January 2012

Precipitation of Phosphate Minerals from Effluent of Anaerobically Digested Swine Manure

Alex Y. Lin
University of South Florida, aylin@mail.usf.edu

Scholar Commons Citation
Lin, Alex Y., "Precipitation of Phosphate Minerals from Effluent of Anaerobically Digested Swine Manure" (2012). *Graduate Theses and Dissertations.*
http://scholarcommons.usf.edu/etd/4359

Precipitation of Phosphate Minerals from Effluent of Anaerobically Digested Swine Manure

by

Alex Yuan-li Lin

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Co-Major Professor: Sarina Ergas, Ph.D.
Co-Major Professor: Jeffrey Cunningham, Ph.D.
Maya Trotz, Ph.D.

Date of Approval:
November 9, 2012

Keywords: struvite, wastewater, confined animal feeding operation (CAFO), fertilizer, synthetic

DEDICATION

I dedicate this thesis to all those that have supported me along the way whether directly or indirectly. I would like to thank members of Intervarsity on the USF campus, members of Community Life Church, and my family for their support and encouragement in many ways. They have shaped my time at USF.

I would like to thank Veronica, Trina, and Tom especially for their time, collaborations, and contributions to my work. They have been a great asset throughout this work. They were the key members in my research community that made the following work possible. I would also like to thank Arlin and others for allowing me some of their time during their busy schedules as well.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant 0965743. This research was supported by research grant No. IS-4360-10 from BARD, the United States-Israel Binational Agricultural Research and Development Fund. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation or of the Binational Agricultural Research and Development Foundation.

I acknowledge my committee members for their time and support in this project. They have allowed me to access many of their resources and have been overall an encouragement throughout this whole process. I have learned many things from them and have grown tremendously under their guidance.

TABLE OF CONTENTS

LIST OF TABLES iii

LIST OF FIGURES iv

ABSTRACT vi

CHAPTER 1: INTRODUCTION 1
- 1.1 Background 1
- 1.2 Factors Affecting Struvite Precipitation 4
- 1.3 Objectives 6

CHAPTER 2: LITERATURE REVIEW 7
- 2.1 Anaerobic Digestion 7
  - 2.1.1 Reactor Systems: CMBR, SBR, and CMFR 7
  - 2.1.2 Three Main Purposes of Anaerobic Digestion 8
  - 2.1.3 Anaerobic Digestion By-Products 9
- 2.2 Struvite Precipitation 10
  - 2.2.1 pH Effects on Struvite Components 11
  - 2.2.2 Methods to Control pH 12
  - 2.2.3 Chemistry of CO_2 Stripping as pH Adjustment 12
  - 2.2.4 Inhibitory Chemical Interferences 13
  - 2.2.5 Growing Struvite Crystals: Nucleation 16
  - 2.2.6 Struvite Fertilizer for Plant Utilization 16
  - 2.2.7 Economic Feasibility 17
- 2.3 Struvite Precipitation of Anaerobically Digested Effluent 18
  - 2.3.1 Predicting Struvite Precipitation 18
  - 2.3.2 Effective pH from Synthetic Wastewater Experiments 21
  - 2.3.3 Examining Struvite Precipitation from AD Effluent 22
  - 2.3.4 Other Factors: Organic Matter and Storage 24

CHAPTER 3: MATERIALS AND METHODS 26
- 3.1 Establishing Operational Procedures for Anaerobic Digesters 26
- 3.2 Effects of Mg:P Ratios for Struvite Precipitation 28
- 3.3 Effect of Organic Matter on Struvite Precipitation 30
- 3.4 Storage of AD Effluent for Struvite Precipitation 31
- 3.5 Analytical Methods 32

CHAPTER 4: RESULTS AND DISCUSSION 34
- 4.1 Anaerobic Digestion Studies 34

4.2 Effects of Mg:P Ratio 36
  4.2.1 Ammonium Removal and Observed Volatilization...............................39
  4.2.2 Calcium Removal and Interference 40
  4.2.3 Magnesium and Phosphorus Removal and the Optimal Mg:P Ratio 41
  4.2.4 Agreement with Other Studies and Carbonate Minerals 42
  4.2.5 Comparisons with Visual MINTEQ v.3.0 43
4.3 Effects of Organic Matter 44
4.4 Effects of Storage..47
  4.4.1 Magnesium Ion Removal from Solution..48
  4.4.2 Ammonium Ion Removal from Solution 49
  4.4.3 Calcium Ion Removal from Solution..50
  4.4.4 Phosphate Ion Removal from Solution 51
  4.4.5 Effects of Forced Precipitation 51
  4.4.6 Overall Storage and Precipitation 55

CHAPTER 5: CONCLUSIONS 57

REFERENCES 60

APPENDIX A: ADDITIONAL MATERIALS FOR CHAPTER 3 67

APPENDIX B: ADDITIONAL MATERIALS FOR CHAPTER 4 70

LIST OF TABLES

Table 2-1: Struvite properties observed at room temperatures 11

Table 2-2: Minerals related to phosphorus precipitation 15

Table 2-3: Major findings of various chemical equilibrium models 20

Table 2-4: Tested pH and molar ratios of synthetic wastewaters 22

Table 2-5: Struvite precipitation findings of synthetic or real anaerobically digested swine manure effluent 25

Table 3-1: Main purposes of experiments 26

Table 3-2: Approximate concentrations of synthetic AD swine manure effluent 29

Table 3-3: Reagents used to create synthetic AD swine manure effluent 30

Table 3-4: Method detection limits (MDL) of IC analyses 33

Table 4-1: Loading rate and methane production comparisons for swine waste AD studies 35

Table 4-2: Summary of total mass differences 37

Table 4-3: Brief economic analysis of Mg use and struvite production 42

Table 4-4: Comparison of real and synthetic effluents' total mass differences................47

Table A-1: Equipment and analyses shared among experiments 69

LIST OF FIGURES

Figure 2-1: Formation of struvite (a) and amorphous calcium phosphate (b) at varying pH values 14

Figure 2-2: Solubility of struvite as Mg:Ca ratio varies with pH 15

Figure 4-1: Methane production and ammonium concentration in reactor 2. 34

Figure 4-2: XRD scans of corresponding Mg:P ratios identified struvite in all samples with mixed purity. 37

Figure 4-3: Reference patterns identified in precipitates were taken from the Panalytic Highscore software 38

Figure 4-4: Precipitation of minerals at varying Mg:P molar ratios show a possible optimum between Mg:P ratios of 1.30-1.78 39

Figure 4-5: Percent compositions of mineral precipitates from Visual MINTEQ....................44

Figure 4-6: Comparison of XRD scans between real and synthetic effluents showing different quantities of each precipitated mineral 45

Figure 4-7: Comparing real, synthetic, and modeled anaerobically digested effluent 46

Figure 4-8: Evidence of CO_2 stripping during storage 48

Figure 4-9: Magnesium concentrations of stored AD effluent over time 49

Figure 4-10: Ammonium concentrations of stored AD effluent over time 49

Figure 4-11: Calcium concentrations of stored AD effluent over time 51

Figure 4-12: Phosphate concentrations of stored AD effluent over time 52

Figure 4-13: Comparison of XRD scans between different storage conditions for day 0 53

Figure 4-14: Precipitation of stored AD effluent in varying storage conditions 54

Figure 4-15: Ion removals from beginning of storage to after forced precipitation 56

Figure A-1: Diagram of bench-scale anaerobic digesters 67

Figure A-2: Sample cation calibration curve for the IC 68

Figure A-3: Sample anion calibration curve for the IC 68

Figure B-1: Methane production and ammonium concentration in reactor 3 70

Figure B-2: XRD scans over time for storage under outdoor, closed to the atmosphere conditions 71

ABSTRACT

Swine production represents approximately 40% of the world's meat production, and its wastes contain high concentrations of organic carbon, nitrogen (N), and phosphorus (P). Anaerobic digestion is an increasingly popular technology for treating animal wastes while simultaneously generating energy. Its propagation and ability to solubilize organic N and P make adding a struvite recovery process attractive. Recovering struvite ($MgNH_4PO_4$) from anaerobically digested swine waste can address global P shortages, meet P discharge guidelines, and produce slow-release fertilizer, which can be sold for revenue.

Anaerobic digesters were operated with at organic loading rates of 3.4-3.9 g volatile solids per liter per day to provide consistent effluent for struvite precipitation studies. Three research questions about struvite precipitation were addressed in this study, specifically what is the (1) required $Mg:PO_4$ ratio, (2) effect of organic matter, and (3) effect of storage time and conditions on struvite precipitation from effluent of anaerobically digested swine manure? $Mg:PO_4$ ratios between 1.3-1.8 were determined to be the economic optimum and precipitated 81-90% of P from synthetic wastewater with calcium phosphate minerals dominating. Under P-limited conditions, a chemical equilibrium model (Visual MINTEQ v.3.0) predicted over 99% P removal with a precipitate mixture of struvite, calcium phosphates, and magnesite. Synthetic wastewater experiments without organic matter removed approximately 85% P with a precipitate mixture of struvite, dolomite, calcite, brucite, and calcium phosphates. Real swine effluent removed more than 95% of P and had a similar mixture of precipitates as synthetic wastewater, but in different concentrations. Organic acids were suspected to prevent struvite formation. Stored anaerobically digested swine wastewater under varying conditions all suggest calcium phosphates form naturally over time. Precipitation of struvite is best carried out as soon as possible to increase the purity of struvite. Although struvite recovery was possible, the conditions for struvite precipitation must be controlled carefully to obtain highly pure struvite.

CHAPTER 1: INTRODUCTION

1.1 Background

Worldwide increases in population and meat consumption have placed greater demands on livestock operations to produce more food per unit area. Pork currently comprises 38% of the world's meat production, which the United States Department of Agriculture (USDA) expects to increase (Davis & Lin, 2009). Confined animal feeding operations (CAFOs), which are common for mass production of pork, create concentrated animal wastes that require treatment. CAFOs typically employ the following techniques to treat their animal wastes: land application, anaerobic lagoons, and composting. Although these conventional techniques have been acceptable for many years, modern large-scale production farms are known to release greenhouse gases (GHGs) such as carbon dioxide (CO_2) and methane (CH_4), thereby contributing to global climate change (Massé et al., 2011). Also, land application, anaerobic lagoons, and composting techniques have also been documented to release organic carbon, nitrogen (N), and phosphorus (P) compounds into the environment (Smith et al., 2001; Ives et al., 2011; Pascoe et al., 2011). These releases can stimulate harmful algal blooms, which lead to eutrophication and subsequently disrupt ecosystems or destroy habitats if left uncontrolled (Burkholder et al., 2007). Land application, anaerobic lagoons, and composting often do not meet the nutrient guidelines set by the National Pollutant Discharge Elimination System (NPDES) permits regulated by EPA (Environmental Protection Agency, 2003) or the national surface water discharge criteria (Environmental Protection Agency, 1986).

Environmental groups and government agencies are seeking ways to reduce these GHG emissions and detrimental discharges (Burkholder, et al., 2007; Massé et al., 2011).

Conversely, if unmanaged GHG emissions and nutrients swine wastes can be captured, then these problems can become opportunities for wastes to become resources. Of the emissions from farms, methane can be used by capturing it and then burning it for energy. This can help address national energy demands in rural areas far from electrical power plants (Newell, 2010). Nutrients, such as P, can also be captured from swine wastes, which have noticeably higher amounts of P than other animal manures, thereby providing a better opportunity to recover P (Moody et al., 2009). P recovery is critical to address the wide need for P in plant fertilizers, and the growing concern of P shortages (Cordell et al., 2009). Phosphorus-rich mines are slowly being depleted and are expected to last between 50 to 400 years based on current usage rates (Bradford-Hartke et al., 2012). Currently, there is no comprehensive solution addressing these issues.

Anaerobic lagoons and anaerobic bioreactors, also known as anaerobic digesters (AD), are similar. Both utilize similar microbiological processes to degrade wastes such as swine manure by converting solids into biogas and soluble compounds and by inactivating pathogens (Burkholder et al., 2007). This means the two systems can both generate carbon dioxide, methane, ammonium, phosphate, bicarbonate, and metal ions, including potassium, magnesium, and calcium from organic materials (Marti et al. , 2008); however, anaerobic digesters allow for the capture of GHGs. In addition to contributing to GHGs, lagoons require large land areas, provide little control over the microbiological processes, and are unstable in performance due to weather and climate (Deng et al, 2008; Mihelcic et al., 2009). Depending on the site, it is also possible for algal blooms to occur in anaerobic lagoons, which can result in odors, aesthetic impairment, and a disruption of the local ecology (Ritmann and McCarty, 2001; Mihelcic et al., 2009). In contrast, an anaerobic digester provides a single outlet for biogas, which can be directed towards stoves to cook food, heaters to warm a facility, or generators to create electricity (Rowse, 2011; Marañón et al., 2011). Applications usually depend on the process size and the quality of the biogas generated. Other benefits of using digesters are the ability to change hydraulic and solids residence times to help mitigate inconsistent feed strengths or the presence of toxic materials in the system. Anaerobic digesters also improve microbial performance by maintaining constant temperature, having fixed stirring rates, and controlling pH. This allows digesters to produce fewer odors, increase pathogen inactivation, and degrade waste materials faster than lagoons (Song et al., 2004; Smith et al., 2005; Chen et al., 2011). The drawback of these systems is a greater generation of dissolved nutrients such as ammonium, phosphate, magnesium, and calcium, all of which require management or treatment (Rittman & McCarty, 2001).

In order to address the problem of depleting P sources, a mineral called struvite ($MgNH_4PO_4$) has been recognized as a possible solid, slow-release fertilizer (Wang et al., 2005; Bauer et al., 2007). Due to its ionic components of magnesium, ammonium, and phosphate, struvite has been suggested as a better fertilizer than calcium phosphates or conventional fertilizers (Wang et al., 2005). All these ionic components are already found in digested wastes. In fact, struvite is commonly found as scale on wastewater treatment plant (WWTP) pipe walls, eventually causing pipe blockages and reducing system performance at WWTPs (Uludag-Demirer et al., 2008). Like municipal wastewaters, swine wastewaters also contain high concentrations of magnesium, ammonium, and phosphate. Doyle and Parsons (2002) found that P can be recovered from swine wastewaters as struvite.

The combination of anaerobic digestion followed by struvite precipitation (SP) can address issues of both energy and P scarcities by generating biogas and struvite. These products can either be used for farming operations or sold to offset operational costs. Struvite precipitation can capitalize on anaerobic digester effluent's greater nutrient content compared to direct struvite precipitation from animal wastes without digestion (Moody et al., 2009), due to the generation of nutrients, ammonium and phosphate, as mentioned previously. However, several other factors reported in literature can also affect struvite precipitation potential: effective pH range, temperature, magnesium to phosphorus ratio (Schuiling & Andrade, 2010), interfering calcium to magnesium ratio (Battistoni et al., 2000), and the effects of aeration (Wang et al., 2006; Dhakal, 2008). It is necessary to understand what factors are involved with precipitating struvite and how these factors affect struvite precipitation from swine manure specifically.

1.2 Factors Affecting Struvite Precipitation

The presence and ratio of magnesium, calcium, phosphate, and organic ions are critical to struvite precipitation because those ions contribute to or interfere with struvite precipitation. Struvite is a mineral with a 1:1:1 molar ratio of magnesium, ammonium, and phosphate (Jaffer et al., 2002). Although ammonium also contributes to struvite formation, anaerobic digester effluent often contains a stoichiometric excess of ammonium, so ammonium is not considered a limiting reactant (Nelson et al., 2003). Magnesium ions are often limiting in anaerobic digester effluent, so it must be added to achieve at least a 1:1 magnesium-to-phosphate (Mg:P) ratio to precipitate struvite. Calcium ions are often present in anaerobic digesters, and they compete with magnesium to form calcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Bauer et al., 2007; Suzuki et al., 2001; Wang et al, 2006). Additionally, organic acids complex with metal ions, which increases solubility of struvite (Wrigley et al., 1992). Since the desired fertilizer product is struvite, any competition is unfavorable.

Another factor potentially affecting struvite precipitation is the storage time of the anaerobically digested effluent before struvite precipitation. Small-scale farms in developed nations or community-scale systems in developing countries may not have daily effluent from anaerobic digesters (Rowse, 2011). These farms typically have their digester effluent flow into anaerobic lagoons or a holding tank until it is applied onto fields (Ohlinger et al., 2000; Perera et al., 2007; Wang et al., 2006). While the effluent is stored, there may be a variety of mechanisms that contribute to changes in the digester effluent quality: volatilization, photochemical reactions, and microbiological activity. Battistoni et al. (2000) described the effects due to aging of digester effluent from WWTPs. However, the exact storage conditions and mechanisms that affect struvite precipitation are unknown. In addition, it is not certain these effects are consistent for swine wastewaters. Any positive effects such as increased struvite production may encourage construction of additional storage units to enhance effluent quality for struvite precipitation. This would result in additional revenue. Negative effects such as decreased struvite purity may encourage the sizing of ADs to obtain daily flow rates for precipitation of fresh effluent. This gap in literature must be addressed to guide implementing struvite precipitation processes for farming operations.

1.3 Objectives

The overall goal of this research is to understand the key parameters affecting struvite precipitation from anaerobically digested swine manure effluent. Specific objectives include the following:

- Quantify suitable swine manure loading rates for consistent anaerobic digester operation without inhibition or failure, so anaerobically digested swine manure effluent is available for struvite precipitation.
- Quantify the effects of Mg:P on the mass of precipitate recovered and the residual ion concentrations in the liquid after struvite precipitation.
- Compare the results of struvite precipitation from synthetic wastewater (no organic matter) to results from actual anaerobically digested swine manure (high dissolved organic matter).
- Quantify how various storage conditions of anaerobically digested swine manure effluent affect the concentration of dissolved ions in digester effluent and the mass of precipitate formed.

CHAPTER 2: LITERATURE REVIEW

2.1 Anaerobic Digestion

Anaerobic digestion is a natural process of complex microbial interactions that primarily converts organic carbon to methane and carbon dioxide. Anaerobic digesters are bioreactor systems that create favorable environments for anaerobic digestion. The type of bioreactor system used depends on the purpose at an industrial, communal, or household level.

