anaerobically digested and centrifuged biosolids. The problem evolves slowly and manifests as iron dependence gradually produces progressively higher organic sulfur odors and deteriorating biosolids quality.

Many facilities add iron salts to the distribution systems to reduce the emission of hydrogen sulfide by precipitating sulfide in the form of FeS. However, it has been suggested that, at some point this practice begins to negatively impact the treatment plant's digestion process and the resulting biosolids.

Over the years, the non-toxic antacid milk-of-magnesia ($Mg(OH)_2$) has emerged as an effective complementary or alternative chemical strategy. Similar to iron, magnesium is an essential element for the proper functioning of biological systems. However it brings the added advantage of being non-hazardous and better suited for digestion. This versatile chemical can be used for pH control in wastewater systems without the negative effects of iron. Iron lowers the pH and results in added solids through precipitation of ferric hydroxide. Iron can also change oxidation-reduction potential, leading to chemical changes that may be undesirable, especially under reduced conditions.

Magnesium hydroxide can reduce the generation of hydrogen sulfide gas, which is corrosive and odorous, due to higher pH conditions. Moreover, it can also be effective in controlling objectionable organic odors. Magnesium hydroxide works not only through pH control so sulfide is present in its ionic forms and not as the gaseous form, but also as a source of divalent cations necessary for settling and digestion. However, most utilities have not switched to magnesium hydroxide yet. Past research shows that iron is effective in increasing the solids destruction and reducing the H_2S odors in sewers. Primarily, the concern is that iron is a "known quantity" while magnesium is not. Specifically, there is

confusion about the control of odors in the collection system and the effect on treatment plant operations from the magnesium addition to the influent. While research at Virginia Tech has shown divalent cations to be beneficial to aerobic biological flocculation (Higgins and Novak, 1997), there is little data to indicate its impact on anaerobic digestion or the generation of odors from digested and dewatered sewage sludge.

Anecdotal and limited research indicates improvement to various plant processes by magnesium hydroxide for the removal of BOD, total suspended solids, ammonia and phosphorus (Bishop, 2006). The effect of magnesium should be to reduce organic sulfur odors. However, iron and magnesium differ in their impact on sludge characteristics. Most of the iron added in the collection system should be removed in the primary clarifier while most of the magnesium will remain in solution and will most likely impact the secondary sludge. It is unlikely that either will have an impact on nutrient removal. However, it is possible that some of the iron added to the collection system will precipitate some phosphorus. If iron is added to the head works, it should remove phosphorus, but recent research at Virginia Tech suggests that this point of addition will have little impact on digestion or odors (Novak and Park, 2010). It is also a concern that too much iron at the head works can be phosphorus-limiting both in secondary treatment and in digesters, as iron-bound phosphorus may be unavailable for the biota. Moreover, the fate of either the magnesium or the iron solids once they enter the treatment plant environment is not clear.

This project focuses on a comparison of the roles of iron and magnesium on solids reduction by anaerobic digestion, anaerobic digestion effluent characteristics and odors in biosolids. The main motive is to assess the advantages of the use of magnesium hydroxide as an additive to the anaerobic digestion process, and compare its performance with iron addition. The following are the objective(s) of this research: Assess the comparative roles of iron and magnesium on solids destruction, effluent characteristics, nutrient removal, gas production, odor generation and overall performance in anaerobic digestion of municipal wastewater sludge.

Chapter 2: Literature Review

2.1 Overview of Anaerobic Digestion (AD)

Anaerobic digestion (AD) of waste water is a widely practiced technique due to its sustainability aspects. Anaerobic wastewater treatment systems are biological systems operating in the absence of oxygen. AD is used for the stabilization of particulate organic matter and production of methane and carbon dioxide rich biogas that can be used as a source of green energy. The microbial communities in anaerobic operations are primarily prokaryotic, with members of both the bacteria and the archaea being involved. Thus the emphasis here would be on the complex and important interactions between the bacteria and the archaea that are fundamental to the successful functioning of the methanogenic communities.

There are a variety of metabolic processes, inhibitory compounds, hydrolytic activities and syntrophic associations that occur during anaerobic digestion. In general, the progression of anaerobic degradation of organic matter moves through four principal reaction steps, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Hydrolysis, acidogenesis and acetogenesis are carried out by members of the domain bacteria while methanogenesis is carried out by methanogens, which are members of the domain archaea.

The digestion process begins with bacterial hydrolysis of the input particulate materials in order to break down insoluble organic polymers such as carbohydrates, proteins and lipids into sugars, amino acids and long chain fatty acids respectively, and make them available for other bacteria. Acidogenic bacteria then convert the sugars, amino acids and long chain fatty acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. The production of hydrogen is very critical because it serves as one of the primary substrates for the production of methane (Grady et al., 1999). The final stage, methanogenesis results in the formation of methane (CH₄). Two types of methanogenic archaea are involved in this process. Aceticlastic

methanogens split acetic acid into methane and carbon dioxide. Hydrogen oxidizing archaea use hydrogen as an electron donor and carbon dioxide as an electron acceptor to produce methane (Grady et al., 1999, Appels et al., 2008). The multistep nature of anaerobic biochemical operations is depicted in Figure 2-1.

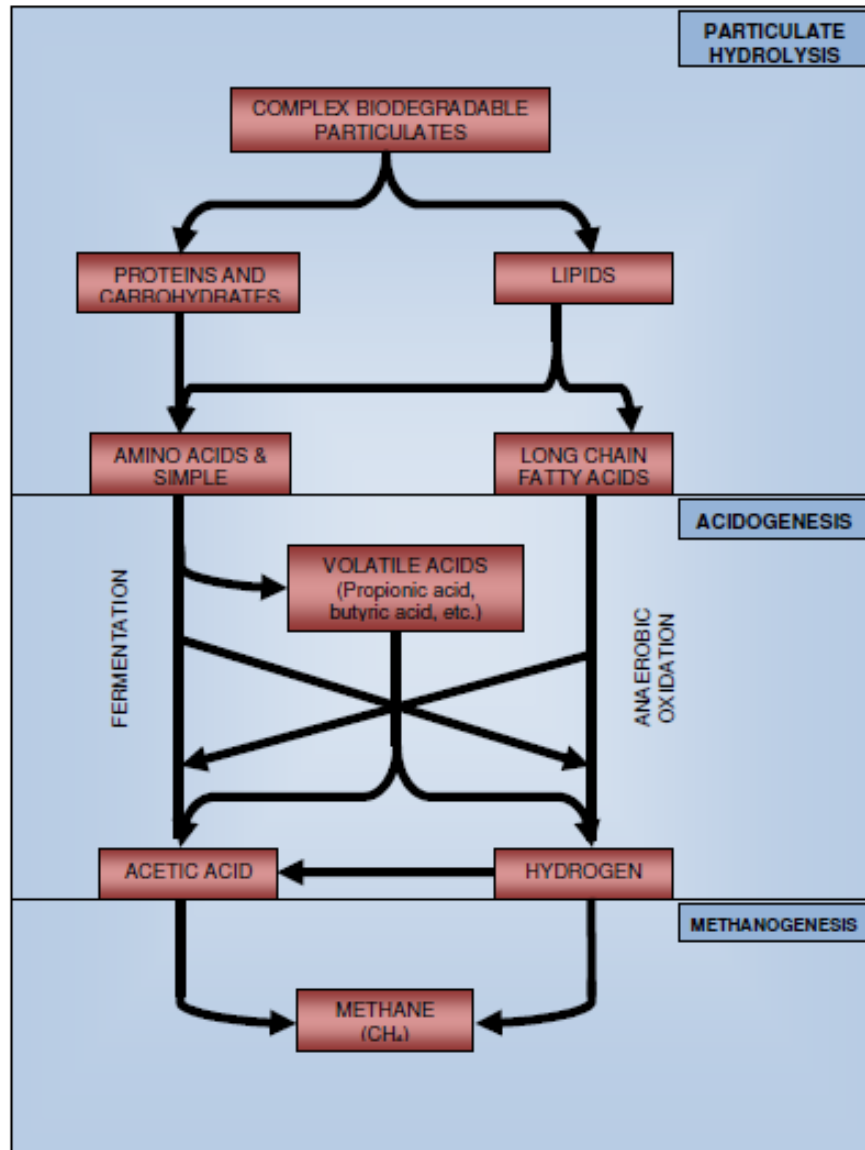


Figure 2-1. Multistep nature of anaerobic operations

Various factors govern the performance of the digester. These are pH, temperature, solids retention time (SRT), alkalinity, biogas production, accumulation of volatile fatty acids (VFAs), organic loading rate, total hydraulic loading and level of xenobiotic compounds.

The optimum pH for anaerobic digestion is 6.8 - 7.4 (Grady et al., 1999). The methanogenic activity will slow down considerably with pH less than 6.3 and higher than 7.8 and this will reduce the biogas production (Leitao et al., 2006). A lower pH will result in the growth of filamentous bacteria and a high pH results in buildup of unionized ammonia (Grady et al., 1999).

Accumulation of VFAs result during overloading and sudden variations in organic loading rates (Leitao et al., 2006). Volatile fatty acids are weak acids that are dissociated at a neutral pH (Grady et al., 1999). The presence of high concentrations of VFAs is detrimental to methanogenic activity through the toxic action of unionized VFAs and they always suggest a reactor imbalance. It is always beneficial to maintain favorable pH and moderate VFA concentration so that no drastic effects are imposed on the system (Cohen et al., 1982).

Major nuisance organisms in anaerobic operations are sulfate reducing bacteria, and they are present in large numbers when the waste water contains a significant amount of sulfate. The main problem with these organisms is that they compete with acetate and hydrogen for the electron donor and this results in production of sulfide and reduces the amount of methane formed (Grady et al., 1999).

Solids retention time plays very important role in the design of the anaerobic process. It represents the average length of time a particulate constituent stays in the reactor. It is the most important design parameter available for an engineer as it is directly related to specific growth rate of biomass in a continuously stirred tank reactor (Grady et al., 1999).

Other factors that affect anaerobic processes include high concentrations of xenobiotic compounds, heavy metals, detergents and oxygen. These will generally result in accumulation of VFAs and a reduction in pH (Leitao et al., 2006).

Temperature plays a very important role in anaerobic digestion. There are two critical temperature ranges mesophilic digestion (35°C - 40°C) and thermophilic digestion (50°C - 60°C). The digestion process can be carried out in one stage or multi stages and under mesophilic or thermophilic conditions.

2.2 Role of Cations, especially Iron, Magnesium and Aluminum

The addition of the cations iron, magnesium or aluminum into activated sludge basins for phosphorus removal is likely to impact both the efficiency of the anaerobic digestion process and the generation of odor-causing compounds following digestion and dewatering. There is limited data on the effect of magnesium additives on anaerobic digestion performance. However, the roles of iron and aluminum have been studied in the past.

Former studies on the effect of iron and aluminum on anaerobic digestion have revealed that iron addition was found to have little impact on the volatile solids destruction and on sludge dewatering properties. Aluminum addition, like iron addition, had little impact on sludge dewatering properties. However, aluminum reduced volatile solids destruction in the anaerobic digesters and this is consistent with other studies. It has been proposed that aluminum binds to organics in sludges, especially proteins and makes these less bioavailable. A similar mechanism has been proposed for iron but a decrease in VS destruction was not seen in the study by Novak and Park (2010).

The literature reports mixed results with regard to the impact of iron on gas production and solids destruction in anaerobic digesters ranging from enhanced digestion to reduced digestion (Dentel & Gossett 1982; Johnson et al., 2003). It is likely that the way in which the iron is added and the nature of the sludges being tested influence the results.

With regards to the reduction in odor causing organic sulfur compounds, the direct addition of both iron and aluminum to an anaerobic digester results in reduced total volatile organic sulfur compounds (TVOSC) generation. It was thought that aluminum might reduce the production of organic sulfur compounds by binding proteins and making these less available. It was also proposed that the iron becomes reduced under anaerobic conditions and precipitates the organic sulfur compounds (Novak and Park, 2010).

Because much of the organic matter in sludge appears to be associated with metals, it was thought that metals and specific metal-associated sludge fractions might provide useful

information about odors and solids reduction by anaerobic digestion. Recent research has focused on developing a better understanding of the composition of sludge, especially the role that metals may play in determining floc structure. It has been found that the cations Ca^{++} and Mg^{++} can influence both the effluent quality from activated sludge and also the settling and dewatering characteristics of the sludge (Higgins and Novak, 1997). More recently it has been shown that the volatile solids destruction by anaerobic digestion of waste activated sludge varies with the iron content in the sludge matrix (Park et al., 2006). As the iron content increased, the volatile solids destruction also increased. It was suggested that activated sludge floc consists of several different fractions, one associated with iron and another associated with Ca^{++} and Mg^{++} and these fractions digest differently (Novak et al., 2003). Park and Novak (2007) suggested that at least three organic fractions exist in sludge and these are iron bound organics that degrade under anaerobic conditions, aluminum bound fraction that generally resists biological degradation under any conditions and a fraction associated with divalent cations that degrade aerobically but not anaerobically. A graphical presentation of these fractions for primary and secondary sludge is shown in Figure 2-2. Since these fractions are thought to respond differently under anaerobic conditions, it was thought that metals in sludge could also impact odor generation from anaerobically digested sludges. This research focused on examining the role of metals with regard to digestibility by anaerobic digestion and the impact of metals on odor generation.

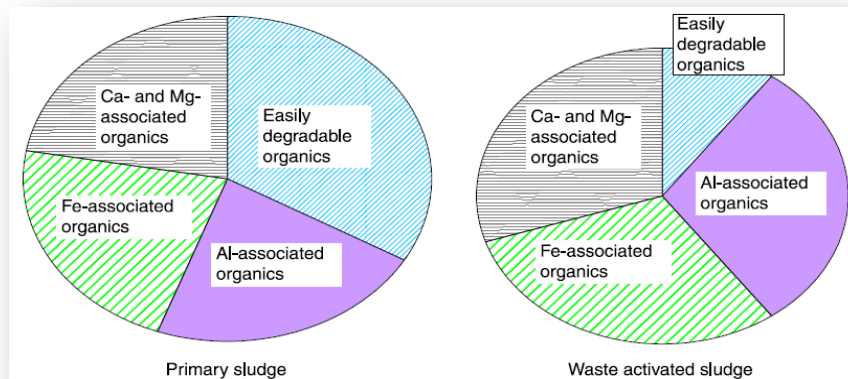


Figure 2-2. Proposed distribution of organics in sludge associated with specific metals (Novak et al., 2007)

The study on the effect of cations on activated sludge showed that the settling and dewatering properties were dependent on both the concentrations and ratios of cations in the feed (Higgins and Novak, 1997). The results of this study demonstrated that the cation content in a wastewater can have a major impact on the settling and dewatering characteristics of an activated sludge. The relative ratios and concentrations of cations play a role in determining settling and dewatering characteristics. When present in the feed, cations become incorporated within the microbe-biopolymer network, creating a dense floc that is more resistant to shear. This results in an improvement in settling and dewatering properties and reduces conditioning requirements. The divalent cations appear to bind mainly protein within the floc matrix. Some activated sludge systems require both calcium and magnesium in the feed while others only require one of these cations for good settling and dewatering properties. The poor settling and dewatering of suspensions receiving low divalent cation concentrations in the feed can also be improved by batch addition of calcium and/or magnesium. Addition of the monovalent cation, sodium, to the feed results in a deterioration in settling and dewatering properties when the monovalent to divalent cation ratio exceeded approximately 2:1, expressed on an equivalent basis.

Cations are an integral part of the floc structure, linking separate biopolymer components together into a floc structure. The cation content of wastewater, especially the ratio of monovalent to divalent cations, has been shown to influence the properties of activated sludge flocs (Higgins and Novak, 1997). A high concentration of monovalent cations is usually associated with a weak floc structure and a large amount of biocolloids in solution.

Cations have been found to influence the settling and dewatering characteristics of biological sludges. It has been shown that iron contributes to floc strength and it appears that the deterioration in sludge dewatering during anaerobic digestion is associated with the reduction and solubilization of iron (Novak et al., 2001). Further, it is the presence of proteins in solution that contributes to poor dewatering and to the demand for conditioning chemicals.

It has been proposed that the stability of biological flocs is due to the presence of iron that binds with the protein content of the biopolymer and this metal-protein complex is both biologically resistant and physically stable (Novak et al., 2001). Anaerobic digestion reduces the iron, weakening the iron-protein bonds resulting in a release of biopolymer into solution. The solution biopolymer contributes to both the decreased dewaterability and the increased demand for conditioning chemicals, primarily associated with the protein fraction in solution.

The shearing of anaerobically digested sludges releases protein into solution. The addition of iron for improving dewatering shows that iron may selectively coagulate solution proteins. It is thought that the iron-protein complexes are relatively resistant to shear accounting for the limited observed release of proteins. The iron content of sludges may be important in determining floc strength but this has not yet been thoroughly investigated. The possible role of iron in floc formulation can also be seen in the conditioning data shown in Figure 2-3 (Novak et al., 2001).

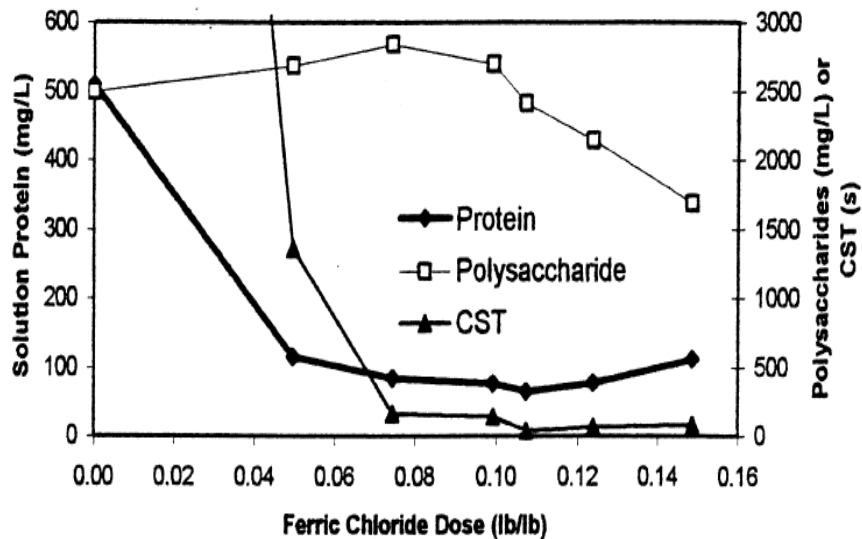


Figure 2-3. Effect of ferric chloride dose on solution protein, polysaccharide and CST

Recent research in our laboratory has focused on developing a better understanding of the role of iron and other cations in sludge digestion and odor generation. Data suggest that both iron and aluminum can decrease the available phosphorus and that may decrease VS destruction. However, iron will change oxidation states under anaerobic conditions and release phosphorus, this might account for the differences between iron and aluminum on digestion efficiency. (Novak et al., 2010). The impact of magnesium and aluminum is less clear but some data indicate that aluminum will reduce solids reduction by anaerobic digestion. This may be due to a direct effect on organic solids bioavailability or due to the removal of phosphorus, making the system nutrient deficient. Little is known about the impact of magnesium on anaerobic digestion. Data presented by Bishop (2006) indicated that magnesium could increase methane production in a batch digestion study and this data was one of the motivations for conducting this research.

2.3 Odors from Dewatered Sludge Cakes

Odor generation from dewatered sludge cakes has been the focus of study by Water Environment Research Foundation (WERF) for the past seven years. This research has shown that anaerobically digested sludges are capable of emitting substantial quantities of organic sulfur compounds, the main odor causing chemicals, and that the odor from dewatered sludge cakes is much greater from centrifugally dewatered sludges than from those dewatered by belt presses. This is thought to be due to the large amount of shear that occurs in a centrifuge (Muller et al., 2004). To evaluate sludge odor generation, a headspace procedure was developed (Glindemann et al., 2006) to measure the gases produced by sludge cakes. This method is designed to mimic the odor generation that occurs from fresh sludge piles.

Murthy et al., (2002) has reported that anaerobically digested biosolids have the potential to produce unacceptable odors. Volatile organic sulfur compounds (VOSCs) are the primary group of compounds associated with odor from anaerobically digested biosolids (Forbes et al., 2003; Higgins et al., 2002). Reduced sulfur compounds include H₂S and VOSCs such as methanethiol (MT), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS). Based on prior research (Adams et al., 2007), it has been found that the total volatile organic sulfur compounds (TVOSCs) concentrations exceeding 500 ppmv can be considered to be odorous sludges while values below 100 ppmv can be considered as very low odor sludges.

These sulfur-based compounds may cause acidification of forests and lakes vastly, while they also attribute to local odor problems from compost sites, wastewater treatment plants and paper and textile industries. They can be a nuisance to local communities or even a threat to the human health at much higher concentration. In this regard, the generation and removal of volatile sulfur compounds from wastewater sludge should be understood to devise countermeasures for enhanced odor removal from dewatered sludge cakes or the accidental emission to the localities, which may cause serious protests or claims.

