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Sustainable Energy and Nutrient Recovery from Swine Waste

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Sustainable Energy and Nutrient Recovery from Swine Waste

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
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DEDICATION

I would like to dedicate this work to my family who has provided me the strongest foundation, which I will keep throughout my life. I am always grateful to them for their love, their joy, and the countless hours spent in selflessly helping me to grow.

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I would like to thank enormously my committee members and especially my advisors for all of their contributions toward the completion of this thesis. They truly sacrificed of their time and ability for me to succeed. I have learned much from them that I will take with me throughout my life. Their compassion stands out as exemplary and distinguished and will always be remembered.

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- Meng Wang and Nathan Manser: collecting *E. coli* data;
- Verónica Aponte-Morales: performing the IX experiment, collecting water quality data and measuring N concentrations after IX, measuring ion concentrations with the IC throughout the entire treatment train
- Merrill Peyton Dillbeck: collecting water quality data and measuring N concentrations before AD, after AD, and after precipitation

Furthermore, their advice, joyful spirit, and accompaniment in this process have been indispensable.

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ABSTRACT

Swine production represents approximately 40% of the world's meat production, and swine wastes contain high concentrations of organic matter, nitrogen (N) and phosphorus (P). Swine production is intensifying as meat demand increases and concentrated animal feeding operations (CAFOs) are becoming increasingly common, making it difficult to treat the waste generated. A system for holistic treatment of swine waste produced in CAFOs was investigated in this study that sustainably generates energy and recovers N and P as saleable fertilizers. The system uses anaerobic digestion (AD) for methane production and solids stabilization, followed by precipitation of struvite ($MgNH_4PO_4 \bullet 6H_2O$) and recovery of N by ion exchange onto natural zeolites. This process is expected to mitigate both eutrophication of receiving waters and greenhouse-gas emissions while generating products that meet agronomic nutrient demands; however, the economic and environmental sustainability remains unknown. The objectives of this study were to: (1) evaluate water quality and the fate of nutrients and ions in each step in the proposed system through pilot and bench scale experiments, (2) evaluate content/quality of struvite precipitates formed in wastewater treatment processes, (3) assess basic composition of zeolite materials that are being considered for use as IX materials, (4) quantify the environmental impact of the proposed system, and (5) estimate the economic benefits and costs of the proposed system.

The results of a bench scale evaluation of the system show that although water quality greatly improves throughout the treatment process, the effluent water quality has high

concentrations of COD (2,803 mg O_2/L) and *E. coli* ($10^{6.3}$ CFU/100ml). This limits reuse options for the reclaimed water, however a variety of on-farm applications may be suitable.

During struvite precipitation, the recovery efficiency of SRP was 87% (60 mg/L recovered); however, although measurements that take into account P in suspended solids show a lower recovery efficiency, they also show higher mass recovery (77% efficiency, 66 mg/L recovered). N recovery during struvite precipitation showed a similar trend, with 49% of TN and 7% of NH_4-N being recovered. Struvite recovery can only occur from NH_4-N and soluble reactive P. The additional recovery observed is likely due to adsorption of the nutrients onto the precipitate. Therefore, to accurately measure and report recovery, measurements of N and P that take into account suspended solids should be used. In most wastes, magnesium is the limiting constituent for struvite formation, but for swine AD effluents, P is the limiting constituent. Therefore, a higher soluble P concentration would increase recovery potential. The majority of the remaining N and P as well as a significant amount of potassium (K) were recovered during IX.

Six struvites from commercial processes as well as our bench-scale experiments were assessed and compared by X-ray diffraction, SEM imaging, and SEM-EDX scans. All samples were confirmed as struvite by XRD, however they varied widely in crystal size and shape. The elemental composition of the samples was similar; however, struvite formed from phosphate mining waste had higher amounts Mg and P, indicating more pure struvite formation. The presence of impurities in some samples was likely due to the reactor design and solids separation methods.

XRD was also used to confirm the identity of zeolites. Three clinoptilolites had similar crystal size and elemental composition except for Zeosand ® which showed a surface roughness,

which likely contributes to higher cation exchange capacity. Chabazite has smaller crystal size and larger pores than clinoptilolite, which also likely contributes to its higher capacity.

Life cycle assessment (LCA) was used to evaluate the environmental sustainability of the system and the results suggested that environmental benefits were provided across almost all impact categories. Two alternatives for raising the pH in struvite precipitation (NaOH addition vs. aeration) and two alternatives for zeolite IX materials (chabazite vs. clinoptilolite) were assessed, but there were negligible differences between alternatives. The system was also assessed at a medium and large scale, and the large scale was more environmentally friendly across all categories. Operational impacts were significantly greater than construction impacts; therefore, the environmental impact of the system can be accurately assessed by only including operation.

A life cycle cost assessment (LCCA) was also performed on the system and showed a payback period of 39 years for a medium sized system and 15 years for a large size. This, however, is when compared to a “business-as-usual” scenario and does not consider renewable energy credits or government grants. Furthermore, although a larger system is more economically beneficial, this must be balanced with quality of animal care. From a cost standpoint, IX recovery using chabazite is not recommended and struvite precipitation using aeration is more economically beneficial than NaOH addition.

CHAPTER 1: INTRODUCTION

The treatment of animal manure represents a significant environmental problem that has grown in importance as meat demand has increased. From 1961 to 1999, worldwide meat demand grew from 9 to 19 kg/capita/yr and is expected to increase to 30 kg/capita/yr by 2025 (Choi, 2007). In particular, swine production represents nearly 40% of the world's meat production, and is a growing international concern (Choi, 2007). Due to this increased demand, large-scale production of swine in concentrated animal feeding operations (CAFOs) has become increasingly common. These CAFOs generate large amounts of waste which contain high levels of organics, solids, pathogens, phosphorus (P), and nitrogen (N), potentially causing significant environmental harm.

While animal manure is often used as a fertilizer on small-scale farms, the excessive amount of waste in CAFOs increases the difficulty of providing efficient and regulated management of animal waste, laying considerable stress on the environment and often exceeding environmental capacity to absorb its impacts (Bernet and Beline, 2009; Chynoweth et al., 1999). Anaerobic Lagoons (AL) are a common inexpensive treatment method for animal manure; however, ALs have high land requirements and are associated with a variety of environmental problems, such as odors, greenhouse gas emissions, and poor effluent quality (Moser, ND). Furthermore, the National Pollutant Discharge Elimination System (NPDES) requirements were recently revised by the United States Environmental Protection Agency (USEPA), now requiring CAFOs to develop nutrient management plans and eventually eliminate the use of open-air and unlined lagoons for waste treatment and storage (USEPA, 2008). The Food and Drug

Administration (FDA) has also proposed legislation to limit use of untreated animal manure by requiring farmers to wait nine months, instead of the current four months, before applying manure as a soil amendment to edible crops (FDA, 2013). These regulations will make manure application impractical and not cost effective for many farms.

The problems associated with conventional methods of CAFO waste treatment encourage development of alternative technologies for treatment of waste. This research investigates a holistic method for treatment of swine waste generated in CAFOs to sustainably generate energy and recover both N and P as saleable fertilizer. The proposed treatment train (Figure 1.1) uses anaerobic digestion (AD) followed by struvite precipitation and ion exchange of ammonium ion (NH_4^+) onto natural zeolites. This system allows for recovery at every stage, thereby minimizing environmental impacts and costs over the system's life cycle.

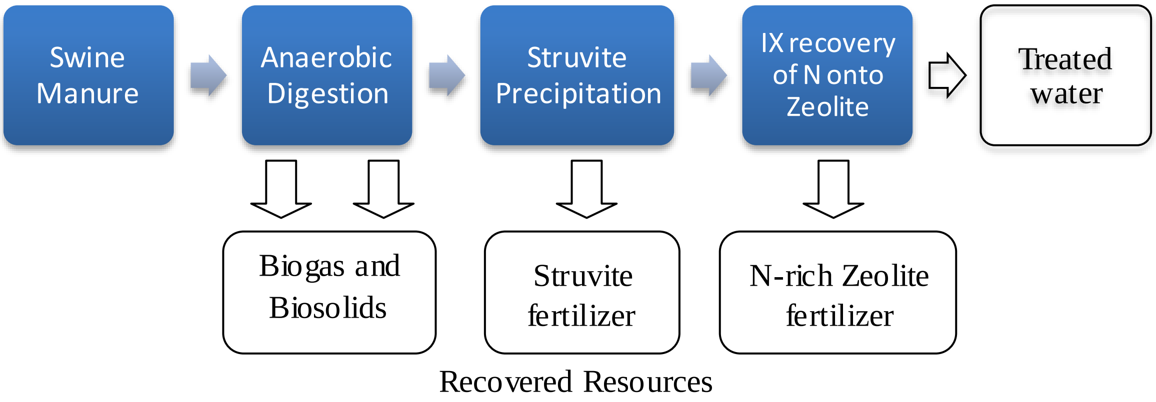


Figure 1.1: Proposed Holistic System for Recovery of Energy and Nutrients from Swine Waste, Showing Resources Recovered.

AD is an alternative technology for treating swine waste, which has the significant advantage of allowing for energy recovery in the form of methane. This methane represents a renewable form of energy, which can be used for a variety of applications including cooking, heating, or co-generation of electricity and can also contribute to the energy requirements of operating the AD system (Westerman et al., 2008). AD also helps avoid the negative environmental effects of improperly managed waste, such as odor problems, attraction of insects and rodents, release of pathogens, contamination of surface water and ground water, and catastrophic spills (Sakar et al., 2009). When treated waste leaves AD, the solid and liquid portions can be separated to allow for recovery of the stabilized biosolids, which can be land applied. Biosolids application is possible because stabilization of organics during AD and reduction of pathogens. The liquid portion of the waste, however, still contains high levels of nutrients such as nitrogen (N) and phosphorus (P) that require further treatment.

Anthropogenic introduction of excessive N and P into water bodies causes eutrophication, leading to algae blooms, which then biologically decompose, creating a high demand for oxygen (Burke et al., 2004). Such demand often leads to hypoxia (lack of oxygen), potentially causing wide-scale death of aquatic life. In addition to these issues, worldwide reserves of phosphate rock, a significant product of the mining industry, are depleting. Therefore, the regulation, recovery, and reuse of N and P, through methods that are economically and environmentally sustainable, are an important challenge.

Recovery of struvite ($MgNH_4PO_4{\cdot}6H_2O$) represents a viable option for removal of both N and P from AD effluent centrate, while also allowing for recovery of the valuable nutrients in the form of a usable and saleable solid fertilizer. This recovery likewise reduces the pressure of demands for non-renewable P resources. Struvite precipitation is usually achieved by magnesium addition and raising solution pH to force supersaturation. Struvite precipitation in municipal waste has been investigated by a number of researchers (Ohlinger et al., 1998; Battistoni et al., 2000; Bouropoulos and Koutsoukos, 2000; Ohlinger et al., 2000; Stratful et al., 2001; Doyle and Parsons, 2002; Jaffer et al., 2002; Le Corre et al., 2007; Bhuiyan et al., 2008; Le Corre et al., 2009; Hao et al., 2009; Galbraith and Schneider, 2009); however, precipitation in anaerobically digested swine waste is less well understood. This unique application can potentially provide significant advantages. Anaerobic digestion allows for release of nutrients into solution, thereby making them more accessible for recovery as a valuable fertilizer through precipitation. Furthermore, ion concentrations within swine waste may decrease the need for chemical addition of magnesium, often the most significant cost in struvite precipitation (Dockhorn, 2009). The use of swine waste as well as the configuration of the digestion and recovery system can affect the quality of precipitated struvite, affecting its value as a fertilizer. Therefore, in this thesis, emphasis is placed on understanding struvite precipitation in anaerobically digested swine waste.

While struvite precipitation is expected to remove a large portion of the P, only a small portion of the dissolved N in solution is removed. The remainder of soluble N, therefore, requires treatment. Biological nitrification-denitrification processes are the most prevalent methods used for removal of reduced N compounds, yet they have limitations such as: COD requirements, which can be costly if external sources are required; temperature dependency and ammonia sensitivity of autotrophic nitrifying bacteria; competition between heterotrophs and autotrophs, which under certain conditions can cause washout and process failure; and long start-up and recovery times after failure (Lahav et al., 2012). Furthermore, most methods for treatment of N merely allow for removal from solution without recovery. Use of ion exchange (IX) onto natural zeolites to remove N from AD centrate avoids many of the disadvantages of biological nutrient removal (BNR) systems. IX also allows for recovery of the N via adsorption onto zeolite followed by field application of the N-rich zeolite material as a fertilizer.

While these additional treatments provide significant advantages by reducing environmental impacts of untreated waste and allowing for pecuniary gain from recovered resources, the life cycle environmental and economic impacts of such treatments are unknown. For example, although eutrophication potential due to untreated effluent is likely to decrease significantly, a rise in eutrophication may be attributed to the construction and operation of additions to the treatment train. A life cycle assessment (LCA) of environmental impacts and life cycle cost analysis (LCCA) can therefore allow for holistic evaluation of additions to the treatment train.

The overall goal of this thesis was to assess environmental and economic impact by constructing a life cycle assessment model of the holistic energy and nutrient recovery system for swine CAFO wastes. To achieve this goal, information regarding the energy and material inputs of the system was required. Bench and pilot scale investigations were carried out to obtain data on performance of each of the additions to the treatment train. Furthermore, data was collected through an extensive literature review as well as surveys and interviews with industry professionals.

Specific objectives of this thesis were to:

1. Evaluate the proposed system in order to understand changes in water quality parameters as well as the fate of nutrients and ions.
2. Evaluate content and crystal characteristics of struvite precipitates formed in various wastewater treatment processes,
3. Evaluate content and crystal characteristics of zeolite materials that are being considered for use as IX materials,
4. Quantify the environmental impact of the proposed system for energy and nutrient recovery,
5. Estimate the economic benefits and costs of the proposed system.

CHAPTER 2: LITERATURE REVIEW

This chapter reviews literature related to the three components of the proposed swine waste treatment process: anaerobic digestion, struvite precipitation, and ion exchange of N using natural zeolites. The literature review focuses most heavily on topics related to struvite precipitation, as this was the primary research focus.

2.1 Anaerobic Digestion of Swine Waste

Field application of manure represents the oldest method for waste treatment known to man, yet due to the high amounts of waste generated by CAFOs, field application of swine manure is considered an unsuitable method of disposal (Bernet and Beline, 2009). Environmental, economic, and regulatory concerns of farmers and governments have led to increased interest in technologies such as AD for treatment of livestock waste. Waste that is not managed properly can have severe effects on the environment including odor problems, attraction of insects and rodents, release of pathogens, contamination of surface water and ground water, and catastrophic spills (Sakar et al., 2009). AD can help prevent such environmental problems while generating energy in the form of biogas to provide pecuniary benefit. The basic goals for AD are to: maximize the degradation of volatile solids (VS), maximize associated methane yield, allow for a continuously high and sustainable organic loading rate (OLR), allow for short hydraulic retention time (HRT) to minimize reactor volume, ensure thorough mixing with an effective transfer of organic material for the active microbial biomass, to release gas bubbles trapped in the medium and to prevent sedimentation (Ward et al, 2008). There are other goals, however, such as reduction of process energy and heat loss, odor control, and to achieve a reliable system with the lowest possible installation and operating cost, all of which likewise contribute to life cycle environmental impact of the system (Chynoweth et al., 1998).

There are a variety of reactor designs commonly used for the AD of livestock manure including batch, continuous single–stage and continuous two–stage reactors, tubular reactors, anaerobic sequencing batch reactors (ASBR), anaerobic filters (AF), upflow anaerobic sludge blankets (UASB), and plug flow reactors (PFR). Reported methane yields for swine manure are generally higher than other livestock wastes, such as cattle manure (Nasir et al., 2012).

2.1.1 Life Cycle Assessments of Anaerobic Digestion Systems

Life Cycle Assessment (LCA) has been utilized by a variety of researchers to understand environmental and human health impacts of AD systems over their life. One of the primary focuses of waste treatment is to reduce ultimate environmental impact; therefore, such assessment helps to quantify impacts not only from the final waste quality but also from the implementation and use of treatment systems. Furthermore, LCA allows for impact assessment of additions to the treatment train as well as comparison between treatment techniques, such as among various AD designs or between AD and other treatments.

Chen et al. (2012) carried out a review of published data and previous LCAs to compare a variety of methods of sewage sludge treatment in the Chinese context such as anaerobic digestion, aerobic digestion, drying, composting, and incineration. They noted that in the future sewage sludge disposal should focus on resource recovery and found that reuse of biosolids in all scenarios was environmentally beneficial and cost effective. Their results showed that AD followed by land application was the most beneficial form of treatment due to low economic and energy costs as well as material reuse. The authors also noted the merit of additional material recovery methods such as struvite precipitation and recommended investigation into the benefits of its addition to the treatment train.

Murray et al. (2008) found similar results through comparing nine alternative treatment schemes and arranging them in order of environmental and economic impacts. Anaerobic digestion (without lime) was found to be generally the optimal treatment technology, while incineration, particularly if coal-fired, was the most environmentally and economically costly. Regarding end use of the sludge, offsets were found greatest in using sludge as a fertilizer, but they determined that all of the beneficial uses of sludge can improve the sustainability of conventional practices.

Most other authors who have conducted LCAs comparing AD to other waste treatment methods have also found AD to be preferable (Edelmann, Baier, and Engeli, 2005; Haight, 2005; Sundqvist, 2005; Chaya and Gheewala, 2006; Synthesis, 2007; Morris and Morawski, 2011; Rigamonti, Grosso, and Giugliano, 2010) although in one case Fruergaard and Astrup (2010) found that mass burn incineration of organic waste with efficient energy recovery was preferable to AD. This, however, is highly dependent on the type of organic waste and the water content. Therefore, AD provides clear environmental advantages over many other types of waste treatment, mainly due to its ability to recover energy as biogas and materials as usable biosolids.

2.2 Struvite Precipitation

The following sections review important literature related to struvite precipitation, including its economic and environmental implications. This subject is the focus on this thesis and is therefore investigated in detail.

2.2.1 Background

When AD is used for manure treatment, the liquid portion of the AD effluent still contains high levels of nutrients. Technologies are available that can recover the resources of N, P, and treated water, while offsetting impact due to discharge of the liquid effluent to the environment. Wilsenach et al. (2003) noted that dilution is never a suitable solution for waste because it destroys exergy (useful energy) and makes the treatment of wastewater costly. Waste streams must therefore be kept as concentrated as possible so that the maximum benefit can be derived from them. Therefore, the wastewater engineering of the future should be a “resource engineer”, considering both water management as well as loss of exergy (Guest et al, 2009; Wilsenach et al., 2003). Therefore, additions to the treatment train, such as struvite precipitation, to provide such resource recovery merit investigation.

2.2.2 Depletion of Phosphorus as a Resource

Phosphorus (P) is a nonmetallic element that is present in all living organisms. It is found in compounds called phosphates, which can include orthophosphate (such as H_3PO_4, HPO_4^{2-} and PO_4^{3-}), polyphosphate (such as adenosine triphosphate (ATP)), and organic phosphate (Metcalf and Eddy, 2004). Because phosphorus is an element it cannot be destroyed, but it can be dispersed to an extent that renders it difficult to recover or utilize (Linderholm, Tillman, and Mattssona, 2012). Phosphate rock reserves are ultimately limited and time horizons of 50-200 years have been suggested for its depletion (Emigh, 1972; Steen, 1998; Cordell et al., 2009; Déry and Anderson, 2007; Barnard, 2009; Van Vuuren 2010).

Phosphorus found in animal waste is a renewable resource and there are currently no environmental or technical reasons to prevent its recovery (Morse et al., 1998). Chen at al., (2012) suggested that AD followed by land application of the biosolids is a particularly good option for treatment of waste because of its low costs, low energy requirements, and suitability for material reuse. The authors, however, also noted that struvite recovery shows great promise, potentially becoming widely implemented in the future. Struvite recovery allows for recovery of P, reducing environmental stressors caused by phosphate mining. Therefore, precipitation of struvite from AD effluent as an additional treatment process provides significant advantages to the treatment system.

2.2.3 Factors Affecting Struvite Precipitation

The composition of struvite, containing equal molar concentrations of N, P, and magnesium, makes it marketable as a fertilizer; however, its nucleation and crystal quality must be controlled (Booker et al., 1999). Table 2.1 shows the general characteristics of struvite. The solubility of struvite is one of the main parameters controlling how precipitation will occur.

Table 2.1: Struvite Characteristics (Le Corre et al., 2009)

Chemical Name:	**Magnesium Ammonium Phosphate Hexahydrate**
Formula	$MgNH_4PO_4 \bullet 6H_20$
Aspect	White glowing crystal
Structure	Orthorhombic (space group Pmn2): regular phosphate octahedra, distorted $Mg(H_2O)_6^{2+}$ octahedral, and ammonium groups all held together by hydrogen bonding
Molecular weight	245.43 g/mol
Specific gravity	1.711 (ρ=1.711 g/cm^3)
Solubility	Low in water: 0.018 g/100ml at 25°C; High in acids: 0.033 g/100ml at 25°C in 0.001 N HCl, 0.178 g/100ml at 25°C in 0.01 N HCl
Solubility Constant	$10^{-13.26}$

Controlling the precipitation of struvite to provide for optimal quality is complex, as it is controlled by a variety of factors, including the crystal state of initial compounds, liquid-solid equilibrium thermodynamics, mass transfer between solid and liquid phases, reaction kinetics, as well as pH of the solution from which struvite may precipitate, supersaturation, mixing energy, temperature, and presence of foreign ions (Le Corre et al., 2009; Cervantes, 2009). Suspended solids can also affect struvite formation at total suspended solids (TSS) concentrations higher than 1000 mg/L (Alp, 2010), and storage in open conditions for periods more than 3 days should also be avoided to prevent ammonia volatilization, which can lead to lower struvite precipitation (Lin et al., 2012).

While struvite formation is complex, two main factors that can be controlled to ensure formation are the presence of magnesium, ammonium, and phosphate ions in molar concentrations of 1:1:1 as well as ensuring a pH range of 8-10 (Battistoni et al., 2000; Le Corre et al., 2009; Ohlinger et al., 1998). Specifically for efficient struvite precipitation in swine waste, a pH range of 8.5-8.7 is needed (Celen et al., 2007; Wang et al., 2004); however, it has been suggested that optimal ammonium removal by struvite occurs between a pH of 8.0-8.5. Above a pH of 8.5, calcium ions have also been found to interfere with struvite formation, creating calcium phosphates (Hao et al., 2009; see discussion in subsequent section on foreign ion effects). Therefore a pH of 8.5 can allow for efficient precipitation while limiting formation of some undesired precipitates.

Ensuring the proper molar ratios may often require addition of a magnesium source such as MgO, $MgCl_2•6H_2O$, or $MgCl_2$ (Choi, 2007). In cases where magnesium ion concentrations are high, further magnesium addition, which incurs higher cost, may not be necessary. The main soluble ions considered in most cases for struvite formation include: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4^-$, $MgOH^+$, Mg^{2+}, NH_4^+ and NH_3 (Cervantes, 2009).

Nucleation of struvite crystal in solution generally falls into two categories: primary nucleation and secondary nucleation (de Haan and Bosch, 2007). Primary nucleation occurs when crystals begin to form without the presence of existing crystals and secondary nucleation is when they form on existing crystals or other objects. When new crystals form in a supersaturated solution spontaneously, this is also called homogeneous nucleation. When they form or on the surface of objects that may be present, this is called heterogeneous nucleation. In homogenous nucleation, a cluster stabilizes after reaching a critical size and can then act as a nucleus for further growth. Homogeneous nucleation requires a high level of supersaturation; therefore, heterogeneous nucleation is more likely to occur and requires less saturation. (de Haan and Bosch, 2007 as cited in Bergmans, 2011). Secondary nucleation involves forming crystals using the presence of existing seed crystals and is used in commercial processes such as Ostara's fluidized bed reactor. This requires an initial purchase of struvite to begin the process. In experiments that tested the effects of seeding with struvite or sand, it was found that sand also increased P removal. The improvements gained, however, were not significant enough to justify additional costs or manipulations, though the author mentioned that more research is necessary in this regard (CEEP, 2003). Reactor designs, such as the fluidized bed reactor (FBR) can help overcome the need to continuously purchase seeding material, as the fluidized bed material serves as seed throughout the process.

In whatever method the crystal begins nucleation, supersaturation is necessary. Raising the pH can allow for supersaturation to be reached and can be accomplished through a variety of methods such as by caustic addition (often NaOH) or CO_2 stripping, using aeration. NaOH can be expensive for large-scale precipitation systems while creating undesirable salinity (Jaffer et al., 2002). The increase in pH due to caustic addition, however, occurs rapidly requiring a low hydraulic retention time (HRT) and small reactor volume and capital costs. Aeration avoids increases in salinity but incurs high energy costs while causing volatilization of ammonia, preventing its recovery. Furthermore, aeration often takes significantly longer than caustic to raise solution pH, increasing the reactor volume required. The slow rise in pH, however, and may also decrease Mg^{2+} requirements by allowing more Mg^{2+} to form struvite as opposed to other precipitates such as bobierrite and magnesite (Song et al., 2011). Therefore, there may be tradeoffs between higher capital costs for using aeration and higher operating costs for using caustic.

After supersaturation is reached in solution, an induction time is required for crystals to begin to form. In experiments involving solutions that lack foreign ions and contain high saturation levels, it has been found that higher saturation generally leads to shorter induction times (Ohlinger et al., 2000; Bouropoulos and Koutsoukos, 2000; Bhuiyan et al., 2008; Galbraith and Schneider, 2009). Other factors, such as level of agitation, can also affect induction times. For example, in solutions with similar saturation levels, the induction time without any agitation was approximately 24 hours, yet with agitation the induction time was only one minute (Le Corre et al., 2009). Induction times of 6-8 minutes are common in commercial fluidized bed struvite reactors (Ostara Inc and KEMA LLC, personal communication, December 4, 2013).

When struvite has been precipitated in piggery lagoons, such as anaerobic lagoons, in some cases the majority of the precipitate was estimated to be calcium phosphates (Barak and Stafford, 2006); however, as manure handling becomes more similar to wastewater treatment, such as by using AD, it is expected to become easier to control the quality and content of the precipitate (Barak and Stafford, 2006). Experiments and pilot scale reactors in Tennessee, USA and Japan for precipitating struvite from swine waste showed a mixture of struvite and calcium phosphates, by monitoring the changes in soluble concentrations; however, most experiments completed by 2003 with swine waste were not conducted with centrate or particularly AD centrate (CEEP, 2003). Other studies have noted that in swine wastes with low carbon/nitrogen ratio due to solids separation, such as centrate, struvite precipitation is more feasible and higher N-removal is achieved (CEEP, 2003). Therefore, understanding and implementing systems to control precipitation can improve precipitation performance.

2.2.4 Effects of Foreign Ions on Struvite Precipitation

The main difficulty in predicting struvite formation in wastewater is that many ionic species can influence the saturation of struvite by reacting with its component ions (Le Corre et al., 2009). Aside from magnesium, ammonium, and phosphate, which make up struvite, other ions are present in AD centrate such as potassium (K) and calcium (Ca). The presence of potassium and calcium as well as other foreign ions can make the thermodynamics of the system much more complicated, changing the availability of ions and possibly changing equilibrium constants. Furthermore, the presence of foreign ions allows precipitates to form other than struvite. Calcium ions can compete with magnesium to form precipitates such as calcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Suzuki et al., 2001; Bauer et al., 2007; Wang et al, 2006). Additionally, organic acids can complex with metal ions, increasing the solubility of struvite (Wrigley et al., 1992). These other precipitates, such as calcium phosphates, can also compete with struvite formation and become incorporated within struvite precipitates as impurities (Hao et al., 2009). The percentage of struvite in the precipitate, however, is expected to increase as magnesium becomes limiting, as the magnesium/phosphate ratio decreases, or as the ammonia/phosphate ratio increases (Gadekar et al, 2009).