2.1.1 Reactor Systems: CMBR, SBR, and CMFR

Reactors are engineered vessels in which chemical or biochemical reactions take place to form specific products. Several reactor systems such as completely mixed batch reactors (CMBRs), sequencing batch reactors (SBRs), and completely mixed flow reactors (CMFRs) are used for anaerobic digestion. The following pros and cons of the various reactors were taken from Crittenden et al. (2005) unless otherwise stated. The benefits of CMBRs are their simple nature, allowing reactions to take place homogeneously until completion. The limitation of CMBRs is the inability to adjust parameters inside the reactor except for temperature and pH. Reaction rates and equilibrium constants for chemical reactions and biological processes can also be found determined using this reactor system (Crittenden et al., 2005; Rittman and McCarty, 2001). Anaerobic digestion studies in the laboratory are typically done in this manner. SBRs allow a series of chemical reactions to take place in the same reactor at different times, which makes them versatile. SBRs can cycle between different conditions, such as aerobic and anoxic phases. If SBRs are held under anaerobic conditions, they are called anaerobic sequencing batch reactors (ASBRs). Angenent et al. (2002) were able to acclimate different methanogenic species to high ammonia levels in a full-scale, farm-based ASBR. In contrast to the previous two reactor systems, CMFRs allow reactants and products to flow in and out of the reactor, and any entering reactant is diluted in the reactor volume. Hydraulic retention time (HRT) is the length of time liquids stay in a reactor, equal to the reactor volume divided by volumetric flow rate. Concentrations inside the reactor are equal to effluent concentrations. Solids or reactive portions of the effluent, typically microbial biomass, can be recycled to create a separate flow of particulates. The length of time that particles stay in a reactor is called the solids retention time (SRT), or the mean cell residence time (MCRT). HRT, SRT, and MCRT are all equal when there is no recycle. CMFRs do not guarantee complete reaction of reactants, but they are useful for handling large quantities of reactants, as in the case for wastewater treatment or large swine CAFOs. It should be clarified that anaerobic digestion is one of many processes that can utilize a variety of reactor systems. Other chemical processes, such as struvite precipitation, can also use these same reactor systems.

2.1.2 Three Main Purposes of Anaerobic Digestion

The three main purposes of anaerobic digestion are decreasing volatile solids (VS) concentrations, generating methane for energy, and removing pathogens. First, anaerobic digestion can decrease the concentration of VS in wastes through a microbial community using organic materials as both their carbon and energy sources (Rittman & McCarty, 2001). Shin et al. (2011) demonstrated how a community of *Lactobacillus*, *Clostridium*, and methanogens coexists and changes as some substrates are degraded and other substrates are generated throughout a batch anaerobic process. Second, anaerobic digestion generates biogas consisting of carbon dioxide, methane, hydrogen sulfide, and nitrogen gas. The methane can be used as a fuel source to provide energy. Rittman and McCarty (2001) state that methane has an approximate energy content of 36 MJ/m^3, which is similar to the energy value of natural gas, 37 MJ/m^3. This is likely due to the high methane content in natural gas. Third, anaerobic digestion can deactivate pathogens (Kim et al., 2002). The effectiveness of treatment depends on the operating conditions such as temperature, pH, hydraulic retention time (HRT), and solids retention time (SRT). Chen et al. (2011) found that removal of *Salmonella sp.* and *E. coli* increased with increasing solids retention time SRT. Certain pathogens, such as *Ascaris*, can also be affected by ammonium concentrations (Pecson and Nelson, 2005).

2.1.3 Anaerobic Digestion By-Products

The by-products of anaerobic digestion consist of gases, dissolved nutrients, and solid particulates. Aside from methane, the other primary constituent of biogas, carbon dioxide, is relatively harmless in its respective concentration. However, the concentrations of dissolved nutrients generated from the anaerobic digestion process can be environmentally detrimental and can vary greatly depending on the operating conditions and substrate. Digested swine waste typically has high concentrations of ammonium and phosphate (Turner and Leytem, 2004), whereas ions such as sulfides, magnesium, sodium, potassium, calcium, and bicarbonate can be present in high concentrations depending on the specific swine operation (Turner and Leytem, 2004; Chen et al., 2007). Untreated total ammonium, total phosphate, and total sulfide at concentrations between 0.10-2.5 mg/L, 25-310 μg/L, and 2 μg/L, respectively, can present surface water quality problems, depending on the pH, temperature, and sensitive species (Environmental Protection Agency, 1986). Referring to Table 2-4 and Parkin & Owen (1986), anaerobic digester effluent can have concentrations two or three orders of magnitude greater than EPA surface water quality recommendation. The solids generated from the anaerobic digestion process consist of microbial biomass, undigested wastes, and recalcitrant material (Rittman & McCarty, 2001), such as cellulose from the pig's diet. These solids are better suited as soil amendments because of lowered pathogens (Harikishan & Sung, 2003) while still containing essential N and P for plant growth (Kinney et al., 2006).

2.2 Struvite Precipitation

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a mineral consisting of magnesium, ammonium, and phosphate, which commonly forms after anaerobic digestion on pipe walls and reactor vessels as scale. The chemical equation (Eq. 1) for struvite formation is given below (Stratful et al., 2001; Zeng and Li, 2006; Huang et al., 2010).

$$Mg^{2+} + NH_4^{+} + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^{+} \qquad \text{(Eq. 1)}$$

The potential to form struvite depends on pH, magnesium concentration, and the presence of interferences. Struvite formation in anaerobic digesters and pipes can be very costly or extremely beneficial if struvite can be captured and sold as plant fertilizer. Below are some parameters of struvite in Table 2-1 for general understanding.

Table 2-1: Struvite properties observed at room temperatures

Color	white, yellow, brown, or gray	
Morphology	Rods, needle-like, or orthorhombic	
Molar Mass	245.42	g/mol
pKsp	13.15	
Reaction Rate Constant	3.7	h^{-1}

Sources: Wang et al. (2005) and Nelson et al. (2003)

2.2.1 pH Effects on Struvite Components

Struvite precipitation is a physical-chemical process that can occur over a range of pH values bounded by the speciation of struvite components, such as ammonium and phosphate. The pK_a of ammonium is approximately 9.24 (Morel & Hering, 1993). Ammonia will dominate at pH values above the pK_a. The Henry's constant of ammonia is high, approximately $\log K_H = 1.76$ M/atm (Morel & Hering, 1993), suggesting significant quantities of ammonia will volatilize and decrease struvite formation. The HPO_4^{2-} form of the phosphoric acid species will dominate between the pK_{a2} of 7.20 and the pK_{a3} of 12.35 (Morel & Hering, 1993). The desired pH range for struvite precipitation would ideally be between pH values of 7.20-9.24. However, Battistoni et al. (2000) report that struvite forms within the pH ranges of 8-10; this is consistent with other researchers (Buchanan et al., 1994; Ohlinger et al., 1998). This pH range available for struvite precipitation also includes effects of the aqueous matrix and interfering ions in solution.

2.2.2 Methods to Control pH

It may be necessary to adjust the pH for struvite precipitation, depending on the aqueous matrix, by using chemical additives or air stripping. Efficient struvite precipitation of swine manure wastewater is reported at a pH range between 8.5-8.7 (Wang et al., 2004; Stratful et al., 2006; Celen et al., 2007). Huang et al. (2010) suggested ammonium removal by struvite is optimized at pH values between 8.0 and 8.5. To raise the pH of digester effluent, chemicals such as sodium hydroxide (Jordaan et al., 2010), magnesium hydroxide (Miles and Ellis, 2001), and magnesium oxide (Moody et al., 2009) have been used. Magnesium hydroxide or magnesium oxide simultaneously provides the magnesium for struvite precipitation and raises the pH of the system; however, these compounds are poorly soluble (Zeng and Li, 2006). In poorly buffered waters, using these compounds also can create a choice between optimizing the pH or providing the magnesium concentration for struvite precipitation. Sodium hydroxide can be expensive for large-scale systems and can create undesirable salinity in the system (Jaffer et al., 2002). For these reasons, air stripping of dissolved CO_2 has been used as the preferred method for raising the pH in anaerobically digested swine wastes (Song et al., 2011).

2.2.3 Chemistry of CO_2 Stripping as pH Adjustment

Anaerobically digested swine manure wastewaters tend to be both saturated with dissolved CO_2 and highly buffered with bicarbonate ions in the aqueous matrix. This is due to microbial processes mentioned in section 2.1.3. of this chapter. The aqueous chemical reactions of CO_2 dissolution are shown in Eq. 2 and Eq. 3, where H_{CO_2} is the Henry's constant for CO_2 (Morel & Hering, 1993).

$$CO_{2\,(g)} + H_2O \leftrightarrow H_2CO_{3\,(aq)} \qquad \text{(Eq. 2)}$$

$$H_{CO_2} = \frac{\{CO_2\}_{(g)}}{\{H_2CO_3\}_{(aq)}} \qquad \text{(Eq. 3)}$$

To maintain equilibrium inside the digester, $H_2CO_{3\,(aq)}$ is deprotonated and acidifies the wastewaters (Eq. 4) (Morel & Hering, 1993).

$$H_2CO_{3\,(aq)} \leftrightarrow HCO_{3\,(aq)}^{-} + H_{(aq)}^{+} \qquad \text{(Eq. 4)}$$

CO_2 can be stripped out of the water by aeration (Wang et al., 2005; Battistoni et al., 1999). The equilibrium shifts, causing both the reverse reaction of Eq. 2 and the reverse reaction of Eq. 4. This means aeration will simultaneously lower the alkalinity in the wastewater and raise the pH. Expensive chemicals for pH adjustment can be avoided, and the required magnesium can be added without considerations of pH.

2.2.4 Inhibitory Chemical Interferences

The term *interference* refers to two different mechanisms that inhibit struvite precipitation. The solubility plots of struvite and amorphous calcium phosphate (ACP) are shown in Figure 2-1. The first mechanism is a situation in which particles or dissolved ions prevent struvite formation simply because of their presence. Schuiling and Andrade (1999) found that suspended solids concentrations greater than 1,000 mg/L interfere with phosphate removal; however, it is not clear whether they actively take part in any chemical reactions. Carbonate (CO_3^{2-}) also interferes with struvite precipitation by changing the reaction rates (Le Corre et al., 2005) and morphology of struvite crystals (Song et al., 2007). This type of interference tends to alter the quantity, quality, and conditions under which struvite precipitation will take place.

The second mechanism is competition for component ions. Several reactions related to struvite precipitation are shown in Table 2-2. Calcium is well known to form amorphous calcium phosphates (Le Corre et al., 2005; Song et al., 2007) or crystal calcium phosphates such as hydroxyapatite (HAP) (Battistoni et al., 1997), which decreases the phosphate available for struvite formation. The solubility of struvite is shown in Figure 4-2 as the magnesium-to-calcium ratio is varied.

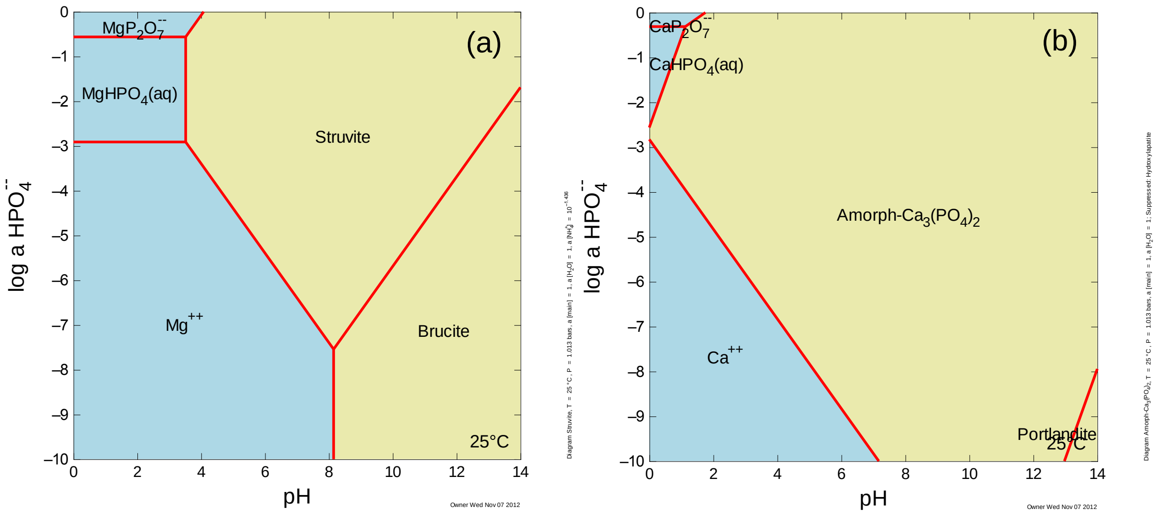


Figure 2-1: Formation of struvite (a) and amorphous calcium phosphate (b) at varying pH values

Another competing ion is potassium (K^+), which forms magnesium potassium phosphate, known as K-struvite or KMP (Marti et al. , 2008). Marti et al. (2008) suggested that K-struvite could form under low ammonium conditions but later found that even low ammonium conditions do not precipitate KMP. Wilsenach et al. (2007) precipitated KMP at similar efficiencies as MAP only when ammonium was completely removed. Inhibition exists only when the competitor ion is present at high concentration relative to the target ion or when the solubility product constant is less than or equal to the target mineral's solubility product constant (Dhakal, 2008; Morel & Hering, 1993). This inhibition affects the quantity and quality of minerals formed but does not affect the conditions under which struvite forms.

Table 2-2: Minerals related to phosphorus precipitation

Mineral	Chemical Formula	pK$_{sp}$	Chemical Reaction
Struvite	$MgNH_4PO_4 \bullet 6H_2O$	13.15	$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+$
K-struvite	$MgKPO_4 \bullet 6H_2O$	10.62	$Mg^{2+} + K^+ + HPO_4^{2-} + 6H_2O \rightarrow MgKPO_4 \cdot 6H_2O \downarrow + H^+$
ACP	$Ca_3(PO_4)_2$	28.25	$3\ Ca^{2+} + 2\ PO_4 \rightarrow Ca_3(PO_4)_2$
Dolomite	$CaMg(CO_3)_2$	16.54	$Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-} \rightarrow CaMg(CO_3)2$
Calcite	$CaCO_3$	8.48	$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
Magnesite	$MgCO_3$	7.46	$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3$

Sources: Visual MINTEQ v.3.0, Wilsenach et al. (2007), Stratful et al. (2001)

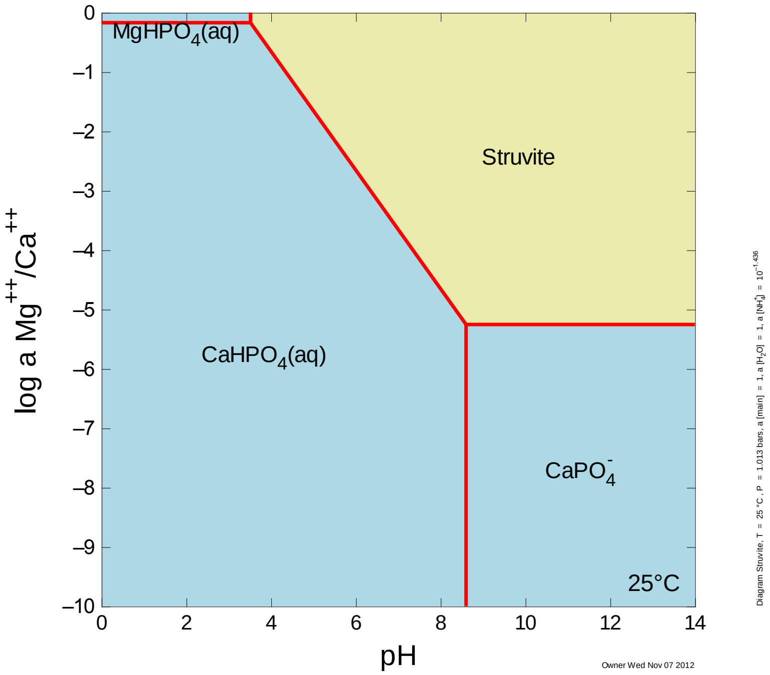


Figure 2-2: Solubility of struvite as Mg:Ca ratio varies with pH

2.2.5 Growing Struvite Crystals: Nucleation

Struvite is a mineral; therefore, crystal growth kinetics apply to struvite precipitation. Struvite nucleation occurs either homogeneously or heterogeneously. Homogeneous nucleation means another phase forms evenly throughout the solution and usually requires heating or cooling. Heterogeneous nucleation occurs in the presence of nucleation sites, which can provide a location for the formation of crystals such as struvite (Stratful et al., 2001). Adding material to provide nucleation sites is referred to as *seeding* the reaction. Battistoni et al. (2002) observed that seeding struvite reactors sped up the rate of struvite formation. Several materials can aid nucleation to hasten crystal growth: metallic surfaces (Suzuki et al., 2006), sand (Doyle & Simon, 2002), and struvite (Le Corre et al., 2007). This is important if larger crystals are desired; however, larger crystals require more time to build the crystal lattice (Doyle et al., 2002; Le Corre et al., 2007; Stratful et al., 2001). Varying reaction times have been given; however, an hour or more will ensure low rates of crystal growth nearing equilibrium (Doyle and Parsons, 2002; Le Corre et al., 2007; Stratful et al., 2001; Zeng and Li, 2006). Therefore, seeding reactors may be useful in an industrial process where large crystal sizes and short reaction times may be desired. Farming operations may infrequently discharge effluent from anaerobic digesters, which allows several hours of crystal growth and makes seeding unnecessary.

2.2.6 Struvite Fertilizer for Plant Utilization

Struvite is a slow-release fertilizer that can be substituted for conventional fertilizer; however, there is surprisingly little research supporting its effectiveness (Liu et al., 2011).

Conventional fertilizers often leach through the soil, run off, or volatilize; however, a slow-release fertilizer allows plants to take up available nutrients as they are released (Johnston and Richards, 2003). This prevents losses due to the mechanisms listed above and can offset operational costs at a farm because of decreased fertilization. Ganrot et al. (2007) showed that struvite performed poorly when supplied to wheat crops; however, they attributed the poor performances to the high pH of the growth media. Ryegrass fertilized by struvite has been reported to yield similar plant dry weights to other phosphate fertilizers (Johnston and Richards, 2003). Another study on maize showed that struvite performance was comparable to combined N and P fertilizer treatments (Liu et al., 2011).