Methanethiol (MT) and dimethyl sulfide (DMS) are the major odor compounds associated with dewatered sludge cakes (Novak et al., 2006). DMS forms under both aerobic and anaerobic digestion of sludge from the degradation of sulfur-containing compounds while MT forms under anaerobic conditions. Verma, (2005) and Higgins et al., (2008) found that iron content of the sludge is correlated with the generation of odor from the dewatered sludge cake. Iron binds the protein in the biosolids, so more iron in the sludge cake will decrease the availability of bound-protein (Higgins et al., 2008). Hydrogen sulfide is present in the raw sludge. If iron is present in the treatment units, H₂S precipitates out as FeS (Novak et al., 2006). So in wastewater with low iron concentrations, H₂S will be a problem. In contrast to these results, Novak et al. (2007) found increasing VOSCs with increase in iron content of the sludge. In their method, the sludge was first dewatered centrifugally, and then dewatered again using a press. The shearing in the centrifuge is thought to release previously undegraded iron-associated proteins in the solid cake and thus the VOSCs generation from the cake increased. So odor generation in a cake solid was also believed to depend on the method and extent of dewatering and shearing.

The impact of cations on odor generation from anaerobically digested sludges was unclear until the study was undertaken to better understand the effects of iron and aluminum salts (added to activated sludge for phosphorus removal) on anaerobic digestion and odor generation potential (Novak et al., 2010). It was logically assumed that odors will reflect solids reduction. Hence, iron was expected to reduce odors while aluminum might increase odors. However, as indicated in the recent WERF III odor study (Adams et al., 2007); addition of aluminum during centrifugal dewatering for sludge conditioning resulted in much lower odor generation from the dewatered sludge cakes.

The importance of this is that when iron or aluminum salts are added for phosphorus removal in the activated sludge system, they can also influence both the efficiency of anaerobic digestion and also the odors that are generated from the dewatered sludge (Verma et al., 2006; Adams et al., 2007). Overall, addition of either iron or aluminum to activated sludge for phosphorus removal does not appear to be detrimental to either

dewatering or organic sulfur generation. Rather it appears to benefit odor control. Iron produced a greater reduction in TVOSCs than did aluminum, as indicated in Figure 2-4 below (Novak et al., 2010).

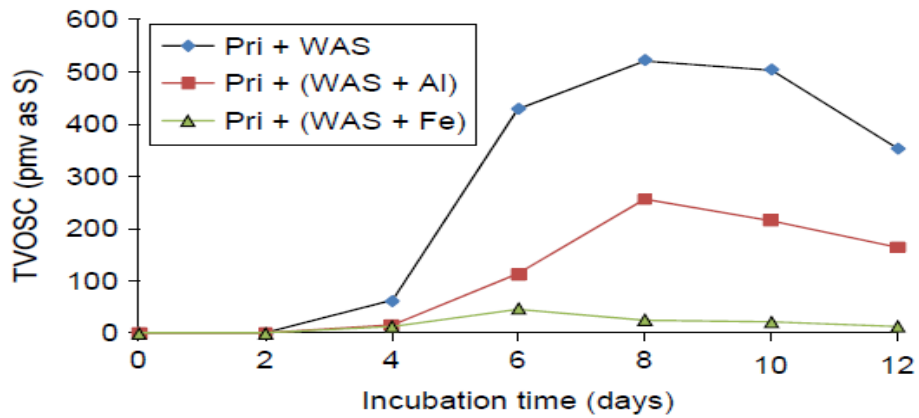


Figure 2-4. TVOSC generation from dewatered sludge cakes (Novak et al., 2010)

2.4 Phosphorus Removal and Recycling as Struvite

2.4.1 Phosphorus Removal from Wastewater

Unlike nitrogen, phosphorus contained in wastewater effluents has to be transformed into a solid to be removed. Traditional phosphorus removal processes work by fixing the phosphorus into the sludge in one of the two ways listed below (Parsons et al., 2009):

1. Chemically by precipitation of soluble phosphorus with aluminum or iron salts into insoluble phosphate compounds. Separation of the precipitates is then achieved by sedimentation, filtration or flotation. Or,
2. Biologically (i.e., biological nutrient removal or enhanced biological phosphorus removal) using the ability of some microorganisms to accumulate phosphates as polyphosphates for their own metabolism.

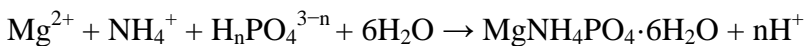
These processes are efficient in the sense that they can reduce phosphorus concentrations in wastewater treated to less than 1 mg/L, but they have certain disadvantages, including the accumulation of phosphorus in the resulting sludge, an increase in sludge volumes, and the spontaneous accumulation of struvite in pipelines and other parts of the treatment works.

Previous studies have reported large increases of soluble magnesium levels in effluents treated with iron metal salts, raising the potential for spontaneous struvite precipitation (Parsons et al., 2009). Finally the phosphorus precipitates generated by these methods are not directly recyclable.

2.4.2 Struvite Precipitation Issues in Anaerobic Digestion

Accumulation of magnesium ammonium phosphate hexahydrate (struvite) on pipe walls and equipment surfaces of anaerobic digestion and post-digestion processes is a problem that plagues the wastewater treatment industry. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is well known for plugging pipes and fouling pumps, aerators, screens, and other equipment. Remediation, when possible, is costly in terms of labor, materials, and system downtime. Struvite precipitation occurs when the combined concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} exceed the struvite solubility product. In the presence of phosphate and ammonia, magnesium forms a number of complexes depending on pH and concentration of the species in solution. However, as speciation of the components is pH dependent; the solubility of struvite also varies with pH. The pH of the anaerobic sludge digestion and post digestion processes is generally higher than the pH of preceding waste treatment processes (Marti et al., 2008). Moreover, although the total concentration of magnesium and phosphate is similar in the processes preceding anaerobic digestion, their dissolved concentrations are lower because much of the constituent concentration is bound in wastewater particles and bacterial cells. Ammonia concentrations in the bulk fluid increase as protein is degraded and dissolved magnesium and phosphate concentrations increase due to cell lysis. Thus, struvite precipitation potential is greater in the anaerobic digestion and post digestion process, since only the dissolved fraction of the components is free to combine to form precipitates (Bhuiyan et al., 2007).

Struvite precipitation is not simply a problem of biological nutrient removal treatment works. However, enhanced biological phosphorus removal processes, which produce a poly-phosphorus rich waste sludge, exacerbate struvite and calcium phosphate deposit problems in anaerobic sludge digestion. Therefore, in these cases, special attention must be paid to control the formation of these deposits. Struvite precipitates in a 1:1:1 molar ratio following the general equation (with $n = 0, 1, \text{ or } 2$):



Accurate determination of struvite solubility requires consideration of ionic strength effects on effective ion concentrations in the aqueous system and inclusion of magnesium phosphate complexes in the analysis. Both factors increase struvite solubility. Ionic strength affects precipitation potential because the electrostatic interactions of ions in solution reduce their activity, or effective concentration, thereby reducing struvite precipitation potential. Magnesium phosphate complex formation reduces the concentrations of Mg^{2+} and PO_4^{3-} ions available for struvite formation (Ohlinger et al., 1998).

The occurrence and development of struvite crystals follows two chemical stages: nucleation (crystal birth) and crystal growth (development of crystals until equilibrium). Predicting or controlling these mechanisms is complex, as it is controlled by a combination of factors including the crystal state of initial compounds, thermodynamics of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases, and kinetics of reaction, as well as several physico-chemical parameters such as pH of the solution from which struvite may precipitate, super-saturation, mixing energy, temperature, and presence of foreign ions (Ohlinger et al., 1999, Corre et al., 2009).

The main difficulty in predicting struvite formation in media such as wastewater is that many ionic species (e.g., Ca^{2+} , K^+ , CO_3^{2-}) can influence the saturation of struvite by reacting with its component ions, Mg^{2+} , PO_4^{3-} , and NH_4^+ . It is therefore necessary to know the availability of free ions (i.e., the ionic activity) for a given pH. A variety of empirical equations have been proposed in the literature (Corre et al., 2009).

2.4.3 Interests in Controlling and Recovering Phosphorus as Struvite (Corre et al., 2009)

(a) Potential pollution reduction: Eutrophication typically occurs in aquatic environments when levels of nutrients (P and N) increase significantly and lead to an excessive growth of algae, which can cause the death of fish and other living organisms and reduce the availability of water resources. Most experimental methods on P-removal from wastewater sludge by struvite crystallization showed relatively high efficiencies (never less than 60%) and would therefore limit problems linked to eutrophication if applied. Struvite crystallization in particular offers the additional advantage of being able to remove nitrogen simultaneously to phosphorus.

(b) Sludge reduction: Sludge disposal and production is effectively a major problem for water companies. Using computer modeling to assess the economic viability of implementing P recovery processes in municipal wastewater treatment plant (WWTP), Woods et al. (1999, 2000) showed that sludge mass could be reduced 8% - 31% by implementing phosphorus recovery by crystallization.

(c) Use as a fertilizer: The agronomic properties of struvite as a fertilizer have been widely discussed. It represents a highly effective source of nutrients (P, N, and Mg). Its low solubility in water (0.018 g/100 ml at 25°C) also presents the advantage of prolonging the release of nutrients during the growing season without danger of burning roots of crops treated. To date, struvite has only been commercialized in Japan as a fertilizer for growing rice and vegetables. It was suggested that struvite is not widely applied as a fertilizer because of its limited availability to farmers and the lack of communication on its applicability and benefits.

(d) Economics: As seen previously, phosphorus recovery from wastewater effluent as struvite presents a number of advantages: it can help to solve and prevent scaling problems in WWTPs, it reduces pollution linked to excess discharge of nutrients (N and P) in wastewater effluents, and its potential reuse as a fertilizer could benefit the wastewater companies. Finally, the implementation of a sustainable process for P reuse

and recycling and the profitability of struvite recovery as a fertilizer will rely on the way potential customers will perceive struvite as a new fertilizer.

Corre et al. (2009) has reviewed the techniques and processes experimented to date by researchers at laboratory, pilot and full-scale to maximize phosphorus removal and reuse as struvite. Struvite crystallization from digested sludge liquors by means of fluidized bed reactors directly integrated in wastewater treatment plant lines are the most common processes studied with success. Furthermore, crystallization studies using synthetic liquors and a pilot scale stirred struvite reactor in order to investigate the conditions at which struvite precipitation can occur have been done (Pastor et al., 2008).

Currently, only few full-scale struvite crystallization plants exist. This is due to the lack of information about the benefits of struvite as a fertilizer, its value on the market, and problems related to the crystallization process such as the need to control the pH and the cost of reagents (Pastor et al., 2010). However, if good phosphorus removal has to be ensured, the techniques still need improvements with regards to quality and quantity of the product formed to be applicable as an economically viable route to recover phosphorus.

2.5 Iron Addition for Phosphorus Removal

Wastewater companies essentially have two options available to remove phosphorus (P), (i) chemical P-removal (CPR) and (ii) biological P-removal (BPR). CPR involves the addition of a chemical coagulant, either aluminum (Al), iron (Fe) or lime and is known to be a reliable process for P-removal, achieving high removal rates and low residual P concentrations.

The impact of chemical phosphorus removal on anaerobic digestion (AD) has long been debated, possibly because there is no general consensus of the definition of impaired AD, but also because of the different assessment methods used. Smith et al. (2008) surveyed 12 wastewater treatment plants to compare the relative digestibility of iron-dosed with undosed activated sludge during two batch test trials. The relative digestibility was assessed by measuring three parameters: (1) biogas volume, (2) biogas composition and hence CH₄ volume and (3) organic matter destruction. Results showed that iron-dosed sludge negatively impacted AD by reducing the volume of biogas (12%) and methane (5.5%) produced from the same amount of volatile solids fed. Possible reasons for reduced biogas production include lower levels of bioavailable P and iron in iron-dosed sludge, which may hinder the ability of micro-organisms to metabolize organic substrate.

The addition of iron hydroxide during the anaerobic digestion of activated sludge, displaying an iron-reducing activity, resulted in the formation of bivalent iron ions, capable of precipitating phosphates (Stabnikov et al., 2004). This study formed the background for developing a new anaerobic technology for the treatment of the wastewater polluted with phosphates or the digestion of activated sludge with high phosphate content. This technology should involve the use of anaerobic sludge with artificially increased iron-reducing activity and the addition of iron hydroxide when anaerobically digesting phosphate- containing substrates.

Another study reports an investigation into the relative digestibility of iron-dosed waste activated sludge (WAS) from a sewage treatment works with chemical phosphorus

removal, in comparison to WAS from a works without phosphorus removal (Johnson et al., 2003). Following conclusions were drawn from the study:

1. The anaerobic digestion of an iron-dosed sludge produced less gas than that of a non-iron-dosed sludge.
2. The use of sulfide and shear, both alone and in combination, brought about a further reduction in the gas production.
3. EDTA addition and pre-acidification improved gas production in comparison to iron-dosed sludge with no pre-treatment. However, the performance was not as good as with non-iron-dosed sludge.
4. The gas production was linearly related to the concentration of bound iron in the sludge.
5. The anaerobic digestion of an iron-dosed sludge gave a lower reduction of volatile solids than that of a non-iron dosed sludge.

2.6 THIOGUARD[®] in Sanitary Treatment Plants and Collection Systems (THIOGUARD[®] White paper)

THIOGUARD[®] is an alkaline magnesium hydroxide slurry, $Mg(OH)_2$, that is beginning to be recognized as having many advantages over the more common alkali sources, such as caustic soda and hydrated lime. Technical grade magnesium hydroxide suspensions are akin to the more familiar pharmaceutical grade "milk of magnesia" used to alleviate acid indigestion, and are therefore a safe non-hazardous product that will not cause chemical burns.

Magnesium hydroxide has found great use in treating industrial metal laden acidic wastewater, where, compared with caustic soda or lime, remove metals at lower pH, produce less sludge volume, and a filter-cake that dewateres more readily. However, it is also beginning to be used in the municipal arena. When comparing the physical and chemical properties of magnesium hydroxide with conventional alkalis, hydrated lime and caustic soda, several advantages are noted. The first is that fewer pounds of magnesium hydroxide are required to neutralize the same amount of acid, 37% more for caustic soda and 27% more for hydrated lime. Another unique characteristic is the maximum pH obtainable during an overdosing situation. Excessive additions of caustic soda and hydrated lime will result in the pH of the waste stream reaching 14 and 12.5 respectively. However, the pH of a magnesium hydroxide slurry is 10.5, and when used to neutralize acidic waste, will only obtain a pH of about 9.0, even when overdosed. This upper pH limit happens to coincide with the upper limit under the Clean Water Act, 1976.

Magnesium hydroxide is supplied as an easily pumpable "latex paint like" aqueous suspension, typically ranging from 55% to 65% solids. It can settle and freezes at 32°F, therefore should be stored in agitated tanks. It can also be supplied as a fine powder.

THIOGUARD[®] magnesium hydroxide slurry offers the following advantages for various physical and biological processes in wastewater treatment:

- Provides alkalinity and nutrient

- Buffers at the pH maximum
- Safe to handle
- Improved clarifier and dissolved air floatation (DAF) performance
- Reduced sludge volume index (SVI)
- More dense filter cake with lower press cycle times
- Enhanced activated sludge performance
- Lower effluent total suspended solids (TSS), phosphorus removal and sludge conditioning
- Metals precipitation and reduced effluent BOD₅

THIOGUARD[®] can also be used for lagoon odor control, and suspended growth nitrification.

Chapter 3: Materials and Methods

3.1 Production and Dosing of Primary Sludge and Waste Activated Sludge Blend

The challenge in this research was to manufacture sludges with the iron and magnesium content to reflect the field conditions. It was thought that by careful addition of chemicals to sewage, sludges could be generated that will be similar to actual field samples.

In the initial phase of the study (Phase I), different sludges from several locations were used to evaluate the effects of magnesium and iron additives on anaerobic digestion of wastewater. For the control, primary (PRI) and WAS were obtained from the Town of Christiansburg Wastewater Treatment Plant (WWTP). This sludge had no additives. A 50%-50% volumetric mix was fed to the control digester. Two more digesters were fed a similar 1:1 volumetric mix of PRI & WAS, one dosed with iron (Fe) and the other with THIOGUARD[®] (Mg(OH)₂). Both the iron and Mg(OH)₂ were being applied full scale in the collection system to control H₂S and were provided by Premier Magnesia, LLC. The iron containing sludge was shipped from Dallas, TX and the magnesium containing sludge was shipped from Tampa, FL.

Since the sludges used in Phase I were from different utilities and comparisons could not be directly made, a second phase was initiated. For Phase II, a 70%-30% mix of PRI and thickened WAS (T-WAS), respectively as percentages by volume was adopted from the same Christiansburg WWTP for all the reactors. This proportion was required since the utility was nitrifying and this led to low alkalinity values in the WAS. If the mix was 50%-50%, the digester pH would not remain above 7.0. The Fe and Mg-reactors were also fed the same sludge blend as the control, and dosed with appropriate amounts of FeCl₃ and MgCl₂ / Mg(OH)₂ respectively. This was proposed so as to simulate the actual plant conditions where typically PRI & T-WAS are blended to provide adequate organic loading to the digesters without overloading them. The total solids percentage for the sludge blend before dosing was kept around 2.5% during the entire study.

3.2 Anaerobic Digester Setup and Operation

High-density polyethylene fermentation reactors supplied by Hobby Beverage Equipment Company (Temecula, California) were used as pilot scale anaerobic digesters. The conical bottom of these vessels was thought to be advantageous in terms of mixing and suspension of grit, similar to the full-scale application of egg-shaped anaerobic digesters. The nominal volume of each vessel was 25 liters (L) and was operated with an active volume of 10 L. The reactors were operated at an SRT of 20 days by maintaining a constant volumetric feeding and wasting rate across each system. Daily batch feeding and wasting was performed at the rate of 0.5L/day to maintain the desired SRT. The reactor vessels were modified to accept a threaded stainless steel thermometer, also supplied by Hobby Beverage. Digesters were operated at 37°C (mesophilic conditions maintained within a constant temperature room). The reactors were named according to the feed dosing that they received and the purpose that they served. Reactors were continuously mixed by digester gas recirculation from the headspace through the conical reactor bottom.

Mixing was achieved by circulating gas from the headspace of each digester and injecting it into a valve at the bottom of the digester. The relatively deep cylindrical shape, combined with steeply sloped conical bottom of the digesters was thought to enhance mixing efficiency in a similar manner to egg-shaped digesters. The degree of mixing could be increased or decreased using 6-600 RPM variable speed peristaltic pumps that circulated the gas (Cole-Parmer, Vernon Hills, Illinois). Normally, the pumps were set at 40% of their maximum speed. This corresponds to approximately 0.7 L/minute with the Cole-Parmer “L/S-18” tubing used on the pump heads. At least five minutes before wasting and feeding, the gas flow rate was increased to 1.4 L/minute to ensure that waste samples were representative of the digester contents. The flow rate was maintained at 1.4 L/minute for about 10 minutes after feeding to disperse the feed.

Conventional mesophilic anaerobic digesters were initially seeded with digested sludge from the Town of Christiansburg WWTP (Christiansburg, VA). The digesters were operated in the following manner:

Unit #1: Control (C): This unit received the Christiansburg sludge blend with no additives. 50%-50% volumetric mix of PRI & WAS was used in the Phase I and 70%-30% volumetric mix of PRI & T-WAS was used in Phase II of the study. This unit served the purpose of a control to compare the roles of various other additives to anaerobic digestion of sludges.

Unit #2: Phase I: Iron dosed (Fe): This unit received the 1:1 PRI:WAS sludge blend from Dallas, TX, which contained additional iron in the form of FeCl_3 . The exact dosing of the chemical was unknown. This reactor served the purpose of assessing the absolute performance of iron in an arbitrary sludge feed, on anaerobic digestion.

Phase II: Iron dosed (C-Fe): This unit received the 70-30 mix of PRI & T-WAS from Christiansburg WWTP, with additional known iron in the form of a daily dose of FeCl_3 in the feed. This unit served the purpose of analyzing and assessing the comparative performance of iron in the control sludge feed, on anaerobic digestion, with respect to the sludge feed without any additives (C-feed) and the sludge feed with magnesium additives (C-Mg-feed).

Unit #3: Phase I: Magnesium dosed (Mg): This unit received the 1:1 PRI:WAS sludge blend from Tampa, FL, which contained additional magnesium in the form of THIOGUARD[®] ($\text{Mg}(\text{OH})_2$). The exact dosing of the chemical was unknown. This reactor served the purpose of assessing the absolute performance of magnesium in an arbitrary sludge feed, on anaerobic digestion.

Phase II: Magnesium dosed (C-Mg): This unit received the 70-30 mix of PRI & T-WAS from Christiansburg WWTP, with additional known magnesium in the form of a daily dose of $\text{MgCl}_2/\text{Mg}(\text{OH})_2$ in the feed. This unit served the purpose of analyzing and assessing the comparative performance of magnesium in the control sludge feed, on anaerobic digestion, with respect to the sludge feed without any additives (C-feed) and the sludge feed with iron additives (C-Fe-feed).