Hao et al. (2009) showed how the presence of foreign ions can change precipitate contents across a pH range of 7-12 by precipitating struvite in both ultra-pure water and tap water that contained about 87 mg/L of calcium. In the tap water, the calcium could not be detected in crystal precipitates formed at pH values below 8.5; however, above a pH of 8.5, struvite formation was limited by formation of compounds such as tricalcium phosphate and monenite. Therefore, if calcium presents an issue for struvite formation, carrying out precipitation at a pH value of 8.5 can still allow for supersaturation, without introducing the effects of calcium.

Mathematical models and software, such as Visual MINTEQ v.3.0 and PHREEQC, have been used to predict possible precipitates formed during precipitation in wastewater. The possible precipitates found are shown in Table 2.2.

Table 2.2: List of Precipitates from Various Wastewaters Predicated in Equilibrium Models (Gadekar et al., 2009; Lin, 2012; Warmadewanthi, J. L., 2009)

Chemical name/Commercial Name	Chemical formula
magnesium ammonium phosphate, struvite	$MgNH_4PO_4\bullet 6H_2O$
magnesium hydrogen phosphate, newberyte (MHP)	MgH_4PO_4
magnesium phosphate, bobierrite (MP8)	$Mg_3(PO_4)_2\bullet 8H_2O$
trimagnesium phosphate, cattite (MP22)	$Mg_3(PO_4)_2\bullet 22H_2O$
hydroxyapatite (HAP)	$Ca_5(PO_4)_3)OH$
tricalcium phosphate, whitelockite (TCP)	$Ca_3(PO_4)_2$
monenite(DCP)	$CaHPO_4$
octacalcium phosphate (OCP)	$Ca_3(HPO_4)_2(PO_4)_4\bullet 5H_2O$
dcalcium phosphate dihydrate, brushite (DCPD)	$CaHPO_4\bullet 2H_2O$
calcium carbonate, calcite	$CaCO_3$
magnesium carbonate, magnesite	$MgCO_3$
nesquehonite	$MgCO_3\bullet 3H_2O$
dolomite	$CaMg(CO_3)_2$
huntite	$CaMg_3(CO_3)_4$
magnesium hydroxide, brucite	$Mg(OH)_2$
potassium struvite	$MgKPO_4\bullet 6H_2O$

2.2.5 Unintentional Struvite Precipitation

Unintentional and uncontrolled struvite precipitation is a common problem in wastewater treatment plants, causing scaling in pipes and reactors (Stratful et al., 2001). Undesired precipitation of struvite, in the form of scale, can be very costly, requiring cleaning or replacement of pipes. While acid washing can remove struvite precipitate, currently the most effective method of struvite scale removal is a hammer and chisel (Stratful et al., 2001). Annual costs for a mid-size wastewater treatment plant (WWTP) (~ 95,000 m^3/day) related to struvite deposit damage can easily exceed $100,000 (Benisch et al., 2000). Such unintentional precipitation not only causes damage to the system but also renders the precipitate unrecoverable. While these scaling issues have been mostly observed in municipal WWTPs, understanding these issues can help ensure that systems for treatment of swine waste generated in CAFOs are designed to prevent unintentional precipitation. Controlled struvite precipitation has been applied to municipal systems, not only to prevent problems throughout the wastewater treatment process but also to avoid phosphorus feedback into treatment plants by centrate recycle, which can responsible for 20-50% of the total phosphorus entering the WWTP (Jaffer et al., 2002).

2.2.6 System Configurations for Controlled Struvite Precipitation

A variety of system configurations and designs can be employed for phosphate recovery. Furthermore, phosphate can be recovered at various points in the wastewater treatment process. These points include the centrate stream, digested sludge, and sludge ash. A summary of common techniques is shown in Table 2.3. While the techniques implemented to date for struvite recovery have mainly been designed for treatment of domestic wastewater and sludges, their success shows great promise for implementing similar type systems for treatment of swine waste, which contains higher levels of nutrients.

Table 2.3: Summary of Phosphate Recovery Techniques (adapted from Bergmans, 2011)

Technique	Company/ Institute	Applied on	Developing Phase	Product	Treatment Principle
AirPrex	PCS	Digested Sludge	Fully Operational	Struvite	Airlift reactor followed by sedimentation
-	Waterschap Velt en Vecht	Digested Sludge	Fully Operational	-	Aeration in a basin, no separation
Crysta-lactor	DHV	Centrate/ plant effluent	Fully Operational	Struvite/Phenyl dichlorophosphate (MPCP)/Potassium metaphosphate (KMP)	FBR
Phosphaq	Paques	Centrate/ plant effluent	Fully Operational	Struvite	CSTR with separation in a special outlet construction
Pearl	Ostara	Centrate / plant effluent	Fully Operational	Struvite	FBR
WAS-STRIP	Ostara	Waste Activated Sludge	Fully Operational	P and Mg rich solution	Anaerobic P+Mg release tank
Seaborne	Seaborne	Centrate	Fully Operational	Struvite	CSTR followed by centrifuge
ASH DEC	ASH DEC	Sludge ash	Developing	P-rich granules	Chemical/thermal treatment of sludge ash
-	Ebara Environmental Engineering	Digested Sludge	Developing	Struvite	CSTR with separation in a hydrocyclone
SEPHOS	Ruhrverbrand	Sludge ash	Developing	$CaPO_4$	CSTR followed by sedimentation
Phred	KLA Environmental Services	Wastewater runoff (1% DS)	Fully Operational	Struvite	FBR
Multiform Harvest	Multiform Harvest	Centrate	Fully Operational	Struvite	FBR

2.2.7 Struvite Precipitation from Anaerobically Digested Swine Waste

Swine waste provides a significant source of P that can be recovered through struvite precipitation. This is due in large part to their diet and digestive functioning. The most significant components of pig diets are seeds (cereal grains) or products from seeds, such as oilseed meal and grain by-products (Kornegay, 2001). A significant portion of the P in these foods is in the form of phytates, which are the salts of phytic acid; however, swine lack the enzyme phytase, which allows for metabolization of phytates, causing high P content in swine wastes (Kornegay, 2001; Lammers et al., 2007; Jongbloed and Kemme, 1990). Dietary supplements of bioavailable P are often required for optimal animal growth (NRC, 1998). Kebreab et al. (2012) summarized common mitigation strategies to increase bioavailable P, which are shown in Table 2.4. One of these solutions is the development of transgenic pigs, whose saliva contains the phytase enzyme, reducing the P content of their manure by 75% (Golovan et al, 2001). However, because of ethical considerations, it is not expected that transgenic pigs will be used in livestock production in the near future (Kebreab et al., 2012). Therefore, swine manure will likely continue to contain high P content in the near future.

Table 2.4: Mitigation Options to Increase P Availability in Swine Diet (Kebreab et al., 2012)

Mitigation	Increase in available P (%)	References
Phytase	2.0-204.7	Kerr et al., 2009; Goebel and Stein, 2011; Rojas and Stein, 2011; Poulsen et al., 2010
Transgenic animal	81.2-90.4	Golovan et al., 2001
Low-phytate plant	38.4-41.3	Hill et al., 2009; Sands et al., 2001
High-phytase plant	18.2-163.2	Zhang et al., 2000
Liquid feeding	18.4-34	Lyberg et al., 2006; Blaabjerg et al., 2010

A number of studies have performed struvite precipitation from both real and synthetic swine waste from raw sources, AD effluent, and AL effluent. Results of these studies were compiled by Lin (2012) and are shown in Table 2.5. These studies show generally high P

Table 2.5: Studies of Struvite Precipitation from Real and Synthetic Anaerobically Digested Swine Waste (Lin, 2012)

Authors	Waste Source*	Reactor Type	Max P removal	Molar Ratios Based on P			Ca:Mg	Minerals Formed
				Mg^{2+}	Ca^{2+}	NH_4^+		
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	13.9	0.75	Struvite, Monetite, Brushite
Huang et al., 2010	AD	Batch	96%	0.16	1.99	32.21	12.22	MgO, MgNaPO4
Jordaan et al., 2010	AD	Batch	80%	2.7	6.47	195.77	2.4	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, Cattite
Korchef et al., 2010	S	Batch	---	0.44	0.06	1	0.13	Struvite
Korchef et al., 2010	S	Batch	75%	1	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	---	1.02	---	Struvite
Ohlinger et al., 1998	S	Batch	---	1	---	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%	1.4	1.63	11.2	1.17	struvite, calcium phosphates
Song et al., 2007	S	Batch	90%	1.4	---	11.2	---	Struvite(diff. 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%	2.5	2.63	38.9	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%	0.2	0.13	1.39	0.67	struvite, calcium phosphates
Wrigley., 1993	AD	Batch	90%	3.91	19.85	210.6	5.08	struvite, apthitatite, thermardite
Ye et al., 2011	AD	Batch	100%	1.85	0.92	8.54	0.5	struvite, calcium phosphates

*Waste source abbreviations: Raw Manure (R), Anaerobic Lagoon Effluent (L), AD effluent (AD), Synthetic Waste (S) removal of at least 75% and in most cases struvite was formed in the precipitation reaction, though often concurrently with other minerals.

2.2.8 Effectiveness of Struvite as a Fertilizer

Struvite contains approximately 5% N and 12% P by weight, with a fertilizer analysis in the oxide form (NPK value) of approximately 5-28-0, meaning that it contains 5% N, 28% P_2O_5 and 0% K_2O. It also contains approximately 10% magnesium which is beneficial for crops such as citrus. Struvite has been proposed as a fertilizer since the mid-1800s. It even chemically forms in soils fertilized with other phosphates such as ammonium phosphate, ammonium polyphosphate, and diammonium phosphate (DAP) when magnesium is present in the soil (Lindsay and Taylor, 1960; Lindsay et al., 1962; Ghosh et al., 1996 as cited in Barak and Stafford, 2006). Therefore, it is often present in soils where traditional phosphate fertilizers have been applied. When applied, the slow release of struvite is due not only to dissolution but primarily to nitrification of its ammonium (Bridger et al., 1962). Many of the agronomy studies assessing the effectiveness of struvite as a fertilizer are from the “grey” literature. While it is not the focus of this review, it should be noted that other precipitates formed by removing phosphate from wastewater do exist, the most common being metal salt precipitation, using metals such as iron and aluminum; however, such precipitates are unrecoverable for industrial processing into fertilizer (Debashan and Bashan, 2004). Struvite, therefore, allows for removal of phosphate while holding significant fertilizer potential.

A number of studies have evaluated the effectives of struvite as a fertilizer by comparison with traditional or alterative P fertilizers. These studies are explained in detail below and their results are summarized in Table 2.6.

Johnston and Richards (2003) compared eleven precipitated phosphate materials for plant growth as compared to monocalcium phosphate (MCP), a water soluble P source. Pot trials on two soils were used, with perennial ryegrass as the test plant. The eleven phosphates included nine different struvites, either recovered from various sources or synthetically formed. The variables measured were grass dry-matter yield, grass P concentration, and uptake of P in the harvested grass. The precipitated phosphates were found to not statistically differ from each other or MCP. This shows that struvites of various sources can all perform at par with traditionally accepted MCP fertilizers.

Table 2.6: Fertilizer Effectiveness of Struvite as Compared to Alternative and Conventional P Fertilizers

P Fertilizer Compared	Plant Growth Results	Source
Monocalcium Phosphate (MCP)	Equal performance with struvite	Johnston and Richards, 2003
Triple Superphosphate (TSP)	Struvite showed equal or superior performance	Cabeza et al., 2011; Weinfurtner et al. N.D as cited in CEEP, 2009
Calcium Phosphate	Struvite superior in neutral soils (calcium phosphate only effective in acidic soils)	Cabeza et al., 2011
Fused Superphosphate-Urea (FSP-urea)	Struvite showed equal or superior performance	Liu et al (2011)
Diammonium Phosphate (DAP)	Struvite showed superior performance. 36 mg struvite-P was equal to: 100 mg DAP-P for dry matter production, 42mg DAP-P for P up-take, and 64.9 mg DAP-P for residual Bray P.	Barak and Stafford (2006)

Cabeza et al. (2011), performed pot and field growth studies with recovered struvites, a recovered calcium phosphate, alkali sinter phosphate (sinter-P), a heavy metal depleted sewage sludge ash (Sl-ash), a cupola furnace slag made from sewage sludge, and a meat-and-bone meal ash (MB). Experiments were performed in both acidic and neutral soils, with triple superphosphate (TSP) providing a measure of comparison. They found that struvite was as equally effective as TSP in both acidic and neutral soils. However, calcium phosphate and sinter-P were only effective in acid soil, while cupola slag was effective in neutral soil. Sl-ash and MB were found to not be effective. Other authors have performed maize pot trials using a similar range of fertilizers (Weinfurtner et al. N.D as cited in CEEP, 2009). They found mixed results but found that recovered struvite products were comparable or slightly better than triple super phosphate.

Liu et al (2011) performed pot experiments with struvite recovered from swine manure slurry (as described in Rahman et al., 2011) compared to fused superphosphate-urea (FSP-urea) for growing maize crop. The plant height and diameter, leaf number and area, biomass yield, nutritional composition of the maize plants, and N_2O emissions were measured. Results showed that plant height and diameter as well as nutritional composition were statistically similar between struvite and FSP-urea. Leaf area and biomass yield, however, were higher in struvite treated maize. Furthermore, N_2O emissions were lower for struvite treated soil, showing that struvite can help reduce greenhouse gas emissions from crop cultivation. Therefore, struvite performed with equal or superior effectiveness as a fertilizer as compared to FSP-urea, a traditional phosphate and nitrogen fertilizer.

Because diammonium phosphate (DAP) is an extremely common fertilizer (more common than MCP), Barak and Stafford (2006) performed pot tests to compare it to struvite as a fertilizer. Two rates of DAP (50 and 100 mg DAP-P/kg) and one rate of struvite (36 mg struvite-P/kg) were tested. All of treatments were brought to a uniform N rate by using urea. Results showed that struvite “outperforms DAP on a unit-for-unit basis” in terms of dry matter production, P uptake, and extractable residual P (Barak and Stafford, 2006). Analysis of dry matter production showed that 36 mg struvite-P/kg treatment was statistically identical to 100 mg DAP-P/kg treatment. Furthermore, examination of the amount of phosphorus up-take in the aboveground plant showed that 36 mg struvite-P/kg treatment was equivalent to 42 mg DAP-P/kg. Analysis of average residual Bray P showed that 36.4 mg struvite-P/kg soil treatment was equivalent to that expected of 64.9 mg DAP-P/kg soil. Therefore, most growth studies show that struvite can perform on par with or outperform conventional fertilizers.

2.2.9 Cost Considerations and Assessments of Struvite Recovery Systems

A number of authors have assessed the market value of struvite fertilizers, with results ranging from $0.198 per kg to $2.64 per kg (Moody et al., 1999; Jaffer et al., 2002; Choi, 2007; Forrest et al., 2008); however, price of struvite fertilizers can vary widely due to a variety of factors, such as size of an order and brand name. Struvite tends to be higher priced than other fertilizers due to the advantage of being slow-release. Moody et al. (1999) and Jaffer et al. (2002) suggested that struvite systems can be economically feasible, while companies such as Ostara Inc., Multiform Harvest, and Kansas Environmental Management Associate's (KEMA) have also demonstrated profitability.

Several businesses have patented, manufactured, and marketed struvite fertilizers, including WR Grace & Company in the 1960s as well as Ostara Inc. and KEMA LLC more recently. WR Grace & Company's struvite was formed by adding magnesium oxide or magnesium hydroxide to monoammonium phosphate. The high cost of production restricted this to high value-added uses, such as floriculture (Barak and Stafford, 2006). Treatment with ammonia of rock phosphate and olivine, to which sulfuric acid has been added, has not been considered an economically feasible process for generating struvite (Barak and Stafford, 2006)

Shepherd et al. (2009) performed a cost analysis on a struvite precipitation from manure slurry utilizing an air sparged tank reactor (ASTR) to raise pH (using aeration) and a hydrocyclone for solids separation. The case study was for a typical swine production facility with 10,000 pigs/year. Economic analysis was performed under the assumption that the system reduced 90% of the dissolved reactive phosphorus (DRP) with 80% recovery, even though their tests showed only an 18% recovery, due to poor hydrocyclone performance. Scaling up of the equipment costs was accomplished by multiplying the pilot scale costs by the ratio of the full scale to pilot scale size (volume, flow rate, horsepower), raised to an economy of scale sizing exponent as shown in Equation 2.1:

$$Cost_{FullScale} = Cost_{PilotScale}\left[\frac{Size_{FullScale}}{Size_{PilotScale}}\right]^{n} \tag{2.1}$$

where n = economy of scale sizing exponent (0.3, Brown, 2003 as cited in Shepherd et al., 2009).

Operating costs were assessed with an annual treatment capacity of 450 million L/year (1,232 m^3/day) and included direct costs of energy and chemical consumption as well as indirect costs of interest, depreciation, and selling price. The selling price, including labor, of the treatment service was set to achieve a 10% return on investment. Therefore, profit was not based on selling the struvite but selling the treatment service. Annual interest was set at 6% for a 10 year loan, a 10% straight line depreciation was assumed for an equipment lifetime of 10 years. $MgCl_2$ was also used with a price of $0.95/kg. The yearly cost of treatment was estimated to be $222,000 equating to $22.20/pig space ($8.88/finished pig, assuming 2.5 turns/year) or $0.0353/L of deep pit manure slurry treated ($0.134/gal). Therefore, the cost can be normalized by the daily treated volume at $608 per 1000$m^3$/day. Custom feeding operations in western Iowa are currently paid an average of $13.50 per finished pig for operational management, facilities, utilities, labor, and manure management. Therefore, the authors concluded that a phosphorus treatment cost of $8.88/finished pig (66% of the total payment per pig) renders an ASTR-hydrocyclone system economically unfeasible for swine finisher manure slurries. The authors' findings, however, do not indicate that other systems, which utilize different system configurations and treat waste exiting from different treatment processes, are not economically feasible. Therefore, investigation into such systems is necessary.

Bergmans (2011) performed a cost analysis on struvite systems taking into account the cost savings due to lower disposal costs because of decreased sludge mass. His assumptions and results are shown in Table 2.7. The assessment shows that economic benefit is not only provided by recovery and sale of struvite but also from savings due to reduction in sludge volume and avoidance of sludge disposal.

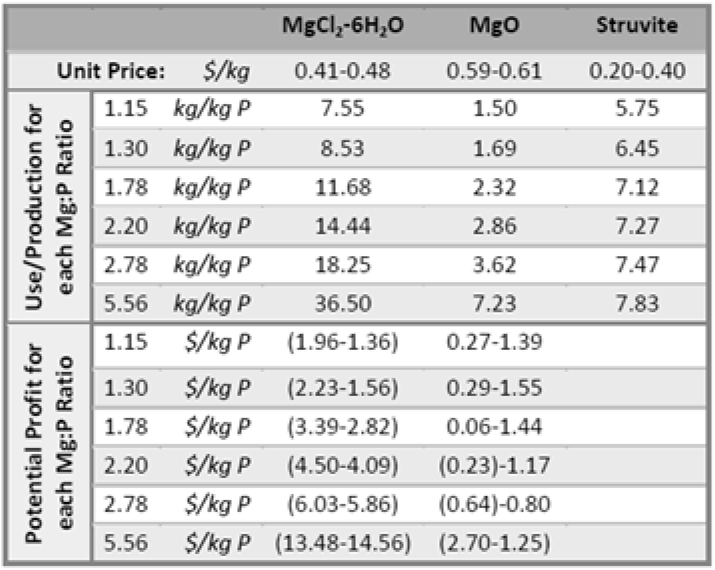
Table 2.7: Struvite System Cost Analysis (Bergmans, 2011)

Assumptions/Calculations **Prices from 2009 converted from Euros to USD with 2009 exchange rate of 0.748 Euro/$ (IRS)**	**Profits ($/year)**
Income from selling struvite	
Digested sludge: 2,000 m^3/day or 730,000 m^3/year	84,225
Struvite formation: 2.3 g/L or 1679 tons/year	
Assumed struvite recovery: 75% or 1259 tons/year	
Selling price of struvite: $66 /ton	
Savings from reduction in sludge volume	
Costs of dewatered sludge disposal avoided: $88 /ton	110,963
Total	195,187

The addition of magnesium to centrate is often required to provide for 1:1 of Mg:P so that most of the P can be recovered. Common forms of magnesium that are used include $MgCl_2$, $MgSO_4$, $Mg(OH)_2$, and MgO is considered the most significant operational expense of struvite precipitation systems and is estimated to contribute up to 75% of overall production costs

(Dockhorn, 2009). Lin (2012) performed an analysis of the cost of magnesium addition, assuming a cost of \$0.41-\$0.48/kg for magnesium chloride or \$0.59-\$0.61/kg for magnesium oxide. He found that MgCl addition was not economically feasible. MgO addition was economically favorable between Mg:P ratios of 1.30-1.78, which are also the most favorable ratios for P removal. His analysis is shown in Table 2.8.

Table 2.8: Analysis of Magnesium Addition Costs (Lin, 2012)



			$MgCl_2$-$6H_2O$	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)

Alternative sources of magnesium have also been investigated. Lahav et al. (2013b) investigated the use of seawater nanofiltration (NF) concentrate as an inexpensive magnesium source. They estimated that costs for magnesium sources such as $MgSO_4$•$7H_2O$ and $MgCl_2$•$6H_2O$ to be \$2.787 and \$1.171 per kg magnesium, respectively. This is significantly higher than Lin's (2012) estimates. They estimated the cost of magnesium from nanofiltered seawater concentrate to be \$0.25 /kg Mg for plants located near the shore. Therefore, even if the price was increased by 100% (\$0.5 /kg Mg) it would still be less than half of their estimated costs for conventional magnesium sources. Disadvantages of using NF concentrate is that it also includes other ions, such as chloride and sodium, which add to the salinity and environmental impact of the wastewater, and calcium that may interfere with struvite precipitation by forming calcium phosphates. The authors, however, considered the advantages to significantly outweigh these disadvantages.

2.2.10 Life Cycle Assessments of Struvite Recovery Systems

Investigation of struvite recovery systems not only requires understanding of the process, but also an understanding of its optimization and application to a variety of system types, while ensuring that it represents a sustainable approach. A handful of LCAs have been performed on phosphorus recovery methods, such as struvite. Kalago and Moneith (2008) note the need for more LCAs to be performed on systems for energy and resource recovery from waste, likewise demonstrating the need for LCAs of other similar systems, such as recovery of N from AD centrate.

Linderholm et al. (2012) carried out an LCA in Sweden in the context of providing phosphorus for application in agriculture. Four methods of recovery and reuse were considered, including: mineral fertilizer, certified sewage sludge, struvite precipitated from wastewater, and phosphorus recovered from sludge incineration. These were assessed using a comparative LCA approach to determine impact in the categories of global warming, eutrophication, energy demand and cadmium flows to farmland. The functional unit chosen was 11 kg P (25.2 kg P_2O_5). The study found that using sewage sludge directly on farmland was the most efficient option in terms of energy and emissions of greenhouse gases, but also added the most cadmium to the soil. Recovery of P from incinerated sludge was the most energy demanding option and gave the greatest emissions of greenhouse gases. Furthermore, it was determined that large-scale recovery of phosphorus as struvite is not a suitable technique for Sweden due to technical and cost reasons. A limitation of the study, however, was that the assessment was only carried out in the Swedish context and does not necessarily apply to other contexts or countries. Moreover, P recovery methods were not compared to a baseline of fertilizer needs. For example, impact credits were given for N content of the recovered material, however, P content did not receive credits. An alternative method for providing a control would be to compare the methods to a baseline of traditional fertilizer application. Furthermore, because struvite recovery and field application of sludge or biosolids are not exclusive processes, they can both be performed to allow for maximum recovery potential.

Britton et al. (2004) looked at struvite precipitation at a wastewater treatment plant in Edmonton, Canada by building a pilot scale system and performing an LCA on the environmental impacts if it was scaled up. It was found that 75% of the phosphorus and 20% of the nitrogen could be recovered. The full-scale design would produce up to 1200 tons of struvite fertilizer per year, with a 20% reduction in phosphorus load and 5% reduction in ammonia load on the wastewater treatment plant (Britton et al., 2004). There would also be a 12,000 ton offset of equivalent CO_2 emissions. This demonstrates a significant advantage of struvite recovery due to its ability to offset environmental impacts.

2.3 Ammonium Removal and Recovery Systems

AD with field application of biosolids, followed by struvite precipitation from the AD centrate allows for recovery of valuable nutrients and energy, however, the centrate still contains high levels of N. This N must not only be removed to avert environmental impacts, but can also be recovered as another valuable resource. Use of natural zeolites for ion exchange (IX) of N has been investigated as a means for recovering N from the centrate.

Natural zeolites are hydrated aluminosilicates that have been used widely in a variety of applications including agriculture (Van Bekkum et al, 2001; Allen et al., 1995; Colella et al., 2002; Colella et al., 2000; Polat et al., 2004; Breck, 1974; Hershey et al., 1980; Mumpton, 1999) and environmental remediation (Misaelides et al., 1999; Bowman, 2003; Chmielewska, 2003a; Chmielewska, 2003b; Tian and Wen, 2004; Pilchowski and Chmielewska, 2003; Puschenreiter and Horak, 2003; Gebremedhin-Vaile, 2003; Ponizovskij, 2003). Zeolites can serve as cation exchange materials that have affinity for ammonium, potassium, sodium and calcium (Breck, 1974; Jorgensen et al., 1976; Gottardi and Galli, 1985; Tomazovic et al., 1996; Huang and Petrovic, 1994; Mumpton, 1999).

A variety of types of zeolites exist, but two types are mined and distributed in industrial quantities, namely Clinoptilolite and Chabazite. Clinoptilolite is the more abundant zeolite, with approximately four productive deposits in the United States. Chabazite, however, is known to often have much higher cation exchange capacities (Levya-Ramos et al., 2010), yet is significantly higher in price. It should be noted, however, that cation exchange capacities and costs of zeolites will differ between deposits, even for the same type of zeolite. St. Cloud Mining Company (Winston, New Mexico) mines what is currently the only high-grade productive large-scale deposit of chabazite in the world, yet a low grade deposit also exists in Italy (D. Eyde, personal communication, December 27, 2013). Due to the low amount of chabazite available as well as technological difficulties in excavation of its high-grade deposit, its cost is estimated at around $3,500 per ton, while clinoptilolite can be estimated at about $250 per ton (D. Eyde, personal communication, December 27, 2013). The high price of chabazite often reserves it for high value applications, yet its higher cation exchange capacity may make it a more economical choice in some applications.

In agricultural and environmental applications (cited above) zeolites have been used successfully as soil amendments and fertilizers as well as for removal of ammonium from wastewaters. Taking advantage of its utility in both of these areas allows for multi-use potential of natural zeolites to remove ammonium from swine centrate as a cation exchange material with subsequent field application as a slow release, N-rich fertilizer and soil amendment. Lind et al. (2000) used struvite precipitation followed by IX with natural clinoptilolite in source separated human urine and found that most of the P and K can be recovered, while 65-80% of the N can be recovered. They noted that a mixture of struvite and ammonia-rich clinoptilolite can serve as a beneficial soil conditioner. Furthermore, because clinoptilolite mixed with apatite is a well-known slow release fertilizer, struvite and ammonia-rich clinoptilolite is likely to have the same qualities (Lind et al., 2000). While zeolites show great potential in such applications, the life cycle environmental impacts and costs of implementing such systems is unknown.