2.2.7 Economic Feasibility

There are many studies advocating struvite production; however, the costs and benefits of struvite production are unclear. The market price of struvite fluctuates; however, Moody et al. (2009) reported a market value of $206 per metric ton based on the N and P values associated with struvite. In comparing only the chemical costs of magnesium dosing and pH adjustment, both Moody et al. (1999) and Jaffer et al. (2002) suggested that struvite production is economically feasible. This promising outlook did not account for capital costs or operational costs. Forrest et al. (2008) suggested that struvite production at a wastewater treatment plant costs $140-$460 per ton, while the market value of struvite is $198-$1,885 per ton. Huang et al. (2010) also suggested that costs could be reduced by recycling struvite for three process cycles. This could save on chemical costs by 81% compared to using pure chemicals (Huang et al., 2010); although, it is not clear if the mass of struvite produced is affected. These estimates suggest that it is possible to produce struvite and make a profit, but the scale of production is not incorporated in these estimates. Businesses such as OSTARA (Vancouver, BC) have been able to profit from the recovery of struvite in WWTPs; however, farming operations may not have flows comparable to wastewater treatment plants or equipment to produce struvite industrially. These studies also do not include an analysis of how the costs of N and P removal are offset by struvite precipitation. To do this, life cycle assessments of different struvite production systems are necessary.

2.3 Struvite Precipitation of Anaerobically Digested Effluent

Struvite precipitation of effluent from anaerobic digesters can be applied to many waste streams, but swine manure is used specifically because of its high P content. Plants typically store phosphorus as phytate; however, pigs can not metabolize phytate because they lack the enzyme phytase (Lammers et al., 2007). A number of models, laboratory experiments, and field studies provide insight into precipitation of struvite from anaerobically digested swine manure effluent. The characteristics of the anaerobically digested swine manure effluent and the system used to precipitate struvite must be considered carefully for production of high purity struvite.

2.3.1 Predicting Struvite Precipitation

Modeling can be an inexpensive and useful way to predict the conditions required and amount of struvite precipitated. Ye et al. (2011) used PHREEQC as an extension of experimental work done with bittern dosages on anaerobically digested swine effluent to identify percentages of ACP and MAP precipitated. Little detail was given regarding their modeling approach; however, modeling after experimental work was already done provided insight into optimal conditions for MAP precipitation (Table 2-2). Miles and Ellis (2001) compared MINTEQA2 results with their experimental treatment of ammonium in anaerobically digested swine wastes from an SBR. MINTEQA2 predicted approximately 88% ammonium removal as struvite compared to 88-98% ammonium removal from experimental results. Wang et al. (2005) used MINEQL with the following conditions: pH ranging between 6-12, pKsp of 12.6, ionic strength (M) of 0.1, and temperature at 25°C. Despite slight deviations, MINEQL accurately predicted experimental findings of synthetic wastewater experiments. $Ca_4H(PO_4)_3 \cdot 3H_2O$ and $CaHPO_4 \cdot 2H_2O$ were predicted to preferentially precipitate when Ca:P ratio is high, inhibiting struvite formation.

Miles and Ellis (2001) and Wang et al. (2005) were able to accurately predict their respective ammonium and phosphate removals. However, several considerations were overlooked in their experiments: calcium is a common interfering ion that Miles and Ellis (2001) do not mention; the presence of particulate matter or dissolved organics can interfere with struvite precipitation (Burns et al., 2010); Wang et al. (2005) simulated anaerobic lagoon wastewater, not effluent directly from an anaerobic digester; it is uncertain whether ionic strength was accurately captured in their model and can affect minimum solubility of struvite (Ohlinger et al., 1998); neither Miles and Ellis (2001) nor Wang et al. (2005) considered carbonate, which can affect precipitation rates (Le Corre et al., 2005).

Table 2-3: Major findings of various chemical equilibrium models

Model		Major Findings
Ye et al., 2011	PHREEQC	• Controlling bittern dosage above 1% minimizes ACP formation • Controlling pH below 9.5 minimizes ACP formation
Miles and Ellis, 2001	MINTEQA2	• Approximate optimum was pH 9.0 • Excess Mg^{2+} and PO_4^{3-} provided best NH_4^+ removal
Wang et al., 2005	MINEQL+ v.4.5	• When Ca^{2+} is present, optimal pH is 8.7 for struvite precipitation • Higher pH leads to precipitation of calcium phosphates • High Ca:P ratio leads to precipitation of calcium phosphates • Addition of Ca^{2+} or Mg^{2+} will remove P
Nelson et al., 2003	MINTEQA2 v.3.11	• Predicted P removal was consistently less than experimentally determined • Correcting charge balance with citrate provided more accurate results below pH 9
Celen et al., 2007	Visual MINTEQ 2.23	• Mg^{2+} is the limiting constituent in their wastewater • Excess Mg^{2+} gives small increase in P removal and does not justify cost • Model did not predict brushite • Predicted 3-14% more required NaOH than experimentally found

Nelson et al. (2003) and Çelen et al (2007) used different versions of MINTEQ and included other considerations, such as reaction kinetics. Their major findings are also included in Table 2-2. Nelson et al. (2003) used MINTEQA2 with HAP excluded because of slow kinetics of formation. Citrate was chosen as an organic anion to balance the charge imbalance from missing deprotonated carboxylic and phenolic groups. Citrate concentrations equal to 0.75 and 0.5 times the anion charge deficits gave the best predictions. Çelen et al. (2007) give great detail regarding the excluded minerals in their model. The following minerals were excluded due to slow reaction kinetics: bobierrite, hydroxyapatite, whitlockite, and dolomite. Çelen et al. (2007) excluded other minerals because of other ions in solution or pH considerations. Magnesium ion can inhibit the growth of octacalcium phosphate, so it was also excluded. Calcium carbonate was removed from the database because magnesium, phosphates, and dissolved organics decrease its precipitation. There were some inaccuracies in the model predictions compared to experimental results, particularly for ammonium due to volatilization.

Nelson et al. (2003) and Çelen et al. (2007) also failed to consider several items. Similar to other authors, they neglected the influences of carbonate and ionic strength in their models. Although both groups, especially Çelen et al. (2007), tried to include relevant minerals in their studies, they did not mention sulfate precipitates or ACP. This contradicts the findings of Battistoni et al. (1999), Song et al (2007), Suzuki et al (2006), Ye et al (2011), Wang et al (2005), and Wrigley et al. (1992), who found amorphous calcium phosphate or magnesium sulfate minerals in their deposits.

2.3.2 Effective pH from Synthetic Wastewater Experiments

As detailed in section 2.2.1, the pH of a system is critical for optimizing struvite precipitation. Several authors are listed in Table 2-3 with their tested synthetic wastewaters and their suggestions. Other authors, listed in Table 2-4, chose their respective experimental pH conditions based on the work done on synthetic wastewaters experiments. The experiments maintained a constant pH ranging between 8.0-9.5 on anaerobically digested effluent.

Ohlinger et al. (1998) reported a pH of 10.3 as the minimum solubility of struvite. Although struvite may be least soluble at that pH, that pH did not recover the most struvite (Song et al., 2007). P removal at high pH tends to form calcium phosphates instead of pure struvite. Wang et al. (2005) stated that a pH near 8.7 would achieve high struvite purity. Song et al. (2007) reported that high purity could be achieved at a pH less than 9.5. The specific pH values for optimal struvite recovery can vary depending on the Mg:P ratio used for precipitation. The optimal pH value will depend on supersaturation with respect to struvite components and cost of raising pH.

Table 2-4: Tested pH and molar ratios of synthetic wastewaters

Author	pH Adj.	Tested pH	Tested Ratios	Suggested pH	Suggested Ratio	Notes
Korchef et al., 2010	CO_2 Strip	7.8-8.6	1.0-5.0 Mg:P	---	No optimum; chemical additions depend on initial concentrations	N:P constant
Korchef et al., 2010	CO_2 Strip	---	0.2-5.0 Mg:P	---		N:P constant
Korchef et al., 2010	CO_2 Strip	8.2-8.6	0.25-3 N:P	---		Mg:P constant
Ohlinger et al., 1998	NaOH	6.3-7.1	0.43: 1.01:1.0 Mg:N:P	10.3	---	---
Ohlinger et al., 1998	NaOH	8.0-8.3	1.0:1.11:1.0 Mg:N:P	10.3	---	---
Song et al., 2007	NaOH	8.0-12.0	1.0-2.0 Mg:P	<9.5	1.4 Mg:P	N:P constant
Song et al., 2007	NaOH	8.0-12.0	0.5-2.0 Ca:Mg	<9.5	---	Mg:N:P constant
Wang et al., 2005	NaOH	7.8-10.5	0.5-2.0 Mg:P	---	---	N:P constant
Wang et al., 2005	NaOH	7.8-10.5	0.5-2.0 Ca:P	8.70	<0.5:2 Ca:Mg	N:P constant

2.3.3 Examining Struvite Precipitation from AD Effluent

In Table 2-4, a number of studies are summarized with the approximate molar ratios used for their experiments. Both synthetic wastewater experiments and experiments using anaerobically digested effluent are presented. Both types of studies have achieved high maximum P removal efficiencies. Many different wastewater compositions have been used, and the values vary considerably among experiments. Actual concentrations of P were lower in lagoon wastewaters (L) than in anaerobically digested effluent (AD). Burns et al. (2010) noted the presence of crystalline precipitates in lagoon sludge, which correspond to low P concentrations in their experimental wastewater. Although the molar ratios vary considerably, Table 2-4 shows that all research with high purity struvite had wastewaters with less than 0.5:1.0 Ca:Mg, except for research conducted by Nelson et al. (2003) and one experiment carried out by Korchef et al. (2010). All other research obtained precipitates with mixtures of MAP, ACP, and magnesium sulfate compounds.

For field experiments in anaerobic lagoons, high P removal was achieved (Nelson et al., 2003; Burns et al., 2010). When experiments were conducted on pilot scale systems by Suzuki et al. (2001) and Song et al. (2011), P removal efficiency decreased. This was likely due to a change in reactor systems from CMBR to CMFR or SBR. No prior studies have considered whether reactor systems will affect the Mg:P dosage that should be used for struvite precipitation. Suzuki et al. (2001) and Song et al. (2011) circumvent these considerations by seeding their reactors with a metallic crystal collector. In this case, struvite crystals adhere to the collector while other precipitates, such as ACP, settle to the reactor bottom. Song et al. (2011) used CO_2 stripping for pH adjustment and reported that no additional chemical addition was necessary to precipitate struvite. These findings suggest that high struvite removal would require both the use of a crystal collector and an appropriate Mg:P dosage. Korchef et al. (2010) stated there was no optimal Mg:P ratio, and high struvite recovery would depend on the initial concentrations of each wastewater.

2.3.4 Other Factors: Organic Matter and Storage

The primary variables studied above were a combination of Mg:Ca:N:P ratios, pH, and the presence of interferences on P removal efficiency and purity; however, several items such as the effect of organic matter and stored anaerobically digested swine manure effluent were not discussed. Only Schulze-Rettmer (1990) mentions the role of organic matter in influencing struvite precipitation. Specifically, he gave citric acid as one of many other complex builders possibly present in wastewater to increase the solubility of struvite. This was also supported a crystal growth and morphology study by Meldrum and Hyde (2001), reporting that citrate or malate complex calcium and magnesium ions. Only Battistoni et al. (1999) mentioned how storage of wastewater affects struvite precipitation. They noticed decreasing phosphate concentrations up to 96% in 2-8 days. There was also an increase in pH over time paired with a loss of bicarbonate alkalinity. Additionally, their phosphate limited wastewater formed mixtures of struvite and hydroxyapatite or hydroxyapatite and an unidentified calcium salt. It is important to note that Schultze-Rettmer (1990) and Battistoni et al. (1999) focused on anaerobically digested municipal effluent; however, the following study targets the knowledge gap of how organic matter and storage affects swine wastewater.

Table 2-5: Struvite precipitation findings of synthetic or real anaerobically digested swine manure effluent

Author	Source	Exp. Type	Max P Removal	Chemical Ratios based on P				Minerals Formed
				Mg^{2+}	Ca^{2+}	NH_4^+	Ca:Mg	
Beal et al, 1999	AD	Batch	98%	0.77	---	7.81	---	Unidentified
Burns et al., 2010	R, L	Batch	91%	---	---	---	---	Quartz, Struvite
Celen et al., 2007	R, L	Batch	98%	0.58	0.44	13.95	0.75	Struvite, Monetite, Brushite
Huang et al., 2010	AD	Batch	96%	0.16	1.99	32.21	12.22	MgO, $MgNaPO_4$
Jordaan et al., 2010	AD	Batch	80%	2.70	6.47	195.77	2.40	Struvite, Calcite
Karakashev et al, 2008	AD	Batch	96%	---	---	59.03	---	Unidentified
Korchef et al., 2010	S	Batch	92%	2.96	0.36	---	0.12	Struvite, Cattiite
Korchef et al., 2010	S	Batch	---	0.44	0.06	1.00	0.13	Struvite
Korchef et al., 2010	S	Batch	75%	1.00	0.09	1.25	0.09	Struvite
Miles and Ellis, 2001	AD	Batch	---	0.86	---	7.15	---	Struvite
Nelson et al., 2003	AD, L	Batch	91%	3.35	6.22	29.38	1.86	Struvite
Ohlinger et al., 1998	S	Batch	---	0.43	---	1.01	---	Struvite
Ohlinger et al., 1998	S	Batch	---	1.00	---	1.11	---	Struvite
Perera et al., 2007	AD, L	Batch	98%	8.47	3.44	29.33	0.41	Struvite
Song et al., 2007	S	Batch	97%	1.40	1.63	11.20	1.17	struvite, calcium phosphates
Song et al., 2007	S	Batch	90%	1.40	---	11.20	---	Struvite (dif. Shapes)
Song et al., 2011	AD	SBR/CMFR	95%/94%	5.82	7.27	92.23	1.25	Mg and Ca phosphates
Suzuki et al, 2001	L	CMFR	73%	2.50	2.63	38.90	1.05	Unidentified (struvite, ACP?)
Wang et al., 2005	S	Batch	74%	0.52	0.31	1.39	0.59	struvite, calcium phosphates
Wang et al., 2005	S	Batch	74%	0.20	0.13	1.39	0.67	struvite, calcium phosphates
Wrigley., 1993	AD	Batch	90%	3.91	19.85	210.60	5.08	struvite, apthitatie, thermardite
Ye et al., 2011	AD	Batch	100%	1.85	0.92	8.54	0.50	struvite, calcium phosphates

CHAPTER 3: MATERIALS AND METHODS

Four experiments were conducted to address each of the four objectives listed in Chapter One. Table 3-1 summarizes the main purposes of each experiment.

Table 3-1: Main purposes of experiments

Experiments	Main Purpose
1. Establishing Anaerobic Digester Operation	Produce consistent effluent for struvite precipitation experiments
2. Testing Mg:P Ratios	Find most effective Mg:P ratio
3. Comparing Effluents	Compare effects of organic matter on struvite precipitation
4. Storage of Anaerobic Digester Effluent	Quantify effects of storage conditions

3.1 Establishing Operational Procedures for Anaerobic Digesters

The first objective was to produce consistent effluent for struvite precipitation experiments by establishing working anaerobic digesters. Bench-scale anaerobic digesters were set up in three 2 L bottles. The working volume of each reactor was 1.5 L. Two holes were drilled into rubber stoppers so that hoses could be connected to the bottles. One hose was attached to a 500 mL SKC Tedlar gas bag (Eighty Four, PA). Volume of biogas collected in the bag was measured by water displacement. The other hose was used for purging the digester headspace with nitrogen gas. The attachments and hosing were affixed with zip-ties and sealed with silicone (Appendix A). The assembly was confirmed to be gas tight by water submersion.

Inoculum was generously donated from a consortium of mesophilic animal manure digesters by Dr. Anne Wilkie from the Department of Soil and Water Science at University of Florida. Swine manure was obtained at Mr. Richard Lyons' farm in Mayo, Florida. This farm had at least 50 sows and 100 piglets at any time. Collected manure was iced during transport and subsequently frozen at -20°C in the lab. The three 1.5 L reactors were each filled with approximately 0.5 L of inoculum and 1 L of 5% volatile solids (VS) feed mixture to achieve a total working volume of 1.5 L in each reactor. Thawed manure and local groundwater were used to create this feed mixture. This feed mixture was used for six weeks to ensure successful reactor start-up.

The three reactors were maintained in the following manner for all anaerobic digestion operations. An SK-727 Amerex Instruments, Inc., shaker incubator (Lafayette, CA) was used to keep temperature at 35°C with gentle shaking at approximately 60 rpm. The pH of the reactors was maintained between 7.0-7.3 by addition of 3M NaOH as necessary. The reactors were operated semi-continuously at a solids residence time (SRT) of 28 days. Three times each week, 125 mL of reactor slurry was removed from each reactor and replaced with 125 mL of feed mixture. The reactors were sparged with nitrogen gas at each feeding event to maintain anaerobic conditions. Gas bags were emptied three times per week after volume measurement by water displacement.

Feed mixtures were changed after each SRT cycle for the three reactors to find a volatile solids (VS) loading rate similar values reported in the literature without ammonium inhibition. In order to do this, anaerobic digesters were operated for a period of 17 weeks with monitoring as described in Section 3.5. The first reactor failed at week 7 due to high VS loading of 9.0 g VS/L-day and did not recover. The first SRT cycle for both reactors 2 and 3 started at week 7. A feed of 3.4 g VS/L-day was used, and a second feed of 6.7g VS/L-day was used at week 13. Reactor 3 had feeds of 3.9 g VS/L-day and 5.1 g VS/L-day at weeks 7 and 13, respectively. Reactors two and three were operated until failure at week 17. From this process, a VS loading rate for consistent anaerobic digester operation without ammonium inhibition or reactor failure was determined at 3.4-3.9 g VS/L-day. Reactors were subsequently restarted at this VS loading rate to provide consistent AD effluent for struvite precipitation studies. Reactors were operated and monitored for three SRT cycles before conducting struvite precipitation studies.

3.2 Effects of Mg:P Ratios for Struvite Precipitation

The second objective was to determine the effects of Mg:P ratios on struvite precipitation. Two synthetic wastewaters were created (Table 3-2). Synthetic wastewater 1 was created based on median values of nutrient concentrations from anaerobically digested swine wastewater reported in the literature (Table 2-5). Using synthetic wastewater 1 allowed for comparison of varying Mg:P molar ratios reported by other authors. The amounts of Fisher Scientific reagent grade chemicals (Fair Lawn, NJ) used to create a 1 L of synthetic wastewater are listed in Table 3-3. Although calcium and magnesium ions were components in the wastewater, these ions were added during experimentation. Stock solutions of $CaCl_2$ and $MgCl_2$ were made separately from the synthetic wastewater to prevent immediate precipitation of calcium and magnesium minerals. The synthetic wastewater and stock solutions were refrigerated at 4°C until use.