3.3 Analytical Methods

The following tests were used to compare the performance of the digesters:

- pH
- Total and volatile solids
- COD
- Alkalinity
- Gas production
- Volatile fatty acids (acetic, propionic, butyric, isobutyric, isovaleric, n-valeric)
- Solution cations and anions
- Total cations
- Dewatering and determination of optimum polymer dose & cake solids concentration
- Odor Analysis

COD, pH, alkalinity, and solids testing were conducted according to Standards Methods for the Examination of Water and Wastewater (APHA, 1999). Total solids (TS) and volatile solids (VS) on the samples (feed and anaerobic effluent) were measured almost twice a week. Volatile solids destruction was determined by the formula $(VS_{\text{initial}} - VS_{\text{final}}) / VS_{\text{initial}}$. The pH was measured on the fresh samples daily by pH probe. For total COD, samples were acidified using concentrated H_2SO_4 to lower the pH to less than 2 before measuring COD. Acidifying the sample fixes the carbon. COD measurements were conducted by the closed reflux method (APHA 1999).

Gas from each digester accumulated in Tedlar bags attached to the digester's collection/recirculation system. The gas flow rate was calculated by measuring the volume of gas in the bags and dividing by the time between measurements. Large volume Tedlar bags were used to prevent the systems from becoming pressurized. Gas composition samples were obtained by transferring one liter of gas from the large bags to smaller bags that had syringe-sampling ports.

Gas samples were analyzed with a Shimadzu model GC-14A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) using the thermal conductivity

detector (TCD). The column used was made from a 4 meter length of copper tubing with a 0.25 inch inner diameter. The column was coiled to fit in the GC-14A oven and packed with Haysep Q media (Supelco, Bellefonte, PA). Helium was the carrier gas, with column flow set at 17 mL/min.

In order to prepare samples for solution ions and volatile fatty acid (VFA) analyses, a 500 mL sample of digester biosolids was centrifuged at 13,500 x g for 25 minutes. 50 mL of the supernatant was frozen for storage until the analyses were performed. At the time of analysis, the sample was thawed, centrifuged at 6,000 x g for 15 minutes, and then filtered through a 0.45 micron syringe filter. From this filtered sample, dilutions were made for solution ions and VFA testing.

Diluted VFA samples were acidified in their individual GC vial by adding concentrated phosphoric acid at a ratio of 1:10. The VFA samples were analyzed on a Hewlett Packard Model 5890 gas chromatograph using a flame ionization detector (FID). A Nukol capillary column (Supelco) was used and samples were injected in splitless mode. The column flow gas was helium with a flow rate of 17 mL/min. Flow rates for the other gases used were as follows: Nitrogen – 13 mL/min, Hydrogen – 45 mL/min, Air – 450 mL/min. Volatile fatty acids are expressed as mg/L of individual species (C2-C7 fatty acids). Individual acid concentrations are converted to acetic acid on a theoretical oxygen demand basis and summed to report Total VFA as mg/L as acetic acid.

Diluted cation samples were analyzed on a Dionex ICS-1000 ion chromatograph utilizing a CS-12 column and conductivity detection with self-generating suppression of the eluent (Dionex Corp., Sunnyvale, CA). 25mM methanesulfonic acid was used for eluent at a flow rate of 1 mL/min. Solution anions were analyzed using an ion chromatograph (Model No. DX-120, Dionex) equipped with AS9-HC column (Model No. 051786, IonPac). The eluent was 9.0 mM Na₂CO₃ and the flow rate was 1.0 ml/min.

Total cations in the biosolids samples were measured in accordance with EPA method 3050B (1996). Each cation (Ca, Mg, Al and Fe) was quantified by an atomic absorption spectrophotometry (Model No. 5100PC, Perkin-Elmer, MA).

The method described by Muller et al. (2004) was used for the sludge dewatering testing and for the preparation of dewatered sludge cakes for organic sulfur analysis. One percent high molecular weight cationic polymer (Clarifloc 3275, Polydyne) was used as the sludge conditioner. The polymer dose that resulted in the lowest capillary suction time or the best dewaterability was selected as the optimum polymer dose. A mixture of optimum polymer and sludge was then sheared in a Waring blender for 30 sec and centrifuged in a lab centrifuge at 10000 rpm (17700 G) for 15 min under the room temperature. The sludge pellet was collected and pressed at 207 kPa for 15 min by a lab press. This provided a dewatered sludge cake similar to that generated by a high solids centrifuge (Muller et al., 2004). These pressed sludge cakes were used for volatile organic sulfur compounds measurement.

Total solids and volatile solids in the cake solids were measured by the method described in Standard Methods for the Examination of Water and Wastewater (APHA 1999). The cake solids were then used to make samples for odor analysis.

Bottles for odor analyses were made using 5 grams of wet cake solids in each 50 mL glass bottle. Triplicate samples were made for each sample. In a full-scale biosolids storage facility, there is no gas transfer inside it and the system is anaerobic. So to make the bottle anaerobic in the lab-scale study, the bottles were sealed with screw caps and Teflon-lined rubber septa and they were then incubated at a constant temperature (at 25°C) during the whole experiment.

Twenty five microliter headspace gas from each incubation bottle was periodically collected and injected into gas-chromatography/mass spectrometry (Model No. GC 6890, MSD 5970, Hewlett-Packard) with a cryo-trapping system. The cryo-trap was employed to accumulate gas samples and to generate narrow chromatographic peaks. A 30 m long and 0.25 mm I.D. column (Model No. 20751-01A, Supelco) was connected to the gas injection inlet (200 °C) and helium was used as a carrier gas (2 ml/min). The oven temperature was increased from 50 °C to 265 °C at a rate of 35 °C/min. Total analysis time was around 8 minutes. Odorous compounds that were measured in the study were H₂S, MT, DMS and DMDS. Peak areas of each organic sulfur compound were integrated

by the data analysis program, G1034C version C.03.00 (Hewlett-Packard). The amount of organic sulfur in each sample was quantified by comparing the sample peak area with the area of a standard gas mixture of known amounts of H₂S, MT and DMS (Scott Specialty Gases Inc., PA). DMDS was quantified using DMS as a reference. All the biosolids organic sulfur odor data are presented as total VOSC (TVOSC), which is the sum of MT, DMS and DMDS.

Chapter 4: Results and Discussion

4.1 Results

As mentioned earlier, the study was performed in two phases. During phase I, three digesters were operated. The first one “C” contained a 1:1 volumetric mix of PRI & WAS from the local Christiansburg WWTP and served as the control. The second and the third digesters, namely “Fe” & “Mg”, received 1:1 PRI:WAS sludge blend shipped by Premier Magnesia, LLC. The Fe-reactor received sludge blend from Dallas, TX and contained additional iron in the form of FeCl_3 . The Mg-reactor received sludge blend from Tampa, FL, and contained additional magnesium in the form of THIOGUARD[®] ($\text{Mg}(\text{OH})_2$).

In Phase II, all the three digesters were fed 70:30 volumetric mix of PRI: T-WAS from the Christiansburg WWTP, so that a uniform base could be established to compare the roles of iron and magnesium additives in the same sludge and maintaining similar conditions as those for the control. The nomenclature of the control was retained as “C”. The second reactor was named as “C-Fe” and had additional known iron in the form of a daily dose of FeCl_3 in the feed. The third reactor was named “C-Mg” and had additional known magnesium in the form of a daily dose of $\text{MgCl}_2/\text{Mg}(\text{OH})_2$ in the feed.

4.1.1 Phase I

The main challenge posed in this phase was to draw a comparison between the performances of the three reactors, and also comment on the use of additives. It was difficult to arrive at specific conclusions because of the different sludges used, however, an effort was made to set up anaerobic digestion studies and see if the addition of chemicals (iron or magnesium) was affecting the anaerobic digestion process. The following results were obtained.

(a) pH:

Figure 4-1 shows the pH values for the three reactors during the course of Phase I.

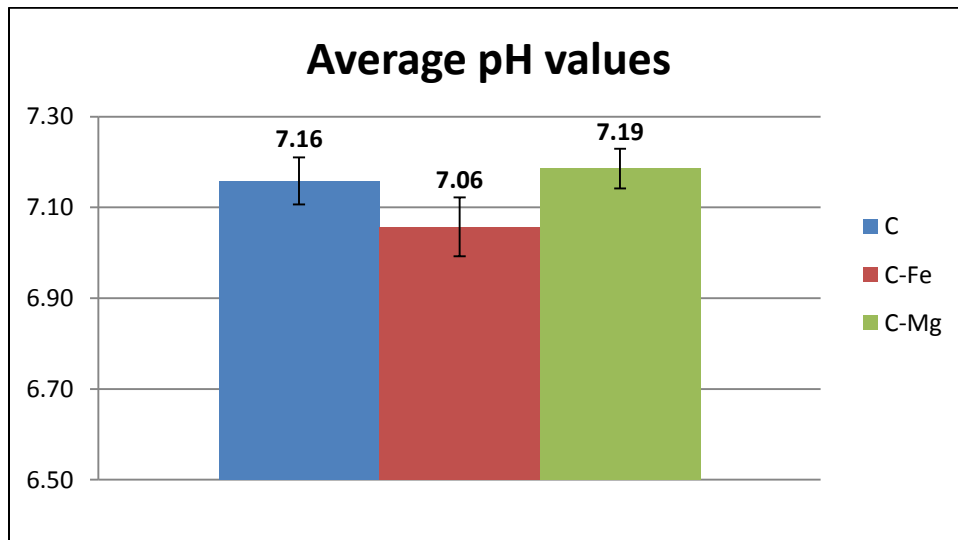
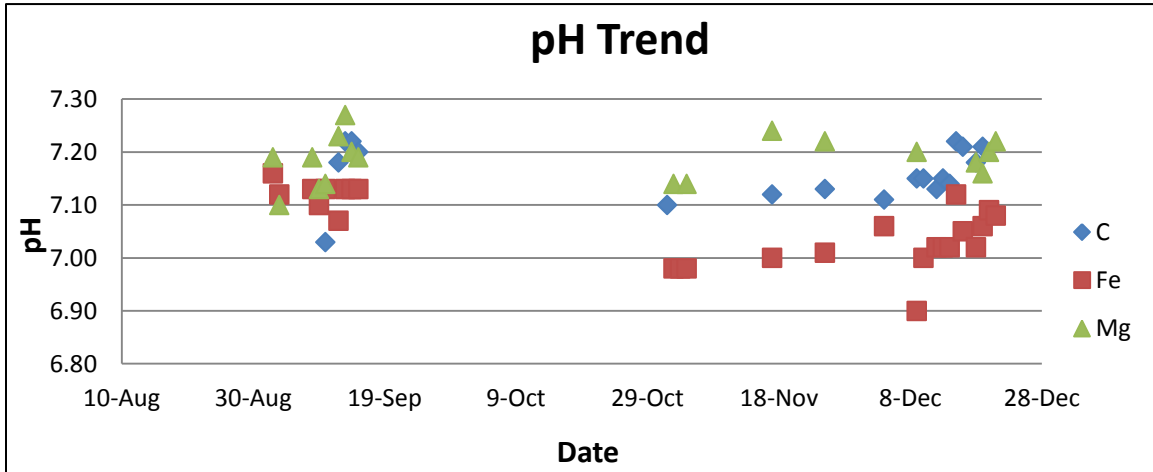


Figure 4-1. pH data for Phase I

It was seen that the average pH value for Mg (7.19) and C (7.16) were higher than that for Fe (7.06). The average pH value for Fe was low compared to those for C and Mg, while the average value for Mg was slightly higher than that of C.

(b) Solids:

Figure 4-2 shows the total solids reduction (TSR) and volatile solids reduction (VSR) profiles for the 3 reactors during the course of Phase I.

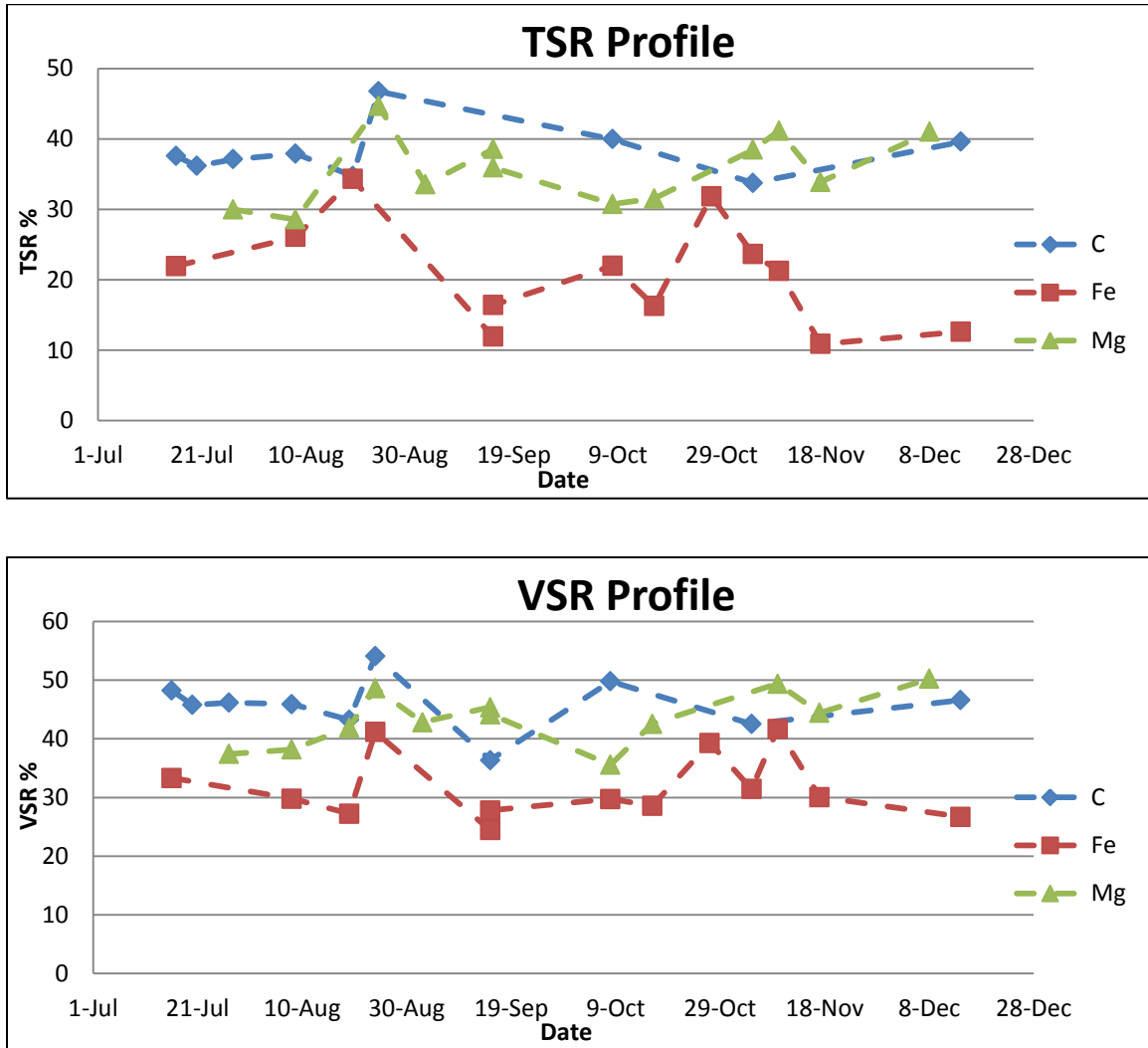


Figure 4-2. Solids reduction profiles for phase I

It can be seen that the Fe-reactor consistently showed lower solids reduction than C & Mg reactors. The solids reductions for C & Mg reactors were comparable and similar. Typical VS reduction for anaerobic digestion is in the range of 40% - 50%. The data show low solids reduction for the iron amended sludge.

(c) Alkalinity:

Figure 4-3 shows the average alkalinity values for the three reactors in Phase I.

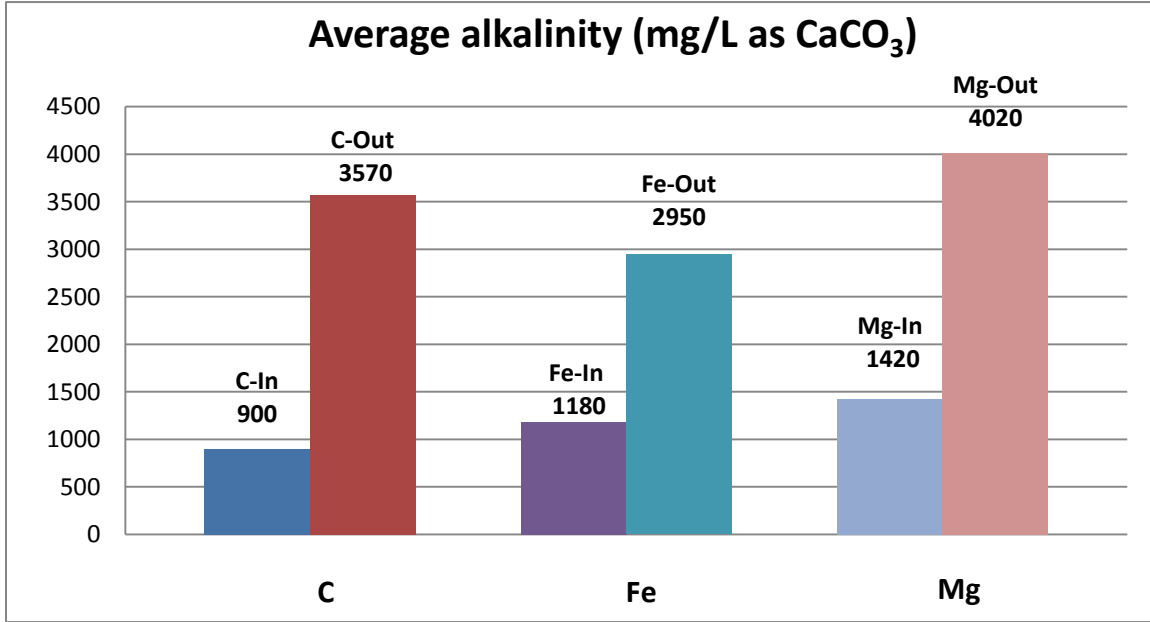


Figure 4-3. Average influent and effluent alkalinity values for phase I

It was observed that the average alkalinity for the effluent of Fe (Fe-Out, 2945 mg/L as CaCO₃) was much lower than those of C (C-Out, 3570 mg/L as CaCO₃) and Mg (Mg-Out, 4015 mg/L as CaCO₃). However, the differences between the values for C & Mg were not high, although the latter recorded a slightly higher value. It was also observed that the influent alkalinity for Mg (Mg-In, 1420 mg/L as CaCO₃) was higher than those for C (C-In, 900 mg/L as CaCO₃) and Fe (Fe-In, 1180 mg/L as CaCO₃).

(d) Odors:

The odor causing TVOSC from biosolids from the three reactors were analyzed and the results are shown in Figure 4-4.

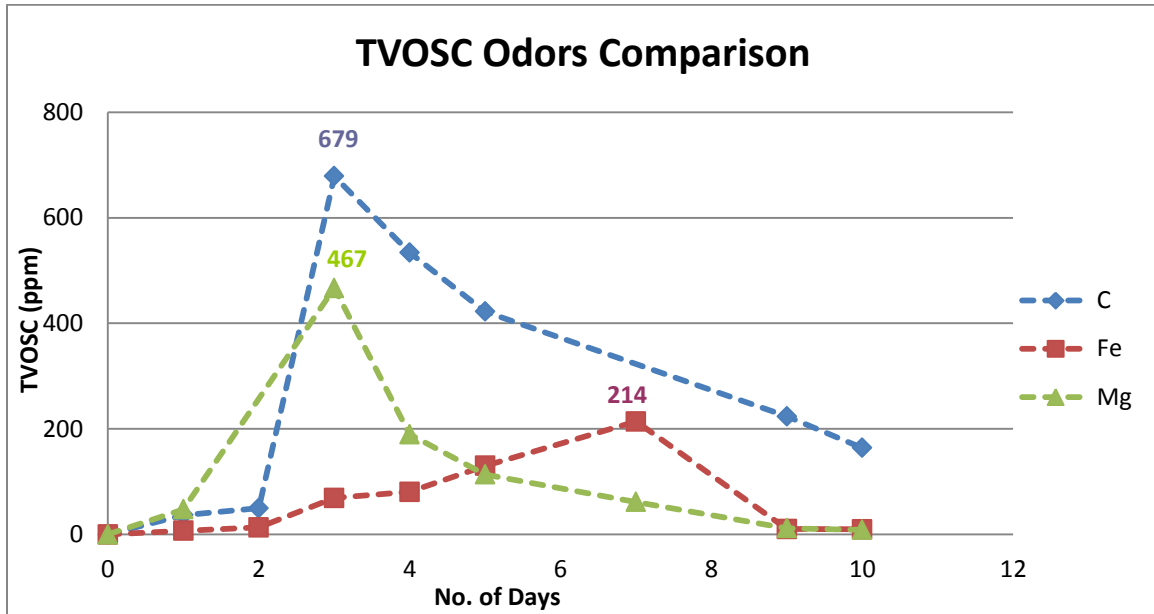


Figure 4-4. TVOSC Odors comparison for Phase I

Since the sludges for all the reactors were different, all of them peaked on different dates. The peak values for Fe (214 ppm) and Mg (467) were distinctly lower than that of C (679 ppm) for the same concentration of solids fed to the reactors. It was clear that iron impacted the sludge and reduced the sulfur odors. Magnesium also seemed to reduce odors to a certain extent, however, because the parent sludges differed, it cannot be precisely concluded that iron or magnesium resulted in lower odors.