2.3.1 Life Cycle Assessments of Ion Exchange Systems

Few studies have assessed life cycle environmental impact of ion exchange systems. Choe et al. (2013) performed an LCA to compare non-selective IX and selective IX for perchlorate removal from drinking water. Non-selective IX resin reaches breakthrough in a much a shorter time because of exchange of non-target ions. The resin, however, is then regenerated using a brine solution which requires disposal (though some modern ion exchange systems can now utilize full brine recycle). The selective IX resin can be used for longer periods for perchlorate removal, but regeneration has been found to be ineffective, and eventual disposal of the resin is therefore necessary. LCA findings showed that non-selective IX had far more associated environmental impact, mainly due to the resin regeneration process. Furthermore, they found that consumables were the most significant contributors to environmental impacts and therefore assessment of consumables can typify impacts of the entire system, as is often the case in water and wastewater treatment systems. They also note that industry has moved toward using selective IX due to its lower costs, while their own cost assessment shows total selective IX costs to be 0.0241 cents per gallon and non-selective to be 0.0459 cents per gallon (in 2010 dollars), approximately double that of selective IX.

The lower environmental impacts and costs of selective IX for perchlorate removal, however, may be particular to the system conditions. The perchlorate concentrations, for example, are relatively low, allowing for selective IX systems to run for a significant length of time before replacement of IX resin. In other types of systems, such as IX of ammonium from wastewater, concentrations are much higher and may require larger amounts of IX material that incur higher environmental impacts and costs. Yet, no previous studies have taken into account recovery of ions (such as ammonia), which could dramatically offset the increased environmental and economic impacts.

In a few cases, life cycle environmental impact of IX has been compared to alternative systems. Choe et al. (2013) compared selective IX to several alternatives for perchlorate treatment of drinking water, including biological reduction with acetate, and catalytic reduction processes, and found that IX had far less impacts than the other systems. However, Ras and von Blottnitz (2012) compared IX to reverse osmosis (RO) for desalination of drinking water and found RO to have lower environmental impacts. The environmental impacts of IX, therefore is likely to be application dependent. No previous LCAs have been found to compare ammonium removal from wastewater to alternative treatments. Therefore, the results for this particular case study are likely to differ from the few previous LCA studies on IX.

CHAPTER 3: MATERIALS AND METHODS

The research performed in this thesis can be organized into two general categories: experiment-based and modeling-based. This chapter describes the materials and methods used in each experimental and modeling-based evaluation.

3.1 Experimental Materials and Methods

The proposed process for recovery of energy and nutrients for swine waste was performed at bench scale within the Environmental Engineering laboratory at the University of South Florida (USF). The goal of the experiments were to demonstrate operational feasibility, provided greater understanding of the performance of the system, and also provided a case study of data and parameters to be used in the LCA and LCCA. The following sections describe the operation of the three major sub-systems as well as parameters measured. A schematic of the entire system, with important sampling points, is shown in Figure 3.1 and Table 3.1 shows the measurements performed at each sampling point.

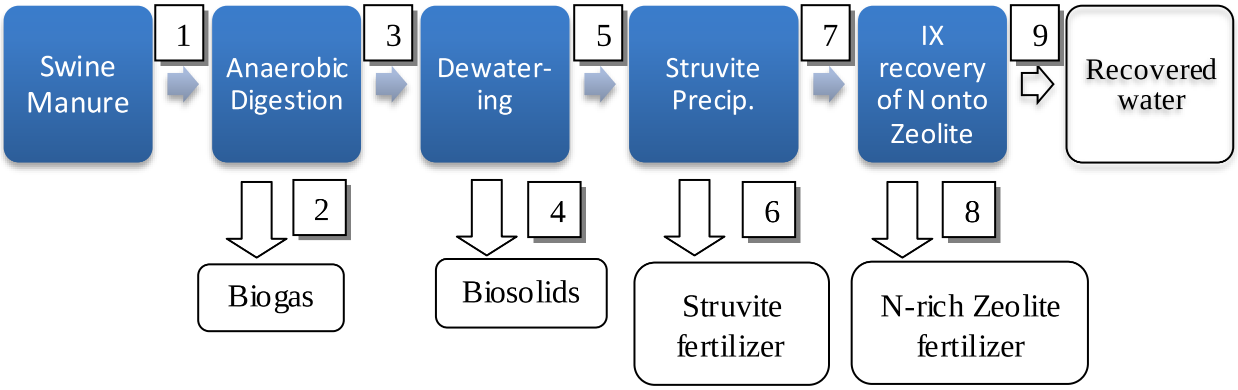


Figure 3.1: Overall Experimental Scheme As Well As Sampling Locations for Laboratory Tests

Table 3.1: Measurements Performed at Each Sampling Point

No.*	Description	Unfiltered Sample Measurements	Filtered Sample Measurements
1	Swine Waste Feed for AD	TN, TS, VS, pH, Alkalinity, VFA,TP,CP, *E. coli*	Soluble COD, Soluble N, SP, SRP,IC
2	Biogas Production	Gas Volume	
3	AD effluent	TN, TS, VS, pH, TP	
4	Biosolids recovery	*E. coli*	
5	Centrate before Nutrient Recovery	Alkalinity, VFA,CP, *E. coli*, TSS	Soluble COD, Soluble N, SP, SRP,IC
6	Struvite Precipitate Recovered	XRD, SEM imaging, SEM-EDX	
7	Centrate after Struvite Recovery	TN, TSS, pH, Alkalinity, VFA, CP, *E. coli*	Soluble N, SP, SRP, IC
8	Zeolite-Nitrogen Recovery	-	-
9	Recovered Liquid Stream	TN, TS, TSS, pH, Alkalinity, VFA, CP, *E. coli*, Conductivity	Soluble N, SP, SRP, IC

*Numbers refer to Figure 3.1

3.1.1 Anaerobic Digestion

A pilot-scale anaerobic digester, with a 30L overall volume and a 26L working volume, was used in this study. The reactor was started using a seed sludge provided by three 2L bench-scale digesters that had been operating in the USF Environmental Engineering laboratory for over a year (Kinyua, 2013). AD sludge from the St. Petersburg, FL municipal wastewater treatment plant was also added as seed during startup. The pilot-scale reactor was utilized to obtain sufficient effluent volumes which were necessary for the ion exchange experiments as well as for generating larger amounts of struvite precipitate needed for XRD analysis. The reactor was modified from an off-shelf 30 Liter (8 gallon) MiniBrew fermentation reactor (Hobby Beverage Equipment Company, Temecula, Ca). The assembly is shown in the Appendix (Figure A.1). A uniform temperature of 35°C was maintained using a Johnson Controls, Inc (Milwaukee, WI) A419ABG-3C electronic temperature controller and a BriskHeat 300 watt, 6 inch wide drum, heavy duty poly drum heater (Columbus, OH). The digester was insulated using standard R-13 fiberglass insulation. Mechanical mixing was achieved by periodic manual agitation of the reactor while the reactor was closed. The reactor was sealed using a Dow Chemical Company “Great Stuff: Gaps and Cracks” insulating foam sealant. The volume of biogas produced was measured by water displacement using a wet tip gas meter (Nashville, TN).

The reactor was operated semi-continuously at a 21-day solids retention time (SRT) by feeding it 2.6L of waste three times per week. This SRT was shown to have the highest gas production in bench scale experiments (Kinyua, 2013). Swine waste was collected weekly from Four Rivers Farm, a small pig farm of less than 30 pigs in Plant City. Due to the nature of the pig farm operation, the waste was not mixed with pig urine; therefore, urea (Urea U15-500; Fisher Chemical; Fair Lawn, NJ) was added to the waste to obtain the desired N concentration. Before feeding, the waste was blended with local groundwater to obtain a consistent solids concentration of 5% (mass/volume). The reactor was operated for three SRTs (63 days) before nutrient removal/recovery experiments were performed. The experiments were performed three times, every other week.

3.1.2 Struvite Precipitation

Effluent collected from the 30L reactor was centrifuged at 4000 RPM for 10 minutes in a Thermoscientific Sorvall Legend RT Plus (Waltham, MA) centrifuge to remove biosolids. Precipitation was performed on the supernatant (centrate) in an approximately 2L well-mixed batch reactor, modified to simulate fluidized bed reactor (FBR) operation. The reactor was seeded with precipitate produced in previous batch experiments. The pH of the centrate was raised to 8.5 by 2N NaOH addition. Although the pH could also be raised using aeration (CO_2 stripping), NaOH was chosen because it is the most commonly used method in commercial systems and our centrate volumes were too low to evaluate both methods and still allow for recovery of the precipitate for crystal characterization. A 2 watt, 5 L/min submersible pump (Zhejiang Sensen Industry Co., Model HJ-311) was used to fluidize and mix the particles for approximately 8 minutes, which is a common operational HRT of full scale FBRs for struvite precipitation, during which induction occurs(Ostara Inc and KEMA LLC, personal communication, December 4, 2013). The centrate was then centrifuged again at 4000 RPM for 10 minutes to remove the solid precipitate from solution. The precipitate was dried in a desiccator at room temperature (~23°C) and preserved for XRD and SEM-EDX analysis.

3.1.3 Ion Exchange Methods

After precipitation of struvite, the centrate was used in ion exchange experiments for N recovery. Two types of natural zeolites were used as ion exchange materials, chabazite (ZS500H) and clinoptilolite (ZK408H). The zeolites used in the experiments were obtained from St. Cloud™ Zeolite (Winston, New Mexico), one of the few producers of natural chabazite in the world. The dry zeolite particle size ranges from 0.6mm to 1.0mm.

Zeolites were washed with deionized water to remove residual powder and dried at 100°C for 24 hours. The zeolite was then pretreated by soaking it in local groundwater (Tampa, FL) for 3 hours and placed on a shaker table at 200rpm. In preliminary experiments this was shown to increase ammonium exchange capacity. Subsequent to pretreatment, the zeolite was again rinsed with deionized water and dried at 100°C for 24 hours.

Previous NH_4^+-N adsorption studies had been conducted in the USF Environmental Engineering laboratory using synthetic AD swine centrate. A concentration of 1000 mg-N/L NH_4^+ was used, with the presence of competing cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}). A dose of 150 g of zeolite per liter of waste resulted in NH_4^+-N recovery of 88% and 46% for chabazite and clinoptilolite, respectively. Based on these results equation 3.1 was used to determine the grams of zeolite to be added in the adsorption batch reactor for N-recovery:

$$M(g\ zeolite) = \frac{150g\ zeolite}{1000\ mg-N/L} * Ci \tag{3.1}$$

where M is the mass of zeolite required and Ci is the initial NH_4^+ (mg-N/L) concentration in the waste. From equation 3.1 it was calculated that approximately 72 g of chabazite and 144 g of clinoptilolite was necessary for at least 80% N-recovery.

The two adsorption batch reactors for N-recovery consisted of a 1 L beaker containing 0.8 L of the real digested swine centrate, following struvite precipitation. Because struvite precipitation raised the pH of the waste to 8.5, the pH was reduced to 7.5 with 4M HCl for efficiency of ion exchange. The corresponding dose of the two types of zeolites were added and mixed at 100 rpm for 24 hours at room temperature using a PB-700 Jartester mixer (Phipps & Bird Inc.; Richmond, VA). Sampling at 4 and 24 hrs were performed since adsorption kinetics for the two zeolites are significantly different.

3.1.4 Analytical Methods

Before and after forced precipitation, concentrations of major cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}) were determined by ion chromatography (IC) (APHA, 2012). IC samples were filtered using Fisher brand 0.45µm syringe filters. A Metrohm 881 Compact IC pro (Riverview, FL) was used for IC analyses. The standards used for the IC analysis include concentrations of 1.0, 2.5, 5.0, 15, 50, and 100 mg/l for all ions. IC detection limits are shown in Table 3.1. The cation eluent consisted of 1.7 mM nitric acid and 0.7 mM dipicolinic acid (pyridine-2,6-dicarboxylic acid) at 32°C with a flow rate of 0.9 mL/min. Sample injection volumes were 20 µL.

Standard methods were used to measure CH_4 content of the biogas (6211 C), COD (5200 B), VS, TS (2540 G), and alkalinity (2320 B) (APHA, 2012). The method described by Montgomery et al. (1962) was used to measure VFA concentrations, with a modified spectrophotometer wavelength of 500nm. TN and Soluble N were measured using the Persulfate Digestion method (Hach Method 10208) using TNTplus 828 Ultra High Range test kits. Samples were measured for pH and conductivity using a Thermoscientific Orion 5-star pH meter (Waltham, MA) and for alkalinity with an 865 Dosimat plus (Metrohm, USA). Method detection limits (MDL) were measured to be 14 mg COD/L for VFA, 30 mg COD/L for COD, and 0.7 mg N/L for NH_4^+-N. *E. coli* was measured by EPA Method 1603, which is a membrane filtration method utilizing mTEC agar as the selective growth medium.

Table 3.2: IC Method Detection Limits (MDLs) (Lin, 2012)*

	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{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	0.31	0.024	0.019
S.D.	6.301	0.01	0.027	0.101	0.072	0.053	0.002	0.099	0.008	0.006

*Concentrations in mg/l

P measurements were performed using the ascorbic acid method (Hach Method 10210) using TNT 845 Ultra High Range test kits. All samples were diluted to the appropriate range. Total P (TP) samples included all solids and represent the entire P content of the manure. Centrate P was measured after centrifugation. Therefore, it includes P contained in suspended particles and represents the P concentration in the centrate which enters the precipitation reactor. Soluble P (SP) was measured after filtration using a Fisher brand (Waltham, MA) 0.45 µm syringe filter. Soluble reactive P (SRP) was measured after filtration but Hach Method 10209 was used to measure only the soluble reactive portion.

Powder X-ray diffraction (XRD) was used to identify the mineral precipitates and was performed using equipment at the Nanotechnology Research and Education Center (NREC) at the University of South Florida. A Philips Panalytical X'Pert MRD (Westborough, MA) was used for XRD measurements. A range of 10° to 75° was used for data collection. The fixed divergence slit (FDS) PreFIX module was used for the incident beam optics, and a 0.1 mm copper attenuator was used for the alignment process. For the diffracted beam optics, a programmable receiving slit (PRS) PreFIX module was used with a nickel filter. The receiving slit was programmed for 0.25mm for the alignment process and a 1mm slit was used for the data scan. The samples were placed on a zero-background reader for sampling.

Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy (SEM-EDX) was also performed at NREC, using a Hitachi S800 (Naka, Japan) for SEM with an EDAX Phoenix Pro (Mahwah, NJ) for EDX. Samples were mounted on carbon tape fixed on an aluminum mount. The chamber pressure was $<10^{-2}$ Pa. The EDX was run for 60 seconds at an accelerating voltage of 15 keV. The sample was tilted 30° using a working distance of about 15mm. For SEM imaging, an accelerating voltage of 5 keV was used. The imaging and EDX were performed using EDAX Genesis software. A ZAF correction was used for quantification of EDX results. While quantitative results for elemental composition were obtained, such results are approximate and provide a comparative assessment between the different samples.

3.2 Life Cycle Assessment Methods

Life cycle assessment (LCA) is a method used to quantify the environmental impacts of a product or process throughout its entire life cycle. The LCA was performed in this study according to International Standard Organization (ISO) standards 14040 and 14044 (ISO 2006a, ISO 2006b). According to the standards, it therefore consists of four main stages as shown in

Figure 3.2. Data was collected for the study from a wide variety of sources, including: literature, vendors, contractors, experts, and our own experiments. LCIs available in Simapro v7.2 were used in this assessment.

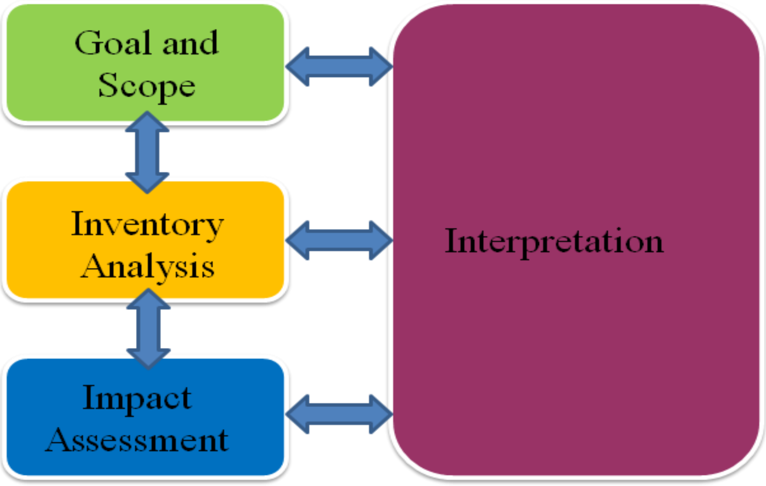


Figure 3.2: Four Main Stages of the LCA

3.2.1 Evaluation Scenarios

Three scenarios were evaluated in this LCA: AD, AD with Struvite Recovery, and AD with Struvite Recovery and N recovery via IX. Each scenario takes into account an addition to the waste treatment train. The evaluation scenarios are described in detail in this section.

Two main overarching scenarios are taken into account in this assessment. The first is based on waste produced from a medium-sized CAFO of about 7,000 pigs. This provides a general case study with values applicable to many average size facilities. The second scenario is based on waste produced from a very large CAFO of about 33,600 pigs or multiple smaller CAFOs with a centralized treatment facility. This provides information on how scale affects environmental impact and costs for the waste treatment system considered. Note that transport of waste to a centralized facility is not taken into account in this assessment. The waste flow information for these two scales, including both raw manure flow and centrate flow, is shown in Table 3.3.

Table 3.3: Waste Flow Information

	Medium Sized CAFO	Large CAFO
Number of Pigs	7,000	33,600
Average weight per pig (lbs)	125	125
Waste generated per pig (kg TS /pig/day)	0.363	0.363
Total waste generated per day (kg TS/day)	2,541	12,197
Solids before AD (5%) (kg/L of TS)	0.05	0.05
Waste flow rate (L/day)	50,820	243,936
Solids after AD (2.5%) (kg/L of TS)	0.025	0.025
TS in AD Effluent (kg/day)	1,271	6,098
% solids capture	90%	90%
Density of biosolids (kg/m^3)	1,550	1,550
% solids of sludge cake	22%	22%
Biosolids recovered (kg TS /day)	1,143	5,489
Biosolids flow rate (L/day)	3,353	16,095
Centrate flow rate (L/day)	47,467	227,841

The first proposed stage in the treatment system is AD of the swine manure. This process generates two recoverable outputs: the biogas energy, which can be converted to heat or electricity, and biosolids, which can be land applied as a fertilizer. A dewatering process, such as by a centrifuge or belt filter press, is also required here to separate the biosolids from the effluent. Without further treatment, however, the centrate contains high concentrations of N and P. Proper land application of the centrate requires expensive infrastructure in the form of underground pipeline or use of tanker trucks. In this scenario it is assumed that the centrate is discharged to surface waters and eutrophication of receiving waters is taken into account. The scenario is illustrated in Figure 3.3, showing the system boundary with inputs and outputs of the system.

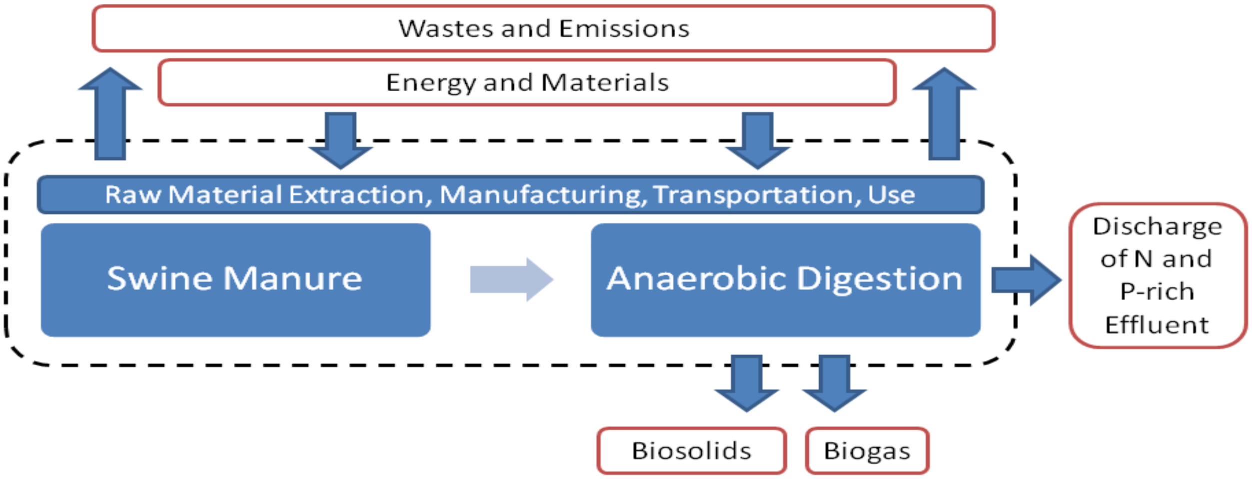


Figure 3.3: Evaluation Scenario 1: Anaerobic Digestion

The second scenario consists of AD followed by struvite recovery from the centrate. Therefore, the main difference is the construction and operation of the struvite reactor, production of recoverable struvite fertilizer, and a change in the nutrient concentrations of the discharged centrate, as shown in Figure 3.4.

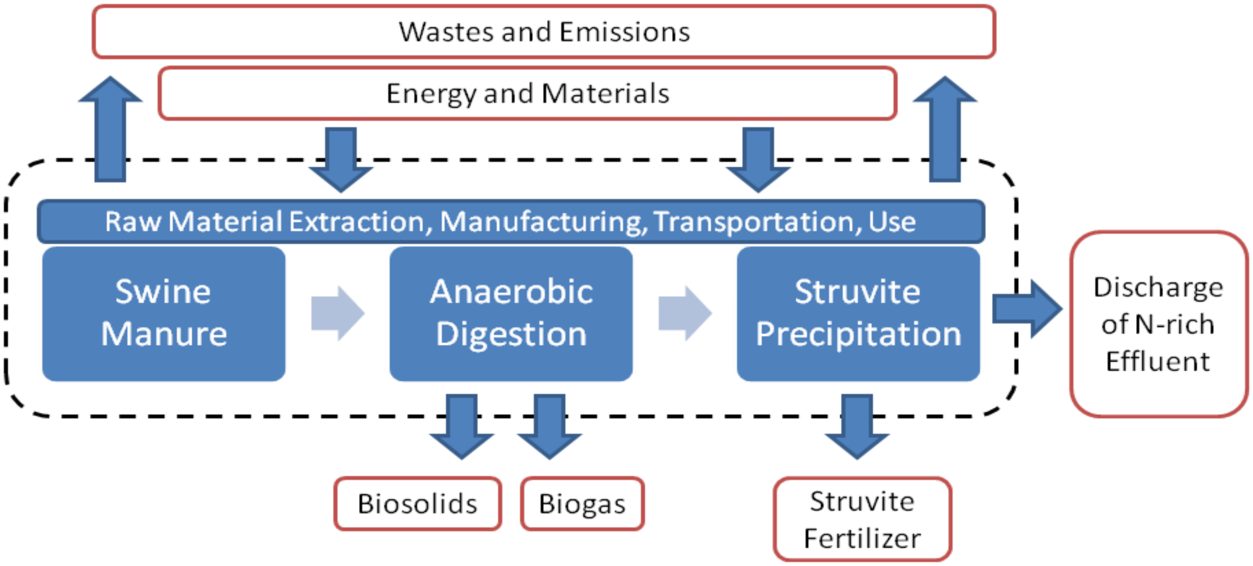


Figure 3.4: Evaluation Scenario 2: AD and Struvite Recovery

The final scenario includes the entire proposed system with all three additions to the treatment train. IX recovery of the N onto natural zeolites via ion exchange produces an N-rich zeolite fertilizer while also allowing for the treated water to be potentially recovered for some uses. However, although AD followed by nutrient recovery significantly treats the water, the reclaimed water may still contain pathogens and organics and is likely not suited to applications requiring high quality water. A potential option may be to reuse it in flushing the swine waste, to allow any remaining nutrients to be recovered in subsequent passes through the treatment system.

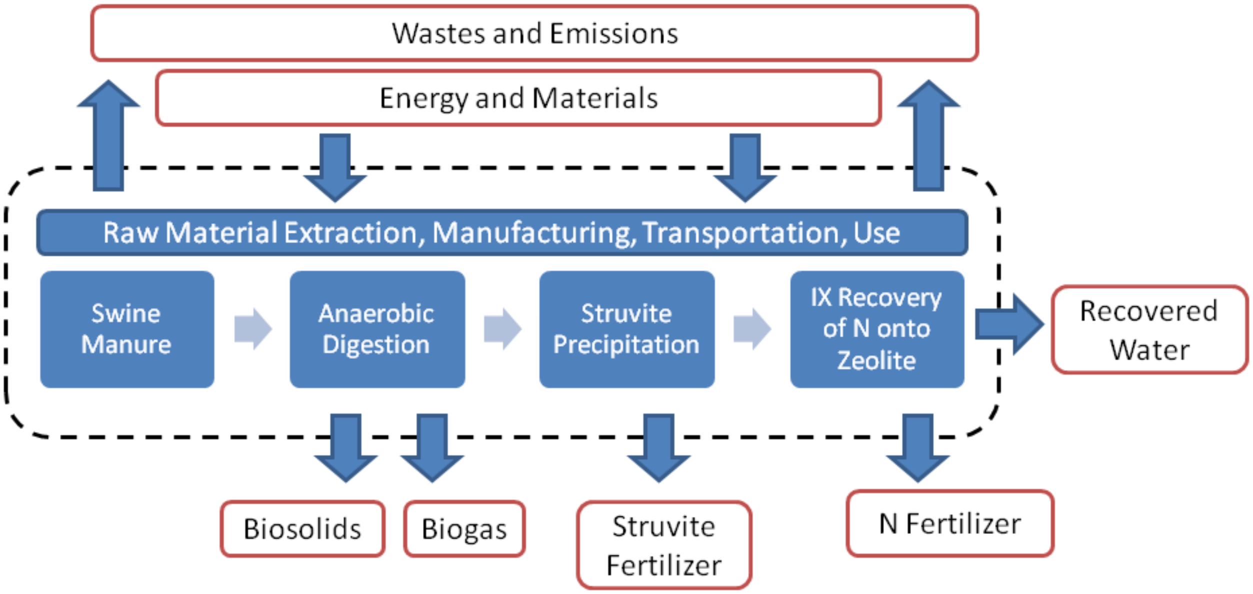


Figure 3.5: Evaluation Scenario 3: AD, Struvite Recovery, and N Recovery

Two alternate scenarios were also considered for struvite recovery and IX. For struvite precipitation, two different methods of raising the pH were considered: NaOH and Aeration (CO_2 Stripping). For IX, two types of zeolites were considered as an exchange material: Chabazite and Clinoptilolite. These alternatives can significantly affect the construction and operation of the system and are therefore expected to affect the environmental and economic impact.

3.2.2 Goal and Scope

The goals of this study are to assess quantitative environmental impacts of energy and nutrient recovery additions to a treatment train for swine waste generated from CAFOs, identify major contributors to the impacts for each process, and identify the effects of scale.

The system boundary is considered to be "cradle to use", and therefore includes raw material extraction, production, transportation, construction, operation, and use of recovered materials and energy. Therefore, construction of significant infrastructure is included, but disposal of that infrastructure is not. The system boundary is depicted in evaluation scenarios (Figure 3.1-3.5) and an overview is shown in Figure 3.6.

Figure 3.6: Overview of System Boundary

The function of the system is considered to be treatment of the swine waste generated at a CAFO. Therefore, the functional unit (FU) is treatment of 50.82 m^3/day of swine waste over the course of 20 years, which is the assumed lifetime of the system. The FU allows for fair assessment of the evaluation scenarios. This FU was chosen because it is the average daily flow rate for a medium sized CAFO.