Table 3-2: Approximate concentrations of synthetic AD swine manure effluent

Ions	Synthetic Wastewater 1	Synthetic Wastewater 2
	mg/L	mg/L
NH_4^+	1220	960
K^+	550	550
Na^+	400	1200
PO_4^{3-}	190	100
SO_4^{2-}	20	20
HCO_3^-	3000	6000
Ca^{2+}	140	220

The testing of Mg:P ratios was performed in triplicate with Mg:P ratios of 1.15, 1.30, 1.78, 2.20, 2.54, and 5.58. Each set of replicates used six 100 mL acid washed beakers filled with 50 mL of synthetic wastewater solution. Each beaker was aerated until it reached a pH of 8.5, then dosed with the appropriate volumes of magnesium chloride and calcium chloride solutions. Following chemical additions, beakers were shaken for 2 hours at approximately 100 rpm using a VWR S-500 Orbital shaker table (USA) and then allowed to settle for 1 hour. The magnesium and calcium added caused precipitates to form in the beakers. The contents of each beaker were filtered using 0.45 μm glass fiber filter circles. The filters and beakers were dried in a desiccator at room temperature (~23°C) and later weighed to find the mass of precipitate. Visual MINTEQ was employed for data comparison, and the solids were preserved for x-ray diffraction (XRD) analyses.

Table 3-3: Reagents used to create synthetic AD swine manure effluent

Chemical Formula	Synthetic Wastewater 1	Synthetic Wastewater 2
NH_4HCO_3	1.852 g	4.410 g
NH_4Cl	2.369 g	n/a
$KHCO_3$	0.836 g	1.118 g
$NaHCO_3$	1.462 g	4.014 g
K_2HPO_4	237 mL	108 mL
K_2SO_4	20 mL	20 mL

Stock Solutions: 1000 mg/L K_2HPO_4 as K^+ and 20 mg/L K_2SO_4 as SO_4^{2-}

3.3 Effect of Organic Matter on Struvite Precipitation

The third objective was to study the effects of organic matter by comparing the differences between real, synthetic, and modeled wastewaters. Initial analyses of laboratory anaerobic digester effluent and groundwater were conducted to create synthetic wastewater 2 with similar composition to real swine wastewater (Table 3-2). Three 100 mL acid-washed beakers were filled with 50 mL of synthetic wastewater. The remaining procedures from aeration to filtration and desiccation were the same as described in Section 3.2. The experiment was dosed with magnesium oxide in place of magnesium chloride to simultaneously raise pH and add magnesium. To understand the effects of organic matter, precipitation from the synthetic wastewater was compared with precipitation from one subsample from the storage of anaerobically digested effluent experiment (Section 3.4). Both were fresh (Day 0), open to the atmosphere, and maintained in indoor conditions.

3.4 Storage of AD Effluent for Struvite Precipitation

The fourth objective was to use AD effluents produced in the laboratory to study how different storage conditions affected struvite precipitation. Storage of anaerobically digested effluent was tested because stored effluent is typically used for crop irrigation (Greaves et al., 1999). The nutrient concentrations of stored anaerobically digested swine effluent could depend upon whether the effluent is stored in an indoor or outdoor environment, as well as whether storage is open or closed to the atmosphere. Storage could affect both the effectiveness of precipitation and available nutrients for plant uptake when using effluents as irrigation water.

To test the effects of storage conditions, three digesters were operated by members in Dr. Ergas' research group for a period of 3 SRTs (84 days) for microbial acclimation at a VS loading rate of 3.4-3.9 g VS/L-day. Effluent from the digesters was collected and stored under different conditions. Three storage variables were tested. First, storage time of the AD effluent was varied at 0, 3, and 7 days. For day 0, storage time is 1 hour. Second, for each of the storage times, the beakers were stored under two different conditions: open to the atmosphere or closed storage sealed with two layers of parafilm. Third, each storage time and beaker were in either a constant temperature room (22 °C) or a container set out in an open field during July or August with temperatures ranging from 22-33°C.

Each experiment began by centrifuging the slurry effluent from the three digesters. Then the supernatants from centrifugation were mixed together. Digester effluent was divided into four 100 mL acid washed beakers for each storage condition, with 50-65 mL of effluent in each beaker. Samples of 0.5 mL were taken each day throughout the experiment. At the end of each storage time, approximately 20 mL of liquid was removed for TS and VS analysis. After the storage period, the stored effluents were precipitated as specified in Section 3.2 from aeration to filtration. The storage of AD effluent experiment was carried out in triplicate.

3.5 Analytical Methods

All the equipment and analytical procedures for the four experiments are summarized in Table A-1. For the first experiment of operating the anaerobic digesters, 50 mL of slurry from the digesters were analyzed once per week. A portion of the slurry was analyzed for total solids (TS) and volatile solids (VS). The remainder of the effluent was centrifuged at 3500 rpm for 10 minutes. The supernatant was diluted for analyses by *Standard Methods* (APHA et al., 2005) for the following parameters: pH, alkalinity, ammonium (NH_4^+), and total phosphorus (TP). NH_4^+ and TP were analyzed using Orbeco kits (Sarasota, FL) equivalent to *Standard Methods*. Gas volumes were measured by water displacement.

For all experiments related to phosphorus recovery, all concentrations of ions were determined by ion chromatography (IC), both before and after forced precipitation. IC samples before precipitation were filtered using Fisherbrand 0.45µm syringe filters. All IC samples after the precipitation process were filtered with Fisherbrand G4 0.45µm glass fiber filter circles of 4.25 cm diameter. These samples were measured for alkalinity and pH with ThermoScientific Orion 5-star pH and conductivity meters (Pittsburgh, PA).

Alkalinity was measured with a 865 Dosimat plus (Metrohm, USA). The 881 Compact IC pro (Metrohm, USA) was used for IC analyses. The range of standards used for IC analysis includes concentrations of 1.0, 2.5, 5.0, 15, 50, and 100 ppm for all ions. Table 3-4 shown below lists the IC detection limits. IC calibration curves are shown in Appendix A. Anions were analyzed using an eluent of 3.6mM sodium carbonate with running conditions of 45 °C and a flow rate of 0.7 mL/min. Cations were analyzed using an eluent of 1.7 mM nitric acid and 0.7 mM dipocolinic acid (pyridine-2,6-dicarboxylic acid) at 32°C with a flow rate of 0.9 mL/min. Sample injection volumes were 20 µL. The IC method detection limits were determined and are shown in Table 3-4.

Table 3-4: Method detection limits (MDL) of IC analyses

	Na^+	NH_4^+	K^+	Ca^{2+}	Mn^{2+}	Cl^-	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}
MDL	19.784	0.031	0.086	0.319	0.225	0.167	0.006	0.310	0.024	0.019
S.D.	6.301	0.010	0.027	0.101	0.072	0.053	0.002	0.099	0.008	0.006

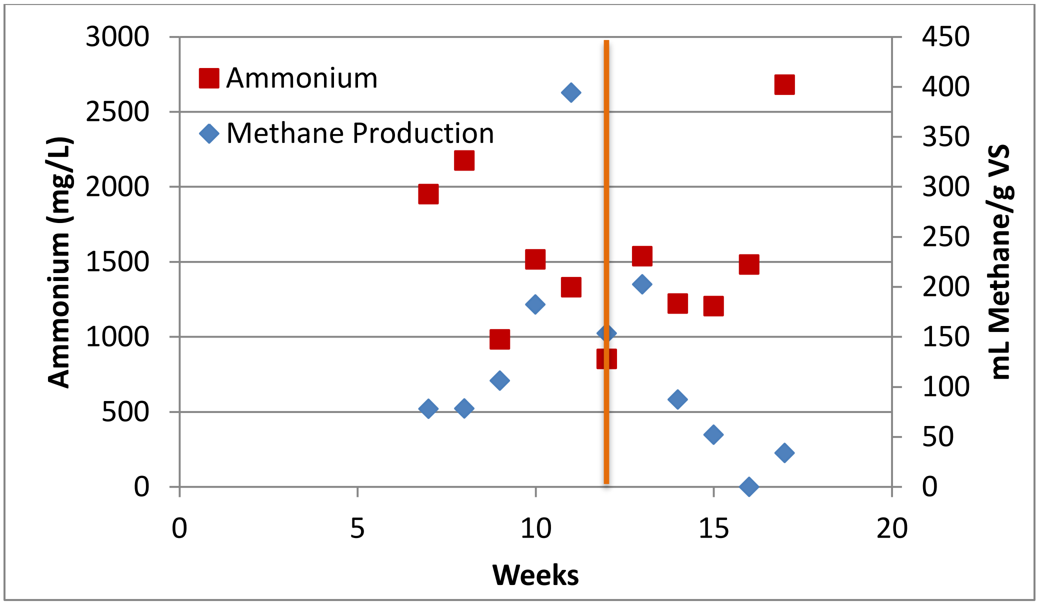
Concentrations in ppm; Obtained from Dr. Ergas' research group

X-ray diffraction using a Philips Panalytical X'Pert MRD (Westborough, MA) at the Nanotech Research and Education Center in the University of South Florida campus was used to analyze precipitates for identification of solid minerals. XRD was only used for phase analysis—determining the presence of crystalline materials. An initial scan of 2-Theta angles between 7.5° and 65° were used to determine the extent of diffraction peaks; however, angles between 10° and 62.5° were used for refined data collection. The PreFIX module used for the incident beam optics was the fixed divergence slit module, and the PreFIX module used for the diffracted beam optics is the programmable receiving slit (PRS) module. A copper mask was used for the incident beam optics. The diffracted beam optics had a nickel filter and the receiving slit was programmed for 0.25mm.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Anaerobic Digestion Studies

Experiments were conducted to find the operating conditions required to provide consistent AD effluent for struvite precipitation. The methane production and the total ammonia nitrogen (TAN) over time for reactor 2 are shown in Figure 4-1. Appendix B contains another plot for reactor 3. Ammonium can inhibit anaerobic digesters at high TAN concentrations and results in low biogas production (Rittman & McCarty, 2001). TAN concentrations in the anaerobic digesters increase due to ammonification of swine wastes in the feed. A VS loading rate between 3.4-3.9 g VS/L-day was suitable for long-term operation without ammonia inhibition or reactor failure. The digesters were operated for 3 SRT cycles before conducting subsequent struvite precipitation studies.



Weeks 7-12: 3.4 g VS/L-day; Weeks 13-17: 6.7 g VS/L-day

Figure 4-1: Methane production and ammonium concentration in reactor 2.

Table 4-1 compares the results of this study with those of other researchers for swine waste anaerobic digestion studies. Successful VS loading rates for mesophilic anaerobic digestion of swine manure fell between 1.0 and 9.1 g VS/L-day. This wide range of values can be explained by the wide range of total ammonia nitrogen (TAN) in the swine wastewater. Hansen et al. (1997) investigated varying temperatures for anaerobic digestion. The temperature most similar for comparison among authors (37°C) resulted in the highest methane production of 0.19 L/g VS. The low methane production of Hansen et al. (1997) compared to other authors was due to ammonia inhibition because of high TAN concentrations. Pagilla et al. (2000) varied the SRT in their study. The 15-day SRT was found to produce the highest methane production of 0.39 L/g VS. A comparison with results from other authors showed that this methane production rate was still low, likely due to the low VS loading rate used.

Table 4-1: Loading rate and methane production comparisons for swine waste AD studies

Author	**Reactor**	**Temp.**	**pH**	**SRT** *days*	**TS** *g/L-day*	**VS** *g/L-day*	**TAN** *g/L-day*
This study	**CMFR**	**35**	**7.0-7.5**	**28**	**4.5-8.5**	**3.4-6.7**	**0.058-0.83**
Chae et al., 2006	CMFR	25-35	7.2-7.4	20	5.7-14.1	3.4-9.1	---
Hansen et al., 1998	CMFR	37-60	7.9	15	---	4.5	5.3
Angenent. et al., 2002	ASBR	22-25	6.7-7.8	15	---	1.7-4.0	0.9-3.7
Boopathy., 2000	CMFR	35	6.9-7.3	14	1.3-10.7	1.0-8.0	0.043-0.34
Pagilla et al., 2000	CMFR	37	7.1	6-15	4.3	2.9	---

Boopathy (2000) and Chae et al. (2006) varied VS loading rates with a temperature of 35°C and SRT of 14 and 20 days, respectively. Boopathy (2000) tested two variables: VS loading rate and the number of baffles. The VS loading rate was gradually increased over time in several baffled CMFRs, so the anaerobic digesters were not overloaded. A medium load of 4 g VS/L-day resulted in a maximum methane production of 0.59 and 0.62 L/g VS in reactors with four and five chambers, respectively. Chae et al. (2006) reported 0.44 L/g VS as the maximum methane production at the lowest VS loading rate of 3.4 g/L-day. These studies suggested that a successful anaerobic digester must maintain a balance between a high VS loading rate for biogas production and a lower VS loading rate due to ammonium inhibition. The optimum VS loading rate of 3.4-3.9 g VS/L-day found in this study concurred with Chae et al. (2006) and Boopathy (2000). The methane produced in this study was not as high compared to Chae et al. (2006) and Boopathy (2000) due to high TAN concentrations in this study (2700 mg/L maximum).

4.2 Effects of Mg:P Ratio

The effects of Mg:P ratios on struvite precipitation using synthetic swine anaerobic digester wastewater based on literature (Table 3-2). The initial pH of the wastewater was between 8.0-8.1. After aeration and precipitation the pH increased to between 8.5-8.6. The XRD analyses of the precipitates revealed struvite, dolomite, brucite, and calcite and were present in the precipitates (Figure 4-2). The reference patterns of identified minerals are shown in Figure 4-3. Multiple minerals were identified within a single sample.

The types of minerals detected by XRD make it impossible to calculate the expected quantities of precipitates. Too many unknown variables exist; however, the expected total mass precipitated was calculated based on known ion removals. The expected and actual mass of precipitate recovered are shown in Table 4-2. The expected mass differs from the actual mass by 2%-57%. This was likely due to added weight from water molecules that can not be taken into account without knowing the corresponding quantities of each minerals precipitated.

Table 4-2: Summary of total mass differences

Mg:P:	1.15	1.30	1.78	2.20	2.79	5.58
Actual Mass (g):	0.0151	0.0201	0.0238	0.0265	0.0278	0.0301
Standard Deviation:	0.0043	0.0065	0.0036	0.0004	0.0003	0.0004
Expected Mass (g):	0.015	0.012	0.013	0.012	0.012	0.013
Standard Deviation:	0.004	0.003	0.006	0.002	3E-04	0.001
% Difference:	2.064	-40.36	-44.1	-56.43	-55.81	-57.2

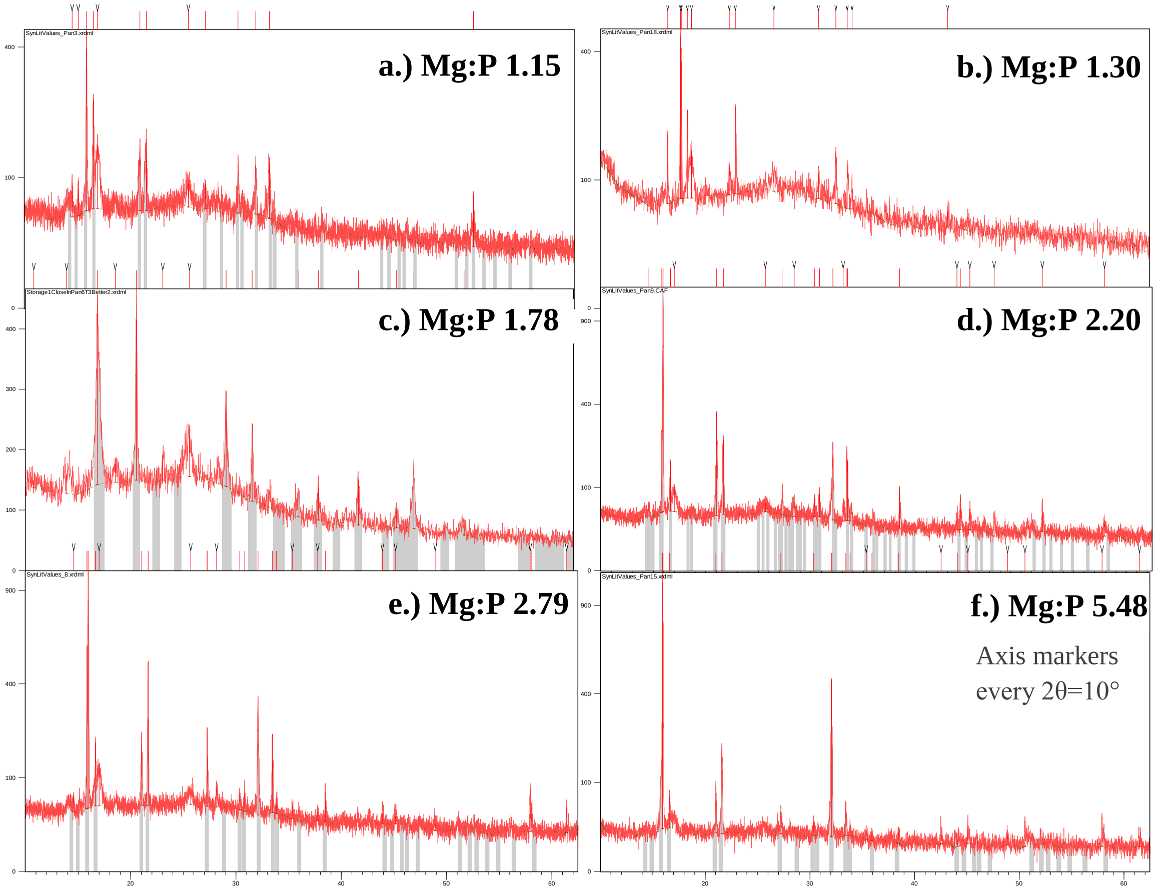


Figure 4-2: XRD scans of corresponding Mg:P ratios identified struvite in all samples with mixed purity.