(e) Ions:

The solution ions were measured using ion chromatographs and the results are shown in Table 4-1.

Table 4-1. Solution Ions data for Phase I

Sample	Ca ⁺⁺ (mg/L)		Mg ⁺⁺ (mg/L)		Na ⁺ (mg/L)		NH ₄ ⁺ as N (mg/L)		K ⁺ (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Control	28.4	23.9	35.2	42.6	31.9	110	269	> 600	150	60.1
Fe	20.3	136	24.4	23.4	35.6	32.1	188	560	141	91.1
Mg	114	570	46.6	44.5	114	98	166	> 600	178	118

Sample	Cl ⁻ (mg/L)		NO ₂ ⁻ as N (mg/L)		NO ₃ ⁻ as N (mg/L)		PO ₄ ³⁻ as P (mg/L)		SO ₄ ⁻ (mg/L)	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Control	33.6	50.3	0.3	n.a.	0.3	0.2	60.7	50.1	3.7	4
Fe	35.5	37.9	n.a.	n.a.	0.3	0.1	31.2	9.5	4.3	2.2
Mg	102	97.9	n.a.	n.a.	0.1	0.6	48.7	43.2	5.3	5.1

n.a = values below detection limit

Much of the ion data was difficult to decipher. However, a general increase in NH₄⁺ as N was observed from influent to effluent in all the reactors, which is generally because of the destruction of proteins in these systems. It was observed that the PO₄³⁻ (mg/L as P) concentration for the effluent of Fe-reactor (9.52 mg/L) was much lower than the other two. This was expected because iron binds to phosphate and removes it from the solution. However, there was no decline in the PO₄³⁻ concentration in the Mg-effluent. This suggested that the magnesium dosing to the Mg-reactor was low, although the magnesium amended sludge showed higher soluble Mg²⁺ as compared to the other two sludges.

Therefore, an acid digestion was performed on the sludges to verify the total cations present in the influents. The results are shown in Table 4-2.

Table 4-2. Total cations data for Fe and Mg influent feeds (in mg of cations/g TS)

Sample	Fe	Al	Ca	Mg	Na	NH ₄ as N	K
Influent							
Fe	5.46	1.83	0.41	0.36	0.30	-	5.22
Mg	3.72	1.63	1.57	0.41	0.76	0.79	10.4

The influent to the Fe-reactor was found to have a concentration of iron (5.46 mg/g TS) that was significantly higher than that of the Mg-reactor (3.72 mg/g TS). However, it was found that the magnesium levels of both the feeds were similar.

The Tampa WWTP added THIOGUARD[®] to the sewer lines. It is possible that the raw water from Tampa was low in background magnesium. So while magnesium increased in the solution, the concentration in the solids was not high compared to other undosed sludges.

The Phase I data did suggest that magnesium could be beneficial for digestion, especially for raising the pH and increasing solids destruction and alkalinity. The data also suggested good digestion performances for the magnesium amended sludge when compared with the iron amended sludge. It also appears that, while direct comparisons cannot be made (due to different parent feed sludges), lower odors values for the dewatered biosolids from the Fe & Mg-reactors may be possible as a result of the iron and magnesium additions.

Therefore, to allow better comparisons, it was decided that all the three reactors would be fed the same sludge, and amendments in the form of known amounts of iron and magnesium added to the iron and magnesium reactors. That would also provide a common basis to assess the comparative performances of the two amendments, iron and magnesium.

4.1.2 Phase II

The challenge in this phase was to manufacture sludges with the iron or magnesium content that reflects conditions that would occur in the field. This is challenging because doses in the field can vary over time and location. However, after discussions with the sponsor (Premier Magnesia, LLC.) and studying of the data from the Tampa and Dallas utilities, it was thought that by careful addition of chemicals to the sludge blend, sludges can be generated that would be similar to actual field samples.

It was initially decided to dose the C-Fe reactor with FeCl_3 (dosage being 300 mg/L as Fe) and C-Mg reactor with a 2:3 mix of MgCl_2 and Mg(OH)_2 (dosage being 200 mg/L). This was allowed to run for around a month. Initially, the pH responded as expected (C-Mg > C > C-Fe), for two to three weeks. Thereafter, the pH for all the reactors, esp. C-Mg and C-Fe, began to drop. During this period, the volatile solids reduction was also low for both the reactors. The possible explanation for this is that the sludge was collected and dosed about every three weeks. The logic was to simulate exposure in the collection system and storage as primary sludge. However, it is likely that the sludge fermented, even though it was stored in a refrigerator, and this resulted in a volatile acid shock to the digesters, thereby rendering them as unrepresentative sludge samples. In fact, the magnesium and iron addition could have resulted in a more rapid fermentation and this could have resulted in a more acidic feed to the digester.

Therefore, it was decided to collect sludge biweekly and dose the sludge feed daily just before feeding. In addition, dosing of Mg was changed to Mg(OH)_2 instead of a mix of MgCl_2 and Mg(OH)_2 . The results were obtained by using the same Christiansburg WWTP sludge blend to all the three reactors (C, C-Fe & C-Mg), with C having no additives, C-Fe receiving a daily dose of FeCl_3 (300 mg/L as Fe) in the feed, and C-Mg receiving a daily dose of Mg(OH)_2 (200 mg/L as Mg) in the feed. The total solids percentage for the sludge blend feed before dosing was kept around 2.5% during the entire study.

(a) pH:

Figure 4-5 shows the pH values for the three reactors during the steady state period of Phase II.

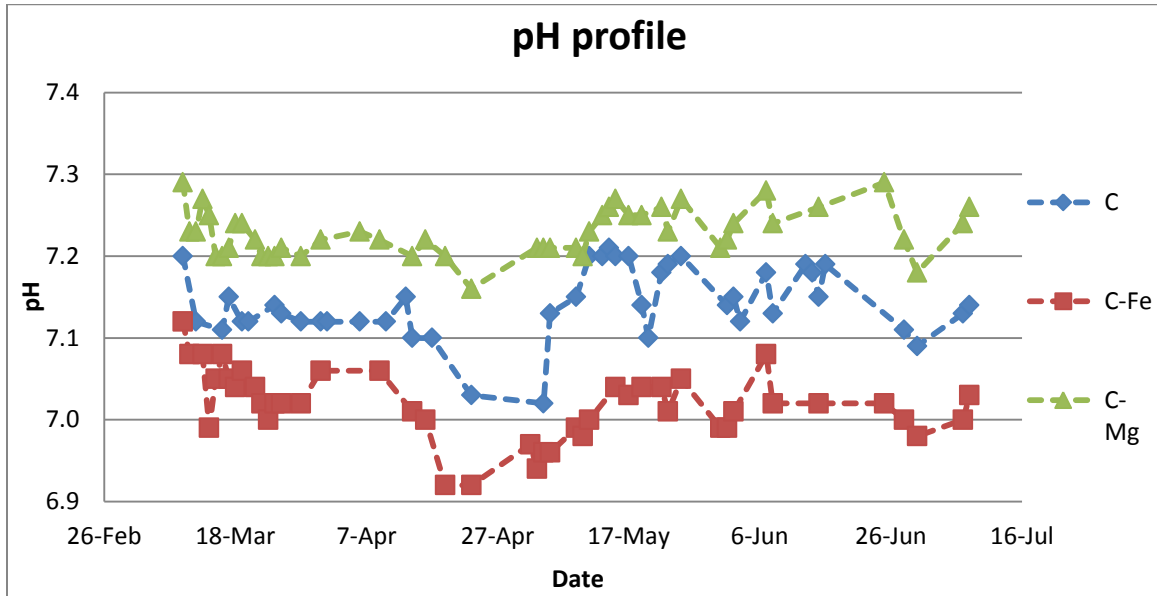


Fig 4-5. pH data for phase II

It is clearly evident from Figure 4-5 that C-Mg reactor maintained the highest pH levels and C-Fe maintained the lowest amongst the three reactors. This is similar to the results from Phase I. The higher pH values of C-Mg can be attributed to the supplementation of OH^- ions by the addition of $\text{Mg}(\text{OH})_2$. The lower pH values in the C-Fe reactor are because FeCl_3 acts as an acid. None of the pH values were out of the “normal” range (6.8 – 7.4) for anaerobic digesters and all would suggest successful digester operation.

(b) Solids:

Data for TSR and VSR are shown in Figure 4-6.

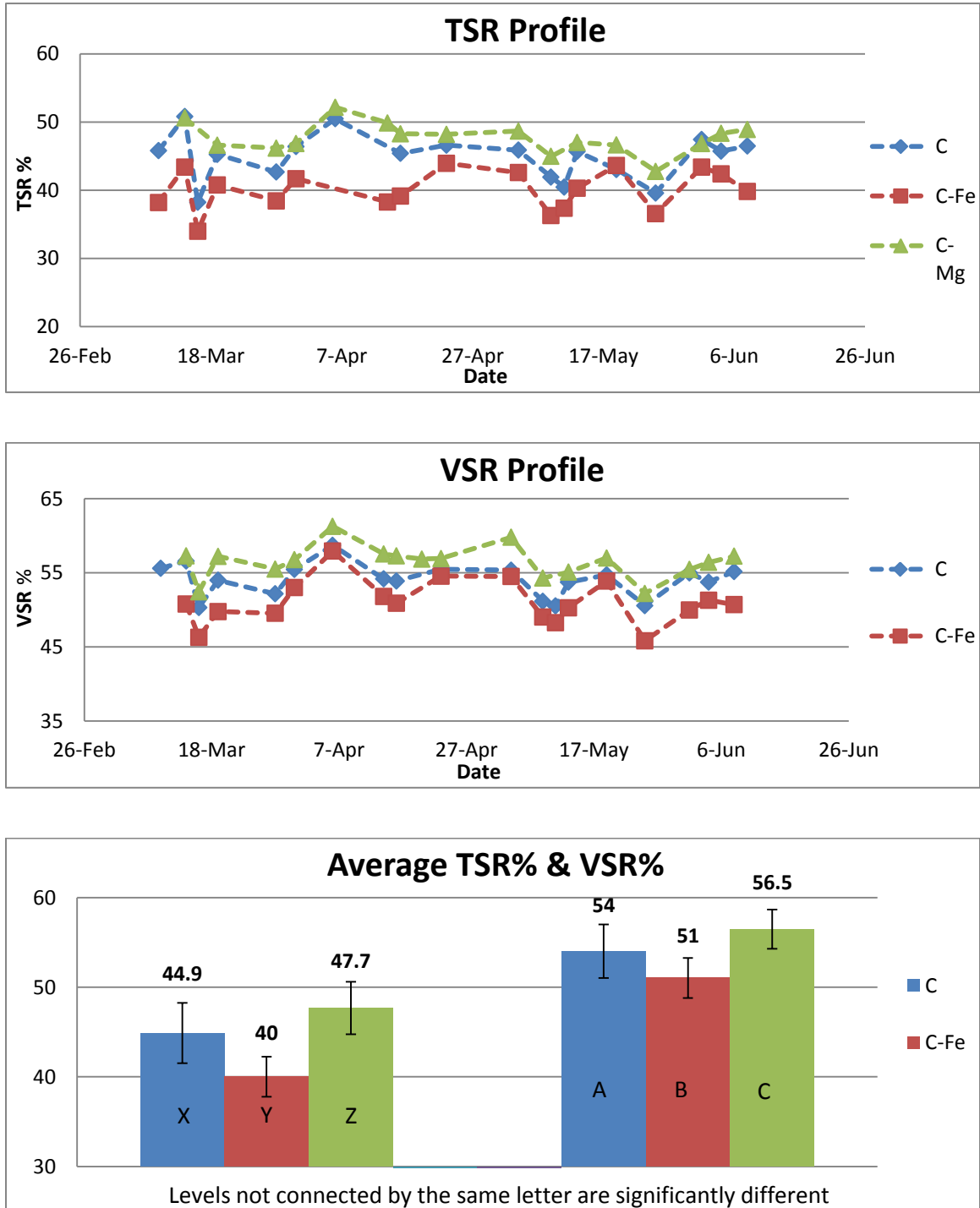


Figure 4-6. TSR and VSR data for Phase II

The data in Figure 4-6 clearly show that the C-Fe digester recorded the least TSR and VSR compared to both the C & the C-Mg digesters throughout the duration of the study. Moreover, the C-Mg digester always recorded the highest values for both the reductions. A one-way ANOVA of the average values for TSR% and VSR% for the three reactors, showed significant differences between the three reactors ($p < 0.0001$). A Tukey HSD post hoc analysis was conducted to analyze the interaction between the average values for the three digesters. The results yielded different levels for all the three values in both the cases (TSR% and VSR% comparisons), which are shown by the different letters in the bar graph (Figure 4-6). The test thus indicated that the comparative performance of the C-Mg digester in terms of solids reduction (both TSR & VSR) was the best for C-Mg reactor, followed by the C reactor and the worst for C-Fe reactor.

(c) COD:

Figure 4-7 show the COD data for phase II.

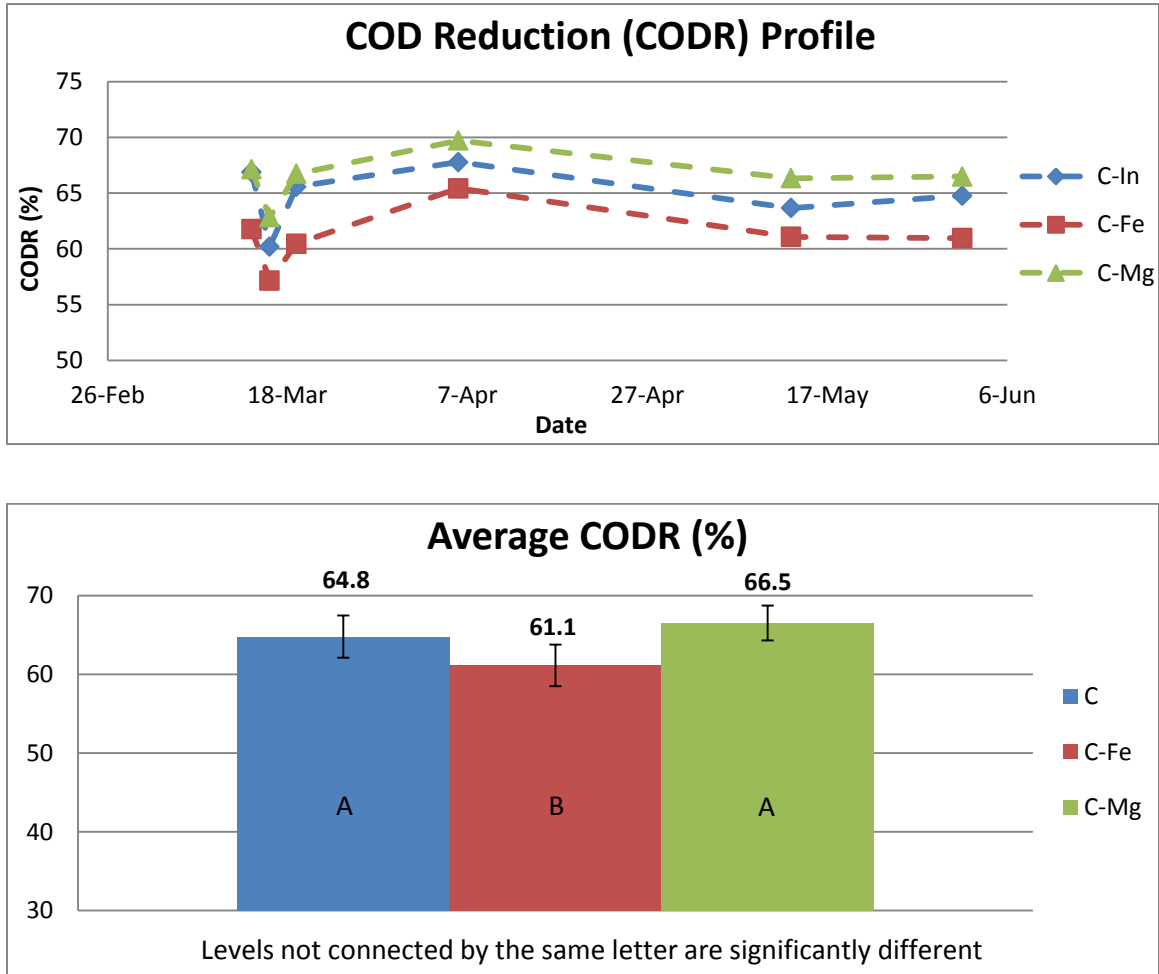


Figure 4-7. COD reduction data for Phase II

The COD reduction (CODR) profiles were similar to the solids reduction profile, with C-Mg values being greater than C followed by the C-Fe values, throughout the study period. However, the data points were not as numerous and hence a one-way ANOVA of the average values for CODR% for the three reactors was performed, which yielded significant differences between the three ($p = 0.0066$). A Tukey HSD post hoc analysis was conducted to analyze the interaction between the average values for the three digesters. The results yielded similar levels for the average values of reactors C & C-Mg

and a different level for that of C-Fe, which are shown by the various letters in the bar graph (Figure 4-7). The test thus indicated that the performance of the C-Mg and C digesters in terms of COD reduction were statistically similar, however, better than that of the C-Fe digester.

(d) Interactions Between the Above Parameters:

The pH, solids and COD are some of the essential parameters determining the efficiency of an anaerobic digestion process. The interactions between these various parameters give an indication of their relative performances and are depicted in the following several graphs.