The impact assessment method chosen for this study is the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI), developed by the US Environmental Protection Agency (EPA). TRACI is chosen because it uses impact assessment methods applicable for North America. The impact categories assessed include: Global warming, acidification, carcinogenics, non-carcinogenics, respiratory effects, eutrophication, ozone depletion, ecotoxicity, and smog.

3.3 Life Cycle Cost Analysis Methods

A Life Cycle Cost Analysis (LCCA) was performed using the same evaluation scenarios used in the LCA. Capital expenses (CAPEX) and operating expenses (OPEX) were collected and calculated using information from literature, commercial manufacturers, and industry professionals.

Uniform present value (UPV) was calculated for the OPEX by multiplying annual operating costs by a UPV factor, found using equation 3.2 with an interest rate of 5% for the system lifetime of 20 years.

$$\text{UPV factor}= \frac{(1-(1+i)^{-n})}{I} = \frac{\left(1-(1+0.05)^{-20}\right)}{0.05} = 12.46 \qquad (3.2)$$

where i is the interest. The CAPEX was not multiplied by any factor because it is already in Net Present Value (NPV).

The payback period was calculated by division of the annual total CAPEX by the OPEX income (not the UPV). Note that the payback period uses cash flows. It does not use net income over the lifetime of the system and does not indicate total profitability of the system; however, it is a useful measure of how beneficial the cash flows of system are.

Total profitability of the system is calculated by adding the present value of the CAPEX to the present value of the OPEX. Therefore, if the present value of the OPEX is negative and its absolute value is larger than the CAPEX, the system will have a lifetime income.

This assessment is calculated as compared to a "business-as-usual" scenario, where no waste treatment is provided. In most cases, the system will be replacing a conventional alternative which has its own associated costs. The costs of conventional systems can be subtracted from the present value of the OPEX and CAPEX to show to comparative costs of implementing the proposed system. The assessment also does not take into account government grants or renewable energy credits which can decrease overall costs and also make initial financing easier; however, financing such as by loans is not taken into account in this analysis. This assessment, therefore, provides an estimate of the economic benefit of the system as well as comparison between alternatives; however, in practical application the system is likely to be more economically favorable.

CHAPTER 4: RESULTS AND DISCUSSION

The experiment-based and modeling-based results are presented in this chapter.

4.1 Experimental Results

The bench scale experiments provided valuable data to demonstrate operational feasibility of the proposed process, generate greater understanding about the performance of the system, and provided a case study of data and parameters to be used in the LCA and LCCA.

4.1.1 Water Quality and System Performance Parameters

Various parameters characterizing the water quality as well as biogas production were measured throughout the treatment process, as shown in Table 4.1. The TS and VS decrease during AD as expected, because of VS destruction. The TS also decreases after the following treatment trains. It is expected that it primarily decreased after struvite precipitation but rose slightly after IX due to breakdown of the zeolite material. The pH shows the expected trend as well throughout the treatment process. During precipitation pH was raised to 8.5 with NaOH, but after solids separation by centrifugation, the pH continued to rise. In order to allow for efficient IX, the pH was decreased back to neutrality with HCl before the IX treatment. The zeolite, however, was observed to naturally raise the pH during ion exchange.

Alkalinity increases, as expected, during struvite precipitation because of NaOH addition. IX causes a drop in alkalinity. The measurement points do not allow us to see the effect of the HCl addition before IX. This can be calculated but these calculations have not been performed in this thesis. Use of HCl before the IX step to decrease the pH decreases alkalinity. Most likely, both zeolites caused an increase in alkalinity, but clinoptilolite less so.

Table 4.1: Measured Water Quality Parameters*

	Units	Before AD	After AD	After Precipitation	After IX (Chabazite)	After IX (Clinoptilolite)
TS	g/L	45±10	38±6	-	8.2±2	5.3±2
VS	g/L	31±6	23±5	-	-	-
pH		8.24 ±0.1	7.28±0.2	8.63±0.03	8.27±0.2	8.10±0.2
Alkalinity	mg CaCO$_3$/L	1,752±43	3,098±114	3,428±177	2,783±123	2,021±203
VFA	mg acetate/L	3,060±2,593	210±182	370±464	40±69	177±153
Soluble COD	mg O$_2$/L	4,760±1,427	1,893±220	-	2,682±480	2,803±549
Salinity	ng/L	-	-	-	3.28±0.6	2.72±0.5
E. coli	log CFU /100 ml	9.7±0.5	-		6.2±1	6.3±1

*Averaged from three experiments performed over six weeks

VFAs decrease during AD, as expected, because methanogens utilize them to produce methane and CO$_2$. VFAs seem to stay relatively consistent throughout the subsequent steps, but minor changes are difficult to detect due to large error. The soluble COD decreases during AD but does slightly increases during struvite precipitation and IX. Prior studies have shown that AD of swine wastes produces effluent that is high in COD but low in BOD (Kinyua, 2014). This is likely the case after precipitation and IX as well. The reclaimed water from this system will therefore still have high COD, which limits options for reuse.

There is a 3 log reduction of *E. coli* throughout the entire treatment train. This shows good removal, but the reclaimed water quality is still poor and further treatment is necessary if it is to be used for irrigation. The *E. coli* in the recovered biosolids was also measured at 10$^{7.1}$ CFU /g dry weight. The salinity of the reclaimed water is low enough that it is suitable for crop use (Bernstein, 1975).

Due to the poor effluent quality, there are few options for the reclaimed water reuse without further treatment. A practical and beneficial reuse option is for washing of the hog pens.

This is likely to avoid any negative effects of pathogens, does not require long distance transport of the water, and allows for compounding recovery of remaining nutrients in the effluent. Zeolite is also commonly known for reducing waste odors. Therefore, the zeolite particulates in the reclaimed water may reduce odor of the waste. Further research would be necessary, however, to determine the effects of the reclaimed water on the treatment system and the number of times the water could be recycled in this manner.

4.1.2 Fate of Phosphorus

A detailed study of the phosphorus concentrations throughout the treatment process was performed in order to fully understand the in its various forms. Therefore, a variety of P measurements were performed, including Total P, Centrate P, Soluble P, Soluble Reactive P, and orthophosphate, as described in Chapter 3. No prior studies are known to have investigated the fate of P through these systems in such detail and this is likely the first to show the fate of P through an ion exchange process with natural zeolites. This fills a gap in the knowledge about the fate of P throughout such processes because it is not well understood how different forms of P, such as organic/inorganic or soluble/non-soluble, change throughout such processes.

The TP, which includes solids, was measured for the raw swine waste (before AD) and the anaerobically digested waste, as shown in Figure 4.1. The concentrations were not significantly different, which is expected for conservation of mass (p-value: 0.20).

The SP concentrations are comparable to literature values for swine waste (see Table 4.2). Nutrients in swine wastes can be extremely variable. This is likely because of differences in feed types, natural biological differences in the swine, and also how the waste is collected. For the waste collection method used in this study, for example, it was not possible to collect urine content. Much of the P in swine waste is contained in the feces due to swine's lack of the phytase enzyme, however, soluble P concentrations may have been higher if more urine collection was possible. Because Mg and N are high in this waste, P is the limiting constituent for struvite formation. Recovery systems are therefore more likely to be economically and environmentally favorable with higher soluble P concentrations in the waste.

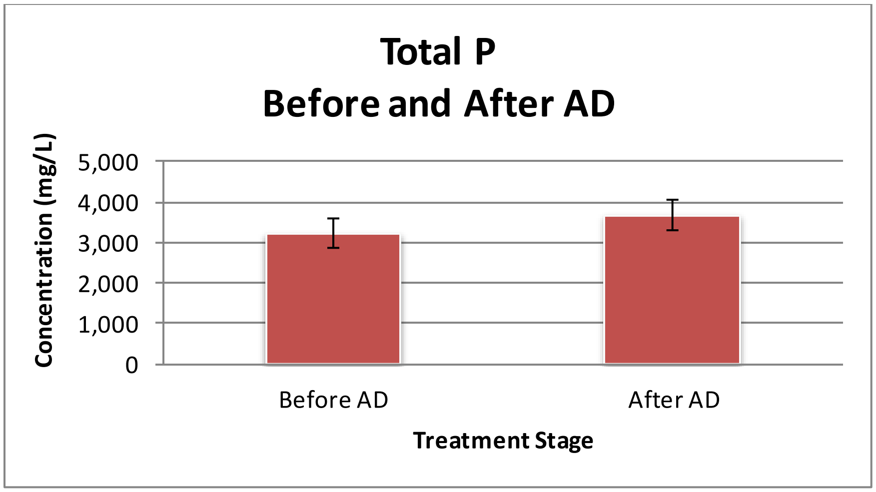


Figure 4.1: Total P Before and After AD (p-value=0.2)

The concentrations of various forms of P were measured throughout the treatment process, from centrifuged samples, as shown in Figure 4.2. The CP represents the entire P in the solution. The large decrease in CP seen after AD is due to a decrease in suspended solids during digestion. This can even be seen by visual detection of AD influent centrate, which is murky, and AD effluent centrate, which is much clearer. SP, SRP, and Ortho P represent soluble forms of P in solution. As expected, the soluble P concentrations increase after digestion.

The P recovery from struvite precipitation (Figure 4.2) is comparable to other precipitation studies (see Table 2.5; note that percent total recovery is calculated as compared to concentrations after AD). It is expected that the P available for precipitation is in the soluble

Table 4.2: Comparison of Swine Waste P Concentrations in Literature

Source	Soluble P (mg/L)	Swine Waste Type
Burns et al., 2010	572	Raw Waste
Huang et al., 2011	161	Raw Waste
Jordaan et al., 2010	41.5 ± 4.8	AD effluent
Jordaan et al., 2010	35.5 ± 1.4	AD effluent
Karakashev et al., 2008	160 ± 20	AD effluent
Miles and Ellis., 2001	153 ± 70	AD effluent
Nelson et al., 2003	57.15 ± 9.4	Anaerobic Lagoon effluent
Perera et al., 2007	42	AD effluent
Suzuki et al., 2002	161	Raw Waste
Suzuki et al., 2006	112	Raw Waste
Suzuki et al., 2006	217	Raw Waste
Suzuki et al., 2006	121	Raw Waste
Suzuki et al., 2006	161	Raw Waste
Suzuki et al., 2006	68	Raw Waste
Suzuki et al., 2006	34	Raw Waste
Suzuki et al., 2006	158	Raw Waste
Suzuki et al., 2006	40	Raw Waste
Suzuki et al., 2006	87	Raw Waste
Song et al., 2011	22-68.7	AD effluent
Wrigley et al., 1992	30	AD effluent
This Study	62 ± 13	Raw Waste
This Study	72.7 ± 8.4	AD effluent

reactive form; therefore, most studies measure recovery efficiency by SP or SRP. Our results show, however, that SRP recovery was 87% (60 mg/L recovered), but the highest mass recovery was from the CP (77% efficiency, 66 mg/L recovered). The difference in concentration between the different forms also decreased after precipitation. Therefore, there may have been removal of additional P by adsorption onto the struvite precipitate. To account for the total P recovered through precipitation it is therefore necessary to measure the recovery efficiency of CP. Most researchers, however, only measure SP or SRP, which fails to take into account the total P available for recovery. IX provides further recovery of the P, removing almost all of the SRP and orthophosphate. This significantly reduces eutrophication potential of the P in the reclaimed

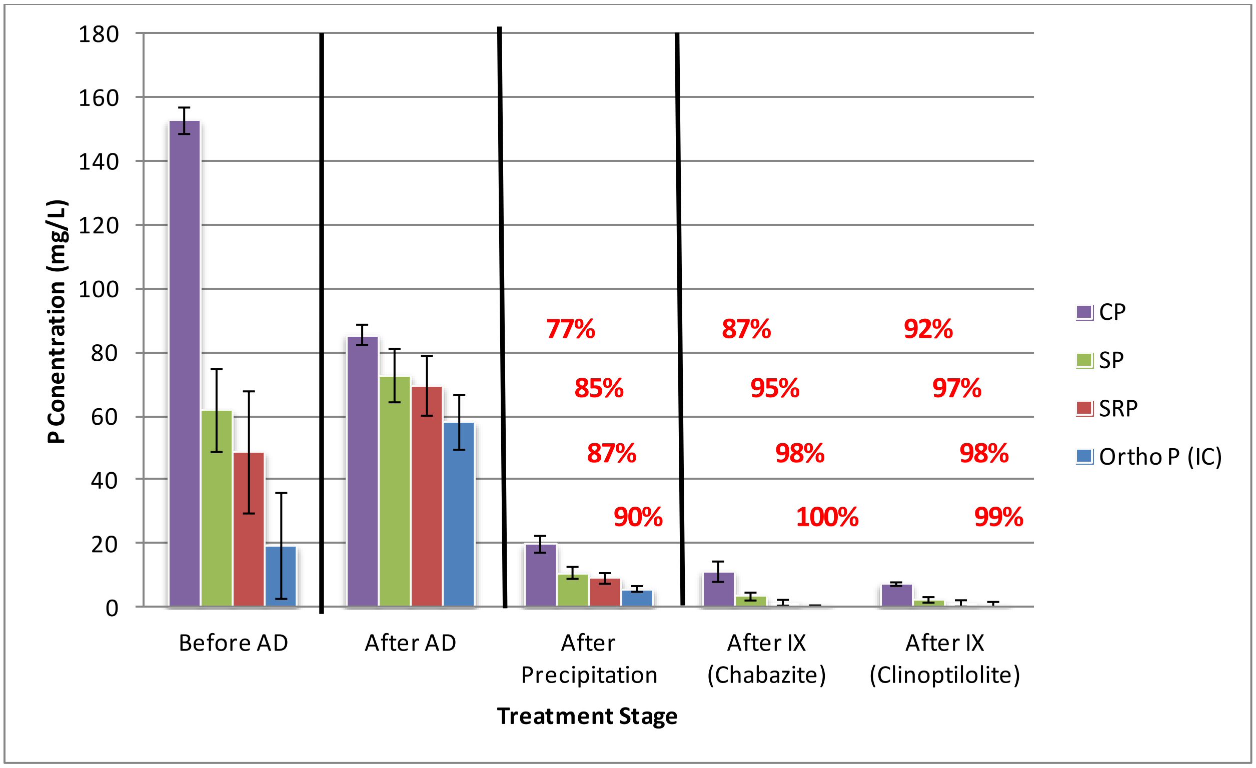


Figure 4.2: Fate of P in Centrate Throughout the Bench-Scale Experiment (Percent Total Recovery Shown in Red)

water. Differences in recovery of P between clinoptilolite and chabazite are small, but clinoptilolite recovers 5% more of CP.

4.1.3 The Fate of Nitrogen

The concentrations of N were measured throughout the treatment process. Recovery of N has the potential to provide significant advantages because it reduces environmental impact of the waste as a water pollutant, allows for financial gain from recovered materials, and offsets traditional N-fertilizer production methods.

The TN measurement includes soluble and particulate forms (including ammonium) in the dewatering centrate, while the ammonium measurement is only in the soluble form. As expected, the ammonium concentration increases after anaerobic digestion (see Figure 4.3).

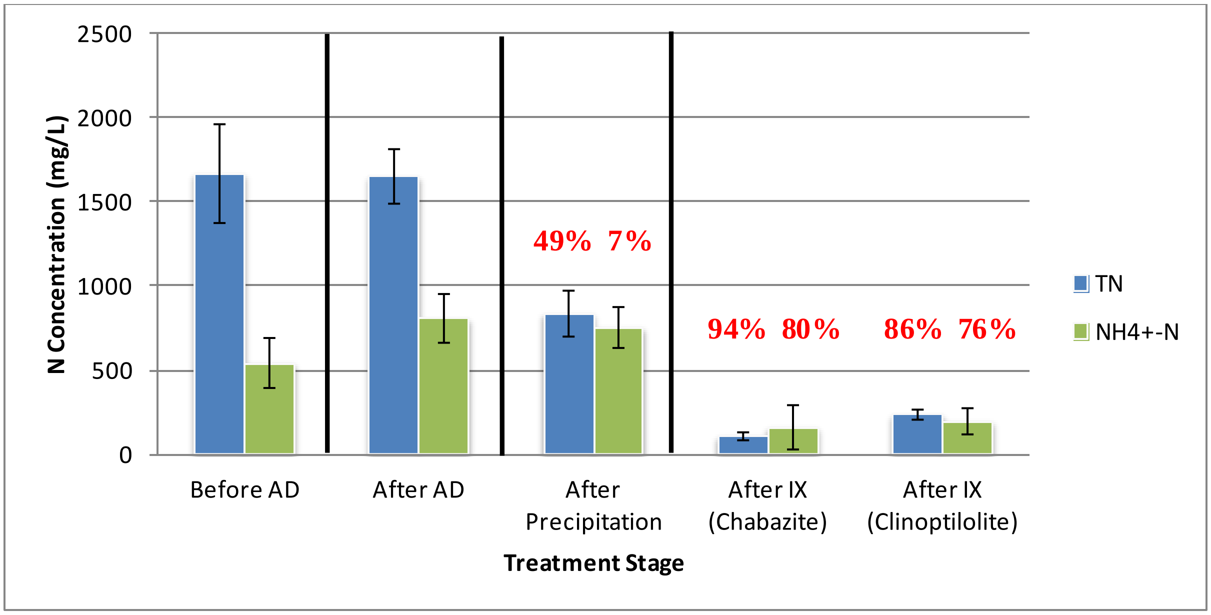


Figure 4.3: Fate of Nitrogen in Centrate Throughout the Bench-Scale Experiment (Percent Total Recovery Shown in Red)

Through struvite recovery, a sharp decrease is seen in TN (49%) was observed, with only a minor decrease in ammonium (7%). Struvite requires a 1:1:1 molar ratio of Mg:N:P. Approximately 1 mmole/l of Mg (24.5 mg/l) was removed, which indicates that 14 mg/l of ammonium-N could form as struvite. However, 54 mg/l of ammonium and 816 mg/l TN was recovered through struvite precipitation. Therefore, it is possible that N was removed by forming other mineral precipitates, but the majority may have been removed by adsorption onto the precipitate.

Through IX, the majority of the remaining N was recovered. At these stages, no statistically significant difference can be seen between TN and ammonium; therefore the N is primarily in the ammonium form. Between the zeolite alternatives, chabazite provides 6-8% higher recovery than clinoptilolite.

4.1.4 Fate of Other Dissolved Ions

The fate of dissolved ions, aside from N and P, were also measured through each treatment stage (Table 4.3). While the fate of most of these ions is of interest, the recovery of K and Mg are particularly interesting to note because K is also a valuable nutrient in the fertilizer industry and Mg is necessary for struvite formation.

Table 4.3: Fate of Other Ions in the Centrate Throughout the Bench-Scale Experiment*

Measurement	Units	AD Influent	AD Effluent	After Precipitation	After IX (Chabazite)	After IX (Clinoptilolite)
Na^+	mg/l	181±8	187±5	638±25	1210±559	972±420
K^+	mg/l	697±87	851±15	845±37	120±110	185±121
Ca^{2+}	mg/l	220±137	327±13	276±59	255±52	248±45
Mg^{2+}	mg/l	71±58	160±30	135±14	139±7	158±29
Cl^-	mg/l	117±9	112±4	117±10	726±77	815±83
NO_2-N	mg/l	0.0±0	0.0±0	0.0±0	0.0±0	0.0±0
NO_3-N	mg/l	0.1±17	0.1±9	0.0±1	0.1±0	0.1±1
SO_4^{2-}	mg/l	1580±2550	1.7±1	2.8±1	369±241	144±337

*Averaged from three experiments performed over six weeks

The recovery of Mg occurs mostly through struvite precipitation, as shown in Table 4.3. Often in struvite precipitation processes, Mg is the limiting constituent and a Mg source must be added to allow for precipitation. For this waste, as is the case of most swine wastes, Mg is plentiful and P is the limiting constituent. It should be noted that groundwater, containing Mg, was used in our experiments. However, the results show that the majority of the Mg available for struvite precipitation is actually released into the soluble form during AD. Therefore, even if the average AD influent Mg concentration was 0 mg/L, the AD effluent concentration would still be 88 mg/L. At this concentration, there is enough Mg to maintain at least the 1:1 molar ratio necessary for struvite formation for phosphate concentrations up to 334 mg/L. Given the concentration shown in Table 4.3 (159.9 mg/L Mg), there would be enough Mg to form struvite for P concentrations up to 608 mg/L. Therefore, if the waste contained more P, it would allow for more recovery of Mg and N, and more struvite overall. Higher recovery could improve environmental and economic performance of the system significantly.

Significant K recovery was achieved through the IX treatment. 86% of the K was recovered using chabazite and 76% using clinoptilolite. Therefore, after IX occurs, the zeolites are not only rich in N but also extremely rich in K. This adds value to the zeolite as a fertilizer and can make it more economically favorable. Calcium also decreases during precipitation, indicating that some of the precipitate likely includes amounts of calcium phosphates (see discussion in section 4.1.5). Calcium phosphates can also be used as a fertilizer (Bauer, 2007; Cabeza, 2011), but calcium is not as commonly required as N, P, and K.

Na and Cl concentrations increase throughout the treatment. The Na increased during precipitation because of the addition of NaOH to raise the pH. During IX, the Na also increased because it desorbed from the zeolite during ion exchange. Cl increases after IX and this is likely because of HCl addition to the centrate before IX to achieve neutral pH required for high efficiency exchange.

Sulfate decreases overall throughout the treatment, but mostly during AD because of anaerobic sulfate reducing bacteria. From experience in our laboratory experiments, the H_2S gas creates odor which is still prevalent after AD, but is significantly reduced after dewatering and entirely gone after struvite precipitation. Sulfate increases after IX, which may be due to bisulfide re-oxidization to sulfate during IX. As expected, nitrate and nitrite concentrations were negligible throughout the tests.

4.1.5 Comparison of Precipitates from Different Struvite Precipitation Processes

Six different precipitates were evaluated with XRD, SEM, and SEM-EDX (Table 4.3). The purpose of this investigation was to characterize the precipitates formed from various processes and compare them. Four of the precipitates analyzed were formed in commercial processes developed by businesses that have successfully implemented struvite recovery at industrial scales. This analysis provides comparison between the precipitates formed in these processes. Furthermore, it provides comparison between the commercially produced precipitates and two that were formed in our laboratory. Comparison of precipitates formed in different operational processes lends understanding as to how differences in process design can affect characteristics of the mineral precipitate.

Table 4.4: Precipitate Sources Analyzed for Crystal Characteristics

Short Name Used	Product Name	P Source	Process	Producer
Airprex	-	Digested Sludge	Airprex	PCS
Phred	**Terraphos**	Animal Wastewater Runoff	Phred	KEMA
Crystal Green Centrate (CG Centrate)	**Crystal Green**	Industrial Phosphate Mining Waste	Pearl	Ostara
Crystal Green Phosphate (CG Phosphate)	**Crystal Green**	Municipal Centrate	Pearl	Ostara
Homogeneous Lab	-	Anaerobically Digested Swine Waste	Homogeneous precip. in batch reactor	Our Lab
Heterogeneous Lab	-	Anaerobically Digested Swine Waste	Heterogeneous precip. in batch reactor	Our Lab

XRD was used to confirm presence of struvite in the samples. Samples were matched using Panalytic’s HighScore software. For all samples, struvite was the best match. The secondary matches seem unlikely, especially considering SEM-EDX results, described below; however, other constituents are likely present in low quantities. Amorphous content also seems present in all the samples. An example XRD scan of the heterogeneous sample produced in our laboratory is shown in Figure 4.4. Most of the scans are similar with some differences in the amorphous content. All of the remaining scans are included in the Appendix.

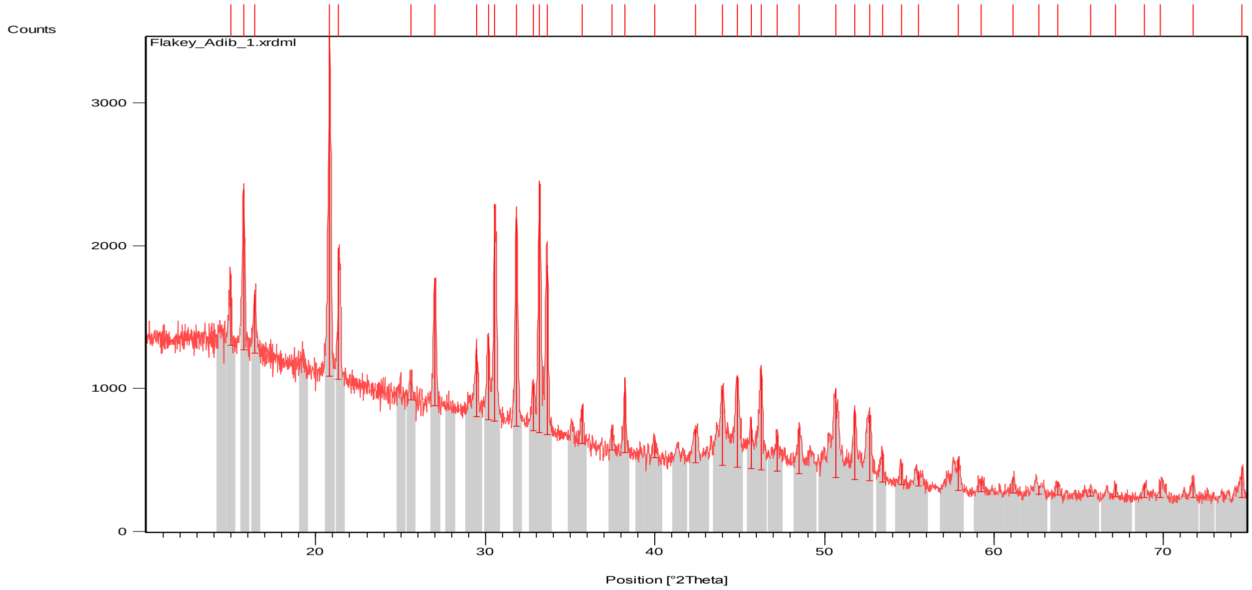


Figure 4.4: XRD Scan of Heterogeneous Struvite Produced in Experiments, Showing Matching Struvite Peaks in Grey.

SEM images were used to observe crystal structure and size and note differences between the precipitates. Often the precipitates varied between its surface and interior and even between core of the interior to its outer rim. Sample of SEM images that show the most unique structures are shown in Figure 4.5. All of the images are included in the Appendix, for reference.

One of the notable differences was that the crystal sizes varied significantly from sample to sample. Airprex and Crystal Green had some of the smallest crystal sizes (around 1 or 2 µm) while our laboratory samples had crystal sizes around 20 µm. Phred samples showed an interesting difference, however. The spherical Phred pellets had crystals at the surface that are >100µm while at the core of the sphere the crystal size was about 2µm (though it has larger pores at the core). The differences between the core and surface of some of the precipitates is likely because they are formed in seeded reactions (heterogeneous precipitation), where seed materials, such as struvite or sand, are added to the reactor before startup so that new crystals can form on them. This has shown to improve overall recovery of P and is an essential aspect of how fluidized bed precipitation reactors function (see discussion in Chapter 2). Ostara's Crystal Green and the Phred precipitates are both formed in FBR processes. Both utilize continuous operation of a FBR to allow struvites formed to serve as seed for new formation, eliminating need for foreign seed addition after startup. Therefore, it is expected that such precipitates will become relatively uniform, unless waste characteristics or operation of the reactor are changed. The Crystal Green tends to be relatively uniform throughout, but the Phred particle analyzed may have been formed with an alternative struvite seed or may vary due to periodic changes in operation. Periodic changes in operation are likely because visual inspection of the Phred cross-section shows changes in color as rings radiate from the center. It is important to note that Crystal Green and Phred are formed in processes that are intended for very different applications. Therefore, differences between them do not indicate superiority of the product, but only preference for certain applications.