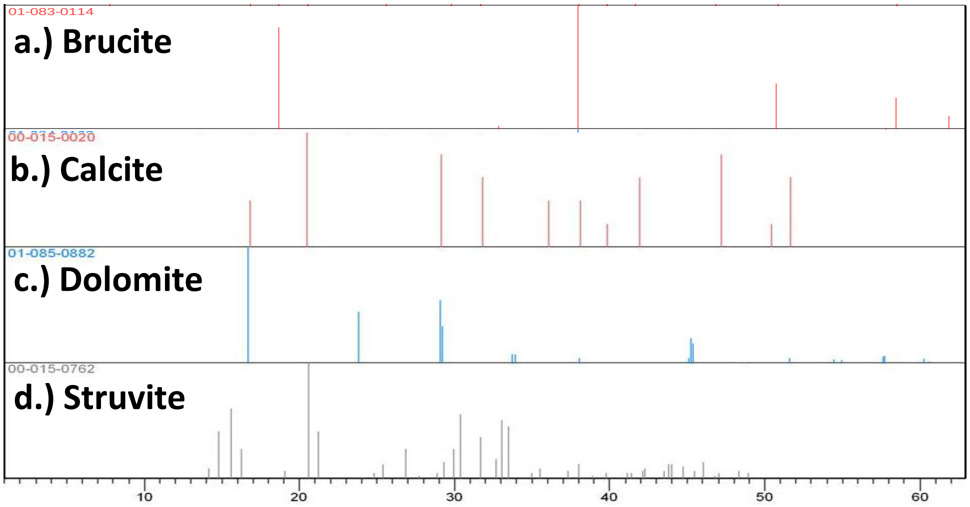


Figure 4-3: Reference patterns identified in precipitates were taken from the Panalytic Highscore software

Ion removals in the laboratory experiment are compared with Visual MINTEQ results in Figure 4-1. The model and laboratory results showed opposite trends with respect to ammonium removal (Figure 4-1a). The model predicted increasing ammonium removal (Figure 4-1b) between 0-2.5%, with increasing Mg:P ratios. However, the experiments showed increasing ammonium removal between 0-4% with lower Mg:P ratios. The model predicted greater than 99% calcium removal (Figure 4-1c); however, actual calcium removals varied between 43-58% for all Mg:P ratios, except for the Mg:P ratio of 1.78 (18% removal). Predicted magnesium removals varied between 79-93% without a noticeable pattern. A decreasing trend was observed in magnesium removal as Mg:P ratio increased; although, magnesium removal was approximately constant between 1.30-1.78. The modeled P removal showed no consistent pattern; however, the experimental P removal (71-97%) increased with increasing Mg:P ratio.

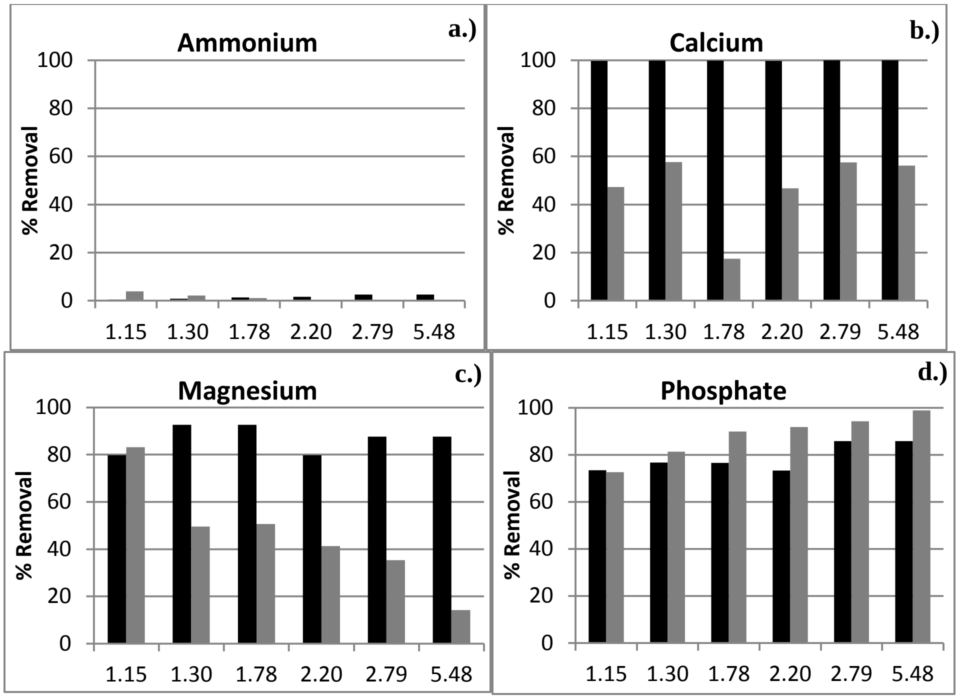


Figure 4-4: Precipitation of minerals at varying Mg:P molar ratios show a possible optimum between Mg:P ratios of 1.30-1.78

4.2.1 Ammonium Removal and Observed Volatilization

Although prior studies have suggested that relatively pure struvite precipitates, experimental results demonstrated low purity struvite was precipitated (Figure 4-4). The idea of low purity struvite was corroborated with XRD scans, shown in Figure 4-2, with weaker relative intensities corresponding to the struvite pattern. When considering ammonium, volatilization and precipitation were the two relevant removal mechanisms. For precipitation, the only known magnesium or calcium mineral with ammonium as its component was struvite (Çelen et al., 2007). The Mg:P ratios of 1.16, 1.30, and 1.78 showed only slight ammonium removals of 3.9%, 2.2%, and 1.1%, respectively, whereas the other molar ratios tested had no detectable ammonium removal. If the amount of magnesium removed was completely due to struvite formation for Mg:P ratios of 1.16

and 1.30, then the respective 2.9% and 1.9% of ammonium was removed as struvite. Correspondingly, 1.0% and 0.3% of ammonium was removed due to volatilization. For the molar ratio of 1.78, it was possible that all of the ammonium removed was due to struvite formation. This left 30% of the magnesium removal unaccounted for and was precipitating in another mineral form. Dolomite (Figure 4-3) was the likely counterpart and was also likely precipitating at the higher Mg:P doses.

4.2.2 Calcium Removal and Interference

Low struvite purity is likely due to interference from calcium competition to form calcium phosphates. The calcium removal at all ratios of Mg:P denoted some level of calcium competition with the least calcium removal at Mg:P ratio of 1.78. This minimum, unfortunately, falls in the same range of Mg:P ratios as magnesium, creating difficulty in obtaining relatively pure struvite when calcium is interfering. Despite the wide variety of data from researchers who precipitated relatively pure struvite, the specific wastewater composition can greatly influence the precipitation of struvite. Wang et al. (2005) found that when the Ca:P ratios was less than 0.5, relatively pure struvite could be produced if the pH was less than 9.2. This means that above 0.5 Ca:P ratio, calcium could inhibit the precipitation of struvite even at pH less than 9.2. In this wastewater, the Ca:P ratio was approximately 1.9, so inhibition of struvite formation was likely. Schulze-Rettmer (1991) suggested that greater Mg:P ratios can overcome this inhibition, but experimental results suggested that a Ca:Mg:P ratio of 1.9:5.5:1.0, or ratios with lower Mg:P, can not overcome the calcium competition. The competition from calcium, however, was overcome in the study by Ye et al. (2011). Maximum struvite purity of 99% was precipitated with some amorphous calcium phosphate (ACP) even when Ca:P ratio was above 0.5. This was possibly due to a large concentration difference between magnesium and calcium (Ca/Mg=0.5).

4.2.3 Magnesium and Phosphorus Removal and the Optimal Mg:P Ratio

The only removal mechanism considered in this experiment for magnesium was precipitation; other mechanisms for removal of ions from solution, such as adsorption, were assumed to be negligible. At Mg:P molar ratios of 1.30 and 1.78, magnesium removals were relatively constant; however, P removal increased (Figure 4-4). This suggested that the additional magnesium was used to remove P directly. Further addition of magnesium decreased the magnesium removal, showing a decrease in effectiveness. Figure 4-4 is plotted as percent removal by concentration, so it showed greater amounts of magnesium added compared to magnesium precipitated. P removal did not increase significantly at higher Mg:P ratios; Song et al. (2007) found similar results.

Assuming all P removed was as struvite, then the profit from struvite ($0.20-0.40/kg) production can be calculated. Assuming a cost of $0.41-$0.48/kg magnesium chloride or $0.59-$0.61/kg magnesium oxide, the magnesium addition cost can also be found (Table 4-3). P removal efficiencies from this study were incorporated into Table 4-3. Calculations showed that magnesium chloride was not economically feasible; however, magnesium oxide was most economically favorable at Mg:P ratios between 1.30-1.78. Previous research reported optimal values of 1.3 Mg:P (Münch and Barr, 2000) or 1.6

Mg:TP (Nelson et al., 2003) for P removal. Despite the percent removals decreasing with Mg:P ratios, the mass of magnesium precipitates increased with increasing Mg:P ratios.

Table 4-3: Brief economic analysis of Mg use and struvite production

			$MgCl_2$-6H_2O	MgO	Struvite
Unit Price:		*$/kg*	0.41-0.48	0.59-0.61	0.20-0.40
Use/Production for each Mg:P Ratio	1.15	*kg/kg P*	7.55	1.50	5.75
	1.30	*kg/kg P*	8.53	1.69	6.45
	1.78	*kg/kg P*	11.68	2.32	7.12
	2.20	*kg/kg P*	14.44	2.86	7.27
	2.78	*kg/kg P*	18.25	3.62	7.47
	5.56	*kg/kg P*	36.50	7.23	7.83
Potential Profit for each Mg:P Ratio	1.15	*$/kg P*	(1.96-1.36)	0.27-1.39	
	1.30	*$/kg P*	(2.23-1.56)	0.29-1.55	
	1.78	*$/kg P*	(3.39-2.82)	0.06-1.44	
	2.20	*$/kg P*	(4.50-4.09)	(0.23)-1.17	
	2.78	*$/kg P*	(6.03-5.86)	(0.64)-0.80	
	5.56	*$/kg P*	(13.48-14.56)	(2.70)-1.25	

Original 2007 cost information was adjusted to 2012 values at 8% interest with annual compounding. Parentheses indicate negative values. Sources for economic analysis: Algeo (2012); ICIS (2012)

4.2.4 Agreement with Other Studies and Carbonate Minerals

The presence of carbonate minerals in this study was unexpected because prior studies did not report carbonate minerals in their precipitates. Prior studies, however, often did not report the amount of alkalinity or bicarbonate in their wastewater. The alkalinity of the synthetic wastewater used in this study was approximately 2,500 mg/L as $CaCO_3$. Of the researchers listed in Table 2-5, Çelen et al (2007) and Song et al. (2007) reported pure struvite in their work when using effluents with 1,500 mg/L as $CaCO_3$ or less. Studies by Suzuki et al. (2001) and Song et al. (2011) reported precipitation of struvite, among other unidentified compounds, when their work used effluents with high alkalinities of 2,100 and 5,900 mg/L $CaCO_3$, respectively. The unidentified compounds could potentially be carbonate minerals.

4.2.5 Comparisons with Visual MINTEQ v.3.0

Visual MINTEQ v.3.0 results did not agree with experimental synthetic wastewater results. The ammonium removal pattern was reversed in comparison to the experimental data, and increased with increasing magnesium addition. The model also showed that there was consistently 99.7% or higher calcium removal, that was not observed in the experimental results. Magnesium removal was also generally higher (80-93%); however, there was no pattern in the model results. Interestingly, the modeled P removal (74-86%) was less than the experimental results, but the pattern of increasing removal with magnesium addition remained. Extensive work by Çelen et al. (2007) suggested that several minerals should not be considered when modeling struvite precipitation because of pH, kinetics, or inhibition by other ions. Since Visual MINTEQ is an equilibrium model, the slow forming minerals cited by Çelen et al. (2007) were excluded from the database, yielding calcium phosphates, magnesite, and calcite with percent compositions shown in Figure 4-5. As magnesium addition increased, the predicted amount of magnesite increased, while the other minerals decreased. This suggested that excessive magnesium inhibited the formation of phosphate minerals. However, experimental results suggested P removal increased with increasing Mg:P ratios. XRD scans also did not agree with Visual MINTEQ. XRD revealed struvite and dolomite. However, Visual MINTEQ did not predict them. Another contradiction with Visual MINTEQ was the presence of magnesite, which was undetected by XRD. Differences from ionic strength or unaccounted inhibitory effects among ions might be responsible for the discrepancies between modeled and experimental results.

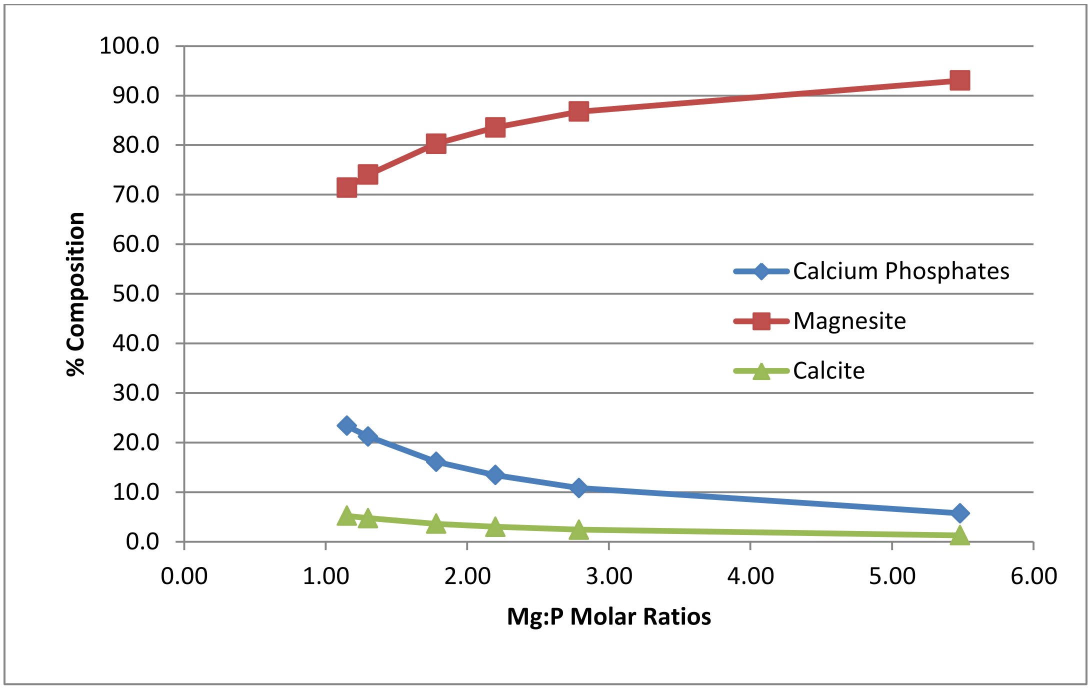


Figure 4-5: Percent compositions of mineral precipitates from Visual MINTEQ

4.3 Effects of Organic Matter

Real, synthetic, and modeled effluents were compared to understand the effects of organic matter on struvite precipitation. Synthetic effluent was created to mimic the nutrient concentrations in anaerobic digester centrate from the lab. The initial pH values of the real and synthetic effluents were 7.5 and 8.2, respectively. The final pH values, after aeration and filtration, were 8.5 and 8.9, respectively. Any decrease in pH due to precipitation was not observable due to carbonate removal from being open to the atmosphere. Korchef et al. (2011) observed similar results in his study using CO_2 stripping. XRD analyses revealed precipitation of different minerals in the real and synthetic effluents (Figure 4-6). Both the real and synthetic effluents showed patterns that could be consistent with struvite, dolomite, calcite, and brucite. Although the amounts of these minerals could not be quantified, the relative intensities in the XRD scans suggested different quantities of these minerals in the two effluents. The larger relative peak at 2θ=17° suggested more dolomite was present in the real effluent's precipitates. For the synthetic effluent, large relative peaks exist at approximately 2θ=20° and 40°, denoting higher quantities of brucite. It was not clear why more brucite would be precipitated in synthetic effluent compared to real effluent.

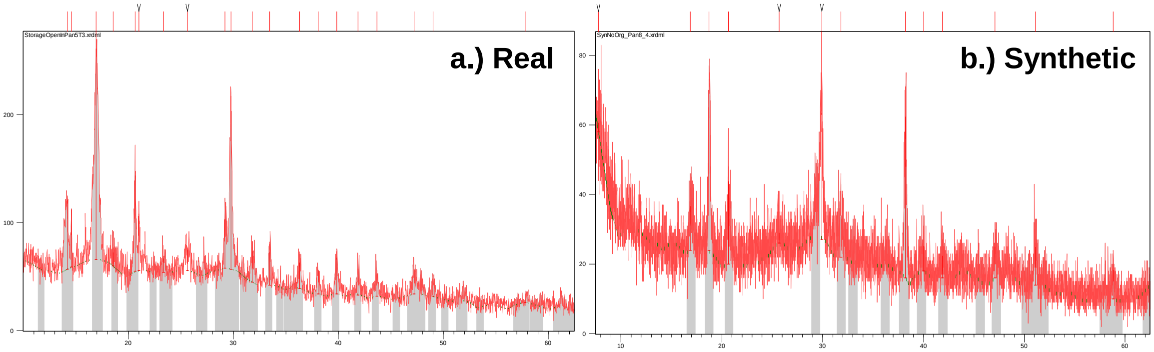


Figure 4-6: Comparison of XRD scans between real and synthetic effluents showing different quantities of each precipitated mineral

There was a significant difference between ion removals in real and synthetic effluents (Figure 4-7). Real effluent had 94% P removal, while synthetic wastewater had 85% P removal. The observed P removal can likely be attributed to both struvite formation and precipitation of other minerals, such as calcium phosphate. More ammonium was removed than would be predicted based on the Mg removal and the chemical formula for struvite. Calculations also confirmed that insufficient phosphate existed in the system for either complete P removal by calcium or magnesium. To account for the observed calcium and magnesium removal, those ions could combine with carbonate. High carbonate concentrations suggested calcium carbonate, magnesium carbonate, or calcium magnesium carbonate might be precipitating, corroborating the XRD findings.