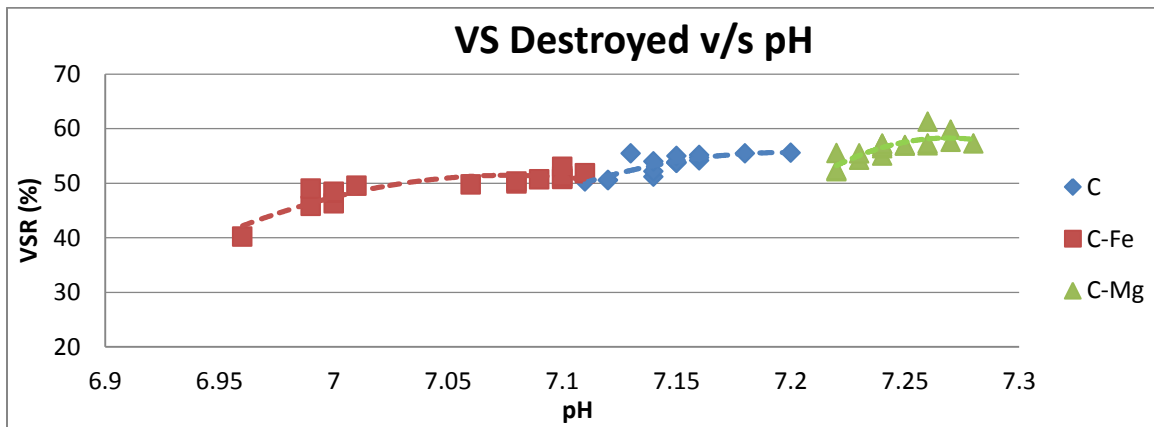


Figure 4-8. Relation between VSR & pH for each reactor during Phase II

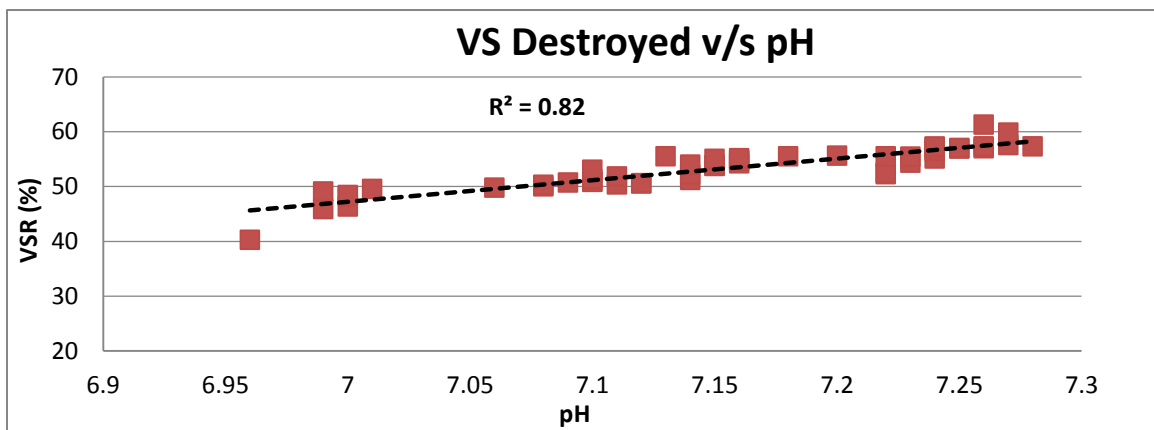


Figure 4-9. Relation between VSR & pH for all reactors combined during Phase II

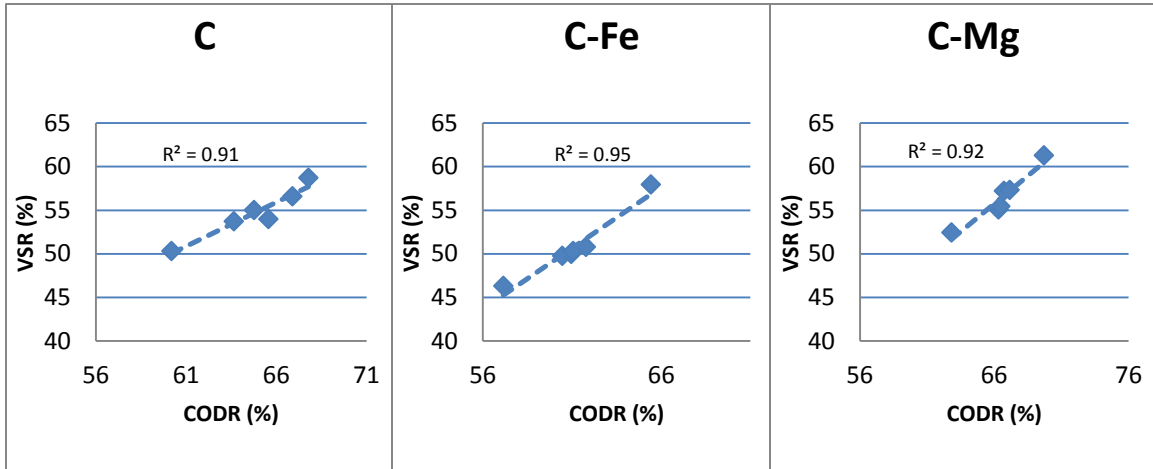


Figure 4-10. Relation between VSR & CODR for each reactor during Phase II

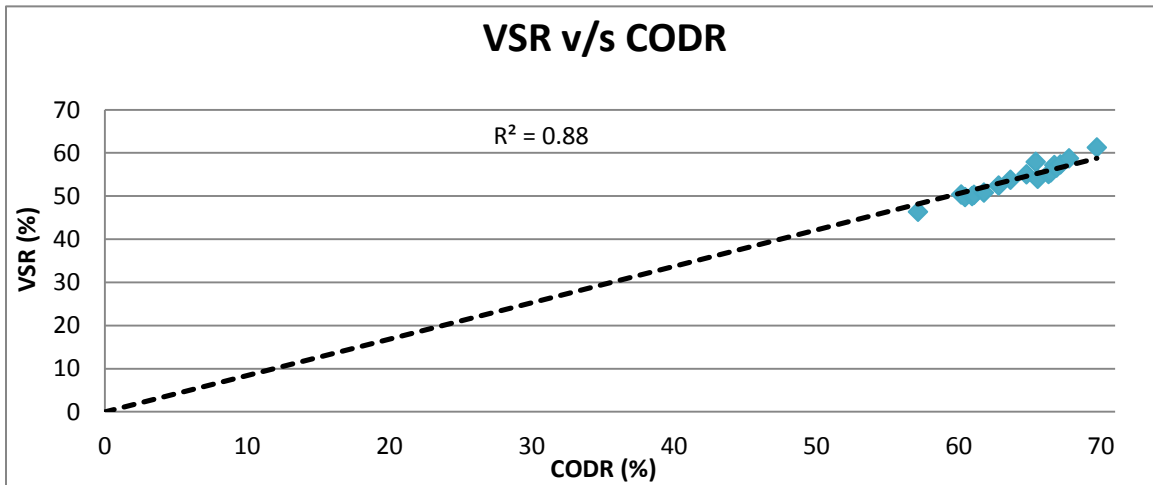


Figure 4-11. Relation between VSR & pH for all reactors together during Phase II

Figures 4-8 and 4-9 show the interaction between VSR and pH for the three reactors. It can be seen that for each reactor, VSR slightly increased with an increase in pH (Figure 4-8). It can also be seen that the values for both pH and VSR were in the higher range for C-Mg reactor, followed by the C and C-Fe reactors respectively. A plot of all the VSR and pH values for all the three reactors combined (Figure 4-9) showed a linear correlation between the two parameters, revealing a positive proportionality.

Figures 4-10 and 4-11 show the interaction between VSR and CODR for the three reactors. It can be seen that for each reactor, the VSR proportionately increased with the increase in CODR (Figure 4-10). It can also be seen that the values for both CODR and VSR were in the higher range for C-Mg reactor, followed by C and C-Fe reactors respectively. A plot of all the VSR and CODR values for all the three reactors combined (Figure 4-11) showed a linear correlation between the two parameters, revealing a positive proportionality. This was consistent with the results of the interaction between VSR and pH. The line for Figure 4-11 was forced through the origin (0,0). So a fit that did not include the origin (0,0) might have provided as higher R^2 value.

(e) Alkalinity:

The alkalinity variation over time was also plotted for both the influents and the effluents, which are shown in Figure 4-12.

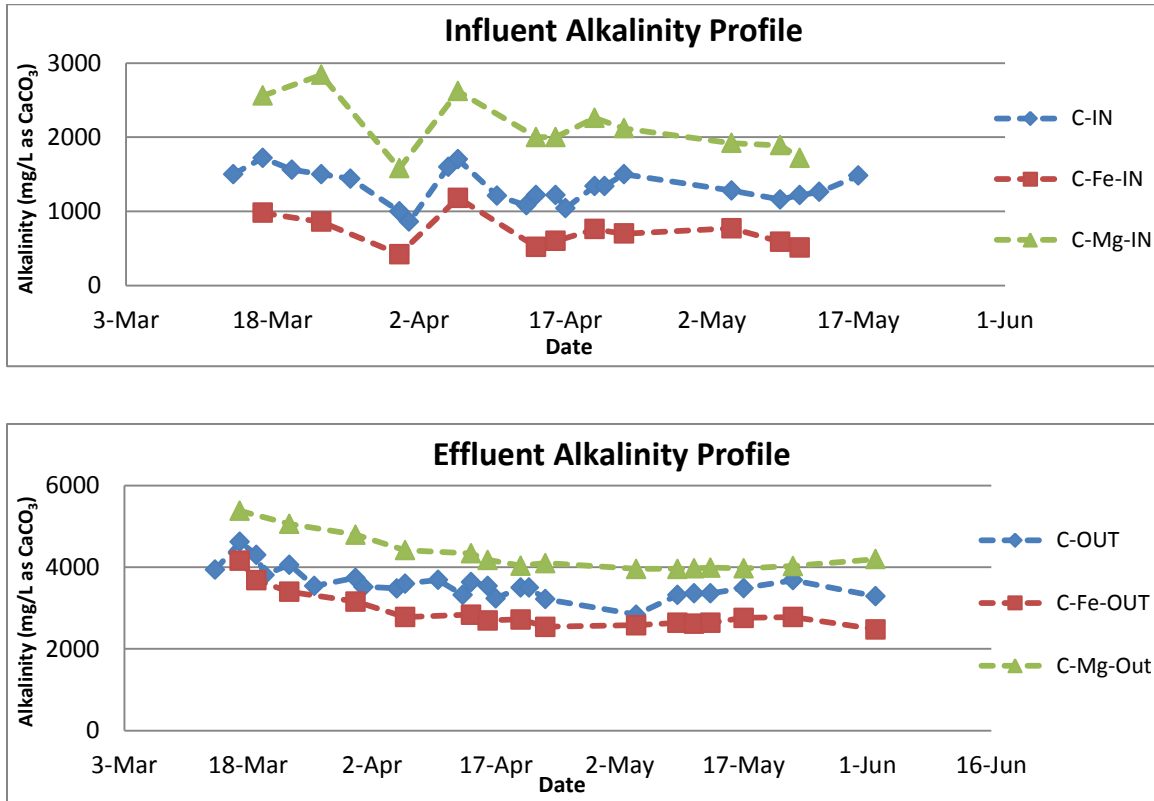


Figure 4-12. Alkalinity data for Phase II

It is evident from the data (Figure 4-12) that the alkalinity values for the C-Mg reactor remained the highest for the entire duration of Phase II, followed by the C reactor. C-Fe reactor recorded the lowest alkalinity throughout the study period. The variations in the influent alkalinity can be attributed to the varying feed composition and minor variations in the solids concentrations over the span of the study. The average alkalinity value for C-Mg effluent was 4260 mg/L as CaCO₃, which is significantly higher than those for C (3580 mg/L as CaCO₃) and C-Fe (2910 mg/L as CaCO₃). The higher alkalinity for C-Mg could be attributed to the increased pH level in the reactor due to the addition of Mg(OH)₂, while the low alkalinity for C-Fe must be due the low pH levels and increased acidity caused by FeCl₃.

(f) VFA:

The VFA data is shown in Figure 4-13.

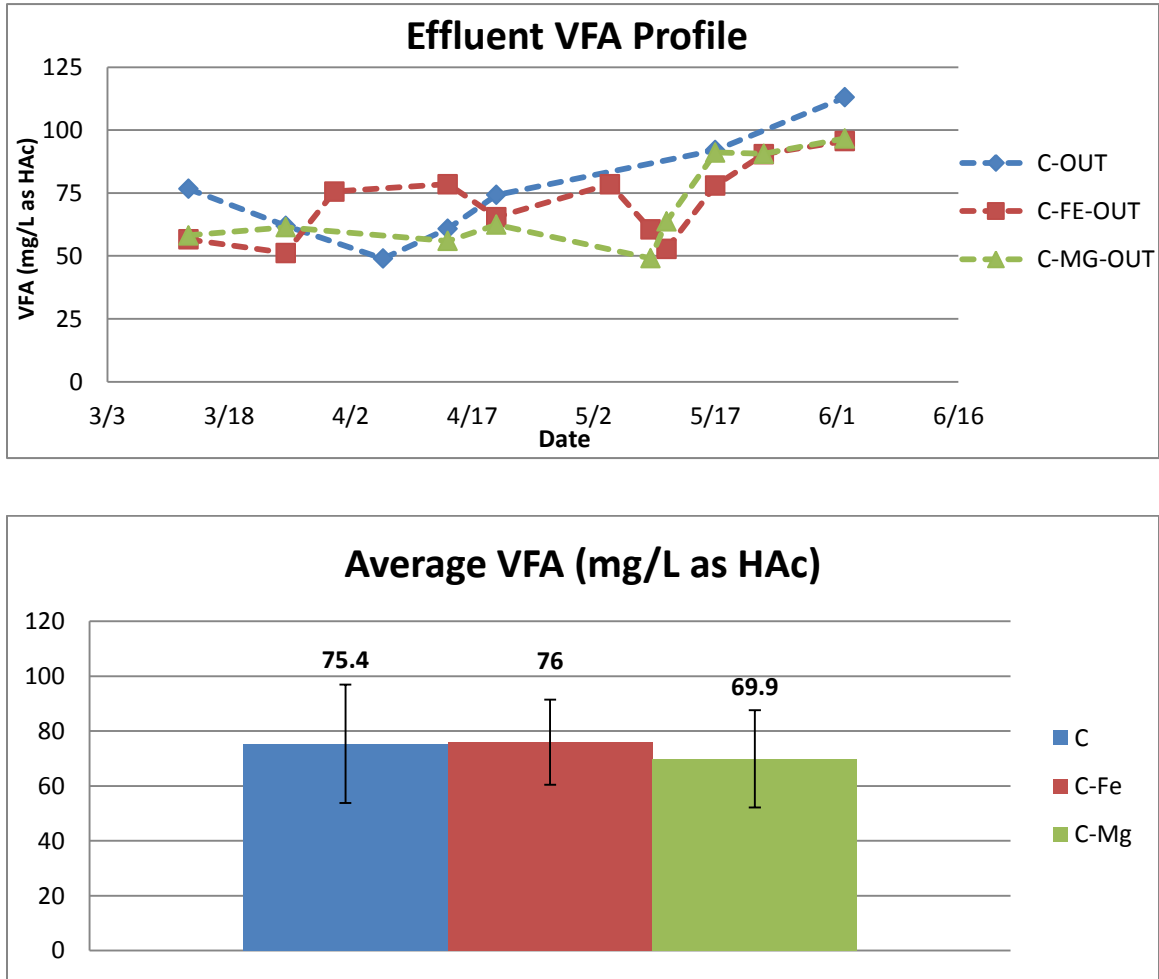


Figure 4-13. VFA data for Phase II

Data (Figure 4-13) indicated that all the VFA values were in the “normal” range and below 100 mg/L as acetic acid, which suggests that all the digesters were functioning normally without upset. The plots do not depict any specific interaction between the three digesters in terms of VFA values. The average VFA value for the C-Mg reactor was the least at (69.9 mg/L as HAc) followed by the C-Fe (75.9 mg/L as HAc) and C (75.4 mg/L as HAc). However, the average values for all the three reactors were statistically similar due to their high standard deviations.

(g) Specific Gas Production:

Figure 4-14 show the gas production data for phase II.

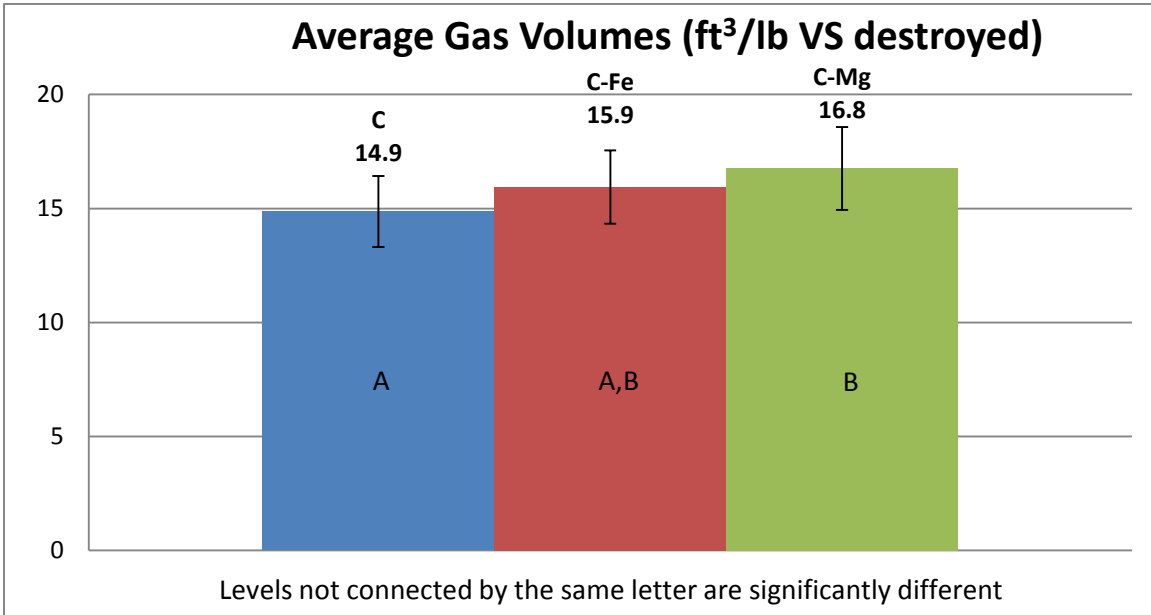
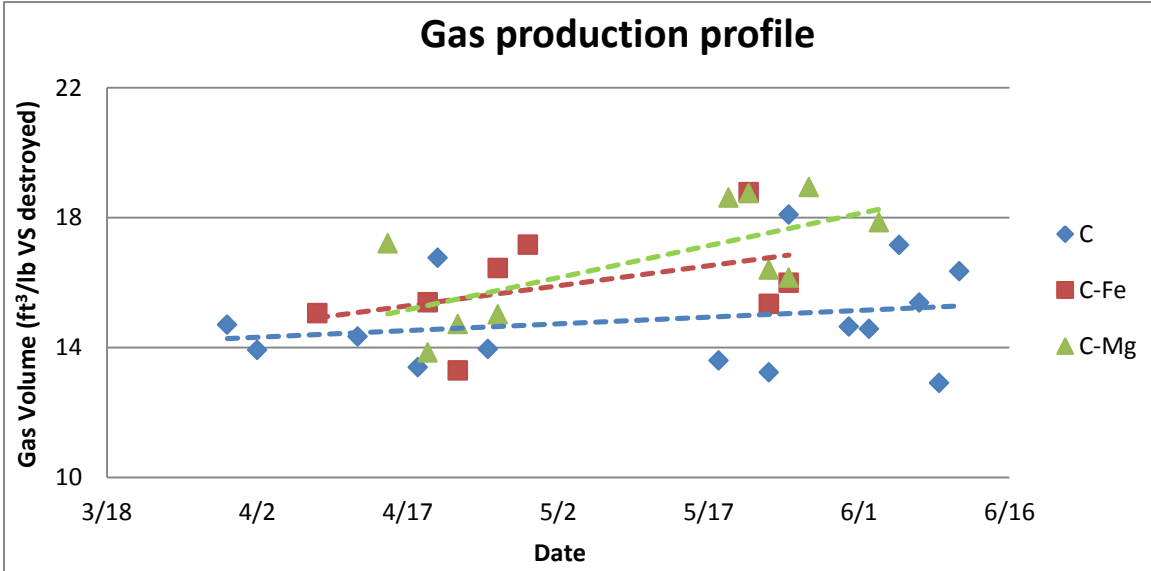
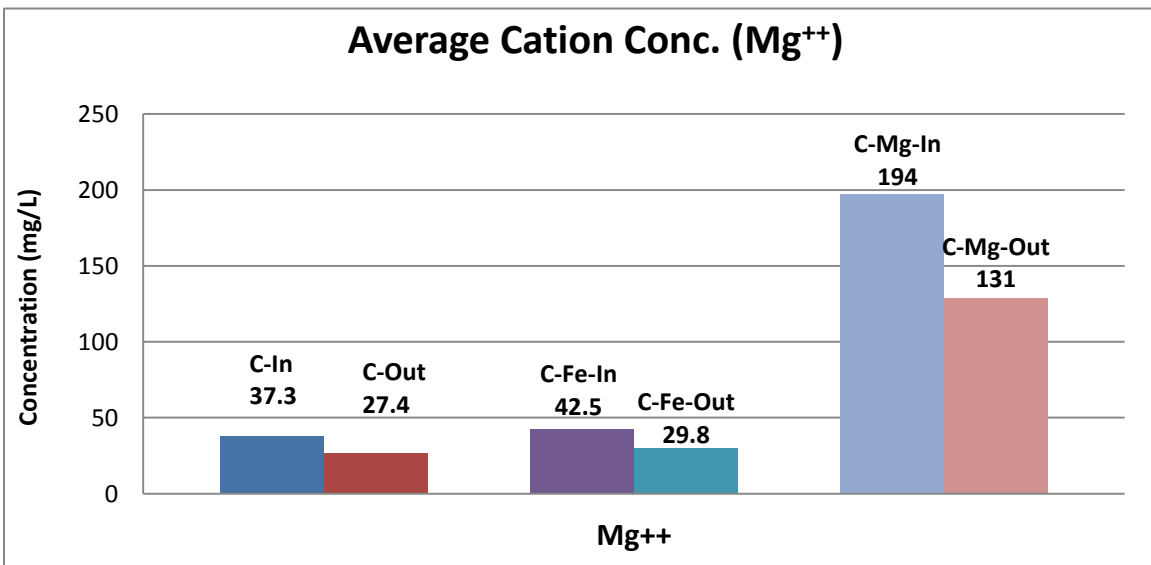
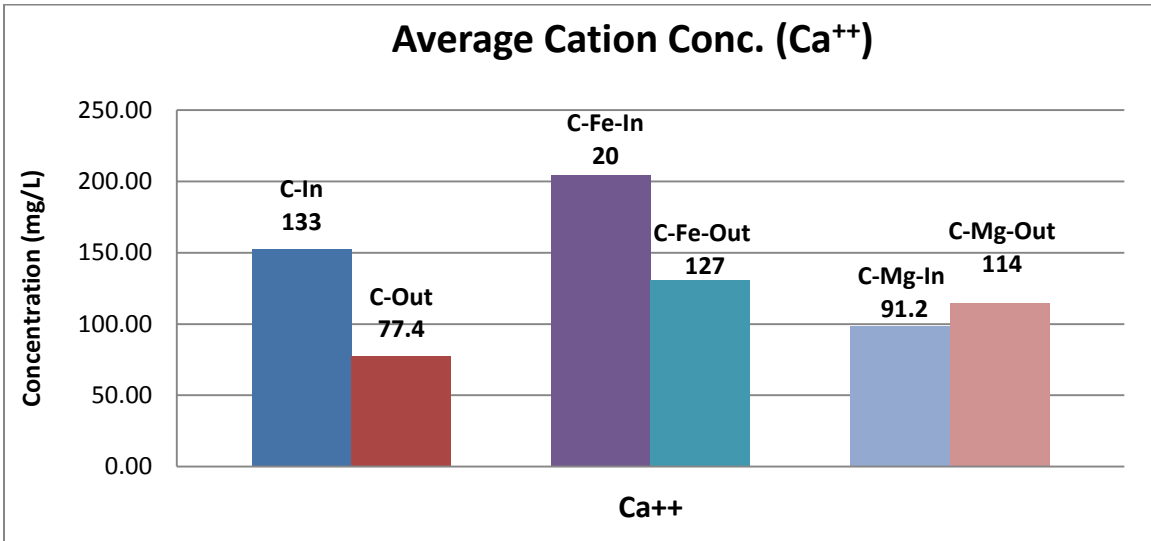


Figure 4-14. Specific gas production data for Phase II

It can be seen that the individual values for gas volumes are scattered. However, the trend lines and the average values suggest that C-Mg had a slightly higher gas production in comparison to the C & C-Fe reactors. A one-way ANOVA of the average gas volumes for the three reactors was performed, which yielded significant differences between the three ($p = 0.0289$). A Tukey HSD post hoc analysis was conducted to analyze the interaction between the average values for the three digesters. The results yielded different levels for the average values of reactors C & C-Mg. However, the average value for C-Fe was assigned the same levels as both C & C-Mg. These levels are shown by the various letters (A and B) in the bar graph (Figure 4-13). The test indicated that the performance of the C-Mg digester in terms of gas production was statistically better than C. However, the C-Fe digester's average gas production was not statistically different from both C and C-Mg.