The variance in crystal size seems to affect the hardness of the precipitate. From a simple tactile evaluation, the precipitates with smaller crystal sizes, such as Airprex and Crystal Green, are very hard and difficult to break or abrade. The laboratory-produced samples, however, are much more brittle and easily crack or abrade. While struvite is considered to be a slow-release fertilizer, this hardness may possibly have an effect on solubility of the precipitate, creating different timing of release. Further studies are necessary, however, to verify this. The cause of the differences in crystal size also requires further investigation

The crystal morphology also seems to differ between samples and even within samples, possibly due to non-contiguous growth. Struvite is essentially orthorhombic, however, the orthorhombic structure is best seen in the Phred samples. The Airprex and Crystal Green samples, however, show more inconsistent crystal shapes. Our laboratory samples show a consistent structure, but it appears more rhombohedral.

SEM-EDX was also performed on the precipitates to evaluate and compare elemental composition. This helps confirm XRD results and suggests presence of other compounds in the precipitate. For most of the samples, the dominant elements were N, O, Mg, and P, which is expected because the formula for struvite is $MgNH_4PO_4 \cdot 6H_2O$. Levels of each constituent, however, differed among the samples along with the quantity of minor constituents such as K and Ca. It should be noted that N levels are not easily measured by SEM-EDX and are therefore, not presented here. The N and O peaks are very close to each other and the EDAX Genesis software likely often misrecognized them. However, all of the samples showed N as present. The results have been separated into three figures due to differences in scale. The Mg and P percentage by weight is shown in Figure 4.6, Ca and K are shown in Figure 4.7, and other minor constituents are shown in Figure 4.8.

Differences in reactor configurations seem to affect the quality of the precipitates. This is mostly clearly seen in the inclusion of non-struvite particulates in some of the samples. FBR configurations seem to decrease the likelihood of other particulates being gathered with the struvite because it selectively separates the struvite solids only after they have grown to the appropriate size. Smaller particulates and suspended solids will therefore continue flow through the reactor. Configurations that use a separate solids separation step are much more likely to

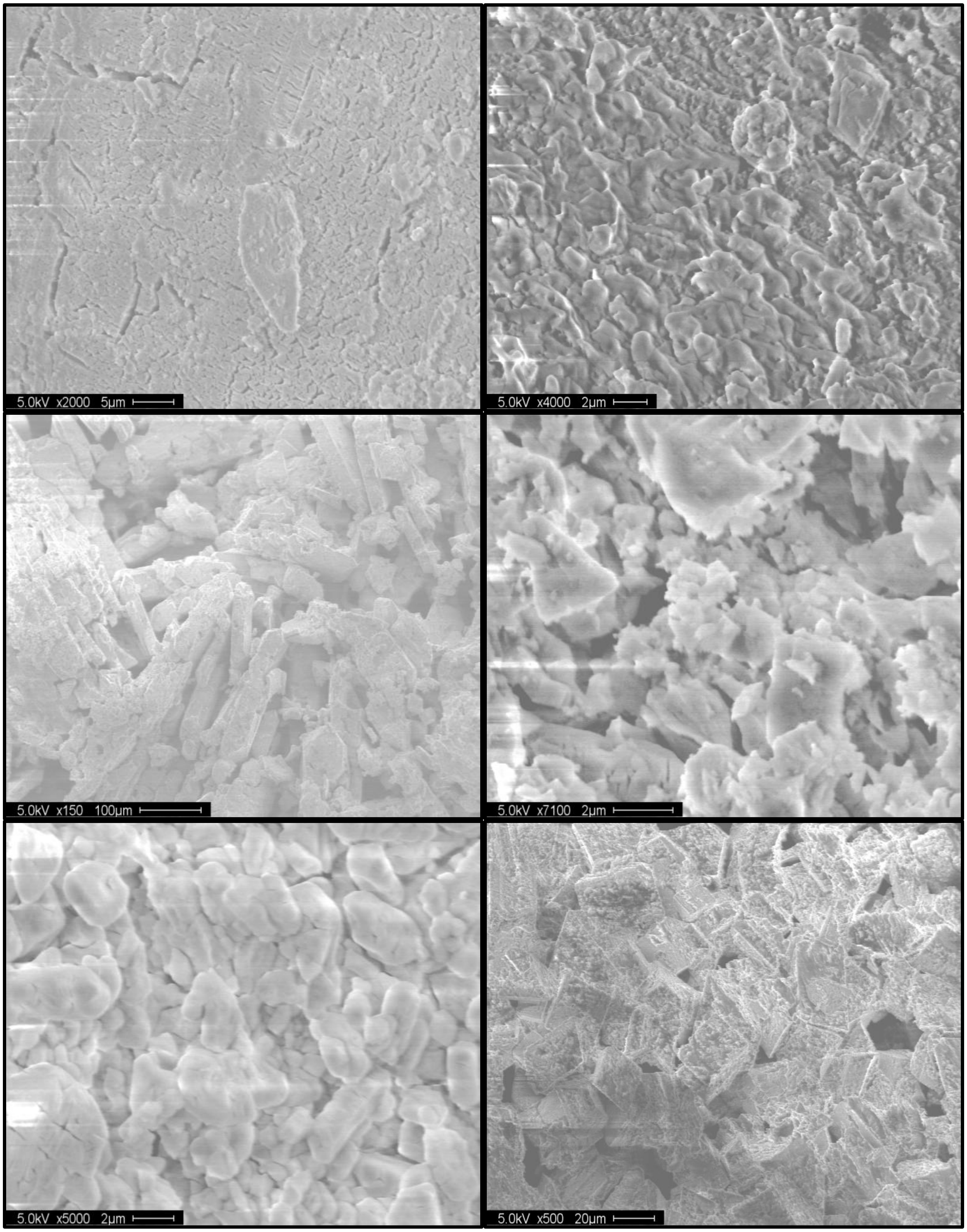


Figure 4.5: Selected SEM Images of Struvite Precipitates. Top Left: Airprex struvite crystal. Top Right: Airprex: Brown flake impurities. Middle Left: Phred Surface. Middle Right: Phred Core. Bottom Left: Crystal Green (phosphate mining). Bottom Right: Homogeneous Lab-produced Sample

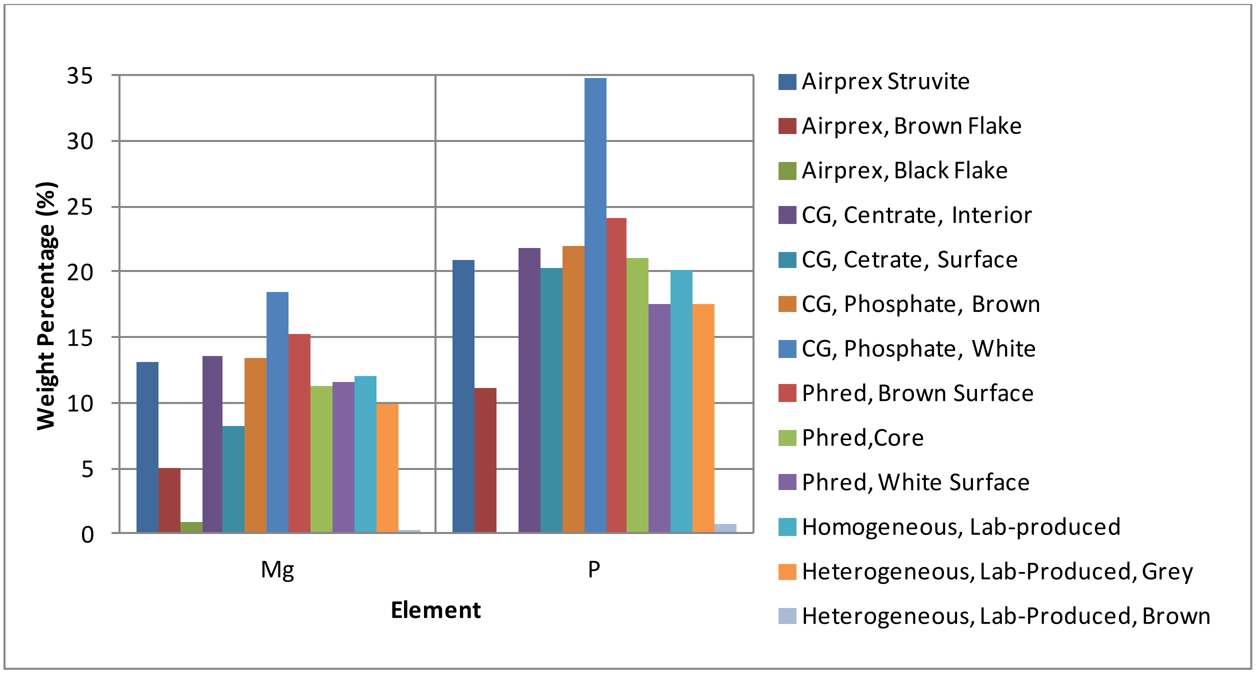


Figure 4.6: Mg and P Elemental Composition of Selected Struvite Samples

include particulates in the precipitate. Airprex utilizes an airlift reactor followed by sedimentation to recover solids. From a visual inspection one can see a significant amount of particulates included in the sample. Two large particulates that appeared as brown and black flakes were analyzed with the SEM-EDX and results showed that one contained elements of struvite but with a significant amount of calcium. Therefore, it is likely a calcium phosphate that formed during precipitation. The other, however, does not show proper Mg and P peaks and is suspected to be composed of biosolids. Our own laboratory samples of struvite were formed in a seeded, well-mixed batch reactor, intended to simulate FBR operation. For the bench-scale design, however, a separate centrifugation step was necessary for solids separation. Often not all of the biosolids particulates were removed during the dewatering step and were likely to enter to precipitation reactor. Furthermore, because separation of the solids after precipitation did not selectively separate certain particle sizes (such as an FBR would), usually biosolids particulates were included in the precipitate. While inclusion of such particulates is not particularly harmful, if a pure struvite is desired then an FBR or other reactor that can provide selective separation is preferable.

Most of the precipitates have a P content of about 20% by weight as shown in Figure 4.6. CG Phosphate, however, has consistently higher P content than the other samples. P content also seems coupled with Mg content; therefore, CG Phosphate also shows a higher percentage of Mg. Some anomalies shown include the Airprex brown and black flakes and the brown surface of the heterogeneous laboratory-produced sample. As discussed above, these are likely impurities mixed with the struvite. The Airprex brown flake is likely a mix of struvite, calcium phosphate, and some sort of sulfur compound while the Airprex black flake and brown laboratory sample are likely biosolids. Aside from these trends, it is not believed that the other minor differences in the Mg and P content are significant and they may even be attributable to uncertainty in readings.

The Ca content is highest in the Airprex brown flake, Phred Core, and heterogeneous laboratory sample. This indicates likelihood of calcium phosphate or other calcium compound presence. During the bench-scale experiments, 1.3 mmole/L (52 mg/L) calcium was removed during precipitation. This is larger than the 1 mmole of Mg removed and would therefore suggest that the precipitate is possibly a majority calcium phosphates; however, XRD confirmed that the precipitates are primarily struvite (see above). The additional Ca may be included as amorphous calcium phosphates, which would not be recognized by XRD; however, SEM-EDX, which recognizes elemental composition in both amorphous and crystalline forms, shows that the weight percentage of Ca is lower than Mg in the precipitate (Figures 4.6 and 4.7). A map of the spatial distribution of elements in the sample also shows that Ca is only present in some locations throughout the sample (see Figure 4.9), whereas N, P, and K are consistently present throughout.

Therefore, although there was high removal of Ca, the analysis indicates that the precipitate is not primarily calcium phosphates. K is also present in the samples. The content is low throughout all samples, but is highest in the heterogeneous lab sample. In general, K content likely signifies some presence of K-struvite.

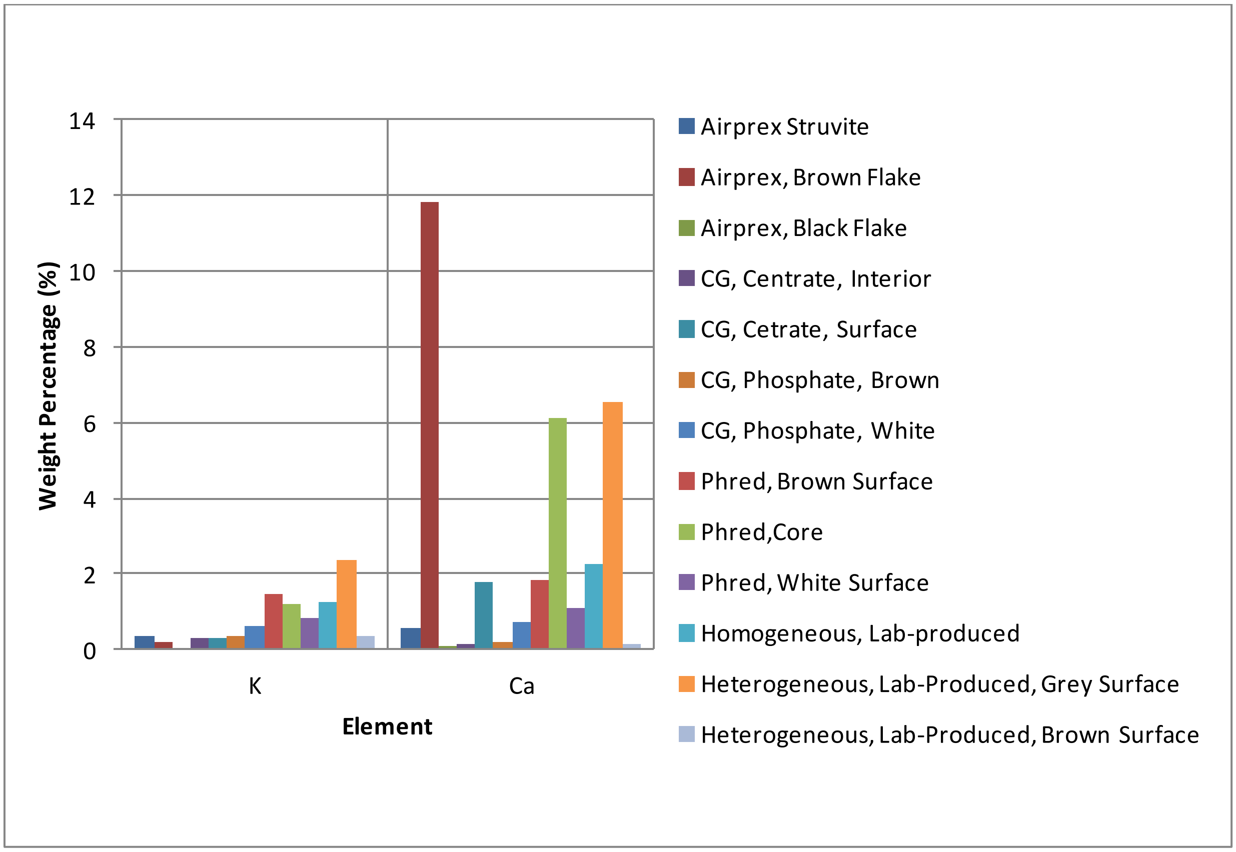


Figure 4.7: K and Ca Elemental Composition of Selected Struvite Samples

A variety of minor constituents are present in the samples as shown in Figure 4.8. Note that the S reading for the Airprex black flake has been removed because it was 20% (much higher than the graph scale). Therefore, this indicates presence of sulfur compounds in the material. Fe is also highest in the Airprex brown and black flakes as well as the brown Phred samples. This may indicate presence of iron phosphate. Aluminum is high in the Airprex impurities as well as the brown heterogeneous lab sample. Because these are expected to be biosolids, SEM-EDX of recovered biosolids could corroborate its elemental composition.

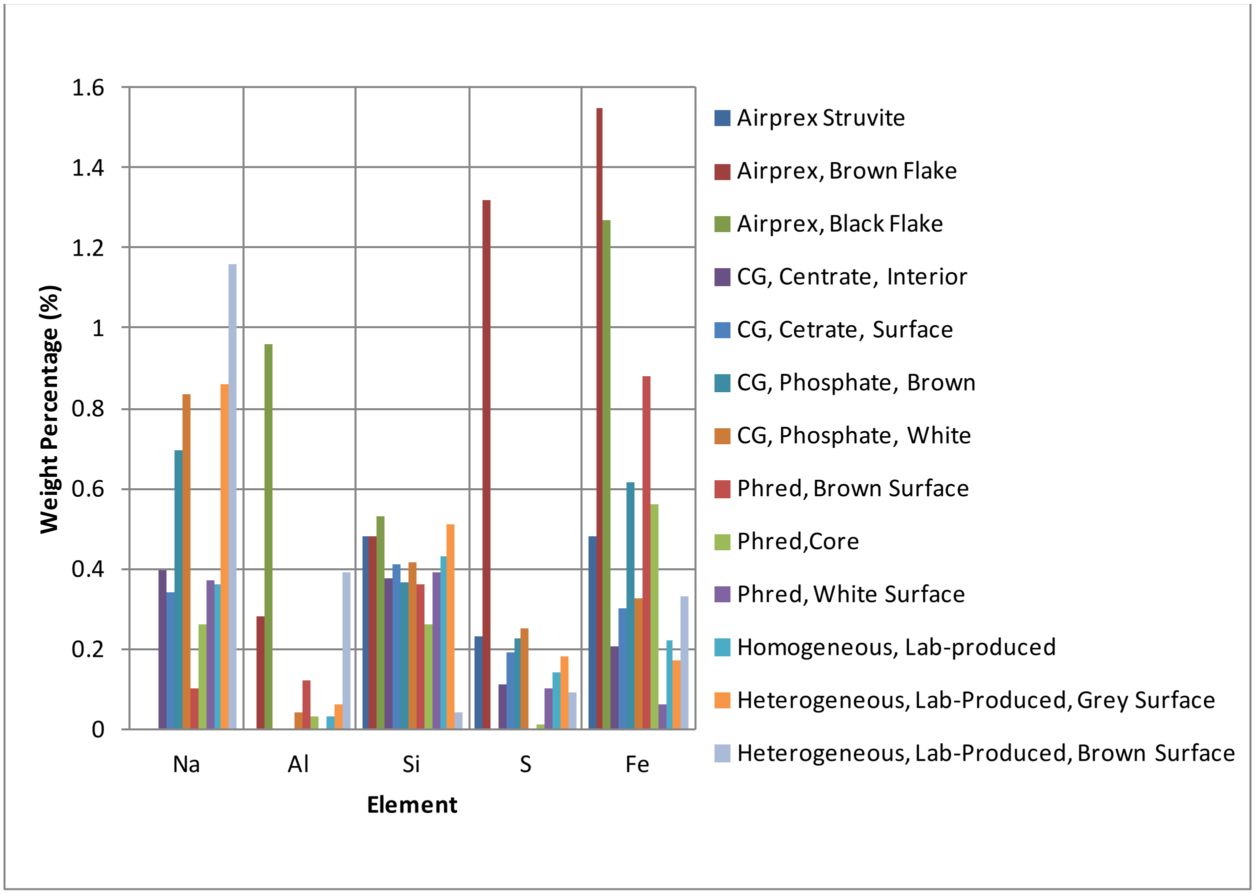


Figure 4.8: Minor Elemental Constituents of Precipitates

The distribution of elements across samples appears to be even, as shown in Figure 4.9. The map of a cross-section of a Phred samples shows even distribution of elements across the sample; however, Ca is concentrated in some areas. Ca and K are also more sparsely present than N, P, and K. The dark sections show absence of elements but are also due to unevenness of the sample surface in some locations. While this scan shows the sample to be generally uniform throughout, a larger scale map of an entire cross-section of a particle may reveal differences noticed throughout cross-sections in the EDX results.

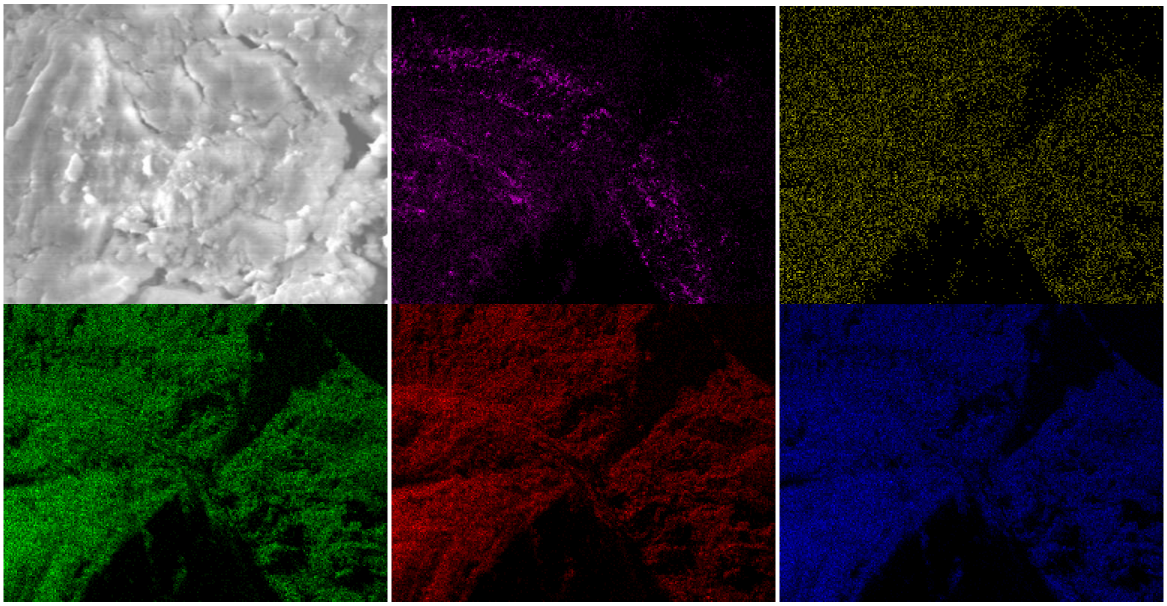


Figure 4.9: Map Showing Location of Elements within a Phred Cross-Section Sample. Top left: SEM Image; Top Middle: Calcium; Top Right: Potassium; Bottom Left: Magnesium; Bottom Middle: Nitrogen; Bottom Right: Phosphorus

4.1.6 Assessment of Four Natural Zeolites

XRD, SEM, and SEM-EDX were performed on four natural zeolites to characterize and confirm their mineral qualities as well as to note differences between them. These zeolites are mined from different sources and isotherm experiments conducted in our laboratory, which are not included in this thesis, have shown that they demonstrate varying ion exchange capacity. Three of the zeolites are expected to be a type of clinoptilolite and one is expected to be a type of chabazite, as shown in Table 4.5. C-Grey and the chabazite were used in the bench-scale experiments.

XRD confirmed that three of the zeolites are clinoptilolite and that the fourth is chabazite. Most of the clinoptilolites matched with both Sodium and Calcium Clinoptilolite. There were some other possible secondary matches, including heulandite, another type of zeolite. The chabazite samples matched best with Calcium Chabazite. There were also several other possible matches, including Gmelinite (another zeolite), Gypsum ($CaSO_4 \cdot 2H_2O$), and Aluminum phosphate. These may be present in some amount, but the fact that they match does not ensure their presence. It only suggests possibility of their presence. When taking into account that the material is chabazite, the software matched the remaining XRD peaks as possibly indicating Indium Selenium, Brushite ($CaHPO_4 \cdot 2H_2O$), Azodicarbonamide ($C_2H_4O_2N_4$), and Quartz (see SEM- EDX discussion below on likelihood of the presence of these compounds). All of the samples seemed to include a large amount of amorphous content. XRD scans for C-Grey and Chabazite are shown in Figures 4.10 and 4.11. The other two clinoptilolite scans are similar to C-Grey and are included the Appendix.

Table 4.5: Zeolites Analyzed by XRD, SEM, and SEM-EDX

Short Name	Zeolite Type	Source Company
C-Yellow	Clinoptilolite (ZS403H)	St. Cloud Mining
C-Grey	Clinoptilolite (ZK408H)	St. Cloud Mining
Zeosand ®	Clinoptilolite	ZeoInc
Chabazite	Chabazite (ZS500H)	St. Cloud Mining

SEM images of the four zeolites show interesting differences between the different samples, as shown in Figure 4.12. The particle size among all the clinoptilolites is approximately 2μm and they all have similar pore sizes of <1μm. The Zeosand, however, has a rough texture which may contribute to higher surface area and higher IX capacity. Isotherm experiments conducted in our laboratory confirm that Zeosand has higher ammonium exchange capacity (data not shown). The chabazite sample shows a much wider range in particle size from approximately 4μm to <1μm. Pore sizes in the chabazite also vary widely but range up to 2μm, significantly larger than the clinoptilolites. Chabazite has higher ammonium exchange capacity than clinoptilolite (see Table 4.12). The small particles and large pores in the chabazite likely contribute to this higher capacity.