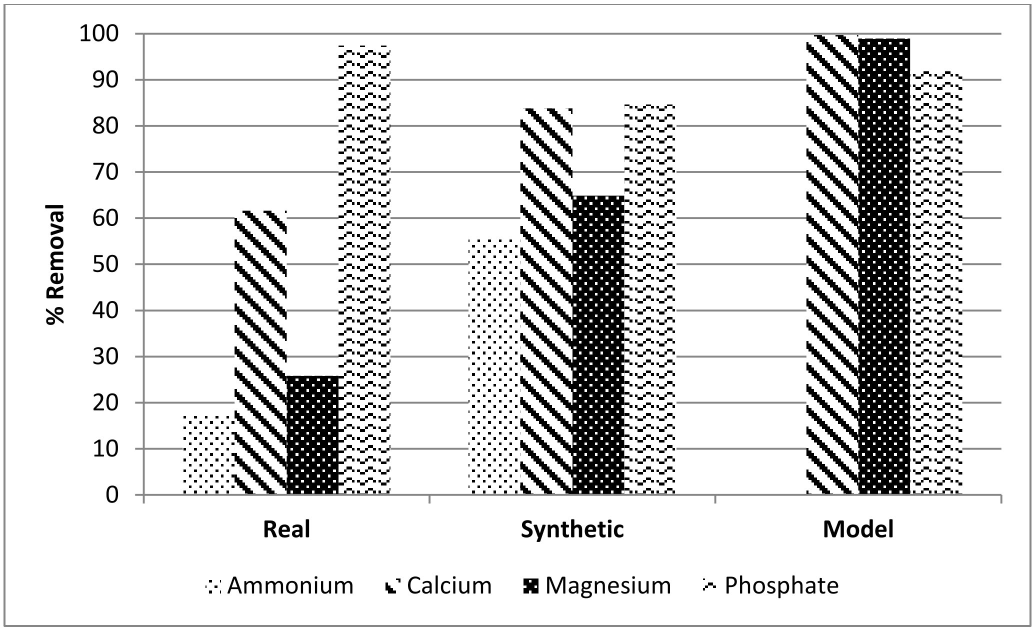


Figure 4-7: Comparing real, synthetic, and modeled anaerobically digested effluent

The ion removal differences (Figure 4-7) between real and synthetic effluents could be due to the presence of organic matter in the real effluent. The calcium removal was approximately two times greater in the synthetic wastewater than the real wastewater. Magnesium and ammonium removal in the synthetic wastewater was about five times greater than the removal in the real wastewater. Although ammonium could have been removed by volatilization, experimental conditions did not favor greater volatilization in one reactor over the other. Schulze-Rettmer (1991) stated that organic acids may increase the solubility of struvite (1991). Volatile fatty acids and other unmeasured organic acids may complex with ammonium, calcium, and magnesium ions, and prevent mineral formation. The expected masses of precipitate based on ion removals are shown in Table 4-4. The real effluent's mass deviated from expected mass because of water molecules in the minerals' lattices. The synthetic effluent's precipitates were improperly dried in an oven, removing mass from ammonium and associated water molecules in the crystal lattice.

Table 4-4: Comparison of real and synthetic effluents' total mass differences

	Real	Synthetic
Actual Mass (g):	0.075	0.039
Standard Deviation:	0.014	0.001
Expected Mass (g):	0.028	0.052
Standard Deviation:	0.009	0.001
% Difference:	-62.43	32.15

The modeled results from Visual MINTEQ v.3.0 did not agree with either the real or synthetic wastewater results. High phosphate, calcium, and magnesium removals were predicted; however, the removals did not correspond to the minerals found by XRD. If slow forming minerals (Çelen et al., 2007) were excluded from the database, then calcium phosphate, calcite, and magnesite minerals were formed with a percent composition of 1.71%, 20.5%, and 77.8%, respectively. Only the phosphate removal from the model matched well with the real and synthetic wastewaters. This suggested other factors, such as ionic strength or organic acids, might contribute to the differences between modeled, synthetic, or real wastewaters.

4.4 Effects of Storage

The fourth experiment tested different storage conditions for anaerobically digested swine manure effluent. The pH of all stored effluents gradually increased over the storage period (Figure 4-8a). Simultaneously, the alkalinity of all stored effluents gradually decreased over time (Figure 4-8b). This suggested that CO_2 stripping occurred during the storage of the effluents. Greater increases in pH were observed in open containers due to greater volatilization of CO_2. As pH increased over time, the supersaturation of struvite components was more likely, and resulted in precipitation of minerals during storage.

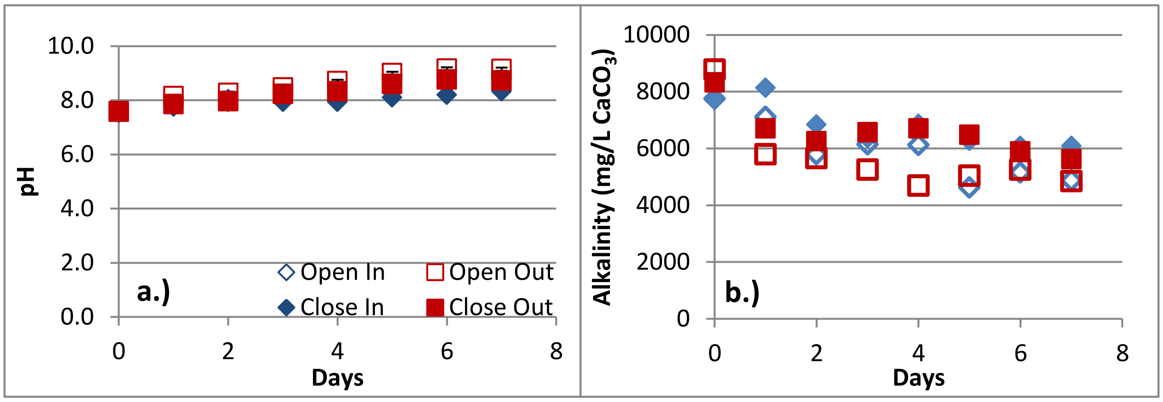


Figure 4-8: Evidence of CO_2 stripping during storage

4.4.1 Magnesium Ion Removal from Solution

Measured magnesium concentrations were sometimes higher than the initial concentration. The experiments were kept in isolated or infrequently traveled places and were unlikely to be contaminated from ambient conditions. This variability was likely caused by dilutions, but in spite of that, magnesium in the system remained relatively constant (Figure 4-9). There was a slight decrease in magnesium concentration on day 7, suggesting another phase formed due to precipitation during storage. This is possible due to increasing pH of the stored effluent from natural CO_2 stripping over time. There was no apparent difference over time between the different storage conditions, so exposure to the atmosphere or temperature do not seem to greatly affect magnesium.

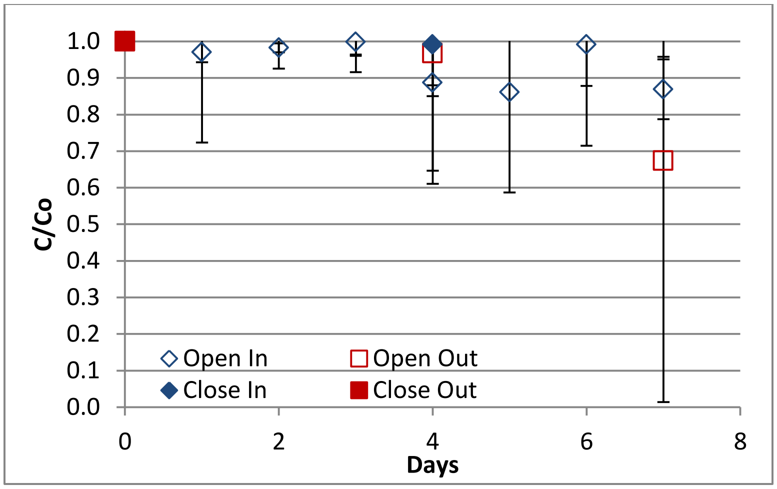


Figure 4-9: Magnesium concentrations of stored AD effluent over time

4.4.2 Ammonium Ion Removal from Solution

The storage of anaerobically digested swine manure effluent revealed that ammonium was being removed through volatilization (Figure 4-10). If precipitation was the cause of decreasing ammonium concentration ratios, then magnesium should have decreased similarly along with ammonium. Instead, the amount of ammonium decrease was much greater than observed in magnesium.

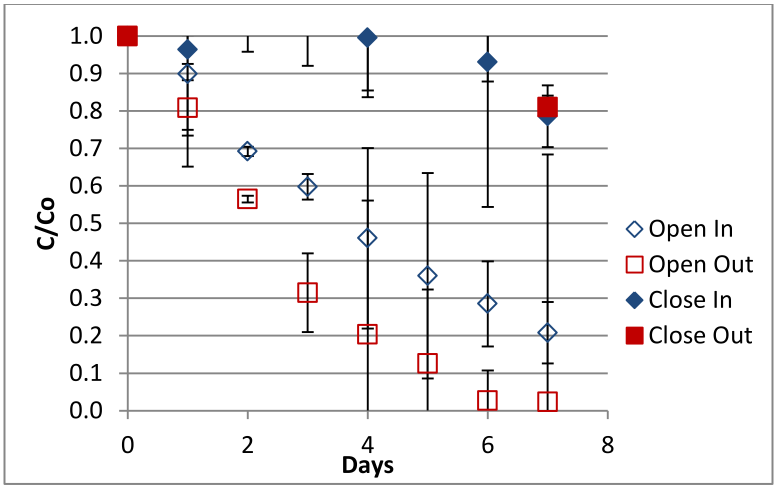


Figure 4-10: Ammonium concentrations of stored AD effluent over time

Open and closed containers responded differently to the storage circumstances. Ratios in closed containers remained relatively constant, with only slight decreases at the end of the storage period. Open containers showed decreasing concentration ratios in the effluent over time. The temperature of the indoor or outdoor environment affected volatilization. The cooler indoor environment had less ammonia volatilization, evidenced by the slope of the points and higher ending concentration ratio. The temperature, however, enhanced volatilization in open containers, not closed containers. The concentration ratios under closed conditions for indoor and outdoor storage were similar, suggesting the main factor limiting the rate of volatilization was a cover. These findings suggested that open storage for less than one day might be acceptable for precipitation of struvite; otherwise, the system might quickly become ammonium limited. Volatilization of ammonia should also be limited because it can be harmful to human health in high concentrations, is an odor nuisance at low concentrations (Airgas, 2011), is a known precursor for PM 2.5 (Key & Kaplan, 2007), and can become nitrogen oxide greenhouse gases (Marañón et al., 2011).

4.4.3 Calcium Ion Removal from Solution

Storage of anaerobically digested swine manure effluent revealed calcium concentration ratios decreased over time, despite the different storage conditions (Figure 4-11). This suggested that the concentration of calcium was not affected by volatilization or temperature. Precipitation could cause a decrease in calcium concentrations over time because of increasing pH. Temperature, interestingly, did not affect the rate of precipitation, noticeable between indoor and outdoor data points. Also, the decrease of calcium appeared almost linear and could be subject to zero order kinetics or was inhibited by the system pH and appears linear due to CO_2 mass transfer limitations.

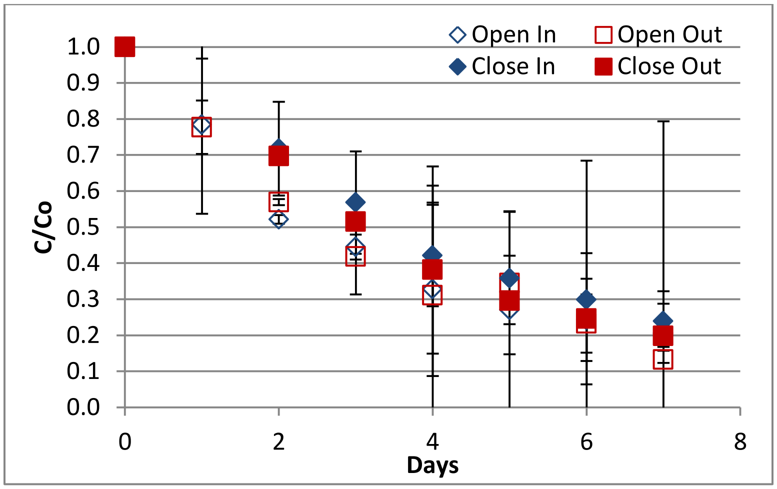


Figure 4-11: Calcium concentrations of stored AD effluent over time

4.4.4 Phosphate Ion Removal from Solution

The phosphate concentration ratios of anaerobically digested swine manure effluent decreased over time due to natural precipitation of phosphate minerals (Figure 4-12). Since there were only slight decreases in the concentration ratios of magnesium, most of these precipitates were likely calcium phosphates. The decrease in phosphate, however, did not appear linear like calcium. This reinforced the idea that the decrease in phosphate was not solely due to calcium but could confirm magnesium precipitation as well. There were no apparent differences between the different storage parameters over time.

4.4.5 Effects of Forced Precipitation

After storage, the anaerobically digested effluent was forced to precipitate. This was done to understand whether additional minerals could be precipitated. The XRD scans of the precipitates for the different storage conditions are shown in Figure 4-13. These scans indicated that calcite, dolomite, and struvite were all possible precipitates formed. The peaks at approximately 2θ=17°, 24°, and 45° denoted the possibility of dolomite formation in containers stored indoors; however, these peaks were not present in outdoor containers. Containers stored indoors also had more pronounced peaks compared to outdoor containers at 2θ=21°, 38°, 42°, and 47°, corresponding to calcite. These findings suggested that storage of anaerobically digested effluent in the outdoor environment decreased the presence of dolomite and calcite. The peaks corresponding to struvite, between 14°-17° and around 30°, showed that struvite precipitation also decreased. Since there was no significant difference between phosphate removals, this suggested that minerals such as amorphous calcium phosphate were formed. XRD comparisons for storage of Day 3 and Day 7 under closed, indoor conditions are in Appendix B.

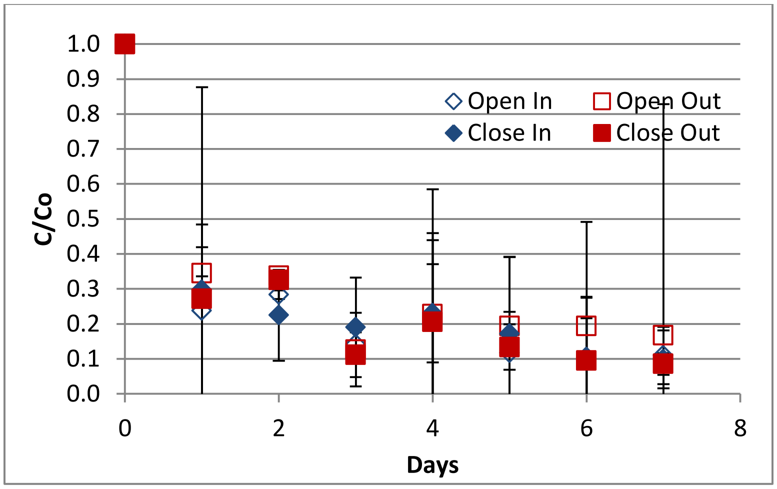
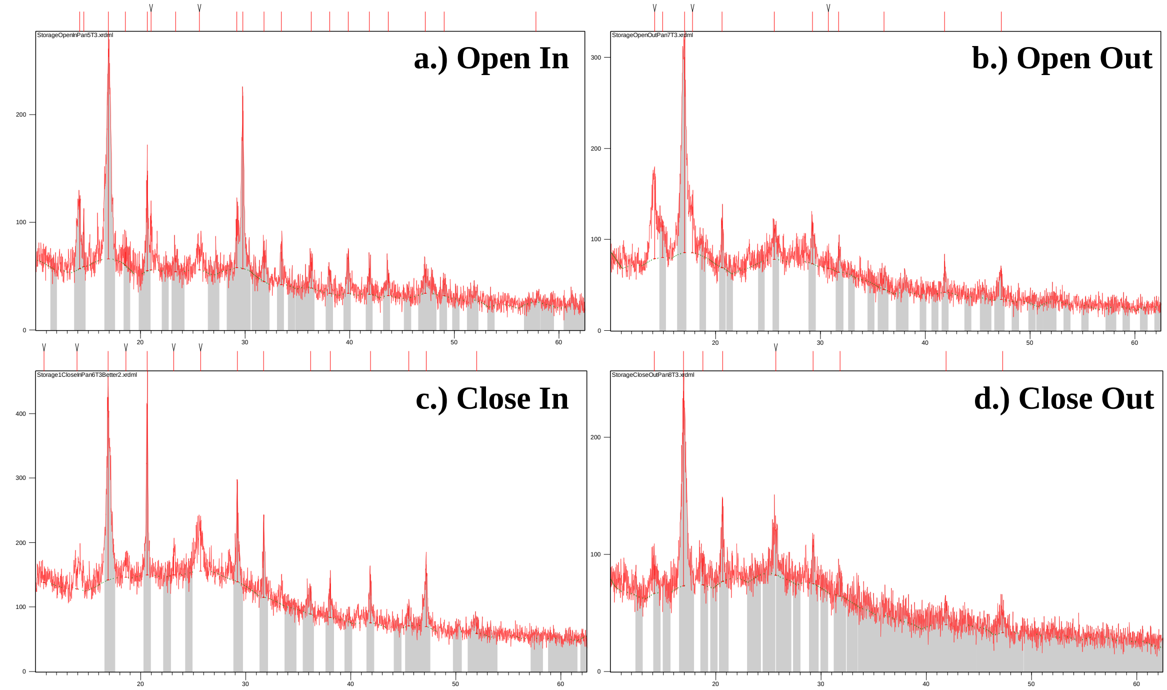


Figure 4-12: Phosphate concentrations of stored AD effluent over time



a.) Open In

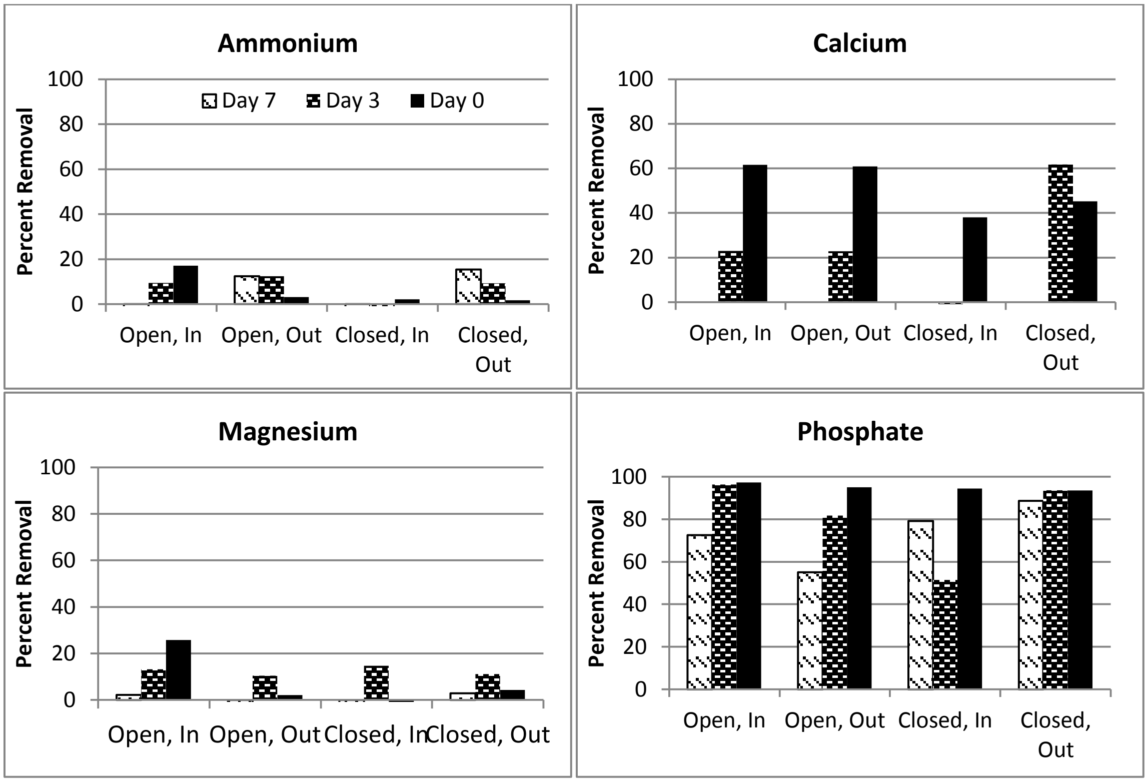
b.) Open Out

c.) Close In

d.) Close Out

Figure 4-13: Comparison of XRD scans between different storage conditions for day 0

The ion removals from forced precipitation are shown in Figure 4-14. Ammonium consistently showed low removals, below 20% among storage conditions. Magnesium also showed low removals (below 25%), and might correspond to precipitation of struvite. Calcium removals were not detected for Day 7. Calcium was likely all removed during storage, so forced precipitation did not remove any additional phosphorus. Forced precipitation did affect Day 0, which generally had higher calcium removal (between 38-61%) and phosphate removal (>90%) than days 3 and 7. Calcium was likely removed as calcite and amorphous calcium phosphate. The maximum P removal was achieved at 96% for day 3, indoor, open-atmosphere conditions. Outdoor, open atmosphere conditions were expected to have the lowest P removal; however, the lowest P removal was 51% at day 3, indoor, close-atmosphere conditions, because natural precipitation would have been carried out longer. The second lowest P removal was 55% at day 7, outdoor, open-atmosphere conditions. Although forced precipitation contributed to high P removal among all storage conditions, the actual phosphate concentrations after storage were very low. The high percent removals corresponded to a difference of less than 2 mg/L phosphate. This means that any additional precipitates were minimal.