(h) Solution Ions:

Soluble cations results are shown in the following figures. Figure 4-14 show the average cations (Ca^{++} , Mg^{++} , Na^+ , NH_4^+ as N and K^+) concentrations for the influent and effluent of all the three reactors for phase II. Figure 4-15 shows the average gain or loss in soluble cations from influent to effluent due to anaerobic digestion, over the study period of Phase II.



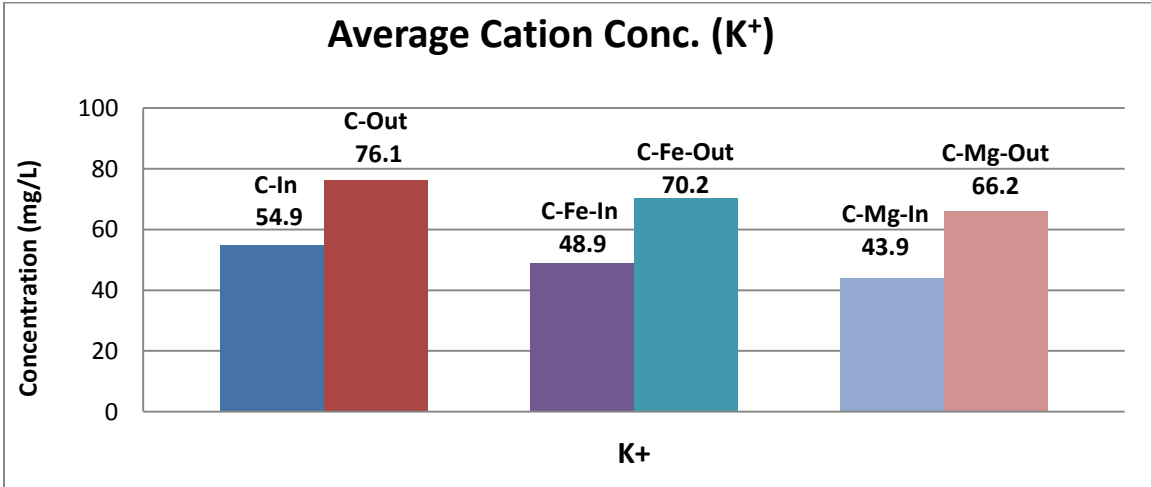
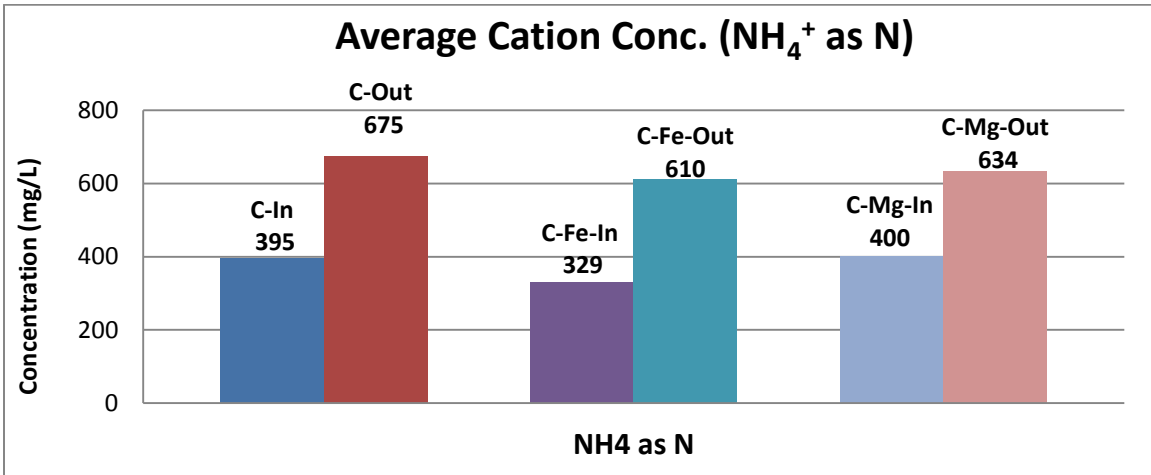
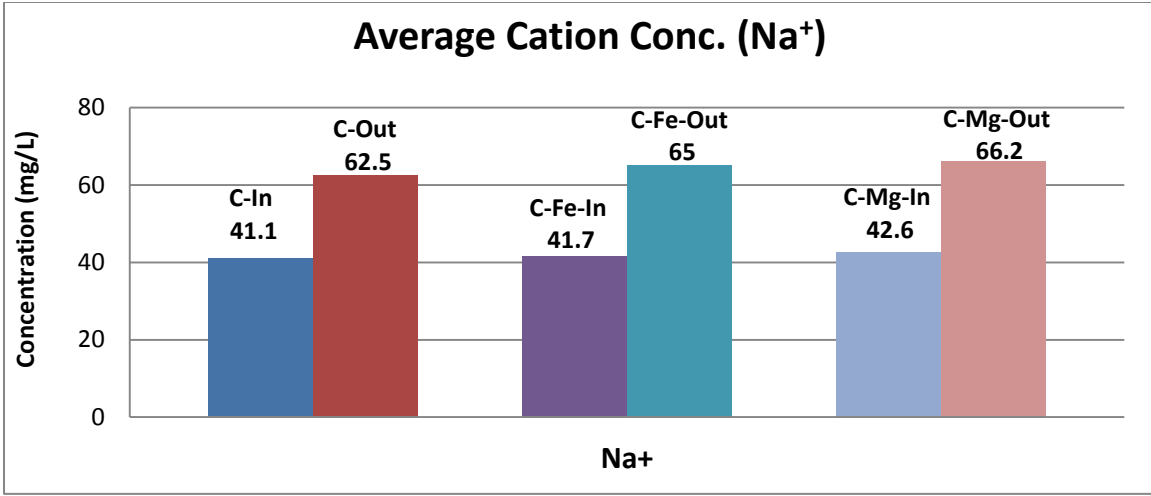


Figure 4-15. Average cations concentration during Phase II

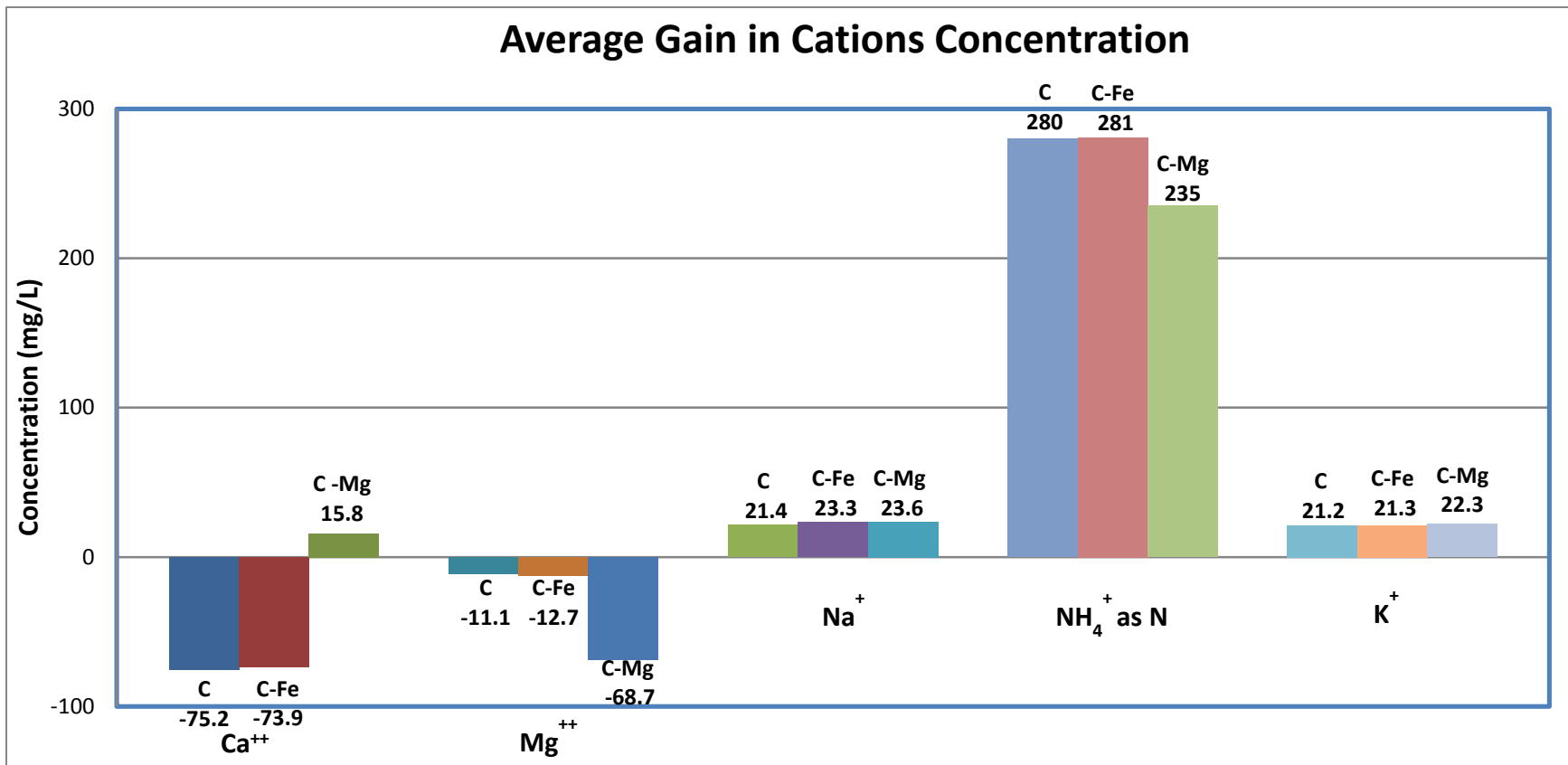


Figure 4-16. Average gain in cations concentration during Phase II

A general decline in Mg^{++} ions from influent to effluent was observed in all the reactors. However, the decline in the C-Mg reactor was the largest (-68.7 mg/L) and considerably higher than those in the C (-11.1 mg/L) and C-Fe (-12.7 mg/L) reactors. A general decline in Ca^{++} ions from influent to effluent was observed in C (-75.2 mg/L) and C-Fe (-73.9 mg/L) reactors. However, in case of C-Mg reactor, an increase in Ca^{++} ions (15.8 mg/L) was recorded. This could be attributed to the fact that the uptake of the divalent Ca^{++} cations, which generally occur in anaerobic digestion, is being substituted by the uptake of divalent Mg^{++} ions in the C-Mg reactor.

A general increase in the monovalent cations Na^+ , K^+ and NH_4^+ as N from influent to the effluent was observed for all the reactors. The average gain in the cations Na^+ and K^+ was almost same for all the 3 reactors. The average increase in the ammonia concentration (NH_4^+ as N) for the C-Mg reactor (235 mg/L) was less than those for the C (280 mg/L) and C-Fe (281 mg/L) reactors, which were almost the same. This gives an indication that some extra ammonia is removed in the C-Mg reactor, as compared to the other two. Because more solids destruction occurred in the C-Mg reactor, ammonia would be expected to be higher unless it was precipitated.

Soluble anions data are shown in the following figures. Figure 4-16 show the average anions (Cl^- and PO_4^{3-} as P) concentrations for the influent and effluent of all the three reactors for Phase II. Figure 4-17 show the average gain or loss in soluble anions from influent to effluent due to anaerobic digestion, over the study period of Phase II.

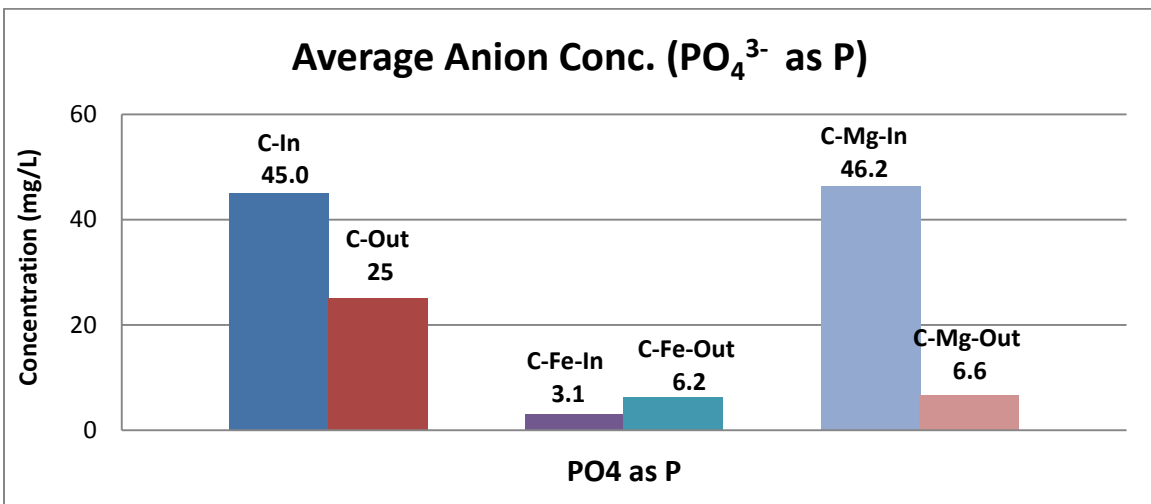
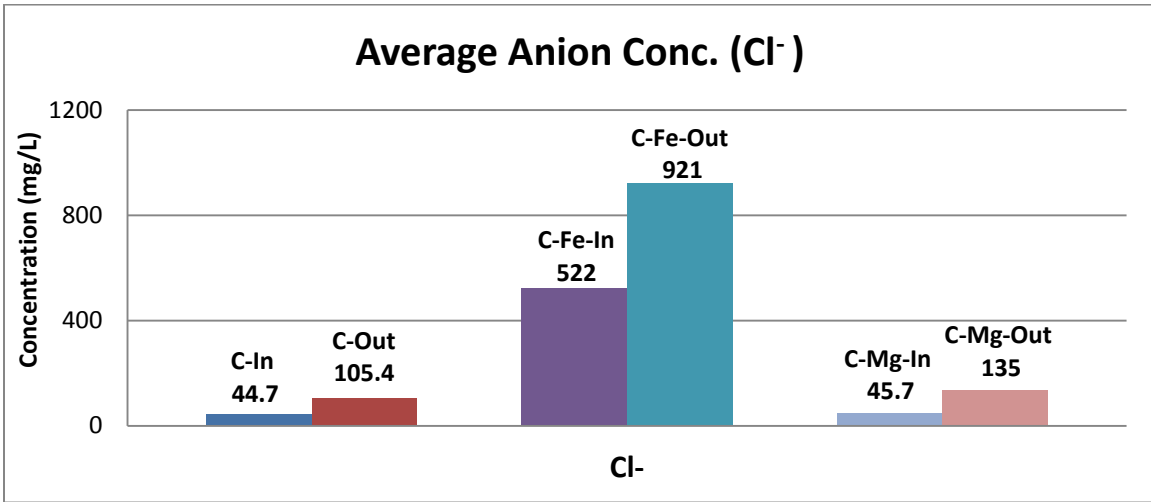


Figure 4-17. Average anions concentration during Phase II

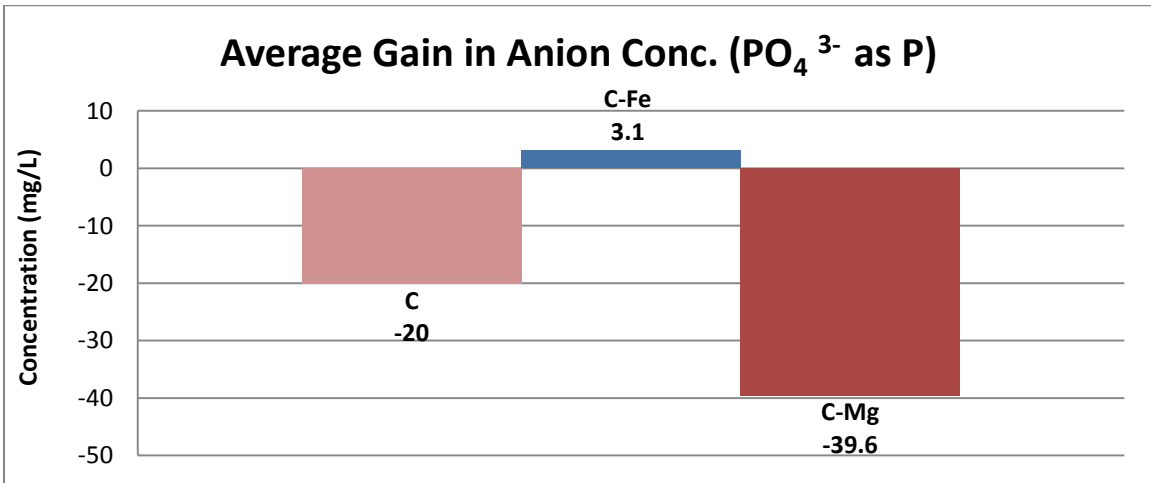
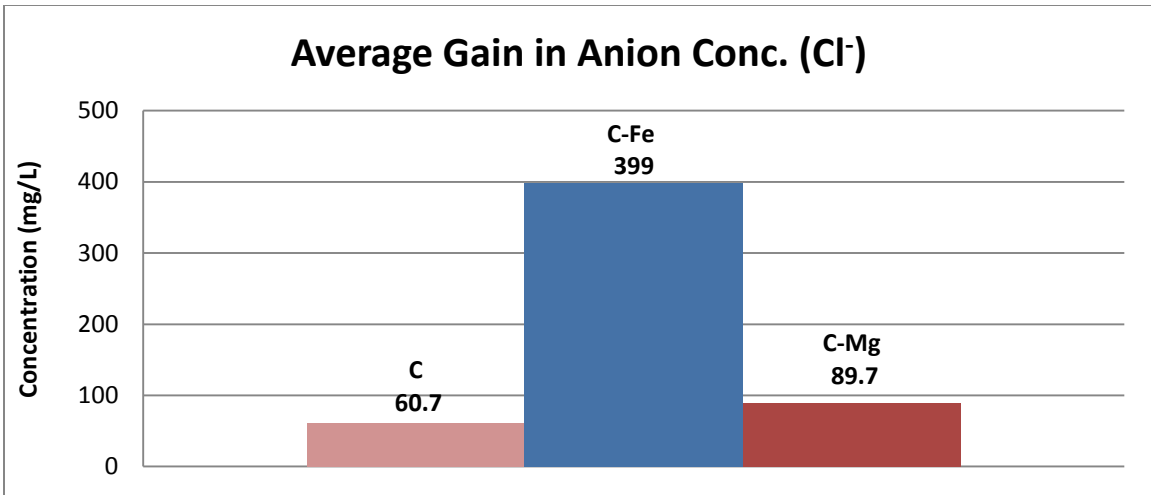


Figure 4-18. Average gain in anions concentration for Phase II

A general increase in Cl^- ions concentration from influent to effluent was observed in all the three reactors. However, the average values of Cl^- ions concentration for C-Fe reactor were much higher than those for C & C-Mg reactors for both the influents and effluents. Thus, the addition of iron as a chloride salt during anaerobic digestion increased the chloride concentration of wastewater substantially. The average values for the concentration of PO_4^{3-} as P were similar in the influents of C (45 mg/L) & C-Mg (46.2 mg/L) reactors. However, it drastically decreased for the C-Fe-In (3.1 mg/L). This is because the iron added to the C-Fe reactor precipitated the available phosphorus. A general decline in the phosphate concentration from influent to effluent was observed in the C & C-Mg reactors. The average effluent phosphate concentrations for C and C-Mg reactors were 25 mg/L and 6.6 mg/L respectively, while it remained low for the effluent of the C-Fe reactor as well (6.2 mg/L). The decline was the highest for C-Mg reactor (-39.6 mg/L). This suggests that the magnesium added to the C-Mg reactor is capable of precipitating phosphate and reducing it to low levels in the effluents, thereby affecting nutrient removal.