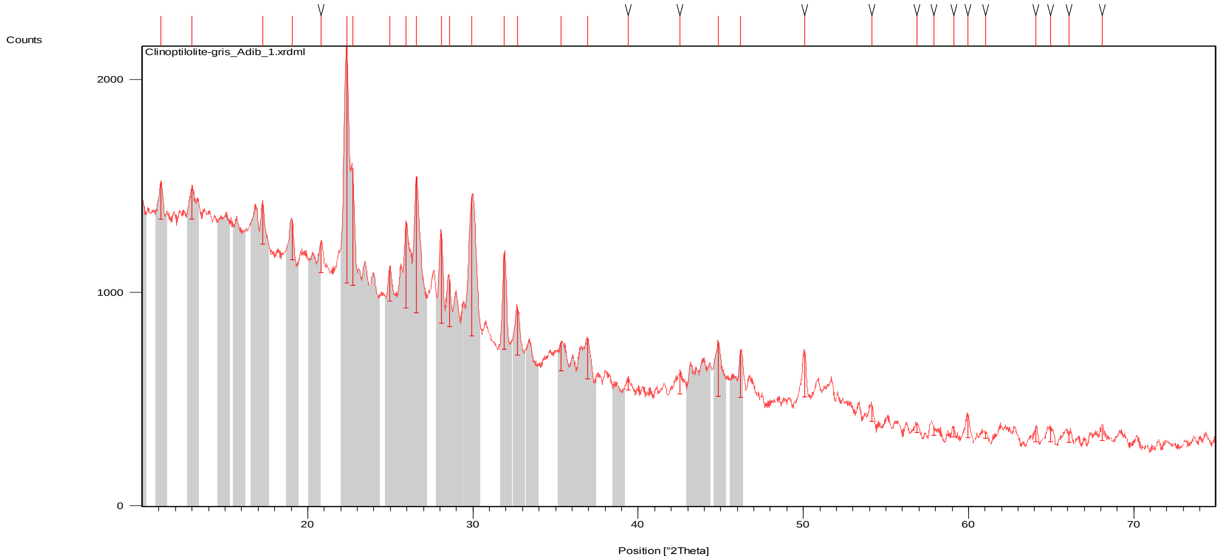


Figure 4.10: XRD Scan of C-Grey showing Ca-Clinoptilolite Match in Grey

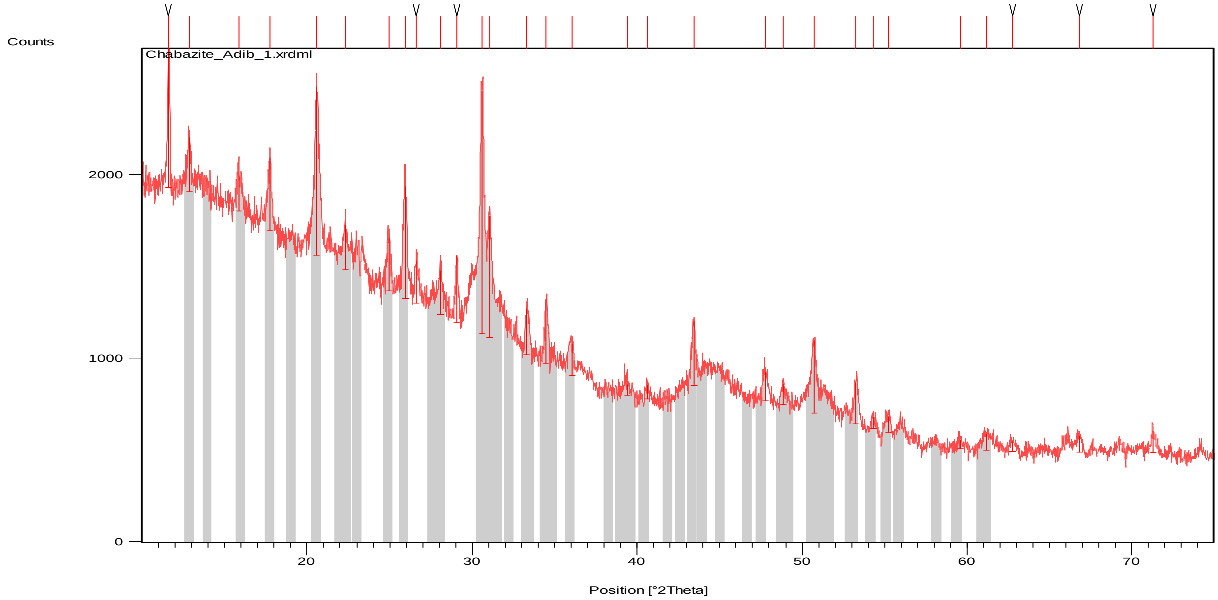


Figure 4.11: XRD Scan of Chabazite showing Ca-Chabazite Match in Grey

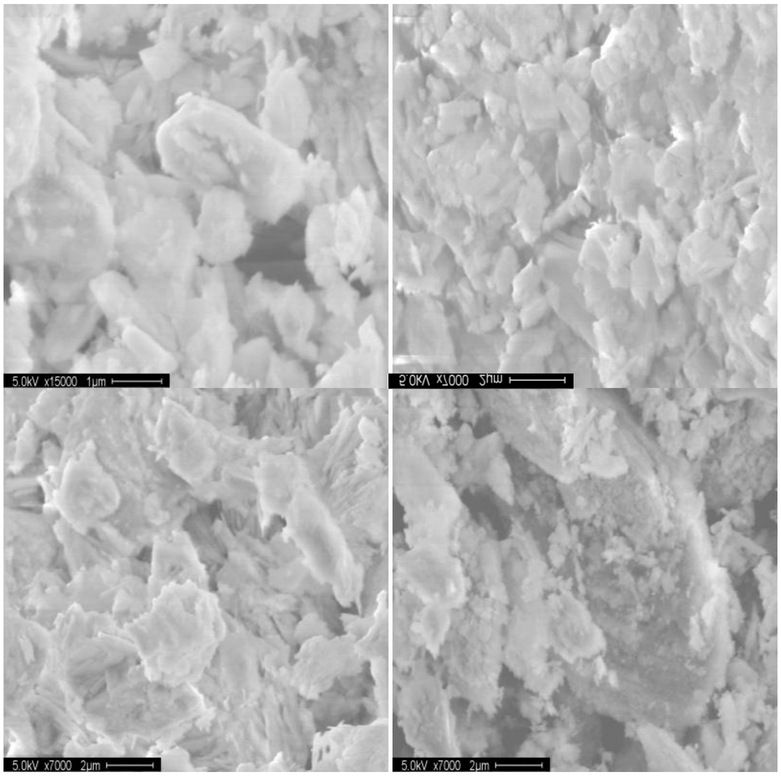


Figure 4.12: SEM Images of Four Zeolites. Top Left: C-Yellow. Top Right: C-Grey. Bottom Left: Zeosand. Bottom Right: Chabazite

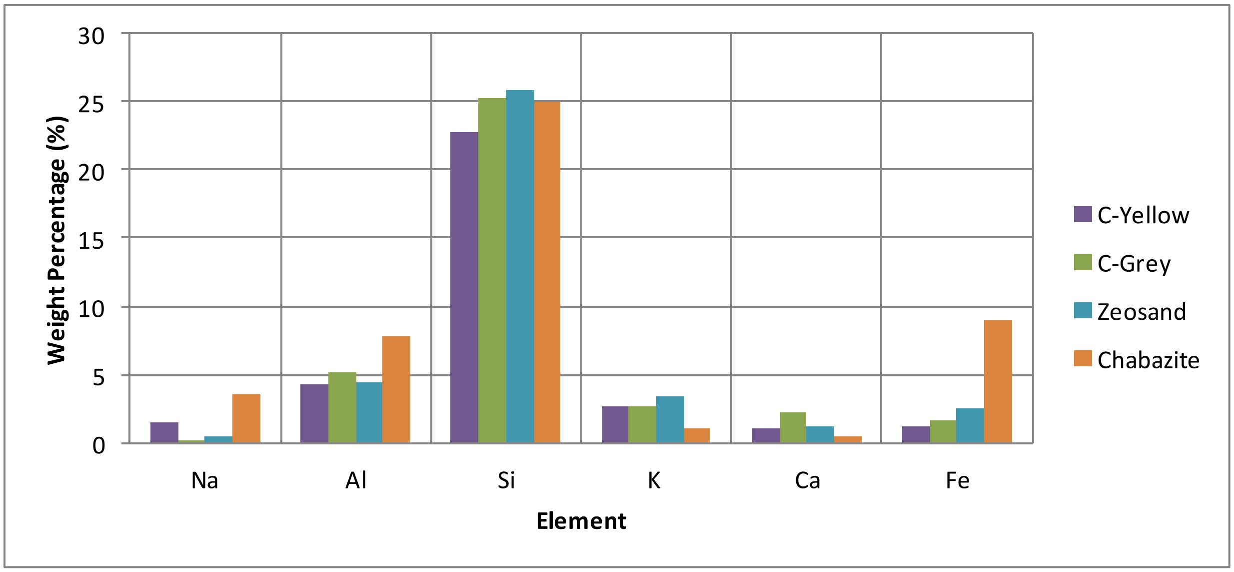


Figure 4.13: Elemental Composition of Zeolites (constituents less than 1% not shown)

SEM-EDX results show the percentage by weight of significant elements in the zeolites. Note that, like the struvites (see above), all of the samples showed N and O presence but amounts are not reported here due to unreliability in readings. Zeolites are aluminosilicates and based on the chemical formulas of clinoptilolite ($(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$) and chabazite ($(Na_2,K_2,Ca,Mg)[Al_2Si_4O_{12}]\bullet 6(H_2O)$), most of the significant elements recorded with the EDX scan match the expected elements, as shown in Figure 4.13. Although XRD analysis showed calcium chabazite to best match the available database in the HighScore software, based on elemental composition sodium chabazite is like a more significant constituent. The XRD peaks between the two are very similar, however, and the HighScore software only estimates a match. The zeolites seem to be a mix of Na, Ca, and K zeolites. The only element that does not seem to match the chemical formula of the zeolites is Fe, which may be due to non-zeolitic amorphous content. Based on the EDX results, from among the alternative mineral matches from the XRD analysis, Azodicarbonamide and Indium Selenium are unlikely candidates. The other alternatives, however, may exist in some quantity. Celadonite is also suspected to exist in the Zeosand, particularly due to its green color. Celadonite also contains Fe.

4.2 Life Cycle Environmental Impact and Cost Assessment

This section evaluates the proposed system for its life cycle environmental impact and life cycle costs. Assessing the life cycle environmental impacts and costs associated with the system allows for a quantitative evaluation of benefit from the system's implementation. While the treatment system is intended to decrease environmental problems, it is not clear as to whether the materials and energy employed in the construction and operation phases incur greater impact than is offset by the waste treatment. Furthermore, quantifying life cycle costs allows for judgment as to the economic expedience. Recovery of materials and energy is expected to significantly decrease environmental impact. Furthermore, it is expected to provide significant economic benefit by decreasing operational costs and possibly providing net positive economic gain.

4.2.1 Life Cycle Inventory

Data for each of the evaluation scenarios was gathered and organized to perform the LCA. Data was collected from a wide variety of sources, including: literature, vendors, contractors, experts, and our own experiments. LCIs available in Simapro v7.2 were used in this assessment. The detailed inventory processes used for each LCI input are provided in the Appendix.

The AD reactor type chosen is a cylindrical completely mixed flow reactor (CMFR) with a 21 day HRT, as shown Table 4.6. A 21 day retention time was chosen because previous experiments have shown that this provides the highest biogas production (Kinyua, 2014). By cogeneration of the electricity, the medium-sized CAFO can produce approximately 82 kW of electricity while the large produces approximately 392 kW.

Table 4.6: AD Operation Information

	Medium Sized CAFO	Large CAFO
Digester Type	Round CMFR	Round CMFR
HRT at Capacity (days)	21	21
Digest Working Volume (m^3)	1,071	5,127
Digester Total Volume (m^3)	1,272	5,650
Working Depth (m)	4.2	4.9
Total Depth (m)	5.0	5.4
Diameter (m)	18	36.5
Cover Type	Floating	Floating
Cover Material	HDPE (80 mil)	HDPE (80 mil)
Temperature maintained (°C)	35	35
Average Methane generated (m^3/kg VS destroyed)	0.35	0.35
Methane Biogas generated per day (m^3/day)	266	1,279
Electricity Production (kW)	82	392
Electricity Produced (kWh/day)	1,958	9,402
Storage Tank Dimensions (m)	5x4x2.6	5x9x4
Storage Tank Volume (m^3)	52	180

Table 4.7: AD Construction LCI*

	Medium Sized CAFO	Large CAFO
Volume of Digester Material (Concrete) (m^3)	134	416
Mass of Cover Material (HDPE) (kg)	502	2,062
Insulation Material (Fiberglass) (kg)	1,034	3,206
Volume of Storage Tank Material (Concrete) (m^3)	17	40
Engine-Generator	Mini CHP Plant	Mini CHP Plant
Steel Pipe Mass (kg)	438	438
PVC Pipe Mass (kg)	46	46
Excavation Volume (m^3)	1,272	5,650
Belt Filter Press (Steel) x2 (kg)	4,536	4,536
Pump	2 pumps	2 pumps
Controls Parts (kg)	2	2
Heater	Furnace heater	Furnace heater
Construction Materials Transport (tkm)	370,967	1,107,845

*Assumed lifetime of 20 years for all construction materials

The information used to build the AD construction LCI (Table 4.7) was primarily based on information provided by contractors and vendors of digesters for swine waste. The construction parts that were expected to contribute the largest impact were included in the assessment. Therefore, smaller parts, such as startup equipment, ventilation accessories, and flare equipment were not included in the inventory. In general, it is expected that the construction will not contribute significantly to the environmental impact when compared to the operation of the system, which is the case for most water and wastewater treatment systems (Choe et al., 2013; Higgins and Olson, 2009; Foley et al., 2010; Pasqualino et al., 2009; Bayer and Finkel, 2006).

The AD operation inventory (Table 4.8) takes into account the most significant energy and materials required for operation of the system. Energy inputs include pump, mixer, heater, and dewatering electricity requirements. However, an energy output is provided by cogeneration of electricity using biogas, which is greater than the energy inputs. Therefore, biogas recovery provides for all of the energy needs of the system while also providing additional energy for use by the CAFO. After digestion, the dewatering allows for recovery of the biosolids. Because P is a depleting nutrient and therefore considered the most important recovered component of the biosolids, the equivalent P_2O_5 content of the biosolids was calculated to estimate the environmental impact offset by biosolids recovery. Avoidance of Diammonium Phosphate (DAP) production was used because the fertilizer includes both N and P and is one of the most commonly used P fertilizers (Barak and Stafford, 2006). After dewatering, the centrate still contain a high nutrient content and must be disposed of. Therefore, the N, P, and K contents of the centrate are considered as discharged to surface waters. This also helps provide a more fair comparison between the first scenario (only AD) and the subsequent two (struvite recovery and IX) which provide recovery of the nutrients from the centrate.

Table 4.8: AD Operation LCI*

	Medium Sized CAFO	**Large CAFO**
Electricity Produced from Biogas (kWh/day)	1,958	9,402
Total Electricity Usage per day (kWh/day)	1,682	6,586
Pumps Electricity Usage (kWh/day)	78	180
Mixer electricity Usage (kWh/day)	396	660
Heater electricity Usage(kWh/day)	1,197	5,663
Dewatering electricity (kWh/day)	11	82
Dewatering Polymer (kg/day)	2	11
P_2O_5 equivalent Avoided (as DAP) by Biosolids Recovery	136	654
Centrate discharged to Surface Water as N (kg/day)	38.3	183.8
Centrate discharged to Surface Water as P (kg/day)	4.1	19.5
Centrate discharged to Surface Water as K (kg/day)	40.4	193.8
Polymer Transport (tkm/day)	2	11

*Value per day shown for ease of understanding, but FU requires actual input to be multiplied over 20 year lifetime

The struvite reactor operation information is shown in Table 4.9. The struvite reactor type chosen in this assessment is an upflow FBR because it is one of the most common commercially operated methods for struvite recovery. No seed is required for FBRs because the bed material is made up of struvite. This allows for heterogeneous precipitation on existing seed material and selective solids separation, as the pellets become large enough to settle. An HRT of 8 minutes was used because this is a common induction time used in commercial reactors (Ostara Inc and KEMA LLC, personal communication, December 4, 2013). The recovery efficiency of struvite is based on our experimental data. A CP recovery efficiency of 77% was used because it takes into account the highest mass recovered (see discussion in section 4.1.2).

Table 4.9: Struvite Reactor Operation Information

	Aeration		**NaOH**	
	Medium Sized CAFO	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Reactor Type	Fluidized Bed Reactor	Fluidized Bed Reactor	Fluidized Bed Reactor	Fluidized Bed Reactor
Reactor Shape	Cylinder	Cylinder	Cylinder	Cylinder
Reactor diameter	0.97	1.61	0.48	0.80
Reactor height	3.20	5.31	1.58	2.64
HRT (minutes)	8	8	8	8
Influent Total P concentration (mg/L)	85.5	85.5	85.5	85.5
P recovery efficiency	77%	77%	77%	77%
Struvite Recovered (kg/day)	24.6	126.2	24.6	126.2

Two main alternatives were considered for how pH was raised in the reactor. The first utilizes aeration for CO_2 stripping while the second uses chemical addition of NaOH. While the induction time for struvite formation is 8 minutes, additional time is required to raise the pH using aeration. This time was approximated at an hour through informal consultation with struvite contractors; however, little literature currently exists on aeration time requirements. The longer HRT for aeration requires a larger reactor which affects the construction materials and capital costs. There is a tradeoff in operation, however, as the aeration-based reactors require more electricity, but NaOH requires manufacturing and transport of the chemical. In our bench scale experiments, we only used NaOH for raising the pH because it is the most commonly used method in commercial systems and our centrate volumes were too low to allow for recovery of the precipitate for crystal characterization using both aeration and NaOH. However, previous bench scale experiments in our laboratory showed issues with foaming during aeration that made reactor operation difficult. Therefore, while the LCA results take account a wide range of system characteristics, other potential issues may arise in large scale operation that require future investigation.

The construction inventory for the struvite reactor (Table 4.10) was based on information provided by contractors and vendors. Most commercial reactors are only provided in a single size; therefore, the information was modified to allow for assessment of various sized reactors. The proportions of the system, however, were kept the same for the different scales. The FBR

Table 4.10: Struvite Reactor Construction LCI*

	Aeration		**NaOH**	
	Medium Sized CAFO	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Steel mass (kg)	4,104	6,181	3,115	3,702
FBR Reactor (carbon steel) kg	1,023	2,817	250	696
Catwalk/Access Platform (carbon steel) (kg)	2,653	2,653	2,653	2,653
Stairs (carbon steel) (kg)	428	710	212	353
Foundation Concrete Volume (m^3)	1.20	2.43	0.50	1.20
Pumps	1 pump	1 pump	1 pump	1 pump
Construction Materials Transport (tkm)	6,987	12,010	4,316	6,585

*Assumed lifetime of 20 years for all construction materials reactor steel mass was modified using the surface area ratio between different sizes, because it is assumed the mass is primarily contained at the surface of the cylinder. The catwalk mass, however, was kept constant because the area required for the catwalk is likely to remain constant. The mass of the stairs was scaled using the height ratio of the stairs. The foundation size also differed depending on the total weight of the system.

Table 4.11: Struvite Reactor Operation LCI*

	Aeration		NaOH	
	Medium Sized CAFO	Large CAFO	Medium Sized CAFO	Large CAFO
Electricity Usage (kWh/day)	96	420	48	180
Aerator Electricity Usage (kWh/day)	48	240	-	-
Pump Electricity Usage (kWh/day)	48	180	48	180
NaOH Usage (kg/day)	-	-	40	192
P2O5 equivalent Avoided (as DAP) Avoided by Struvite Recovery (kg/day)	14	65	14	65
Centrate discharged to Surface Water as N (kg/day)	37.2	178.6	37.2	178.6
Centrate discharged to Surface Water as P (kg/day)	0.9	4.6	0.9	4.6
Centrate discharged to Surface Water as K (kg/day)	40.1	197.2	40.1	197.2
NaOH Transport (tkm/day)	-	-	40	192
Struvite Transport (tkm/day)	2.5	11.8	2.5	11.8

*Value per day shown for ease of understanding, but FU requires actual input to be multiplied over 20 year lifetime

The struvite reactor operation inventory takes into account significant energy and material usage. Electricity usage is primarily attributed to pump operation, required for upflow fluidization, and aeration requirements. A tradeoff between the two alternative reactor types (aeration vs. NaOH) can be seen here, because the aeration requires more electricity while NaOH requires chemical manufacturing and transport. After precipitation, the centrate still contains nutrients. Therefore, the remaining N, P, and K contents of the centrate are discharged to surface waters to provide a more fair comparison between this and the final scenario that allows for recovery of the remaining nutrients via IX.

The IX reactor type used in this assessment is a fixed bed reactor (see Table 4.12). The information used in the assessment is based mostly on data from our experiments and some data acquired from engineering contractors of IX systems for drinking water treatment. Because IX for recovery of nutrients onto zeolites is an emerging technology, practical aspects of the operation, particularly the loading and transport of the zeolite, require further investigation at the pilot scale. The results of our investigation indicate that replenishment and transport of the zeolite is necessary approximately once per week. Therefore, pilot scale and full scale systems must be designed to allow for ease in loading and unloading the zeolite material. Furthermore, because it is an emerging technology, minimal construction information is available for the system (see Table 4.13). A steel process vessel, approximated as a cylinder, was considered the main construction material. K recovery is taken into account in this assessment because it is a valuable nutrient and high recovery is achieved, but the operation of the system is designed around ammonia recovery performance.

Two main alternatives were considered for IX material: use of chabazite and use of clinoptilolite as the zeolite type. Clinoptilolite is the most commonly used zeolite and has the most known deposits (D. Eyde, personal communication, December 27, 2013). Chabazite is less commonly used and the only high quality deposit in the United States (one of the only in the world) is located in Arizona and operated by St. Cloud Mining. The cost of chabazite is therefore much higher than clinoptilolite. However, based on experiments performed in our laboratory, the ammonium cation exchange capacity (see Table 4.12) is almost an order of magnitude higher than that of clinoptilolite. Therefore, less chabazite is needed for the same treatment volume. Furthermore, experiments show that IX using chabazite occurs with higher efficiency within a much shorter retention time than clinoptilolite (4 hrs vs. 24 hours). The clinoptilolite-based system therefore requires a larger reactor and higher capital cost. Thus, significant tradeoffs exist between the two alternatives.

Table 4.12: IX Reactor Operation Information

	Chabazite		Clinoptilolite	
	Medium Sized CAFO	Large CAFO	Medium Sized CAFO	Large CAFO
Reactor Type	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed
Reactor Shape	Cylinder	Cylinder	Cylinder	Cylinder
Diameter	1.78	3.00	3.24	5.46
Height	3.19	5.38	5.81	9.79
HRT (hours)	4	4	24	24
Zeolite exchange capacity (g NH4/kg zeolite)	508	508	59	59
Ammonia influent concentration (mg/L)	784	784	784	784
Ammonia recovery efficiency	94%	94%	86%	86%
Total N adsorption capacity (kg N adsorbed)	326	1,562	229	1,094
Days before zeolite must be emptied (days)	9.33	9.31	7.14	7.12
Potassium influent concentration (mg/L)	865.7	865.7	865.7	865.7
Potassium recovery efficiency	94%	94%	71%	71%
Zeolite Usage Rate (kg/day)	69	330	542	2,603

Table 4.13: IX Reactor Construction LCI*

	Chabazite		Clinoptilolite	
	Medium Sized CAFO	Large CAFO	Medium Sized CAFO	Large CAFO
Mass of Steel in Reactor (Steel) (kg)	2,028	5,761	6,720	19,083
Steel Transport (tkm)	2,028	5,761	6,720	19,083

*Assumed lifetime of 20 years for all construction materials

Aside from operational differences between chabazite and clinoptilolite, there are significant differences in the mining of the materials. Zeolites are considered soft minerals, as opposed to a hard mineral such as limestone. Clinoptilolite mining occurs in open pit mines and overburden waste material ranges from1-10 feet in thickness. Clinoptilolite deposits can be about 75 feet thick, which is the case with Zeosand. The clinoptilolite is blasted, crushed, and transported to the mill. The mill produces little waste and does not use water. When the clinoptilolite deposit is depleted, overburden is put back on the site and is seeded with native vegetation (P. Bunger, personal communication, March 3, 2013). The main difference between clinoptilolite and chabazite mining is that the chabazite deposit is very thin, sometimes only 1 foot (0.3m) in thickness. This requires much more energy and labor for overburden removal per amount of chabazite recovered and often requires toilsome manual digging (D. Eyde, personal communication, March 3, 2013). Because of the differences in mining of the zeolites, it is estimated that mining of approximately 10 tons of clinoptilolite is equivalent to 1 ton of chabazite (D. Eyde, P. Bunger, personal communication, March 3, 2013).

The only existing LCA that has been performed on zeolites took into account average manufacturing of synthetic zeolites (Fawer et al., 1998). This does not fairly evaluate the impact of natural zeolite and also does not take into account the significant differences in the mining of chabazite and clinoptilolite. In order to fairly evaluate the environmental impact of the zeolites, bentonite provides a suitable approximation of the impact of natural clinoptilolite mining (D. Eyde, P. Bunger, personal communication, March 3, 2013). Furthermore, to take into account the higher impact of mining chabazite, the chabazite mass inputs to the LCI (as bentonite) are multiplied by a factor of 10.

Before IX is performed, the centrate pH must be lowered to neutrality to ensure efficiency ion exchange. This requires chemical addition and transport as shown in Table 4.14. The zeolite usage rates and transport differ significantly between chabazite-based and clinoptilolite-based reactors due to the difference in cation exchange capacity and HRT requirements described previously. The recovered zeolite contains high levels of N and K, with K being the largest constituent. Therefore, to take into account the environmental impact offset by their recovery, the K_2O content was calculated as Potassium Nitrate (KNO_3), which includes both the K and N contents. This KNO_3 was considered as an avoided product. After IX is performed, it is also assumed that the water can be reclaimed. See section 4.1.1.1 for discussion on potential uses of the reclaimed water.

Table 4.14: IX Reactor Operation LCI*

	Chabazite		**Clinoptilolite**	
	Medium Sized CAFO	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Avoided K_2O equiv.(as KNO_3) by N & K Recovery (kg/day)	41	223	38	169
Equivalent Zeolite Usage Rate as Bentonite (kg/day)	688	3,304	542	2,603
HCl dry mass needed (kg/day)	57	276	57	276
Avoided Water Production (L)	47,467	227,841	47,467	227,841
HCl Transport (tkm/day)	57	276	57	276
Zeolite Transport (tkm/day)	76	363	596	2,863

*Value per day shown for ease of understanding, but FU requires actual input to be multiplied over 20 year lifetime

4.2.2 Impact Assessment

The impact assessment was conducted for each treatment train with all alternatives, in both the medium and large scales. Comparisons were performed for each scenario to provide understanding of how choice of alternatives can affect impact. The results for the treatment system designed for waste from a medium-size CAFO are presented, along with a comparison between the medium-size and large systems. The results of the large system are included in the Appendix.

The assessment results comparing alternatives of additions to the treatment train generally shows that implementation of the treatment system provides environmental and human health benefits in most categories and minimal impact in others, as shown in Figure 4.14. The alternatives that include IX generate impact in ozone depletion, mainly because of HCl and zeolite production. This is likely because some HCl production can produce chlorofluorocarbons (CFCs) which deplete the ozone. Alternative acids and acid production methods are currently under investigation. AD and struvite precipitation generate eutrophication impact, which is offset after IX is put in place. This is because these scenarios consider nutrients in the untreated centrate as being discharged to surface waters, as described in section 3.2.1. The discharge to surface waters primarily causes eutrophication. When IX is implemented, however, the centrate is considered as treated and suitable for some of reclaimed use, as discussed in section 4.1.1.1. The rest of the impact categories show nearly neutral or negative impact, demonstrating that implementation of the system benefits the environment and human health. There are also negligible differences between using aeration vs. NaOH for struvite precipitation or between clinoptilolite and chabazite usage. This is likely because the aeration requires more energy, but NaOH use requires production of the chemical. Furthermore, chabazite has an ammonium exchange capacity that is approximately an order of magnitude higher than clinoptilolite, requiring 10 times as much clinoptilolite for treatment. However, chabazite mining creates an estimated 10 times more impact than clinoptilolite, balancing the environmental impact.

A comparison between impacts due to operation and construction was also performed, as shown in Figure 4.15. Across all impact categories and scenarios, the impact due to operation outweighs construction so significantly that usually construction impacts are not visible in the figure. Therefore, environmental impact of the system can be accurately assessed by only analyzing the materials and energy required for operation without accounting for construction. This can be implemented in future research to make completion of the LCI more feasible. Furthermore, it implies that it is important for operational parameters to be precise in order for the assessment to be accurate, while accuracy of construction parameters used in this study is not essential.

The impacts of each alternative of the entire treatment train for waste from a medium-size system were also compared to the large scale, as shown in Figure 4.16. This takes into account the functional unit (FU) of the system which is treatment of 50.82 m^3/day of swine waste over the course of 20 years (see section 3.2.2). The comparison was performed for a system that uses aeration and clinoptilolite because these showed low impact and the lowest costs (see section 4.2.3); however, results were similar for all other system choices. Across all categories the large scale system is more environmentally friendly than the medium –scale system, creating an "economies of scale" effect with environmental impact. In this case, because the system is beneficial to the environment, the larger system creates more benefit than the medium-size system. Furthermore, this assessment shows that when the system has a negative effect on the environment, this effect decreases on a per FU basis as the scale increases. This is shown by how the larger system produces less impact in ozone depletion, ecotoxicity, and smog.

Each individual treatment train alternative was also analyzed to show their contributors to impact, as shown in Figures 4.17-4.21. Because results show that operational impacts are the far more significant than construction, only the operational parameters were included. For AD, the most significant contributor to negative environmental effects is electricity usage. The majority of this electricity requirement comes from heating the system to 35°C. However, energy production from biogas and avoided DAP production from the recovery of biosolids overcomes the impact and produces a benefit to the environment.

Between the two alternatives of struvite production using aeration or NaOH, their trends across impact categories are very similar, as shown in Figure 4.18-4.19. The main difference is the higher electricity requirements of aeration and chemical usage of NaOH, as described above. As expected, however, these impacts balance, causing both struvite precipitation methods to have a similar impact on the environment.