The different shadings denote precipitation of AD effluent at different days: (Day 7) diagonal hatches, (Day 3) bricks, and (Day 0) solid.

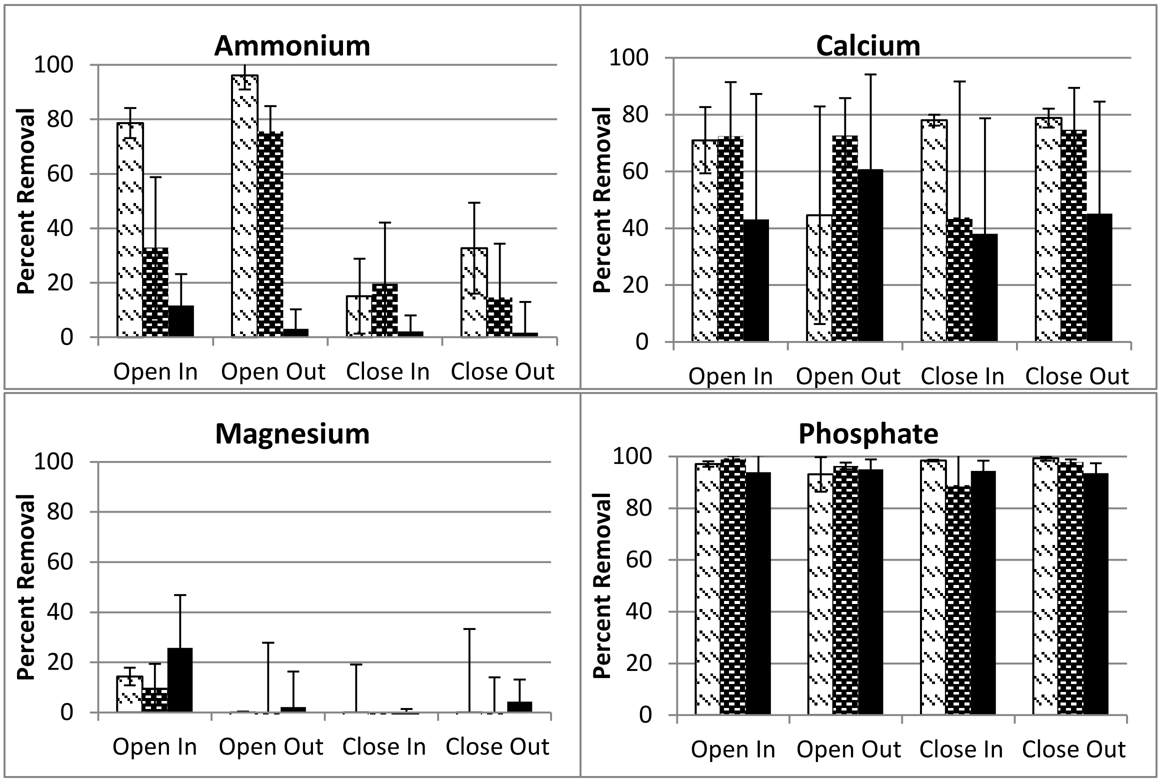
Figure 4-14: Precipitation of stored AD effluent in varying storage conditions

Comparing the ion removals, the highest P removal did not correspond with the highest calcium, magnesium, or ammonium removal. The lowest P removal also did not correspond with the lowest calcium, magnesium, or ammonium removal. As an example of what is meant, the highest removal of phosphate occurs at day 3 under indoor, open-atmosphere conditions, but the highest calcium removal occurs at day 3 under outdoor, close-atmosphere conditions. Also, the highest magnesium removal occurs at day 3, indoor, close-atmosphere conditions. XRD scans confirmed that the discrepancy between

P removal and cation removals might be due to certain storage conditions favoring the precipitation of phosphate minerals while other conditions favor carbonates. As mentioned previously, quantification of these minerals was possible through chemical modeling software; however, modeling approaches reported in literature could not accurately model real anaerobically digested swine manure effluents.

4.4.6 Overall Storage and Precipitation

The overall ion removals from the beginning of storage to after forced precipitation are shown in Figure 4-15. There was overall high ammonium removal, largely due to volatilization. Low magnesium removal was observed overall, so little struvite was precipitated except for containers open to the atmosphere, stored indoors. Moderate to high calcium removal was observed, especially when the anaerobically digested effluent was stored for longer periods of time. Phosphate removal was high at any storage period, suggesting that storage only promoted calcium phosphate minerals to precipitate. Since the additional calcium removal during storage did not match the additional phosphate removed, this showed that as the effluent was stored, calcium was likely precipitating as a calcite mineral. Again, XRD scans confirmed that calcite was present in the precipitates.



The different shadings denote precipitation of AD effluent at different days: (Day 7) diagonal hatches, (Day 3) bricks, and (Day 0) solid.

Figure 4-15: Ion removals from beginning of storage to after forced precipitation

CHAPTER 5: CONCLUSIONS

Swine production represents approximately 40% of the world's meat production, and its wastes contain high concentrations of organic carbon, nitrogen (N), and phosphorus (P). Anaerobic digestion is an increasingly popular technology for treating animal wastes while simultaneously generating energy. Its propagation and ability to solubilize organic N and P make adding a struvite recovery process attractive. Recovering struvite ($MgNH_4PO_4$) from anaerobically digested swine waste can address global P shortages, meet P discharge guidelines, and produce slow-release fertilizer, which can be sold for revenue. In this thesis, the precipitation potential of minerals from effluent of anaerobically digested swine manure was investigated. The overall objectives and major findings of this thesis are listed below with the respective suggestions for swine farmers.

1. Quantify suitable swine manure loading rates for consistent anaerobic digester operation without inhibition or failure, so anaerobically digested swine manure effluent is available for struvite precipitation.
    - *Major Finding:* Effective volatile solids (VS) loading rate without ammonium inhibition or failure was 3.4-3.9 g VS/L-day.
    - *Suggestion*: Farmers should be careful not to overload their anaerobic digesters. Farmers could determine an appropriate loading rate by measuring VS concentration in the feed and subsequently increase the VS concentration in the feed based on calculations.

2. Quantify the effects of Mg:P on the mass of precipitate recovered and the residual ion concentrations in the liquid after struvite precipitation.
    - *Major Finding:* The cost effective Mg:P ratios were between 1.30-1.78.
    - *Suggestion*: The magnesium addition should correspond to the phosphate concentration in the anaerobically digested effluent. Farmers could test available P in the effluent, and the appropriate amount of magnesium to add can be calculated.
3. Compare the results of struvite precipitation from synthetic wastewater (no organic matter) to results from actual anaerobically digested swine manure (high dissolved organic matter).
    - *Major Finding:* There were significant differences between real, synthetic, and modeled effluents. Neither models nor synthetic wastewaters without organic matter could accurately predict the behavior of real anaerobically digested effluent.
    - *Suggestion*: Jar tests should be performed with real effluent of anaerobically digested swine manure, rather than relying on synthetic wastewater or modeled results.
4. Quantify how various storage conditions of anaerobically digested swine manure effluent affect the concentration of dissolved ions in digester effluent and the mass of precipitate formed.
    - *Major Finding:* Covering the storage container significantly decreases ammonia and carbon dioxide volatilization. Also, increased storage time

decreases the constituents available for struvite precipitation because these volatilize or precipitate during storage.

- *Suggestion*: Farmers should precipitate minerals as soon as possible to recover as much P as possible in the form of struvite.

Future work on struvite precipitation can focus on interferences, modeling, and practical applications for farmers. Specifically, the competitive interference of Ca:Mg ratio would affect the addition of Mg and could possibly determine the profitability of an operation. Also, identifying the type of organic matter present in digester effluent and how it affects struvite precipitation could lead to improving struvite precipitation efficiency. While simple lab tests could easily determine the necessary parameters for struvite precipitation, accurate models might be less time consuming and inexpensive. Testing field applications of struvite precipitation would also provide useful information about system efficiency, scale-up, user friendliness, and interest among farmers.

REFERENCES

Airgas. (2011). *Material Safety Data Sheet Ammonia.* Radnor, PA: MSDS.

Algeo, T. (2012, January). *Highlights of the BlueTech webinar: nutrient recovery from agricultural, industrial and municipal wastewaters.* Retrieved November 5, 2012, from BlueTech research an O2 environmental company: http://www.bluetechresearch.com/nutrient-recovery-webinar-highlights/

Angenent, L. T., Sung, S., & Raskin, L. (2002). Methanogenic population dynamics during startup of a full-scale anaerobic sequencing batch reactor treating swine waste. *Water Research, 36*(18), 4648-4654.

Battistoni, P., Fava, G., Pavan, P., Musacco, A., & Cecchi, F. (1997). Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results. *Water Research, 31*(1), 2925-2929.

Battistoni, P., Pavan, P., Prisciandar, M., & Cecchi, F. (2000). Struvite Crystallization: A Feasible and Reliable Way to Fix Phosphorus in Anaerobic Supernatants. *Water Resources, 34*(11), 3033-3041.

Bauer, P. J., Szogi, A. A., & Vanotti, M. B. (2007). Agronomic Effectiveness of Calcium Phosphate Recovered from Liquid Swine Manure. *American Society of Agronomy, 99*, 1352-1356.

Boopathy, R. (1998). Biological treatment of swine waste using anaerobic baffled reactors. *Bioresource Technology, 64*(1), 1-6.

Bradford-Hartke, Z., Lant, P., & Leslie, G. (2012). Phosphorus recovery from centralised municipal water recycling plants. *Chemical Engineering Research and Design, 90*(1), 78-85.

Burkholder, J., Libra, B., Weyer, P., Heathcote, Koipin, D., Thorne, P. S., et al. (2007, February). Impacts of Waste from Concentrated Animal Feeding Operations on Water Quality. *Environmental Health Perspectives, 115*(2), 308-312.

Burns, R., Moody, L., Walker, F., & Raman, D. (2010). Laboratory and In-Situ Reduction of Soluble Phosphorus in Swine Waste Slurries. *Environmental Technology, 22*(11), 1273-1278.

Çelen, I., Buchanan, J. R., Burns, R. T., Robinson, R. B., & Raman, D. R. (2007). Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research, 41*(8), 1689-1696.

Chae, K., Jang, A., Yim, S., & Kim, I. S. (2008). The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure. *Bioresource Technology, 99*(1), 1-6.

Chen, Y., Cheng, J. J., & Creamer, K. S. (2008). Inhabition of anaerobic digestion process: A review. *Bioresource Technology, 99*(10), 4044-4064.

Chen, Y., Fu, B., Wang, Y., Jiang, Q., & Liu, H. (2012). Reactor Performance and bacterial pathogen removal in response to sludge retention time in a mesophilic anaerobic digester treating sewage sludge. *Bioresource Technology, 106*(February 2012), 20-26.

Cordell, D., Drangert, J.-O., & White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change, 19*, 292-305.

Davis, C., & Lin, B.-H. (2009). *Factors affecting U.S. pork consumption.*

Deng, L., Zhen, P., Chen, Z., & Mahmood, Q. (2008). Improvement in post-treatment of digested swine wastewater. *Bioresource Technology, 99*(8), 3136-3145.

Dhakal, S. (2008). *A Laboratory Study of Struvite Precipitation for Phosphorus Removal from Concentrated Animal Feeding Operation.* Rolla: University of Missouri-Rolla.

Doyle, J. D., & Parsons, S. A. (2002, March 15). Struvite formation, control and recovery. *Water Research, 36*(16), 3925-3940.

Environmental Protection Agency. (1986). *Quality Criteria for Water.* Washington DC: EPA.

Environmental Protection Agency. (2003, February 12). Rules and Regulations. *Roles and Responsibilities, 68*(29), p. 7188.

FisherScientific. (n.d.). *Catalogs*. Retrieved November 2, 2012, from FisherScientific: http://www.fishersci.com/ecomm/servlet/cmstatic?href=index.jsp&store=Scientific&segment=scientificStandard

Forrest, A., Fattah, K., Mavinic, D., & Koch, F. (2006). Use of natural zeolite at different does and dosage procedures in batch and continuous anaerobic digestion of synthetic and swine wastes. *Resources Conservation & Recycling, 134*(5), 26-41.

Ganrot, Z., Dave, G., Nilsson, E., & Li, B. (2007, March 1). Plant availability of nutrients recovered as solids from urine tested in climate chamber on Triticum aestivum L. *Bioresource Technology, 98*(16), 3122-3129.

Hansen, K. H., Angelidaki, I., & Ahring, B. K. (1998). Anaerobic digestion of swine manure: inhibition by ammonia. *Water Research, 32*(1), 5-12.

Harikishan, S., & Sung, S. (2003). Cattle waste treatment and Class A biosolid production using temperature-phased anaerobic digester. *Advances in Environmental Research*, 701-706.

Huang, H., Xu, C., & Zhang, W. (2011). Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology. *Bioresource Technology, 102*(3), 2523-2528.

ICIS. (2012). *Indicative Chemical Prices A-Z.* (J. Chang, Ed.) Retrieved November 5, 2012, from ICIS: http://www.icis.com/chemicals/channel-info-chemicals-a-z/

Ives, S., Cotching, W., Sparrow, L., Lisson, S., & Doyle, R. (2011). Plant growth and soil responses to soil applied organic materials in Tasmania, Australia. *Soil Research, 49*(7), 572-581.

Jaffer, Y., Clark, T., Pearce, P., & Parsons, S. (2002). Potential phosphorus recovery by struvite formation. *Water Research, 36*(7), 1834-1842.

Johnston, A., & Richards, I. (2003). Effectiveness of different precipitated phosphate as phosphorus sources for plants. *Soil use and Management, 19*(1), 45-49.

Jordaan, E., Ackerman, J., & Cicek, N. (2010). Phosphorus removal from anaerobically digested swine wastewater through struvite precipitation. *Water Science & Technology, 61*(12), 3228-3234.

Karakashev, D., Schmidt, J., & Angelidaki, I. (2008). Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure. *Water Research, 42*(15), 4083-4090.

Key, N. D., & Kaplan, J. D. (2007). Multiple Environmental Externalities and Manure Management Policy. *Journal of Agricultural and Resource Economics, 32*(1), 115-134.

Kim, M., Ahn, Y.-H., & Speece, R. (2002). Comparative process stability and efficiency of anaerobic digestion; mesophilic vs. thermophilic. *Water Research, 36*(17), 4369-4385.

Kinney et al. (2006). Survey of organic wastewater contaminants in biosolids destined for land application. *Environmental Science and Technology*, 7207-7215.

Korchef, A., Saidou, H., & Amor, M. B. (2011). Phosphate recovery through struvite precipitation by CO2 removal: Effect of magnesium, phosphate and ammonium concentrations. *Journal of Hazardous Materials, 186*(1), 602-613.

Lammers, P. J., Stender, D. R., & Honeyman, M. S. (2007). *Nutrients for Pigs.* Iowa State University. Ames: Iowa Pork Industry Center.

Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth, 283*(3-4), 514-522.

Le Corre, K., Valsami-Jones, E., Hobbs, P., Jefferson, B., & Parsons, S. (2007). Struvite crystallisation and recovery using a stainless steel structure as a seed material. *Water Research, 41*, 2449-2456.

Liu, Y., Rahman, M., Kwag, J.-H., Kim, J.-H., & Ra, C. (2011). Eco-friendly production of maize using struvite recovery from swine wastewater as a sustainable fertilizer source. *Journal of Animal Science, 24*(12), 1699-1705.

Liu, Z., Zhao, Q., Wang, K., Qui, W., Li, W., & Wang, J. (2008). Comparison between complete and partial recovery of N and P from stale human MAP crystallization. *Journal of Environmental Science, 7*, 223-228.

Marañón, E., Salter, A., Castrillón, L., Heaven, S., & Fernández-Nava, Y. (2011). Reducing the environmental impact of methane emissions from diary farms by anaerobic digestion of cattle waste. *Waste Management, 34,* 1745-1751.

Marti, N., Bouzas, A., Seco, A., & Ferrer, J. (2008). Struvite precipitation assessment in anaerobic digestion processes. *Chemical Engineering Journal, 141*(1-3), 67-74.

Marti, N., Ferrer, J., Seco, A., & Bouzas, A. (2008). Optimisation of sludge line management to enhance phosphorus recovery in WWTP. *Water Research, 42*(18), 4609-4618.