The cations and anions data also suggest the possibility of struvite formation in the C-Mg reactor due to the addition of magnesium. The indications of these are decreased levels of magnesium, ammonium and phosphate ions in the C-Mg effluent as compared to the other two effluents.

(i) Odors, Dewatering and Cake Solids:

The effluent from each reactor was tested for the optimum polymer dose (OPD) by performing a capillary suction time (CST) test. The effluent biosolids were also tested for the cake solids concentrations and odors. The odor tests revealed low absolute values for all the sludges and for both the runs, which were much lower than the expected ranges of 100 to 1000 ppmv. It was then found out that the large Waring Blender used for shearing the mixture of optimum polymer and sludge during Phase II, had a “G” value which was lower than what it was initially thought to be. This caused incomplete shearing of the sludge blend, thereby causing the odor levels to stay low. However, the values found were thought to be acceptable on a relative basis.

Therefore, the values relative to the Control have been reported in the results for comparison. The peak value for the control in both the runs was set at 1, and rest of the odor values are relative to this peak in each run. The results of the tests are shown in the following figures and tables.

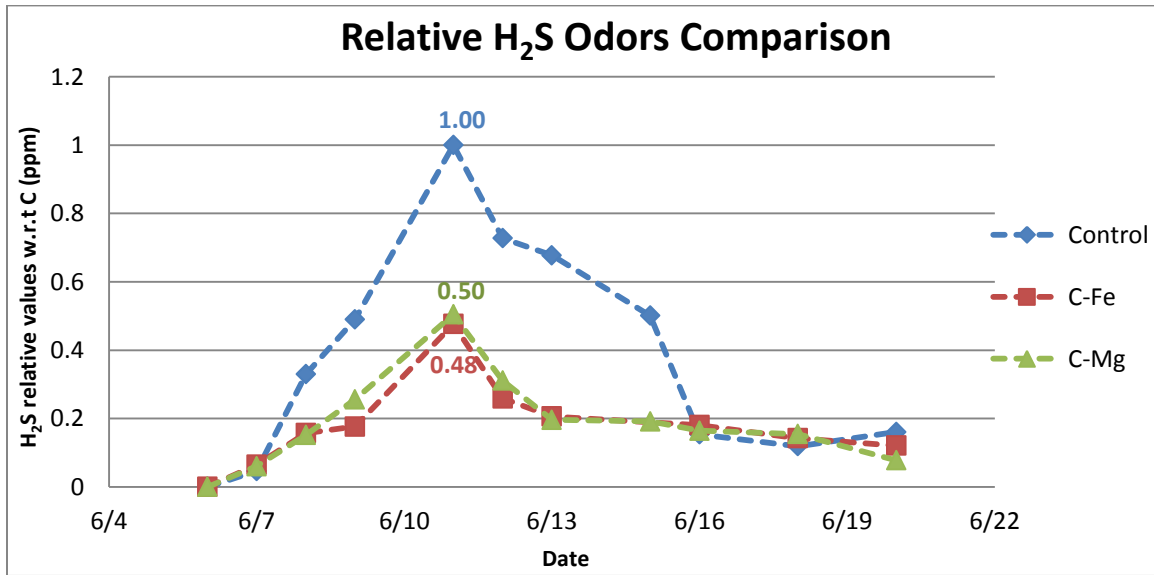


Figure 4-19. H₂S Odor data for Phase II

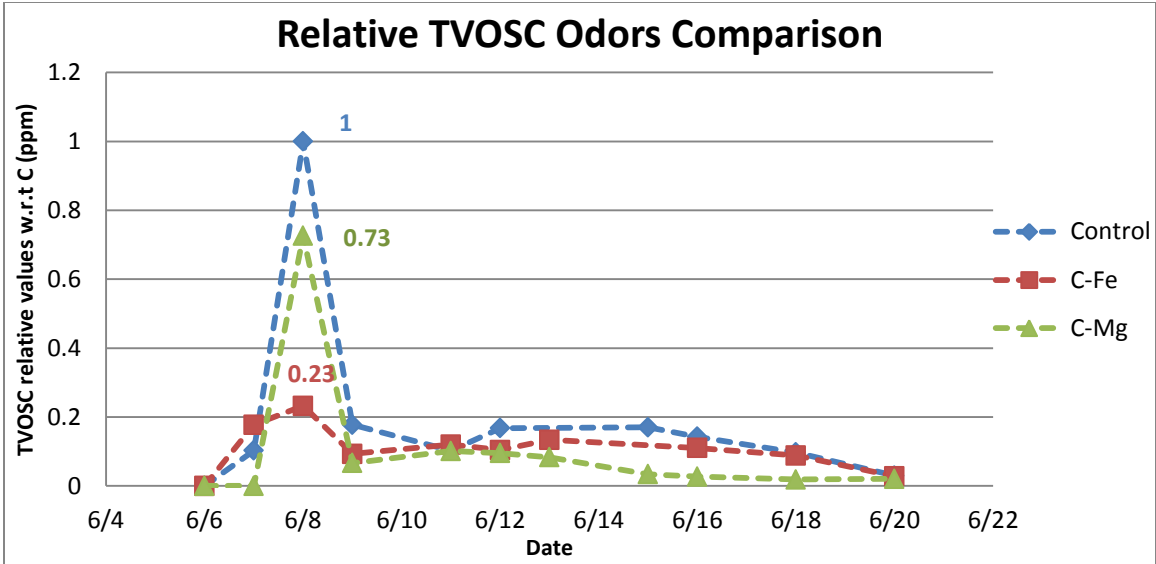


Figure 4-20. TVOSC Odor data for Run 1 (6-7-11) during Phase II

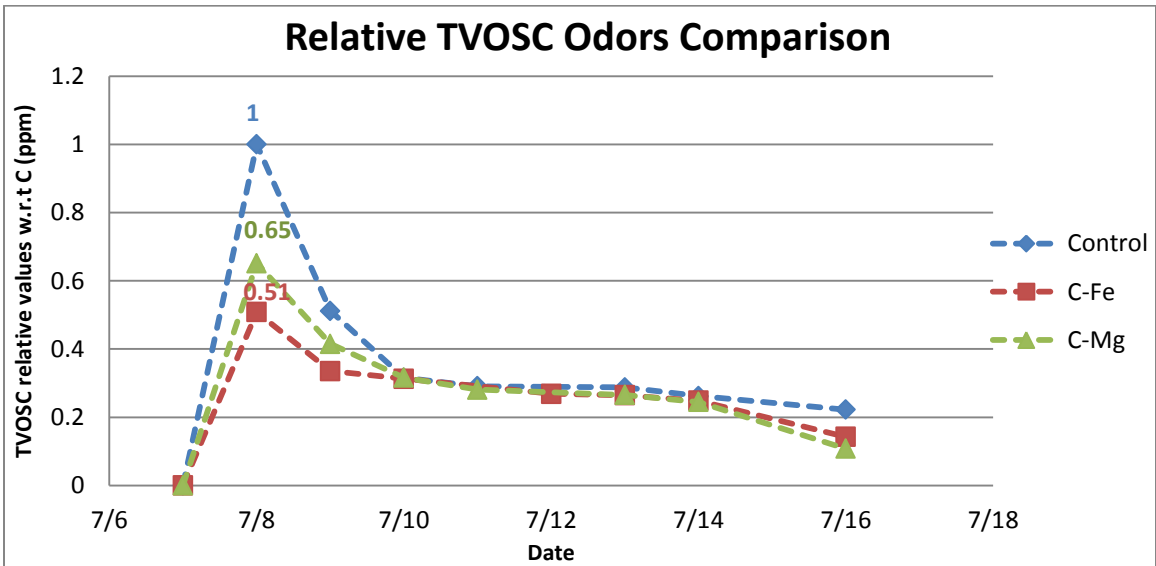


Figure 4-21. TVOSC Odor data for Run 2 (7-8-11) during Phase II

Table 4-3. Optimum Polymer Dose and Cake Solids data for Odor Run 1

Optimum Polymer Dose (ml of 1% Clarifloc/100ml of sample)		
C	C-Fe	C-Mg
7.5	8	7

Percent Cake Solids (%)		
C	C-Fe	C-Mg
19.6	18.6	18.5

Table 4-4. Optimum Polymer Dose and Cake Solids data for Odor Run 2

Optimum Polymer Dose (ml of 1% Clarifloc/100ml of sample)		
C	C-Fe	C-Mg
7.5	8	7

Percent Cake Solids (%)		
C	C-Fe	C-Mg
22.9	23.4	24.9

Figure 4-18 shows that the H₂S odors peaked on the fifth day of the run. Data for TVOSC odors (Figures 4-19 and 4-20) show that all the three samples peaked quite early (2nd or 3rd day of the run) and peaked at the same times during a run. A comparison of the peaks shows that the iron and magnesium amended reactors had lower values than the control, both in terms of H₂S and TVOSC odor production. For the H₂S run, the C-Fe reactor recorded a 52% reduction in the peak value from the C reactor's peak value, while C-Mg reactor recorded a 50% reduction. In the two TVOSC runs, the C-Fe reactor recorded 77% and 49% reductions respectively in the peak values from that of the C reactor, while the C-Mg reactor recorded reductions of 27% and 35% respectively. The decline in the TVOSC odors after peaking is rapid (in a day or two), while in case of H₂S odors, it declines more slowly (three to four days). The odor data is clearly indicative of the fact that both iron and magnesium additives help in reducing both the H₂S and TVOSC odors. From the data, it appears that iron is more effective than magnesium for TVOSC odor reduction, however, their performance in terms of H₂S odor reduction is comparable.

The optimum polymer dose for C-Fe effluent was the highest (8 ml clarifloc/100 ml sample) followed by C reactor's effluent (7.5 ml clarifloc/100 ml sample) and the least

for C-Mg effluent (7 ml clarifloc/100 ml sample). This might indicate that the C-Mg effluent exhibits slightly better dewatering properties than the other two sludges. However, the data are not conclusive.

The cake solids concentrations for all the three reactors were similar in the first run. However, during the second run, C-Mg recorded a higher cake solids concentration (24.9%) as compared to the other two reactors which were similar. This might also be indicative of enhanced dewatering properties attributed due to the addition of magnesium salt. However, the cake solids data was not highly conclusive due to variability in both the runs and the lack of sufficient data to do a statistical analysis. Moreover, no specific correlation could be established between the percent cake solids and odors in biosolids. It can also be believed that, since the sludge is anaerobically digested after addition of the metal ion coagulants, there is little impact on sludge dewatering properties.

(j) Chemical Precipitation Experiment:

This experiment was conducted on the request by the sponsor (Premier Magnesia, LLC.) to ascertain the effect of addition of magnesium hydroxide to the anaerobically digested sludge, on the phosphate concentration of the effluent. The idea was to assess the efficiency of addition of $Mg(OH)_2$ to a sludge storage tank for removal of phosphates prior to dewatering.

A jar test was conducted on the effluent of the mesophilic control digested sludge. The experimental setup consisted of five beakers containing 100 ml each of the control (C) reactor's effluent. Differing amounts of $Mg(OH)_2$ were added to four beakers in the increments of 100 mg/L, starting with 200 mg/L. One beaker had no $Mg(OH)_2$ added and thus served as a control. The sludges in all the beakers, after dosing with $Mg(OH)_2$, were rapid mixed for around 10 seconds, and then mixed at 30 rpm for around half an hour. This was done to ensure proper mixing and flocculation. The effluent of each beaker was then analyzed for soluble phosphate concentration. The results of the same are presented in Figure 4-21.

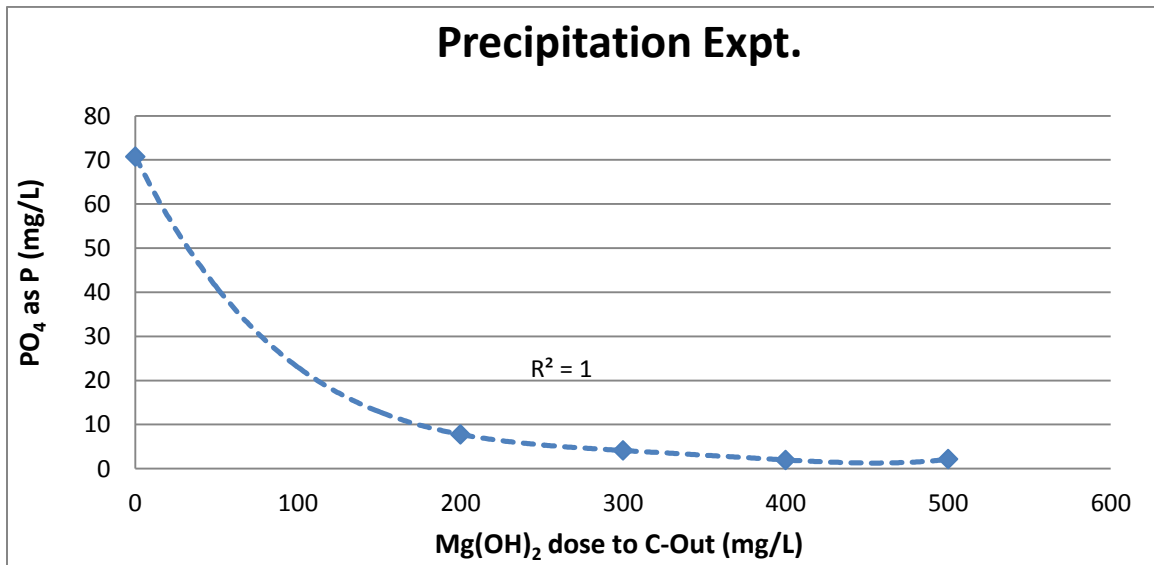


Figure 4-22. Relation between soluble phosphate and $Mg(OH)_2$ dose for precipitation experiment

The results of the precipitation experiment show that the phosphate levels in the effluent decreased with increasing $\text{Mg}(\text{OH})_2$ dose. It was seen that an addition of 200 mg/L of $\text{Mg}(\text{OH})_2$ resulted in around 89% decrease in the phosphate concentration. The phosphate concentration declined exponentially from 70.7 mg/L for control without any $\text{Mg}(\text{OH})_2$ added, to 1.97 mg/L for 400 mg/L of $\text{Mg}(\text{OH})_2$ added.

These results indicate that addition of $\text{Mg}(\text{OH})_2$ to the effluent of anaerobically digested sludge, before it is sent to dewatering, would be very helpful in reducing the phosphate levels in the centrate after dewatering, which is normally circulated back to the head works or discharged into the sea. This would help keep a check on the effluent nutrient levels. Moreover, it is also possible that addition of $\text{Mg}(\text{OH})_2$ removes phosphate in the form of insoluble struvite or other precipitates, resulting in better dewatering and production of nutrient rich and higher percentage cake solids which could be land applied.

4.2 Discussion

Phase I of this study involved the anaerobic digestion of different sludges, one receiving $Mg(OH)_2$ in the collection system, one receiving iron in the collection system and one with no additives. These were all from different utilities. Hence, it was difficult to establish a conclusive comparison between them. The results suggested that the additives did not adversely impact anaerobic digestion of wastewater sludges. In fact, better digestion performance was observed for the magnesium amended sludge as compared to the iron amended sludge with regards to pH, solids destruction and alkalinity. Lower TVOSC odors were detected for both of the amended sludges when compared to the control without any additives. The phosphate removal for the iron amended digester was good; however, little phosphorus removal was observed for the magnesium amended digester. It was also observed that the magnesium amended sludge had low magnesium concentration in the solids but it was high in the solution phase. The results looked positive and provided a good background for the Phase II of the study.

The Phase II of the study provided more conclusive data, which could be directly compared since same sludge was used for all the reactors. Most of the data obtained in the Phase II indicate the improved performance of the C-Mg reactor as compared to the C and C-Fe reactors and reinforce the results and indications of Phase I. Only in the case of COD reduction was the performance of C-Mg reactor similar to that of C reactor. For rest of the parameters tested like pH, solids destruction, alkalinity, specific gas production, etc., the C-Mg reactor showed improved performance compared to the control. Comparing C-Fe with rest of the reactors, the data revealed that addition of iron generally decreased the digestion efficiency. This is indicated by a lower pH, lower solids destruction and lower alkalinity values. However, the C-Fe reactor exhibited higher phosphate removal and lower odors in the dewatered sludge cakes, as compared to the other reactors. The specific gas production for the C-Fe reactor was also statistically similar to the other reactors, though total gas production for the C-Fe reactor would be lower than that for the C-Mg reactor, due to lower volatile solids reduction.

The comparatively poor results shown by the iron amended reactor overall can be attributed to the general reduction in pH and prevalence of comparatively acidic environment. The iron behaves as an acid and tends to lower the pH and alkalinity values, which are essential parameters for the effective functioning of an anaerobic digester. However, the addition of magnesium hydroxide supplements the OH⁻ ions thereby increasing the pH, alkalinity and enhancing the buffering capacity of the sludge and also the overall digestion efficiency in the magnesium amended digester.

Previous literature and current study also indicates that chemical phosphorus removal in wastewater treatment plant can be realized by the addition of iron salts (Mamais et al., 1994, Johnson et al., 2003). However, this practice has two major drawbacks: one is that the chloride concentration in wastewater is increased and the other is that phosphorus recovery from ferric phosphate is nearly impossible. Addition of magnesium hydroxide, on the other hand, has the advantage of being not only able to increase the pH to favor the precipitation of phosphates, but also able to generate more usable phosphate salts, e.g. struvite, which can be recovered. This is particularly true if magnesium hydroxide is added to anaerobic digester supernatant, as this side waste stream contains a high concentration of phosphate and ammonium.

Odor data revealed that both iron and magnesium additives helped in reducing both the H₂S and TVOSC odors. Magnesium addition was about equally as beneficial as iron addition for H₂S odors removal, however, it was less effective for the reduction of TVOSC odors. Both iron and magnesium seem to be capable of precipitating sulfides and controlling the generation of hydrogen sulfide gas which is corrosive and odorous. It also appears that these metals, particularly iron, seem to be capable of binding to organics in sludges, especially proteins, and make these less bioavailable, thereby causing lower odors in dewatered sludge cakes. The observed decrease in the VSR% for the iron amended reactor throughout the study period supports the proposition of the above mechanism for iron. Iron may bind to proteins, making them less bioavailable and that might account for the lower VS reduction. Different mechanisms can be proposed for the magnesium's capability in controlling odors. These include adsorption, neutralization, pH

elevation and stabilization, species complexation, biological interference, and oxidative catalysis.

The oxidation of sulfides occurs both organically and inorganically, through biological and/or chemical mechanisms. Biological mechanisms depend on microbial activity, which is subject to environmental factors such as temperature, pH, food availability and an oxygen source. Although research has indicated that sulfides will rapidly oxidize in the presence of dissolved oxygen, chemical mechanisms rely on pH, redox potential, oxygen source and metal ions for catalysis and rate of oxidation. Oxidative catalysis with magnesium hydroxide occurs from the addition of the light metal cation Mg^{2+} and pH elevation, which affects both chemical and biological pathways.

The supplementation of OH^- ions by the magnesium hydroxide causes a shift in the soluble sulfide equilibrium ($H_2S = H^+ + HS^-$) to reduce the occurrence of hydrogen sulfide gas. It is also possible that magnesium hydroxide particles react directly with H_2S converting H_2S to magnesium polysulfide.

4.3 Proposed Mechanisms of Mg(OH)₂ Functioning

The enhancement of anaerobic digestion due to the addition of Mg(OH)₂ can be broadly explained by the following rationale:

4.3.1 Dissolved Mg(OH)₂ Can Neutralize the Volatile Fatty Acids Produced by the Acidogens, Resulting in a Better pH Environment for the Methanogens.

There are two possible explanations:

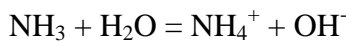
(a) Increase in pH Leads to Enhanced Digestion Operability

Like all biochemical operations, pH has a significant impact on the performance of anaerobic processes, with activity decreasing as the pH deviates from an optimum value. This effect is particularly significant for anaerobic digestion because the methanogens are affected to a greater extent than the other microorganisms in the microbial community. As a consequence, there is a greater decrease in the methanogenic activity as the pH deviates from their optimum value. A pH range of 6.8 to 7.4 generally provides optimum conditions for the methanogens, whereas a pH between 6.4 and 7.8 is considered necessary to maintain adequate activity. A decrease in pH increases the production of higher molecular weight VFAs which might cause inhibition. The pH sensitivity of the methanogens, coupled with the fact that VFAs are intermediates in the stabilization of organic matter, can result in an unstable response by anaerobic digestion to a decrease in pH. If the increased VFA production rate exceeds the maximum capacity of the methanogens to use acetic acid and H₂, excess VFAs will begin to accumulate, decreasing the pH. The decreased pH will reduce the activity of the methanogens, thereby decreasing their use of acetic acid and H₂, causing a further accumulation of VFAs, and a near cessation of methanogenic activity (Grady et. al., 1999)

For the anaerobic digestion process functioning within the acceptable pH range, the pH is controlled primarily by the bicarbonate buffering system. In extreme cases, addition of chemicals for pH adjustment is a wide practice. The addition of hydroxide by adding lime, sodium hydroxide, potassium hydroxide, or Mg(OH)₂ adjusts the pH because the

hydroxide ion reacts with carbon dioxide to form bicarbonate alkalinity. The cations associated with pH adjustment chemicals can also impact the anaerobic process. It is also possible that the addition of divalent Mg^{++} ions improves bioflocculation and thereby has a positive effect on the sludge settleability and dewaterability. An increase in the pH caused by $Mg(OH)_2$ addition would also cause the dissociation of acetic acid into its constituent ions, thereby avoiding a possibility of any sort of inhibition for the digestion process.