Among the two zeolite alternatives for IX, the results are very similar, as shown in Figures 4.20-4.21. The main difference lies in the high transport requirements of clinoptilolite. In contrast to the AD and struvite systems, however, the IX system produces a negative effect on the environment across all categories. This can also be seen in Figure 4.14. Although addition of IX to the treatment train still allows the system to provide a net environmental benefit, the benefit decreases in all impact categories except for eutrophication, because it prevents discharge of N and P. Its impact is mainly due to HCl and zeolite production and processing, which overcome the benefits provided by avoided KNO_3production. KNO_3 has more impact than DAP on a per kg N basis (their common constituent), which indicates that a difference in the type of fertilizer production avoided is not the reason why the AD and struvite production scenarios are more beneficial.

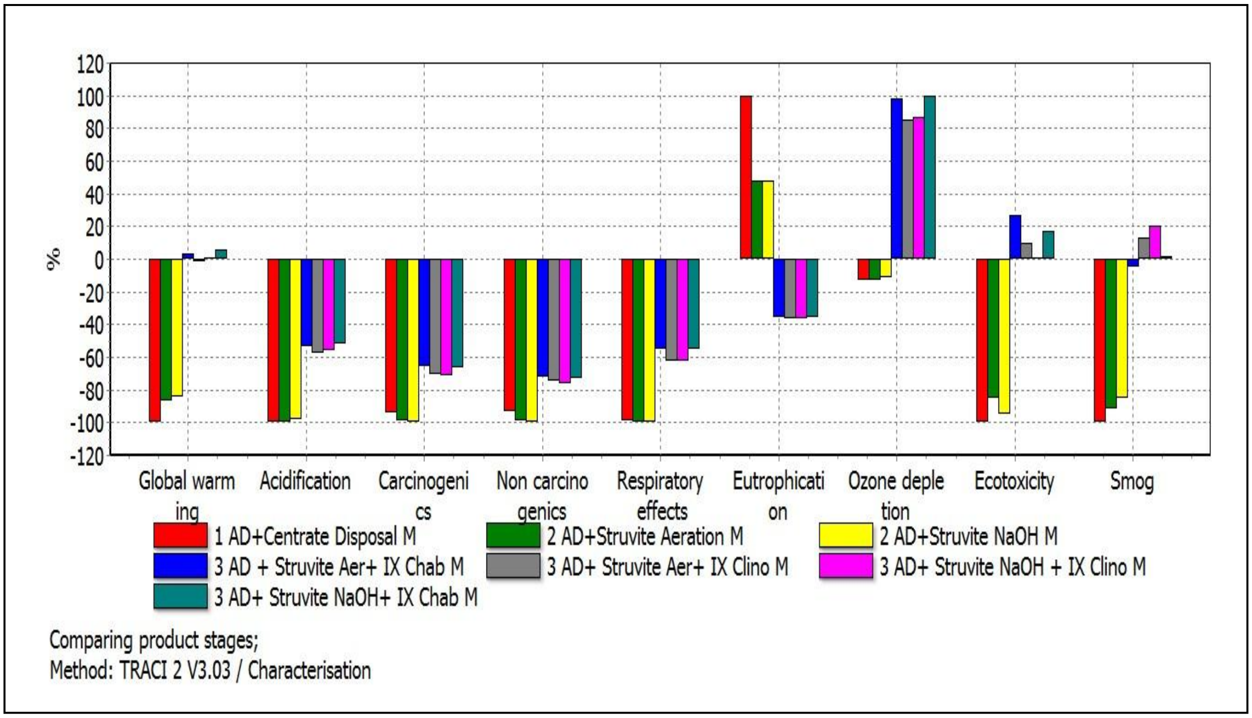


Figure 4.14: Impact Assessment Comparing Additions to the Treatment Train for Medium Size CAFO

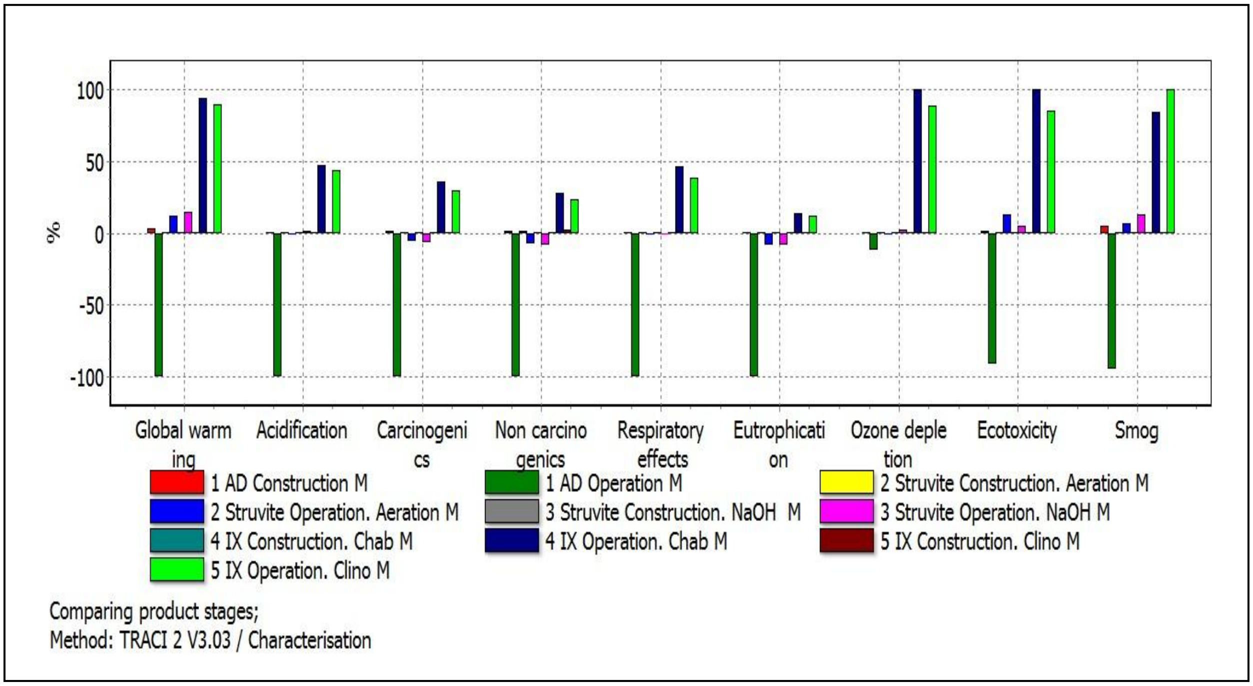


Figure 4.15: Impact Assessment Comparing Construction vs. Operation for Medium Size CAFO

Figure 4.16: Impact Assessment Comparison Between Systems for Medium and Large CAFO, Using Aeration and Clinoptilolite

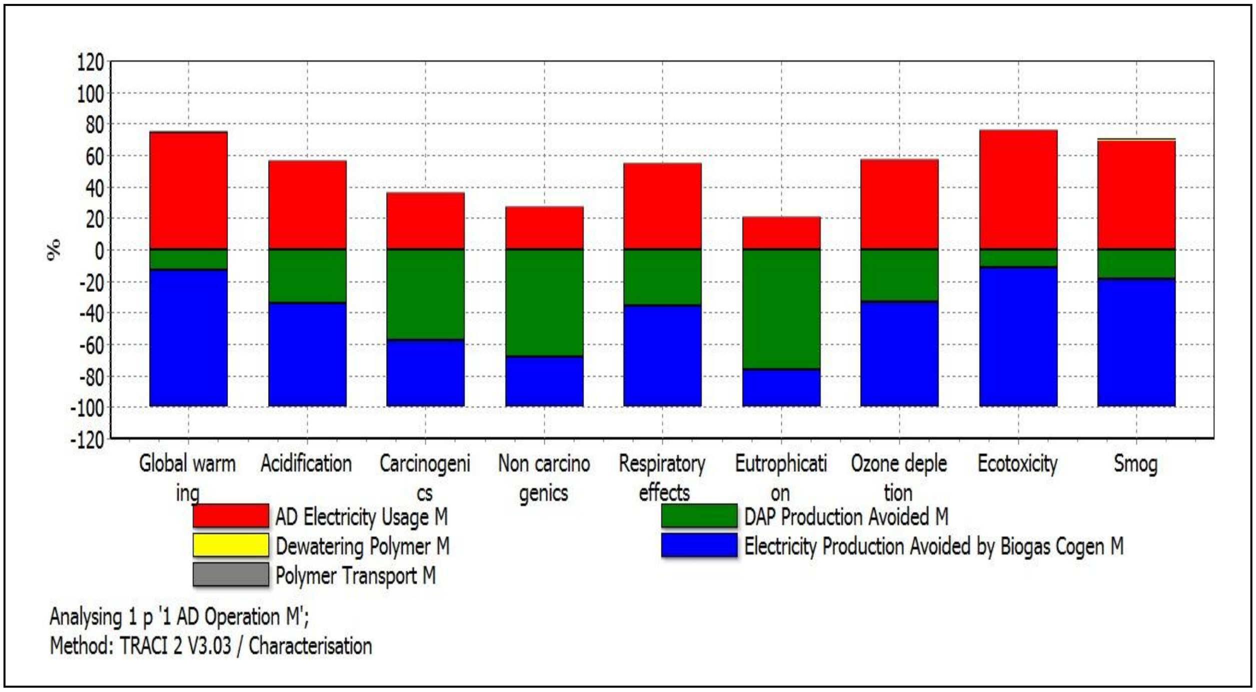


Figure 4.17: Impact Analysis of AD for Medium Size CAFO

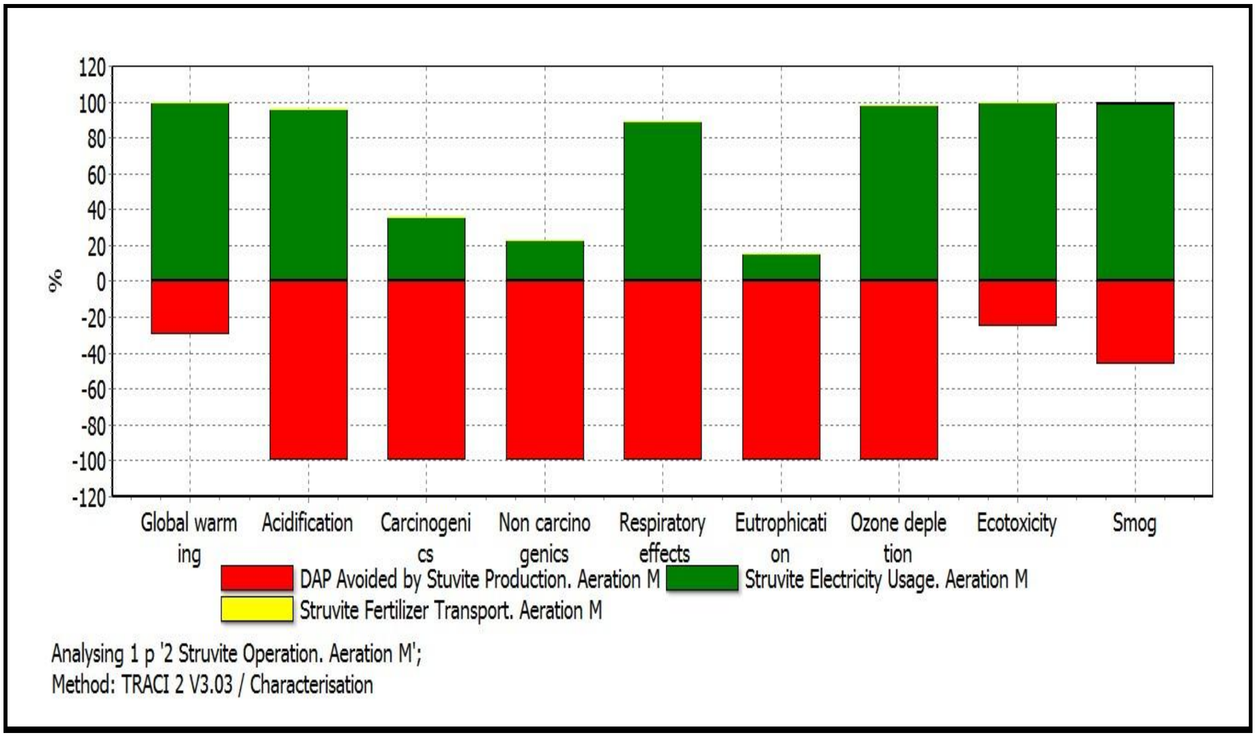


Figure 4.18: Impact Analysis of Struvite Precipitation Using Aeration for Medium Size CAFO

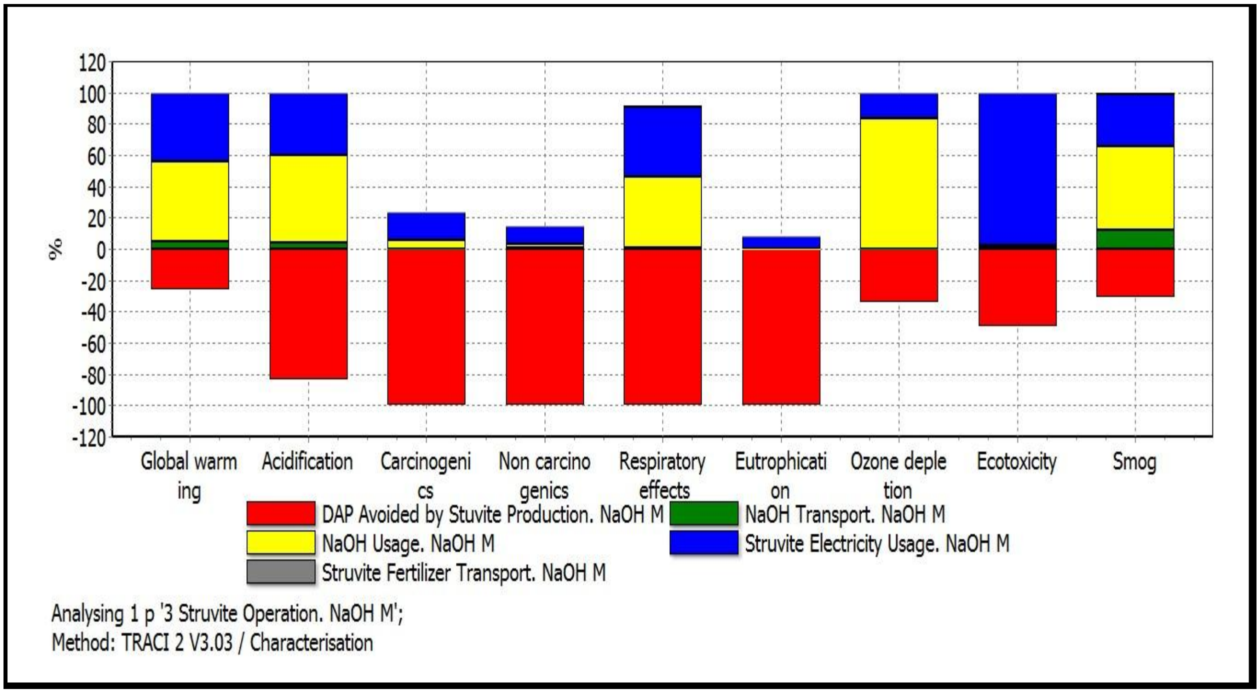


Figure 4.19: Impact Analysis of Struvite Precipitation Using NaOH for Medium Size CAFO

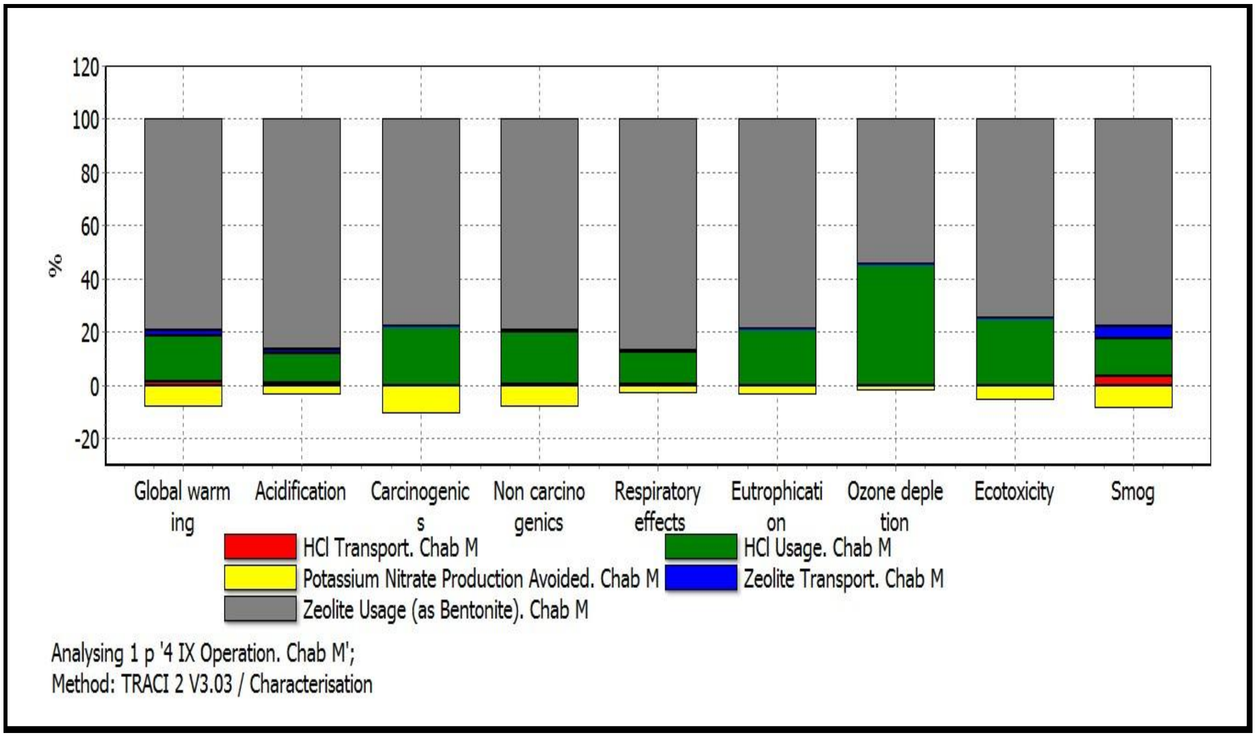


Figure 4.20: Impact Analysis of IX using Chabazite for Medium Size CAFO

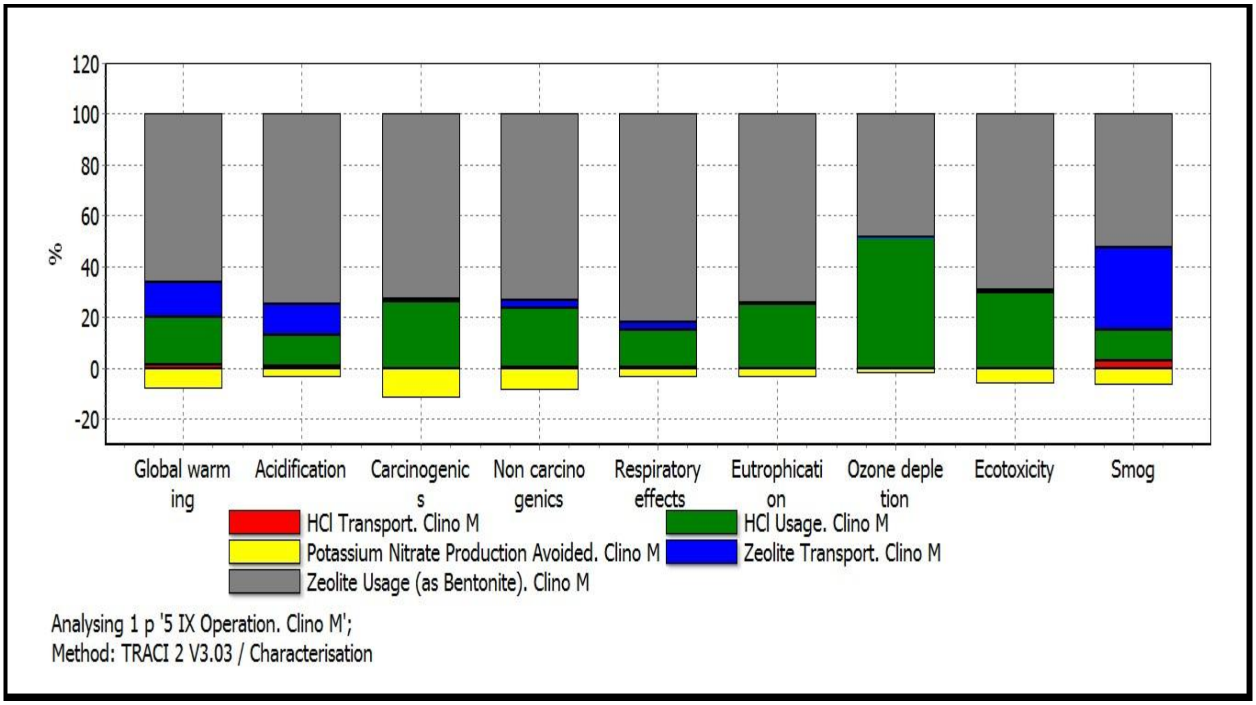


Figure 4.21: Impact Analysis of IX using Clinoptilolite for Medium Size CAFO

4.2.3 Life Cycle Cost Analysis

An LCCA was performed on the same two cases considered in the LCA section of this thesis: a medium-sized and a large-sized CAFO treatment system. The alternatives for the struvite precipitation and IX systems that were considered in the LCA were also considered in the LCCA. This section presents the LCCA results and discusses their implications on the economic viability of treatment options and the effects of scale.

4.2.3.1 AD Costs

The estimated construction and operation cost summaries for the AD designed for treatment of waste from a medium-sized and a large-sized CAFO (or centralized waste treatment) are shown in Table 4.15. AD construction cost data were obtained from manufacturer of swine and dairy anaerobic digesters. The total capital expenses (CAPEX) can be considered very high for most CAFO owners (over $1 million and over $2.3 million). Because of the high CAPEX, financing will be a necessity for most CAFOs. Financing options, however, have not been considered in this analysis. In many states, government grants assist with financing. Other economic incentives such as renewable energy credits can also reduce overall cost of such systems, but are not taken into account in this assessment.

The largest cost is due to equipment purchases, including dewatering equipment (i.e. belt filter presses). This is beneficial for the larger scale system because equipment costs increase nonlinearly due to economies of scale effects, making the larger scale system more cost competitive. Detailed itemization of the estimated construction costs for both systems are provided in the Appendix.

The estimated operational cost summaries for both systems are shown in Table 4.16. The main operating expense (OPEX) for AD is from electricity use and the net OPEX is favorable, providing net revenue for both systems. In this assessment it was assumed that biogas is recovered and cogeneration is used to produce electricity for use by the CAFO. Therefore, its cost offsets were calculated based on national average rates of 9.64 cents/kWh (EIA, ND). Furthermore, it was assumed that biosolids will be sold. Often biosolids are sold at minimal cost, but a typical price, which was used in this assessment is about $10 per yard ($13.08 per m^3) (AD manufacturer, personal communication, March 3, 2013; Goldstein and Block, 1997). The system, therefore, generates net revenue because of the two main recovered products.

Table 4.15: CAPEX Summary for Anaerobic Digester for Medium and Large-size CAFOs

	Cost			
Cost Category*	**Medium Sized CAFO**		**Large CAFO**	
Site Work	$	185,208	$	656,088
Equipment	$	698,656	$	1,354,712
Engineering Utility, Construction Management, Startup, Commissioning	$	136,006	$	288,209
Total Cost	**$**	**1,019,870**	**$**	**2,299,009**

*Detailed capital costs are provided in the appendix

Table 4.16: OPEX Summary for Anaerobic Digester for Medium and Large-size CAFOs

	Cost ($/day)	
Cost Item	**Medium Sized CAFO**	**Large CAFO**
Electricity cost	162.16	634.87
Electricity Cost offset	(185.09)	(906.34)
Revenue from biosolids	(43.86)	(210.52)
Dewatering polymer cost	0.33	1.57
Total OPEX	**(66.46)**	**(480.42)**

4.2.3.2 Struvite Precipitation

CAPEX for struvite precipitation reactors were estimated for four scenarios considering aeration vs. NaOH addition and waste treatment from medium vs. large scale CAFOs. Construction cost data was obtained from commercial manufacturers. Note that a base case scenario was modified to develop the CAPEX for each, based on changes in system size, flow rate treated, and equipment (i.e. aerators). Furthermore, the reactor design evaluated was a fluidized bed reactor (FBR) (see section 4.2.1 for discussion on system design choice). Materials costs were scaled based on flow rate using Equation 2.1, where n=0.65 for a Crystallizer (Guthrie, 1969). Mobilization/freight was scaled using weight percentage, assuming that costs follow a linear trend based on shipping weight. Lastly, aerator costs were scaled depending on the flow rate and estimated amount of aerators required. The other cost items were assumed to be consistent in this assessment. These assumptions and scaling methods allow for a general comparison and understanding of how costs may differ from scenario to scenario, but are only best estimates.

Very little information is available on cost data for struvite precipitation reactors in the literature because most designs are proprietary. It should be noted that these costs are based on a scenario that uses a simple FBR design constructed with “off the shelf” parts. Reactors employed commercially, however, vary widely in reactor type as well as other aspects of reactor use and configurations (see Table 2.3). Other designs may likely be more expensive than the values presented here, yet many companies prefer to implement more expensive reactors to create a more uniform precipitate that is more easily certified for fertilizer sale and marketed as a high quality product. Therefore, there are tradeoffs depending on the intended use of the precipitate. Section 4.1.2 discusses the possible differences in precipitates in more detail.

The CAPEX for aeration reactors are always higher than for reactors that use NaOH addition because raising the pH by aeration requires a much longer retention time and therefore a larger reactor. There are tradeoffs, however, in OPEX, as shown in Table 4.18. The use of NaOH incurs a high cost that greatly overcomes revenue due to struvite, especially at larger scales. However, while aeration incurs electricity requirements, the electricity costs are far lower than NaOH costs and are outpaced at larger scales by struvite revenue, causing large scale aeration based reactors to provide better revenue than all other scenarios. Note, however, that aeration requirements for raising the pH are only an estimate, as there is little literature available for optimum aeration rates for struvite precipitation. The NaOH requirements are also estimates, based on our laboratory experiments (see Sensitivity Analysis for discussion on impact of estimates).

Table 4.17: CAPEX for Struvite Precipitation Reactors

		Cost ($)			
		Aeration		**NaOH Addition**	
Category	**Notes**	**Medium Sized CAFO**	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Materials	Includes custom fabricated parts, "off-the-shelf" parts, concrete, and installation materials.	67,081	179,776	16,691	44,731
Labor for Install	Electrical, pipe fitting, concrete pouring, etc.	40,280	40,280	40,280	40,280
Equipment for Install	Includes crane for erection	10,395	10,395	10,395	10,395
Mobilization/ freight	Mobilizing install crew and freight on fabricated items	7,477	11,261	5,676	6,744
System Startup and Training	System commissioning, safety and operation training for employees	8,000	8,000	8,000	8,000
Aerators		140	700		
Total Cost		**133,373**	**250,411**	**81,042**	**110,150**

Two things will primarily affect the OPEX: the flow rate of the system and the concentrations of Mg, P, and N in the centrate (particularly whichever is the limiting nutrient). This is because deriving revenue from struvite precipitation is driven by the amount of struvite that can be recovered. In swine waste, Mg and N are usually plentiful and therefore P is the limiting nutrient for struvite precipitation. Therefore, having a higher P concentration in the waste would make all of the scenarios more economically favorable.