Massé, D., Gilbert, Y., & Topp, E. (2011). On farm biogas production: a method to reduce GHG emissions and develop more sustainable livestock operations. *Animal Feed Science, 102*(2), 436-445.

Meldrum, F. C., & Hyde, S. T. (2001). Morphological influence of magnesium and organic additives on the precipitation of calcite. *Journal of Crystal Growth, 231*(4), 544-558.

Mihelcic, J. R., Fry, L. M., Myre, E. A., Phillips, L. D., & Barkdoll, B. D. (2009). *Field Guide to Environmental Engineering for Development Workers.* Reston, VA: American Society of Civil Engineers.

Miles, A., & Ellis, T. (2001). Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Water Science and Technology, 43*(11), 259-266.

Moody, L., Burns, R., & Stalder, K. (2009). Effect of Anaerbic digestion on struvite production for nutrient removal from swine waste prior to land application. *Applied Engineering in Agriculture, 25*(1), 97-102.

Morel, F. M., & Hering, J. G. (1993). *Principles and Applications of Aquatic Chemistry.* New York: John Wiley and Sons, Inc.

Münch, E. a. (2000). Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research, 35*(1), 151-159.

Musvoto, E., Wentzel, M., & Ekama, G. (2000). Integrated chemical-physical processes modelling--II simulating aeration treatment of anaerobic digester supernatants. *Water Research, 34*(6), 1868-1880.

Nelson, N. O., Mikkelsen, R. L., & Hesterberg, D. L. (2003). Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. *Bioresource Technology, 889*(3), 229-236.

Newell, R. (2010, December 16). Annual Energy Outlook 2011 Reference Case. (U.S.E.I.A., Interviewer)

Ohlinger, K., Young, T., & Schroeder, E. (1998). Predicting struvite formation in digestion. *Water Research, 32*(12), 3607-3614.

Pagilla et al. (2000). Aerobic thermophilic and anaerobic mesophilic treatment of swine waste. *Water Research*, 2747-2753.

Parkin, G. F., & Owen, W. F. (1986). Fundamentals of anaerobic digestion of wastewater sludges. *Journal of Environmental Engineering*, 867-920.

Parsons, D. a. (2002). Struvite formation, control and recovery. *Water Research*, 3925-3940.

Pascoe, E. (2011). Solve the pile problem. *Practical Horseman*, 50-56.

Pecson, B. M., & Nelson, K. L. (2005). Inactivation of Ascaris suum eggs by ammonia. *Environmental Science and Technology, 39*(20), 7909-7914.

Perera, P. A., Han, Z.-Y., Chen, Y.-X., & Wu, W.-X. (2007). Recovery of nitrogen and phosphorous as struvite from swine waste biogas digester effluent. *Biomedical and Environmental Sciences, 20*(5), 343-350.

Rittman, B. E., & McCarty, P. L. (2001). *Environmental Biotechnology: Principles and Applications.* New York: McGraw-Hill Higher Education.

Rowse, L. (2011). *Design of Small Scale Anaerobic Digesters for Application in Rural Developing.* Civil and Environmental Engineering. Tampa: University of South Florida.

Schuiling, R. D., & Andrade, A. (2010). Recovery of Struvite from Calf Manure. *Environmental Technology, 20*(7), 765-768.

Schulze-Rettmer, R. (1991). The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate. *Water Science Technology, 23*, 659-667.

Shin, S. G., Yoo, S., Hwang, K., Song, M., Kim, W., Han, G., et al. (2011). Dynamics of transitional acidogenic community along with methanogenic population during anaerobic digestion of swine wastewater. *Process Biochemistry, 46*(8), 1607-1613.

Smith, K., Jackson, D., & Withers, P. (2001). Nutrient losses by surface run-off following the application of organic manure to arabl land. 2. Phosphorus. *Environmental Pollution, 112*(1), 53-60.

Smith, S., Lang, N., CHeung, K., & Spanoudaki, K. (2005). Factors controlling pathogen destruction during anaerobic digestion of biowastes. *Waste Management, 25*(4), 417-425.

Song, Y., Yuan, P., Zheng, B., Peng, J., Yuan, F., & Gao, Y. (2007). Nutrient removal and recovery by crystallization of magnesium ammonium phosphate from synthetic swine wastewater. *Chemosphere, 69*(2), 319-324.

Song, Y.-C., Kwon, S.-J., & Woo, J.-H. (2004). Mesophilic and thermophilic temperature co-phase anaerobic digestion compared with single-stage mesophilic- and thermophilic digestion of sewage sludge. *Water Research, 38*(7), 1653-1662.

Song, Y.-H., Qiu, G.-L., Yuan, P., Cui, X.-Y., Peng, J.-F., Zeng, P., et al. (2011). Nutrients removal and recovery from anaerobically digested swine wastewater by struvite crystallization without chemical additions. *Journal of Hazardous Materials, 190*(1-3), 140-149.

Stratful, I., Scrimshaw, M., & Lester, J. (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Research, 35*(17), 4191-4199.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y., Yasuda, T., et al. (2006). Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology, 98*(8), 1573-1578.

Turner, B. L., & Leytem, A. B. (2004). Phosphorus compounds in sequential extracts of animal manures: chemical speciation and a novel fractionation procedure. *Environmental Science and Technology, 38*(22), 6101-6108.

Uludag-Demirer, S., Demierer, G., Frear, C., & Chen, S. (2008). Anaerobic digestion of dairy manure with enhanced ammonia removal. *Journal of Environmental Management, 86*(1), 193-200.

Wang, J., Burken, J. G., ASCE, M., Zhang, X. (., & Surampalli, R. A. (2005). Engineered Struvite Precipitation: Impacts of Component-Ion Molar Ratios and pH. *Journal of Environmental Engineering, 131*(10), 1433-1440.

Wilkie, A. (2011, November 18). Animal Manure Digesters. (A. L. Rowse, Interviewer)

Wilsenach, J., Schuurbiers, C., & Loosedrecht, M. v. (2007). Phosphate and potassium recovery from source separated urine through struvite precipitation. *Water Research, 41*(2), 458-466.

Wrigley, T., Webb, K., & Venkitachalm, H. (1992). A laboratory study of struvite after anaerobic digestion of piggery wastes. *Bioresource technology, 41*(2), 117-121.

Ye, Z.-l., Chen, S.-H., Lu, M., Shi, J.-W., Lin, L.-F., & Wang, S.-M. (2011). Recovering phosphorus as struvite from the digested swine wastewater with bittern as a magnesium source. *Water Science & Technology, 64*(2), 334-340.

Zeng, L., & Li, X. (2006, November 30). Nutrient removal from anaerobically digested cattle manure by struvite precipitation. *Journal of Environmental Engineering Science, 5*, 285-294.

APPENDIX A: ADDITIONAL MATERIALS FOR CHAPTER 3

The following tables and figures are related to Chapter 3: Materials and Methods.

Figure A-1: Diagram of bench-scale anaerobic digesters

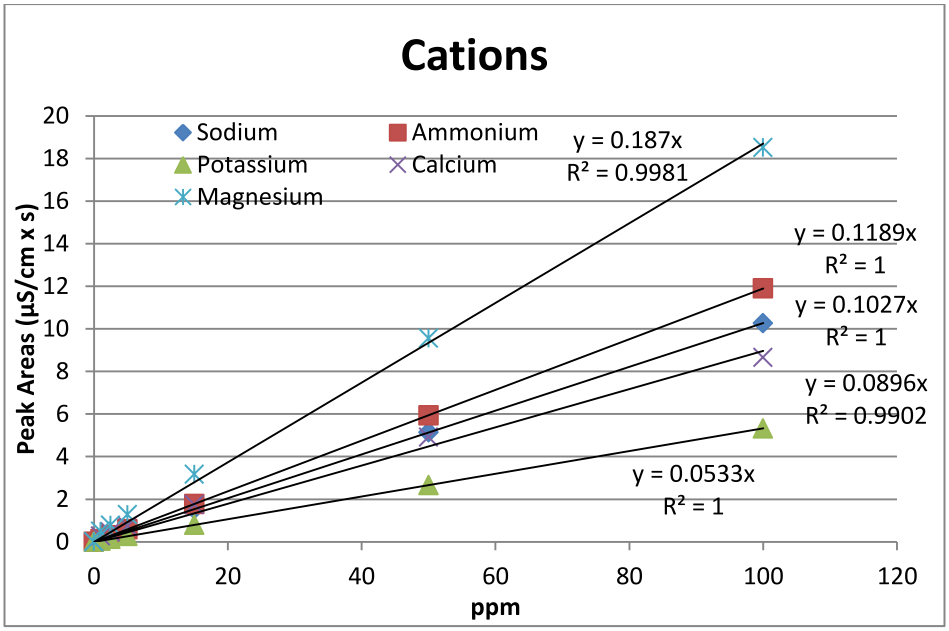


Figure A-2: Sample cation calibration curve for the IC

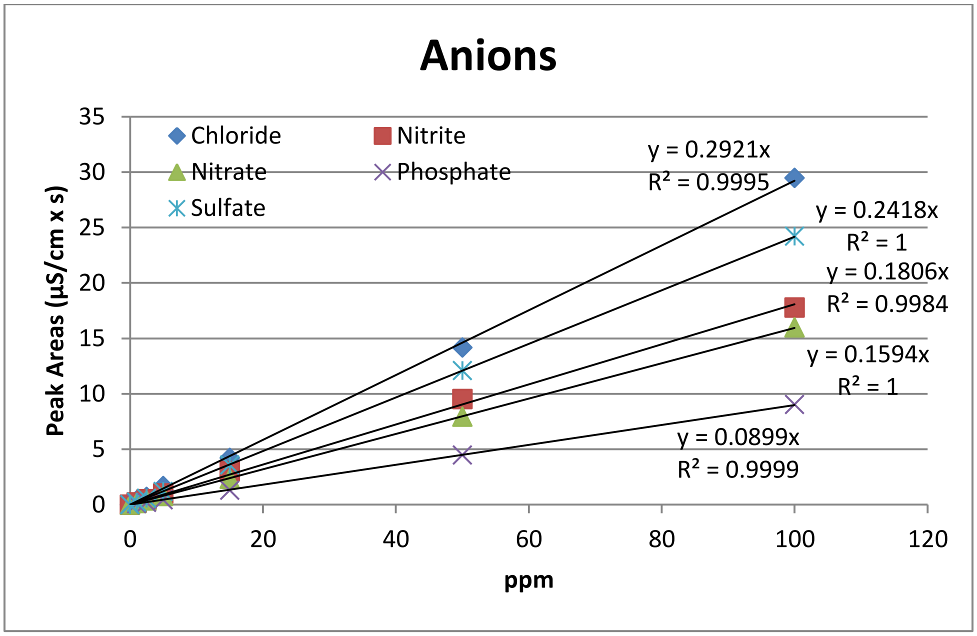


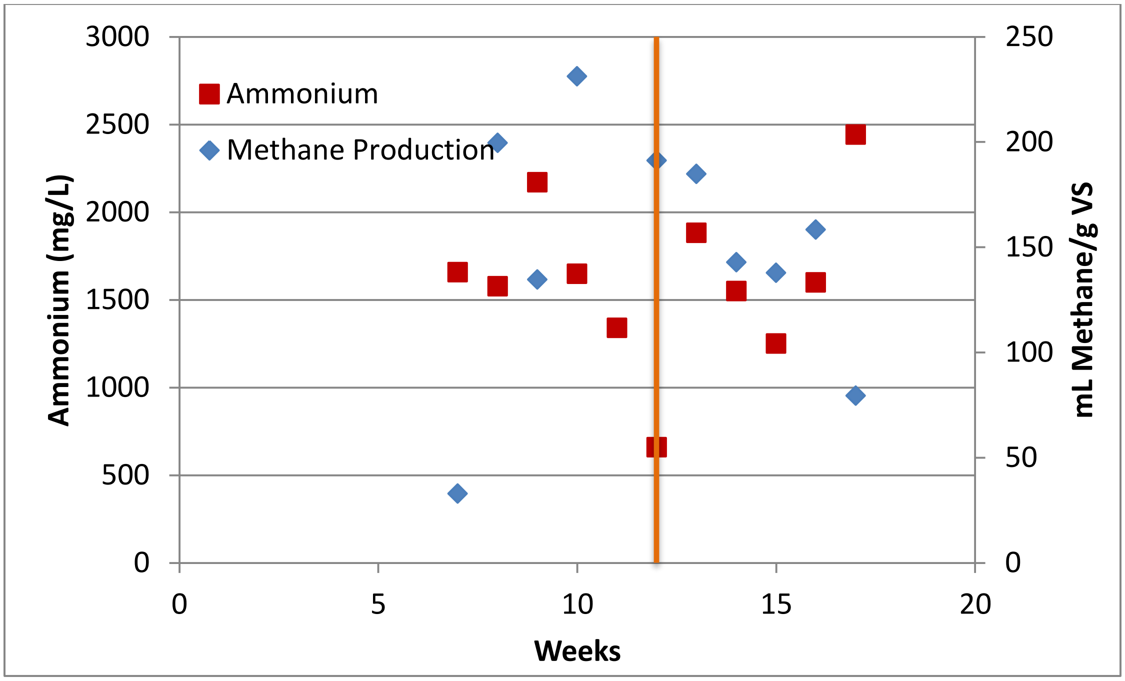
Figure A-3: Sample anion calibration curve for the IC

Table A-1: Equipment and analyses shared among experiments

Experiment	Equipment and Analyses		
Testing Mg:P Ratios with Synthetic Wastewater Values from Literature	***Chemical Equilibrium Modeling Software***: Visual MINTEQ v.3.0	***Alkalinity***: 865 Dosimat plus (Metrohm, USA) End-point titration method	VWR S-500 Orbital shaker table, Fisherbrand 0.45µm syringe filters, Fisherbrand G4 0.45 um glass fiber filter circles (All from Pittsburgh, PA), Tetra Whisper 100 (USA) ***Conductivity and pH***: ThermoScientific Orion 5-star ***Ion Chromatography*** (IC): 881 Compact IC pro (Metrohm, USA) *Metrosep A Supp 7-250/4.0:* Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} *Metrosep C4-150/4.0:* Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+} ***X-Ray Diffraction***: Philips Panalytical X'Pert MRD (Westborough, MA)
Effects of Organic Matter			
Effects of Precipitation on Stored Anaerobic Digester Effluent	Thermo Scientific CL 2 Centrifuge (Pittsburgh, PA) ***pH***: Eutech Instruments Waterproof pH Testr 10 (Vernon Hills, IL)		
Anaerobic Digestion of Swine Wastes			---------------------N/A-------------------

APPENDIX B: ADDITIONAL MATERIALS FOR CHAPTER 4

The following tables and figures are related to Chapter 4: Results and Discussion.



Weeks 7-12: 3.9 g VS/L-day; Weeks 13-17: 5.1 g VS/L-day

Figure B-1: Methane production and ammonium concentration in reactor 3

APPENDIX B (CONTINUED)

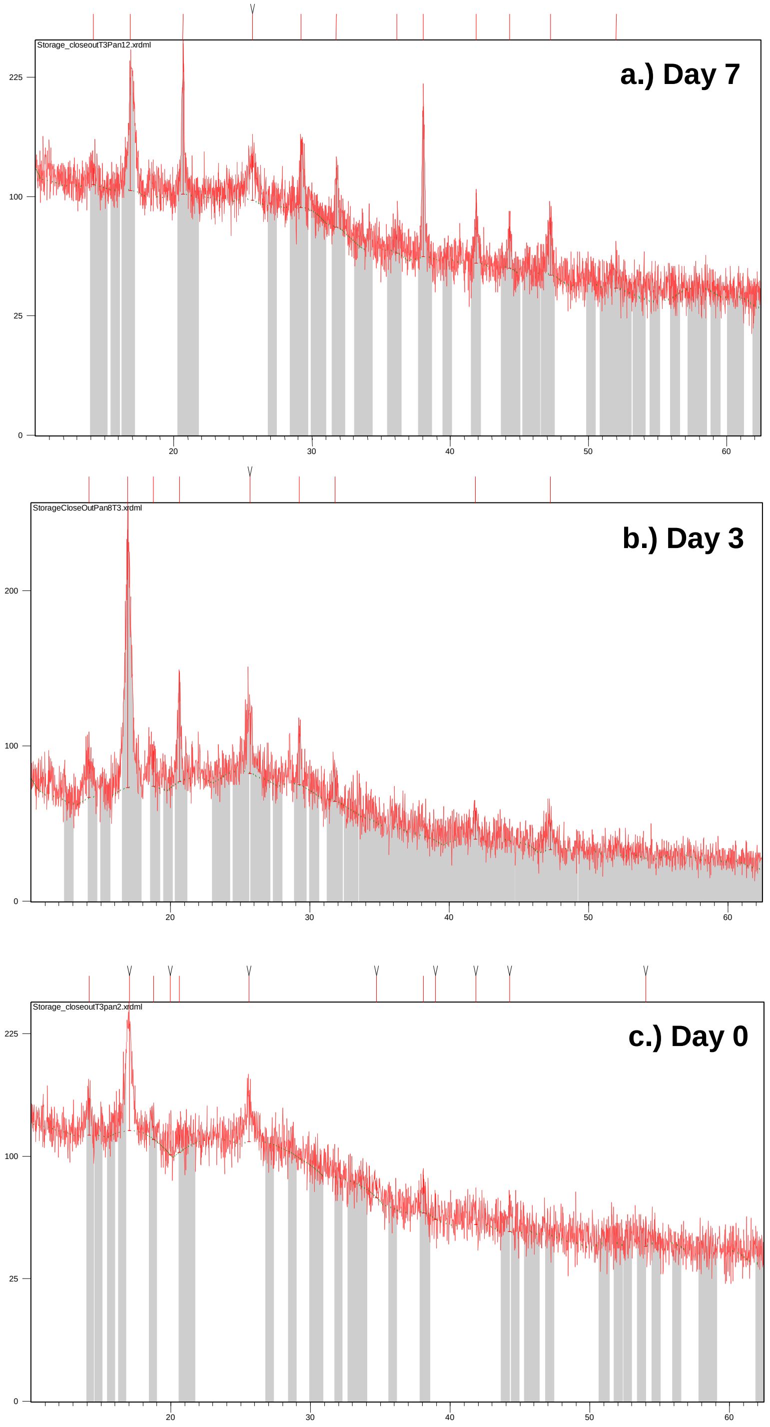


Figure B-2: XRD scans over time for storage under outdoor, closed to the atmosphere conditions