It could be argued that an increase in pH might cause ammonia toxicity. Ammonia is a weak base and dissociates in water:



Both species are inhibitory, but at significant different concentrations. Free ammonia (NH_3) is more inhibitory and can cause a toxic response at concentrations of about 100 mg/L as N. On the other hand, ammonium ion (NH_4^+) concentrations as high as 7000 to 9000 mg/L as N have been successfully treated without a toxic response. Moreover, ammonium ion is also an antagonist for inhibition by potassium (Grady et al., 1999). The pK_a for the dissociation of ammonia is approximately 9.3, so ammonia is present primarily as the ionized species at the pH values typically occurring in anaerobic processes. The proportion of total ammonia that is present as free ammonia increases with both pH and temperature.

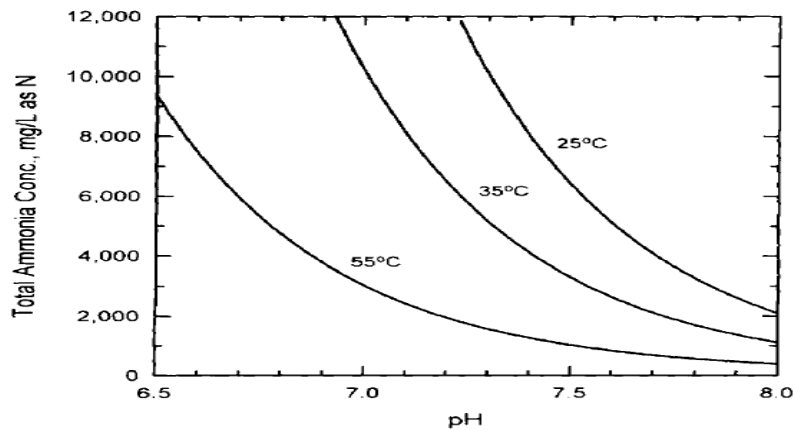


Figure 4-23. Effects of pH and temperature on the total ammonia-N concentration necessary to give a free ammonia concentration of 100 mg/L as N. (Grady et al., 1999)

As illustrated in Figure 4-22, vastly different total ammonia concentrations can result in a toxic free ammonia concentration (100 mg/L as N), depending on the pH and temperature. For mesophilic conditions (35°C), the total ammonia concentration can exceed 5000 mg/L as N and the free ammonia concentration will still be below 100 mg/L as N at pH values of about 7.2-7.3, which were typically observed in the magnesium hydroxide amended reactor (C-Mg). However, for thermophilic conditions (55°C), the total ammonia concentration must be maintained below 2000 mg/L as N to keep free ammonia concentrations below toxic levels. Even for mesophilic operating conditions, total ammonia concentrations of about 2000 mg/L can result in toxic free ammonia concentrations (100 mg/L as N) as the pH approaches 7.5 to 8.0.

Hence, ammonia inhibition is not much of a concern for mesophilic digestion of sludges amended with magnesium hydroxide.

(b) Reduced Long Chain Fatty Acid Inhibition

One characteristic of anaerobic processes is their sensitivity to inhibition by chemicals present in the wastewater or produced as process intermediates. Inhibition causes a reduction in the maximum specific growth rate of microorganisms, thereby requiring an increase in the SRT of a biochemical operation to produce the same effluent that would be produced in the absence of the inhibitor. However, if the inhibitor concentration is increased sufficiently, a toxic response is exhibited and the microorganisms are killed causing total process failure (Grady et. al., 1999).

Anaerobic digestion is often preferred for lipid-rich wastewaters because it allows the energy content of the wastes to be recovered as methane. One of the major challenges faced in AD of lipid-rich wastes is the toxicity of long-chain fatty acids that are produced by the hydrolysis of lipids. Free long-chain fatty acids, which affect the stability and permeability of cytoplasmic membranes, have been reported to inhibit the growth and metabolism of a wide variety of microorganisms, including fermentative acidogens,

hydrogen producing acetogens and aceticlastic methanogens. The toxicity of long-chain fatty acids to these important members of anaerobic microbial communities can also result in the inhibition of the degradation of other important wastewater constituents, such as protein and carbohydrates (Zhengkai, L., et al., 2006).

Previous studies have demonstrated that divalent cations, such as Ca^{++} , Fe^{++} and Mg^{++} can reduce the toxicity of long-chain fatty acids to sensitive members of methanogenic microbial consortia by forming insoluble complexes with reduced bioavailability (Hanaki et al., 1981). The anions of most of the long-chain fatty acids remain in ionic form in the activated sludge. It is possible that the divalent cation Mg^{++} replaces the H^+ or Na^+ attached to the anion (which is responsible for keeping it in the ionic form) and bridges with the fatty acid anion, thereby preventing it from ionizing or forming acid. Thus, it is possible that addition of $\text{Mg}(\text{OH})_2$ provides divalent Mg^{++} cations which bind to the long chain anions and prevent the formation of long chain fatty acids, thereby preventing inhibition to digestion process.

4.3.2 Stimulatory Effects of Light Metal Cation Mg^{++}

Light metal cations include sodium, potassium, calcium, and magnesium. They may be present in the influent, released by the breakdown of organic matter (such as biomass), or added as pH adjustment chemicals. They are required for microbial growth and, consequently, affect specific growth rate like any other nutrient. Consequently, they must be available if anaerobic treatment is to occur. While moderate concentrations stimulate microbial growth, excessive amounts slow it, and even higher concentrations can cause severe inhibition or toxicity. Table 4-5 indicates the concentration ranges over which these various responses occur.

Table 4-5. Stimulatory and Inhibitory Concentrations of Light Metal Cations (Grady et al., 1999)

Cation	Concentration, mg/L		
	Stimulatory	Moderately Inhibitory	Strongly Inhibitory
Sodium	100 - 200	3,500 – 5,500	8,000
Potassium	200 – 400	2,500 – 4,500	12,000
Calcium	100 – 200	2,500 – 4,500	8,000
Magnesium	75 - 150	1,000 – 1,500	3,000

The light metal cations exhibit complex interactions in their effects on microbial growth. For example, inhibition can be increased when two light metal cations are present at their moderately inhibitory concentrations. This is known as a synergistic response. Secondly, the inhibition caused by one light metal cation can be increased if the other light metal cations are present at concentrations below their stimulatory concentrations. Finally, the presence of one light metal cation at its stimulatory concentration can reduce the inhibition of another. This phenomenon is known as antagonism (Grady, et. al., 1999). Table 4-6 summarizes antagonistic responses for the light metal cations and ammonia.

Table 4-6. Antagonistic Responses for Light Metal Cations and Ammonia (Grady et al., 1999)

Inhibitor	Antagonist
Na ⁺	K ⁺
K ⁺	Na ⁺ , Ca ⁺⁺ , Mg ⁺⁺ , NH ₄ ⁺
Ca ⁺⁺	Na ⁺ , K ⁺
Mg ⁺⁺	Na ⁺ , K ⁺

In this study, the C-Mg reactor was dosed with about 200 mg/L as magnesium, which caused the Mg^{++} released into the bulk solution to fall very close to that stimulatory range of 75 – 150 mg/L (Grady et al., 1999). This concentration used (200 mg/L) was much lower than the lowest value (1000 mg/L) for causing even a moderate inhibition, and hence is believed to have been stimulatory to the anaerobic sludge digestion process. Moreover, it can also be seen from Table 4-6 that magnesium acts as antagonist to inhibition by monovalent potassium ions, which have the tendency to adversely affect the digestion process when present in excess.

4.3.3 Phosphate Removal Efficiency and Struvite Formation Potential

Mg^{++} released from the dissolution of $Mg(OH)_2$ and the enhanced polyphosphate hydrolysis, and degradation of organic solids, can react with phosphate to form struvite or a mixture of struvite and other phosphate salts, thereby lowering the level of nutrient concentrations in the bulk solution of the $Mg(OH)_2$ amended digester. The efficiency of phosphate removal is believed to be dependent on the initial phosphate concentration in sludge and also the chemical dosage of magnesium. The higher the dosage and the higher the initial phosphate concentration, the larger the concentration product for insoluble phosphate salts (viz. struvite, magnesium phosphate, calcium phosphate and hydroxyapatite, etc.), hence the larger the driving force for the completion of the precipitation reactions.

Chapter 5: Conclusions

This research investigated and compared the potential applications of magnesium hydroxide and iron chloride in enhancing anaerobic sludge digestion efficiency, removing nutrients from anaerobic supernatant and controlling objectionable odors from dewatered biosolids. The following conclusions can be reached.

1. $\text{Mg}(\text{OH})_2$ added to an anaerobic digester improved its performance. Better pH conditions, larger solids and COD reductions, better alkalinity and buffering conditions and larger biogas production were achieved in the $\text{Mg}(\text{OH})_2$ amended sludge digester. The addition of iron decreased the pH, solids and COD reduction and the alkalinity in the iron amended digester.
2. Both magnesium and iron were found very effective in removing phosphorus.
3. $\text{Mg}(\text{OH})_2$ addition can help considerably in reducing the level of nutrients in the supernatant that must be returned to the plant's headworks (this is a current practice that adversely affects the overall treatment efficiency) and increasing the nutrient content in the generated biosolids for agricultural use and land application.
4. Both magnesium and iron were found to be effective in controlling objectionable odors in dewatered cake solids. They were almost equally effective in removing the H_2S odors, while iron effected greater TVOSC odor reduction.
5. Addition of $\text{Mg}(\text{OH})_2$ to the anaerobic digester posed concerns for struvite formation and its recovery thereafter.

The conclusions and inferences from this study are applicable to the addition of appropriate dosage of $\text{Mg}(\text{OH})_2$ to anaerobic digesters upfront. The results may not be extrapolated for the use of this chemical elsewhere in the wastewater treatment scenario, although there is a good potential for research on that front.

Chapter 6: Engineering Significance and Future Recommendations

This research was aimed at finding an economically feasible alternative to the use of iron in collection systems. Specifically, the use of magnesium hydroxide instead of iron salts was of interest. Excessive iron addition can lead to a decrease in the available phosphorus for the biota, thereby causing hindrance to the anaerobic digestion process, and increased organic sulfur odors from anaerobically digested and centrifuged biosolids. For example, the Los Angeles County Sanitation District (LACSD) uses large amounts of iron in their collection system in an attempt to control hydrogen sulfide (Johnson et al., 2003). Consequently, LACSD has the highest influent iron concentrations of any plant we have investigated over the past seven years. This research can be considered transformative for the amenities in terms of reducing the dependence on iron and opening avenues for the use of a chemical which is non-toxic and brings the added advantages of being non-hazardous and better suited for digestion. This would greatly help the treatment facilities to get rid of iron and other toxic additives to the sewer lines for better treatment and reduced odors from the dewatered sludges. This should be able to provide a sustainable, reliable and cost-effective technology for wide usage and acceptability by the wastewater treatment facilities employing anaerobic digestion.

There is need for additional research with regards to analyzing the general efficacy of $Mg(OH)_2$ in the overall wastewater treatment processes. Few areas with regards to the effects of magnesium salts in anaerobic digestion too need to be further studied. These include:

1. Use of various other magnesium salts like magnesium chloride, etc. Moreover, various forms of magnesium or alternative sources of magnesium hydroxide can also be thought of as potential additives to enhance anaerobic digestion in wastewater.
2. Effects of magnesium hydroxide addition on sludge settleability and validation of the sludge dewatering properties and cake solids concentration and composition.

3. Potential for controlled crystallization of struvite and recovery of phosphate from struvite and other precipitates of anaerobic digestion.
4. Impacts of magnesium additives on the degradation of grease.
5. Impacts of magnesium additives on the organic loading rate to the digester.
6. Effects of magnesium on thermophilic anaerobic digestion.

REFERENCES

1. Adams, G., Forbes, R., Witherspoon, J., Hargreaves, R., and Morton, R. (2008) Recent findings on biosolids cake odor reduction” Results of WERF phase 3 biosolids odor research. *Journal of environmental science and health Part A, Toxic/hazardous substances & environmental engineering* 43: 1575-1580.
2. Appels, L., Baeyens, J., Degreve, J., and Dewil, R. (2008) Principles and potential of anaerobic digestion of waste-activated sludge. *Progress and Combustion Science* 34: 755-781.
3. Bhuiyan, M.I.H., Mavinic, D.S., and Beckie, R.D. (2007) A solubility and thermodynamic study of struvite. *Environmental Technology* 28(9): 1015-1026.
4. Bishop, P.L. (2006) Control of struvite deposition in wastewater treatment plants. *Proceedings of the 11th Annual Central States Water Environment Association Education Conference.*
5. Bouzas, A., Seco, A., and Ferrer, J. (2008) Struvite precipitation assessment in anaerobic digestion processes. *Chemical engineering journal (Lausanne, Switzerland: 1996)* 141: 67-74.
6. Carliell-Marquet, C. and Smith, J.A. (2008) The digestibility of iron-dosed activated sludge. *Bioresource technology* 99: 8585-8592.
7. Cohen, A., Breure, A. M., van Andel, J. G., and van Deursen, A. (1982) Influence of Phase Separation on the Anaerobic Digestion of Glucose-II. *Water Research* 16(4): 449- 455.
8. Cord-Ruwisch, R., Ho, G., Costa, M., and Spencer, P. (2006) Solutions to a combined problem of excessive hydrogen sulfide in biogas and struvite scaling. *Water science and technology* 53: 203-210.
9. Dentel, S.K., and Gossett, J.M. (1982) Effect of chemical coagulation on anaerobic digestibility of organic materials. *Water Research* 16(5): 707- 718.

10. Dezeeuw, W.J. and Lettinga, G. (1980) Use of anaerobic digestion for wastewater treatment. *Antonie Van Leeuwenhoek Journal of Microbiology* 46(1): 110-112.
11. Forbes, R. H., Hentz, L., Adams, G., Witherspoon, J., Murthy, S. N., Card, T., Hargraves, R., Glindemann, D. and Higgins, M. J. (2003). Impacts of In-Plant Operational Parameters on Biosolids Odor Quality: Preliminary Results of WERF Phase 2 Study.
12. Glindemann, D., Murthy, S.N., Higgins, M.J., Chen, Y-C., and Novak, J.T. (2006) Biosolids incubation method for odorous gas measurement from dewatered biosolids cakes, *Journal of Residuals Science and Technology* 3(3): 153-160.
13. Grady, C.P. L., Daigger, G.T., and Lim, H.C., (1999) *Biological Wastewater Treatment*, Marcel Dekker, New York.
14. Hanaki, K., Matsuo, T., and Nagase, M. (1981) Mechanism of inhibition caused by long-chain fatty acids in anaerobic digestion process. *Biotechnology and Bioengineering*, 23: 1591-1610.
15. Higgins, M.J., Adams, G., Chen, Y.C., Erdal, Z., Forbes Jr, R.H., Glindemann, D., Hargreaves, J.R., McEwen, D., Murthy, S.N., Novak, J.T. and Witherspoon, J. (2008). Role of Protein, Amino Acids, and Enzyme Activity on Odor Production from Anaerobically Digested and Dewatered Biosolids. *Water Environment Research* 80(2): 127-135.
16. Higgins, M.J., and Novak, J.T. (1997) Characterization of exocellular protein and its role in bioflocculation. *Journal of Environmental Engineering-ASCE* 123(5): 479-485.
17. Higgins, M.J., and Novak, J. (1997) The effect of cations on the settling and dewatering of activated sludges: Laboratory results. *Water Environment Research* 69: 215-224.

18. Johnson, D.K., Carliell-Marquet, C., and Forster, C. (2003) An examination of the treatment of iron-dosed waste activated sludge by anaerobic digestion. *Environmental technology* 24: 937-945.
19. Leitao, R.C., van Haandel, A.C., Zeeman, G., and Lettinga, G. (2006) The effects of operational and environmental variations on anaerobic wastewater treatment systems: A review. *Bioresource Technology* 97(9): 1105-1118.
20. Mamais, D., Pitt, P.A., Cheng, Y.W., Loiacono, J., and Jenkins, D. (1994) Determination of ferric chloride dose to control struvite precipitation in anaerobic sludge digesters. *Water Environment Research* 66: 912-918.
21. Maqueda, C., Rodriguez, J.L.P., and Lebrato, J. (1994) Study of Struvite Precipitation in Anaerobic Digesters. *Water Research* 28(2): 411-416.
22. Mavinic, D., and Beckie, R. (2007) A solubility and thermodynamic study of struvite. *Environmental technology* 28: 1015-1026.
23. Marti, N., Bouzas, A., Seco, A. (2008) Struvite precipitation assessment in anaerobic digestion processes. *Chemical Engineering Journal* 141(1-3): 67-74.
24. Muller, C.D., Verma, N., Higgins, M.J. and Novak, J.T. (2004). The role of shear in the generation of nuisance odors from dewatered biosolids, *Proceedings WEFTEC*, New Orleans, LA. Oct 3–6.
25. Muller, C.D., Park C., Verma N., and Novak J.T. (2007) The influence of anaerobic digestion on centrifugally dewatered biosolids odors, *Proceedings to WEF Residuals and Biosolids Management*, Denver, Colorado, Apr 15-18.
26. 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*.

27. Murthy, S., Higgins, M., Chen, Y., and Novak, J. (2006) Biosolids incubation method for odorous gas measurement from dewatered sludge cakes. *Journal of residuals science and technology* 3: 153-160.
28. Novak, J.T., Muller, C.D., and Murthy, S.N. (2001) Floc structure and the role of cations. *Water Science and Technology* 44: 209-213.
29. Novak, J.T., and Park, C. (2010) The effect of iron and aluminum for phosphorus removal on anaerobic digestion and organic sulfur generation. *Water science and technology* 62: 419-426.
30. 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(13): 3136-3144.
31. Novak, J.T., Verma, N., and Muller, C.D. (2007) The role of iron and aluminium in digestion and odor formation. *Water science and technology* 56: 59-65.
32. Ohlinger, K.N., Young, T.M. and Schroeder, E.D. (1998) Predicting struvite formation in digestion. *Water Research* 32(12): 3607-3614.
33. Park, C., Abu-Orf, M.M., and Novak, J.T. (2006) The digestibility of waste activated sludges. *Water environment research* 78: 59-68.
34. Parsons, S.A., Corre, K.L., Jones, E.V., and Hobbs, P. (2009) Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology* 39(6): 433-477.
35. Pastor, L., Mangin, D., Barat, R., Seco, A., 2008. A pilot-scale study of struvite precipitation in a stirred tank reactor: conditions influencing the process. *Bioresource Technology* 99(14): 6285–6291.
36. Pastor, L., Mangin, D., Ferrer, J., Seco, A. (2010) Struvite formation from the supernatants of an anaerobic digestion pilot plant. *Bioresource Technology* 101: 118-125.

37. Rodriguez, J., and Lebrato, J. (1994) Study of struvite precipitation in anaerobic digesters. *Water research (Oxford)* 28: 411-416.
38. Stabnikov, V.P., Tay, S.T.L., Tay, D.K., and Ivanov, V.N. (2004) Effect of iron hydroxide on phosphate removal during anaerobic digestion of activated sludge. *Applied Biochemistry and Microbiology* 40: 376-380.
39. Verma N. (2005) Anaerobic digestion: Factors effecting odor generation, *Master of science thesis for Virginia Polytechnic Institute and State University*; Blacksburg VA, USA.
40. Woods, N.C., Daigger, G.T., and Sock, S.M. (2000). Sewage sludge reductions offered by phosphate recycling. *CHIMICA Oggi-Chemistry Today* 18(5): 68–70.
41. Woods, N.C., Sock, S.M., and Daigger, G.T. (1999). Phosphorus recovery technology modelling and feasibility evaluation for municipal wastewater treatment plants. *Environmental Technology* 20(7): 663-679.
42. Wu, Q., Bishop, P.L., Keener, T.C., Stallard, J., and Stile, L. (2001) Sludge digestion enhancement and nutrient removal from anaerobic supernatant by $Mg(OH)_2$ application. *Water Science and Technology* 44: 161-166.
43. Young, T., and Schroeder, E. (1998) Predicting struvite formation in digestion. *Water research (Oxford)* 32: 3607-3614.
44. Zhengkai, L., Wrenn, B.A., Venosa, A.D., Effects of Ferric Hydroxide on Methanogenesis from Lipids and Long-Chain Fatty Acids in Anaerobic Digestion. *Water Environment Research*, 78: 522-529.