Table 4.18: OPEX for Struvite Precipitation Reactors

	Cost ($/day)			
	Aeration		NaOH Addition	
	Medium Sized CAFO	Large CAFO	Medium Sized CAFO	Large CAFO
Struvite	(9.08)	(43.59)	(9.08)	(43.59)
Electricity	9.25	40.49	4.46	16.74
NaOH			20.04	96.20
Total OPEX	0.17	(3.10)	15.42	69.35

In an alternate scenario where the soluble P concentration in the AD effluent is 160 mg/L, often seen in some swine waste AD effluents (see Table 4.2), the operating costs of the system can change significantly, as shown in Table 4.19. This makes both aeration and NaOH addition more economically favorable.

Table 4.19: OPEX for Alternate Struvite Scenario with 160 mg/L Soluble P

	Cost ($/day)			
	Aeration		**NaOH Addition**	
	Medium Sized CAFO	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Struvite	(21.09)	(101.24)	(21.09)	(101.24)
Electricity	9.25	40.49	4.46	16.74
NaOH			20.04	96.20
Total OPEX	**(11.84)**	**(60.75)**	**3.42**	**11.71**

Another possible alternate scenario that can be taken into account is where more electricity is required for aeration. This is possible because the current assessment is based on a best estimate and little literature is available on required aeration rates. To assess the potential of an extreme change, if aeration electricity requirements were to double, the OPEX would significantly increase, as shown in Table 4.20. The OPEX would still be less than the NaOH alternative, but a large scale system would be needed to generate revenue from struvite precipitation.

Table 4.20: OPEX for Alternative Aeration-based Scenario with Doubled Electricity Requirements

		Cost ($/day)	
		Medium Sized CAFO	Large CAFO
72.7 mg/L Soluble P	Struvite	(9.08)	(43.59)
	Electricity	13.88	63.62
	Total OPEX	4.80	20.03
160 mg/L Soluble P	Struvite	(21.09)	(101.24)
	Electricity	13.88	63.62
	Total OPEX	(7.21)	(37.61)

4.2.3.3 IX using Natural Zeolites

The CAPEX for the IX reactors is based on cost information obtained from a manufacturer of IX systems for drinking water treatment. The most significant capital costs are estimated to be only due to construction and materials of the IX reactor. Just like the other treatment stages, each scenario requires a different size reactor due to differences in retention time. To calculate for this difference, retention time was held constant and a theoretical flow rate was calculated for each scenario and used in Equation 2.1. The reactor is a steel process vessel; therefore, n=0.71 was used in the equation (Brown, 2003).

Table 4.21: CAPEX for IX Reactor

	Cost ($)			
	Chabazite		**Clinoptilolite**	
	Medium Sized CAFO	**Large CAFO**	**Medium Sized CAFO**	**Large CAFO**
Reactor Cost	46,299	140,749	165,820	503,961

The reactor design used is a fixed bed reactor, therefore energy for mixing is not required. Furthermore, that pumping is not required because it is assumed that centrate will already have velocity from flowing out of the upflow FBR used for struvite precipitation. The main costs are therefore due to purchasing of zeolite to replenish the reactor and HCl addition to lower the pH to neutrality after struvite precipitation, which is necessary to achieve high IX efficiency. The costs are offset, however, by recovery of the zeolites as well as the nutrients adsorbed. It is assumed that clinoptilolite will have a 5% depreciation in value from its original cost of $200 per ton; however, it increases in value because of nutrients adsorbed to it after IX. It is also assumed that chabazite and clinoptilolite will have an equivalent value as a fertilizer (not taking into account nutrients). When accounting for the nutrients they hold, chabazite is more valuable because it has higher adsorption capacity. This assumption was made because there is no significant difference in performance of the zeolites as a fertilizer or soil amendment and the value to the consumer will likely be the same. With these assumptions, the cost per ton of chabazite with its nutrients was calculated to be about $945 per ton and the cost of clinoptilolite with its nutrients is about $270 per ton. This is reasonable because chabazite contains more nutrients per ton. Furthermore, the nutrients are mostly N and K, and the cost of Potassium Nitrate fertilizer is approximately $800-1,000 per ton.

Because zeolite usage is the main operating expense, clinoptilolite is better able to recover its costs and produce a revenue. Both scales of clinoptilolite usage produce a net revenue, while both chabazite scenarios generate a net cost. This cost or revenue is exacerbated at larger scales, making clinoptilolite more economically desirable and chabazite less so. Therefore, if zeolite recovery for agricultural use is intended, clinoptilolite is the recommended as the best choice. Furthermore, clinoptilolites vary in IX capacity; therefore, use of a higher capacity clinoptilolite can further increase economic feasibility. Because of the high cost of chabazite, ammonium recovery is not recommended as the best application for its use. Chabazite, however, has been shown to be extremely useful in other high cost applications that it has been shown to perform well in, such as nuclear waste treatment applications and selective cesium removal from seawater (D. Eyde, personal communication, December 27, 2013)

Table 4.22: OPEX for IX System

	Cost ($/day)			
	Chabazite		Clinoptilolite	
	Medium Sized CAFO	Large CAFO	Medium Sized CAFO	Large CAFO
Zeolite cost per day	240.93	1,156.49	108.45	520.58
Total Fertilizer revenue	(63.15)	(321.02)	(148.97)	(708.81)
N Fertilizer cost offset	(23.08)	(110.78)	(21.12)	(101.36)
P Fertilizer cost offset	(0.49)	(4.69)	(0.72)	(5.07)
K Fertilizer cost offset	(26.50)	(142.76)	(24.11)	(107.83)
Zeolite Cost offset	(13.08)	(62.78)	(103.03)	(494.55)
HCl Cost	14.36	68.95	14.36	68.95
Total OPEX	**192.15**	**904.42**	**(26.16)**	**(119.28)**

4.2.3.4 Overall Cost Analysis

The overall LCCA summaries for each CAFO size are shown in Tables 4.23 and 4.24. The payback period for the mid-size CAFO is approximately 39 years, longer than the lifetime of the system (assumed 20 years). However, overall system costs decrease significantly with larger scales, decreasing the payback period to 15 years. AD incurs the largest capital cost to the system but also provides the highest revenue. IX using natural clinoptilolite also provides a net revenue to the system. IX using chabazite, however, is not recommended. Struvite precipitation does not provide a net revenue based on current operation parameters, but change in the concentration of soluble P in the centrate can significantly improve economic feasibility of the system.

Table 4.23: Overall LCCA Summary for Medium-Size CAFO

	Cost Item	Base Date Cost ($)	Present Value ($)	Lifetime Cost ($)	Payback Period (Years)
AD	CAPEX	1,019,870	1,019,870	717,615	42
	OPEX (Annual)	(24,258)	(302,254)		
Struvite (Aeration)	CAPEX	133,373	133,373	134,159	-
	OPEX (Annual)	63	786		
Struvite (NaOH)	CAPEX	81,042	81,042	151,192	-
	OPEX (Annual)	5,630	70,150		
IX (Chabazite)	CAPEX	46,299	46,299	920,168	-
	OPEX (Annual)	70,134	873,869		
IX (Clinoptilolite)	CAPEX	165,820	165,820	46,864	17
	OPEX (Annual)	(9,547)	(118,956)		
Total (Lowest Cost Choices)	CAPEX	1,319,063	1,319,063	898,638	39
	OPEX (Annual)	(33,742)	(420,425)		

Table 4.24: Overall LCCA Summary for Large-Size CAFO

	Cost Item	Base Date Cost ($)	Present Value ($)	Lifetime Cost ($)	Payback Period (Years)
AD	CAPEX	2,450,956	2,450,956	266,044	14
	OPEX (Annual)	(175,354)	(2,184,912)		
Struvite (Aeration)	CAPEX	250,411	250,411	236,295	-
	OPEX (Annual)	(1,133)	(14,116)		
Struvite (NaOH)	CAPEX	110,150	110,150	425,554	-
	OPEX (Annual)	25,313	315,404		
IX (Chabazite)	CAPEX	140,749	140,749	4,253,960	-
	OPEX (Annual)	330,113	4,113,211		
IX (Clinoptilolite)	CAPEX	503,961	503,961	(38,528)	12
	OPEX (Annual)	(43,538)	(542,489)		
Total (Lowest Cost Choices)	CAPEX	3,205,328	3,205,328	463,811	15
	OPEX (Annual)	(220,025)	(2,741,517)		

4.3 Alternative Process Designs

Alternative process and reactor configurations could possibly provide environmental and economic advantages. A wide variety of alternative configurations can be imagined. A few promising alternatives are discussed in this section. Preliminary tests on some of these alternatives have already been performed in our laboratory.

One of the possible alternatives is an integration of the nutrient recovery stages. Performing IX of N and struvite precipitation within the same reactor is an attractive alternative because it provides advantages of utilizing one reactor for the two processes (lower capital cost). Furthermore, previous tests in our laboratory have shown that a neutral pH is required for efficient IX to take place. Centrate leaving AD is already at approximately neutral pH, but in the current process, struvite precipitation raises the pH to 8.5 and the pH is then dropped back down to 7 before IX by HCl addition. Zeolite contact with the waste also naturally raises the pH to approximately 8.5. Therefore, placing IX directly after AD would automatically precipitate struvite. By integrating the two processes, both NaOH and HCl addition could be eliminated completely, reducing operating costs significantly.

From an operational standpoint, integrating IX with struvite precipitation provides several challenges and poses some unanswered questions. One of the operational challenges is solids separation of the struvite precipitate as well as the zeolite. For example, zeolite could possibly be placed within the existing fluidized bed reactors for struvite precipitation. However, larger reactors would be required (high capital cost) and it is unclear how efficient recovery of the zeolite would be performed. Furthermore, it is unknown as to whether placement of zeolite within the FBR would affect the struvite precipitation reaction, uniformity of struvite pellets (size and shape), the quality of the precipitate, or the solids separation of the struvite. Other reactor configurations are possible, such as a CMFR or fixed bed followed by solids capture by centrifuge or hydrocyclone. Yet, future research is needed to evaluate the alternatives. Lastly, given the advantages such integration can provide, the environmental and cost disadvantages from large zeolite requirements may still outweigh the advantages.

To avoid the disadvantages caused by large zeolite usage, an alternative IX material may be utilized. An alternative material that we have considered is biochar that can be produced from the biosolids generated from dewatering AD effluent. Biochar can be produced from the biosolids by pyrolisis and this biochar has been found to have a moderate cation exchange capacity. Therefore, if the biochar can be used as an alternative IX material, zeolite usage could be significantly reduced. Biochar is widely known as a beneficial soil amendment. Furthermore, biosolids-based biochar already contains high amounts of nutrients and the additional adsorbed N makes it even more attractive. From some preliminary studies, however, IX capacity of biochar is not very high and it is unknown as to how much biochar could be produced. Therefore, complete elimination of zeolite usage is unlikely. Pyrolisis also requires energy usage. Future research, however, is necessary to determine if its advantages outweigh the disadvantages from a life cycle perspective.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The following selections summarize conclusions and recommendations for the experimental, LCA, LCCA work described in this thesis.

5.1 Experimental Conclusions

Water quality is greatly improved throughout the treatment process, but due to poor effluent quality, there are few options for reusing the reclaimed water without further treatment. Reuse for flushing of the hog pens provides a practical use of the reclaimed water. It is also advantageous because it does not require long distance transport of the water and allows for compounding recovery of remaining nutrients in the effluent. Further research would be necessary, however, to determine the effects of using the reclaimed water in the treatment system.

The P recovery percentage during struvite precipitation was 87% from SRP (60 mg/L recovered) but the highest mass recovered was from CP (77% efficiency, 66 mg/L recovered). It is expected that precipitation only occurred from SRP, but there was adsorption of P onto the struvite precipitate. Therefore, to account for the total P recovered through precipitation it is necessary to measure the recovery efficiency of CP (includes P in suspended solids). The remainder of the P is largely recovered during IX, achieving up to 100% recovery of orthophosphate. Differences in recovery of P between clinoptilolite and chabazite are small, but clinoptilolite recovers 5% more of CP.

A total mass of 816 mg/L N was recovered through struvite precipitation. Recovery of ammonium was 7% but the recovery of TN was 49%, possibly due to adsorption of N onto the precipitate. To account for recovery of N through struvite precipitation the TN must therefore be measured and this is recommended as a method for future research. Through IX, the majority of the remaining N was recovered. At these stages, no statistically significant difference can be seen between TN and ammonium; therefore the N is almost entirely in the ammonium form. Between the zeolite alternatives, chabazite provides 6-8% higher recovery than clinoptilolite.

The recovery of Mg occurs mostly through struvite precipitation. Often in struvite precipitation processes, Mg is the limiting constituent and a Mg source must be added to allow for precipitation. In the case of most swine wastes, however, Mg is plentiful and P is the limiting constituent. If the waste contained more P, then it would allow for more recovery of Mg and N, and more struvite overall. Calcium also decreases during precipitation, indicating that some of the precipitate likely includes small amounts of calcium phosphates, but XRD and SEM-EDX analysis indicate that the calcium phosphates are a relatively small portion of the precipitate.

Significant K recovery was achieved through the IX treatment. 86% (725 mg/L) of the K was recovered using chabazite and 76% (660 mg/L) using clinoptilolite. Therefore, after IX occurs, the zeolites are not only rich in N but also extremely rich in K. This adds value to the zeolite as a fertilizer and makes it more economically favorable.

All of the precipitates were confirmed as struvite by XRD. The crystals varied widely, however, with crystal sizes ranging from 2um to 100um. The crystal size may affect the hardness and dissolution rate of the precipitates, but further experiments are necessary to confirm this. The crystal morphology also seems to differ, but the cause is unknown. The elemental composition of the precipitates is generally similar, with some exceptions. For example, CG Phosphate contains higher P and Mg contents than other precipitates and some of the precipitates contain higher calcium levels. There were also differences observed between the core and surface of some precipitates, likely due to changes during operation or use of seed materials. Some of the precipitates also included impurities that are likely calcium phosphates and biosolids. The inclusion of these impurities is expected to be due to choice of reactor design and solids separation methods.

XRD confirmed that three of the zeolites are clinoptilolite and one is chabazite. The particle size among all the clinoptilolites is approximately 2µm and they all have similar pore sizes of <1µm. The Zeosand, however, has a rough texture which may contribute to higher surface area and higher IX capacity. The chabazite sample shows a much wider range in particle size from approximately 4µm to less than 1µm. Pore sizes in the chabazite also vary widely but range up to 2µm, significantly larger than the clinoptilolites. This likely contributes to its higher IX capacity of the chabazite. The elemental composition of the zeolites matches their chemical formulas except for Fe, which is likely due to non-zeolitic amorphous content. Based on elemental composition, the zeolites seem to be a mix of Na, Ca, and K zeolites.

5.2 LCA Conclusions

The assessment results comparing alternatives of additions to the treatment train generally shows that implementation of the treatment system provides environmental and human health benefits in most categories and minimal impact in others. Furthermore, across all categories the large scale system is more environmentally friendly than the medium –scale system, creating an “economies of scale” effect with environmental impact. There are negligible differences between using aeration vs. NaOH for struvite precipitation or between clinoptilolite and chabazite usage. This is likely because the aeration requires more energy, but NaOH use requires chemical production. Furthermore, chabazite has an ammonium exchange capacity that is approximately an order of magnitude higher than clinoptilolite, requiring 10 times as much clinoptilolite for treatment. However, chabazite mining creates an estimated 10 times more impact than clinoptilolite, thereby balancing the environmental impact.

Across all impact categories and scenarios, the impact due to operation outweighs construction significantly. Therefore, environmental impact of the system can be accurately assessed by only analyzing the materials and energy required for operation without accounting for construction. This can be implemented in future research to make completion of the LCI more feasible. Furthermore, it implies that it is important for operational parameters to be precise in order for the assessment to be accurate, while accuracy of construction is not essential.

5.3 Life Cycle Cost Analysis Conclusions

The payback period for the mid-size CAFO is approximately 39 years, which is longer than the lifetime of the system (assumed 20 years). However, overall system costs decrease significantly with the larger scale, decreasing the payback period to 14 years. AD incurs the largest capital cost to the system but also provides the highest revenue. IX using natural clinoptilolite also provides a net revenue to the system. IX using chabazite, however, is not recommended from an economic standpoint. Struvite precipitation does not provide a net revenue based on current operation parameters, but change in the concentration of soluble P in the centrate can significantly improve economic feasibility of the system.

5.4 Recommendations for Future Research

A number of research gaps have been identified that require further investigation. Furthermore, full scale implementation of systems may require further testing at the pilot scale. Recommendations for future research in these areas are summarized in the following points:

- Need for pilot testing of struvite reactors that use aeration because they are less common and may have unknown operational issues such as foaming observed in bench scale experiments performed in the USF Environmental Engineering laboratory.
- Because IX recovery of N is an emerging technology, practical aspects of the operation, particularly the loading and transport of the zeolite, require further investigation at the pilot scale
- Further research is necessary to determine the effects of using reclaimed water in the treatment system to wash out the hog pens again. Furthermore, the number of times the water could be recycled in this manner would need to be evaluated. This reuse can provide the benefit of recovery of residual nutrients while the zeolite particulates in the reclaimed water may reduce odors of the waste.
- Alternative materials, such as biochar made from AD biosolids of the system, may serve as a more cost effective and environmentally friendly ion exchange material. However, it is not yet known if the biosolids can produce enough biochar and what the tradeoffs in energy and material usage may be.
- Alternative configurations such as IX and struvite precipitation in a single step are feasible. Practical aspects of functioning, such as solids separation (for recovery and for separation solids from the effluent) and whether to conduct homogeneous or heterogeneous nucleation must be investigated. The quality of the precipitate that would form in such reactions is also unknown.
- While struvite is considered to be a slow-release fertilizer, the hardness may possibly have an effect on dissolution rate of the precipitate. This hardness may also be correlated to

differences in crystal size of the precipitates. The cause of the differences in crystal size also requires further investigation.

REFERENCES

AgSTAR. (n.d.). Projects. Environmental Protection Agency. Retrieved February 26, 2014, from http://www.epa.gov/agstar/projects/index.html

Allen, E., & Ming, D. (1995). Recent progress in the use of natural zeolites in agronomy and horticulture. In D. Ming, & F. Mumpton, *Natural Zeolites* (pp. 477-490). Brockport, New York: International Committee on Natural Zeolites.

Alp, O. (2010). Further Treatment of Digested Blackwater for Extraction of Valuable Components. PhD Thesis. Hamburg, Germany: Hamburg Technical University.

APHA. (2013). *Standard methods for the examination of water and wastewater* (32nd ed.). Washington, D.C: American Public Health Association.

Barak, P., & Stafford, A. (2006). Struvite: A Recovered and Recycled Phosphorus Fertilizer. *Presented at Wisconsin Fertilizer Aglime & Pest Management Conference.*

Barnard, J. L. (2009). Elimination of Eutrophication Through Resource Recovery. In K. Ashley, D. Mavinic, & F. Koch, *International Conference on Nutrient Recovery from Wastewater Streams* (pp. 1-22). London: IWA Publishing.

Bartoli, A., Garcia-Belinchon, C., Hidalgo, J. M., Rouge, P., Febragas, C., Fortuny, M., . . . Prado, O. J. (2003). Technical and Economic Analysis of Real Anaerobic Digester Centrate by Means of Partial Nitrification and Sustainable Heterotrophic Denitrification. *Water Science and Technology, 67*(12), 2807-2813.

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*(5), 1352-1356.

Bayer, P., & Finkel, M. (2006). Life cycle assessment of active and passive groundwater remediation technologies. *Journal of Contaminant Hydrology, 83*, 171−199.

Beal., L., Burns, R., & Stalder, K. (1999). Effect of anaerobic digestion on struvite production for nutrient removal from swine waste prior to land application. Paper No. 994042. *1999 ASAE International Meeting in Toronto, Canada.* St. Joseph, MI.

Benisch, M., Clark, C., Sprick, R. G., & Baur, R. (2000). Struvite deposits: a common and costly nuisance. *Water Environment and Technology, 14,* 51-54.

Bergmans, B. (2011). Struvite recovery from digested sludge. MS Thesis . Delft, Netherlands: Delft University of Technology.

Bernet, N., & Beline, F. (2009). Challenges and Innovations on Biological Treatment of Livestock Effluents. *Bioresource Technology, 100*(22), 5431-5436.

Bernstein, L. (1975). Effects Of Salinity And Sodicity On Plant Growth. *Annual Review of Phytopathology, 13*(1), 295-312.

Bhuiyan, M. H., Mavinic, D. S., & Beckie, R. D. (2008). Nucleation and Growth Kinetics of Struvite in a Fluidized Bed Reactor. *Journal of Crystal Growth, 310*(6), 1187-1194.

Blaabjerg, K., Jørgensen, H., Tauson, A.-H., & Poulsen., H. (2010). Heat-treatment, phytase and fermented liquid feeding affect the presence of inositol phosphates in ileal digesta and phosphorus digestibility in pigs fed a wheat and barley diet. *Journal of Animal Science,* 876–885.

Bouropoulos, N., & Koutsoukos, P. (2000). Spontaneous Precipitation of Struvite from Aqueous Solutions. *Journal of Crystal Growth, 213*(3-4), 381-388.

Bowman, R. (2003). Application of surfactant-modified zeolites to environmental remediation. *Microporous Mesoporous Materials, 61,* 43–56.

Breck, D. W. (1974). *Zeolite molecular sieves: Structure, chemistry and use.* New York: Wiley.

Bridger, G. L., Salutsky, M. L., & Starostka, R. W. (1962). Micronutrient Sources, Metal Ammonium Phosphates As Fertilizers. *Journal of Agricultural and Food Chemistry, 10*(3), 181-188.

Britton, A., Sacluti, F., Oldham, W., Mohammed, A., Mavinic, D., & Koch, F. (2007). Value From Waste – Struvite Recovery at the City of Edmonton's Gold Bar WWTP. *IWA Specialist Conference: Moving Forward - Wastewater biosolids sustainability,* (pp. 1-8). Moncton.

Brown, R. C. (2003). *Biorenewable Resources: Engineering New Products from Agriculture.* Ames, Iowa: Iowa State Press.

Burke, S., Heathwaite, L., & Preedy, N. (2004). Transfer of Phosphorus to Surface Waters: Eutrophication. In E. Valsami-Jones (Ed.), *Phosphorus in Environmental Technologies: Principles and Applications* (pp. 120-146).

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.

Cabeza, R., Steingrobe, B., Romer, W., & Claasen, N. (2011). Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. *Nutrient Cycling in Agroecosystems, 91*(2), 173-184.

CEEP. (2003). Piggery waste: Struvite formation for N-removal. Japan: P-recovery from piggery wastewaters; Tennessee: Struvite recovery from swine wastes. *SCOPE Newsletter*(50), pp. 5-6.

CEEP. (2009). Fertilizer value from recovered phosphates. *SCOPE Newsletter*(74), p. 5.

Celen, 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.

Cervantes, F. (2009). *Environmental Technologies to Treat Nitrogen Pollution.* London: IWA Publishing.

Chaya, W., & Gheewala, S. (2007). Life cycle assessment of MSW-to-energy schemes in Thailand. *Journal of Cleaner Production, 15*(15), 1463-1468.

Chen, H., Yan, S. H., Ye, Z. L., Meng, H. J., & Zhu, Y. G. (2012). Utilization of Urban Sewage Sludge: Chinese Perspectives. *Environmental Science and Pollution Research*.

Chmielewska, E. (2003a). Adsorption of arzenate and chromate from waters on hydrofobised zeolitic media. *Turkish Journal of Chemistry, 27*(5), 639–648.

Chmielewska, E. (2003b). Remediation of specifically polluted waste effluents using natural zeolites. *Environmental Protection Engineering*, 35–42.

Choe, J. K. (2013). Comparative Assessment of the Environmental Sustainability of Existing and Emerging Perchlorate Treatment Technologies for Drinking Water. *Environmental Science and Technology*.

Choe, J. K., Mehnert, M. H., Guest, J. S., Strathmann, T. J., & Werth., C. J. (2013). Comparative Assessment of the Environmental Sustainability of Existing and Emerging Perchlorate Treatment Technologies for Drinking Water. *Environmental Science and Technology, 47*(9), 4644-4652.

Choi, E. (2007). *Swine Waste Management*. London: IWA publishing.

Chynoweth, D. P., Wilkie, A. C., & Owens, J. M. (1998). Anaerobic Processing of Piggery Wastes: A Review. *Proceedings of the ASAE Annual International Meeting*. Orlando, Florida, USA.

Chynoweth, D. P., Wilkie, A. C., & Owens, J. M. (1999). Anaerobic Treatment of Piggery Slurry - Review. *Asian-Australasian Journal of Animal Sciences, 12*(4), 607-628.

Colella, C. (2002). Application of natural zeolites. . In *Handbook of porous solids* (pp. 1156–1189).

Colella, C., & Mumpton, F. (2000). *Natural zeolites for the third millenium*. Napol: De Frede-Editore.

Collivignarelli, C., & Bertanza, G. (1999). Simultaneous Nitrification and Denitrification Processes in an Activated Sludge Plants:Performance and applicability. *Water Science and Technology, 40*(4-5), 187-194.

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

De Gussem, K., Wambecq, T., Roels, J., Fenu, A., Gueldre, G. D., & Steene, B. V. (2011). Cost Optimisation and Minimisation of the Environmental Impact through Life Cycle Analysis of the Waste Water Treatment Plant of Bree (Belgium). *Water Science & Technology*, 164.

de Haan, A., & Bosch, H. (2007). *Fundamentals of Industrial Separations*. De Gruyter, Walter, Inc.

Debashan, L. B. (2004). Recent Advances In Removing Phosphorus From Wastewater And Its Future Use As Fertilizer (1997-2003). *Water Research, 38*(19), 4222-4246.

Déry, P., & Anderson, B. (2007). *Peak phosphorus. Energy Bulletin August 13. EEA, 2001. Eutrophication in Europe's coastal waters. Topic report 7/2001.* Copenhagen: European Environment Agency.

Dockhorn, T. (2009). About the Economy of Phosphorus Recovery. In *International Conference on Nutrient Recovery from Wastewater Streams. Vancouver, Canada* (pp. 145–158). London, UK: IWA publishing.

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

Edelmann, W., Baier, U., & Engeli, H. (2005). Environmental aspects of the anaerobic digestion of the organic fraction of municipal solid wastes and of agricultural waste. *Water Science and Technology, 2*, 203-208.

EIA. (n.d.). Independent Statistics and Analysis. U.S. Energy Information Administration. Retrieved February 24, 2014, from http://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_5_6_a

Emigh, G. (1972). World phosphate reserves, are there really enough. *Engineering and Mining Journal, 173*(4), 90–95.

Fawer, M., Postlethwaite, D., & Klüppel, H. (1998). Life cycle inventory for the production of zeolite a for detergents. *The International Journal of Life Cycle Assessment, 3*(2), 71-74.

FDA. (2013). Standards for the Growing, Harvesting, Packing, and Holding of Produce for Human Consumption; Proposed Rule. [Docket No. FDA-2011-N-0921]. RIN 0910-AG35.

Foley, J. M., Rozendal, R. A., Hertle, C. K., Lant, P. A., & Rabaey, K. (2010). Life cycle assessment of high-rate anaerobic treatment, microbial fuel cells, and microbial electrolysis cells. *Environmental Science and Technology, 44*, 3629−3637.

Forrest, A., Fattah, K., Mavinic, D., & Koch, F. (2006). Use of natural zeolite at different dosage and procedures in batch and continuous anaerobic digestion of synthetic and swine wastes. *Resources Conservation & Recycling, 234*(5), 26-41.

Fruergaard, T., & Astrup, T. (2010). Optimal utilization of waste-to-energy in an LCA perspective. *Waste Management, 31*(3), 572-582.

Gadekar, S., Pullammanappallil, P., & Varshovi, A. (2009). Validation of a comprehensive chemical equilibrium model for predicting struvite precipitation. In *International conference on nutrient recovery from wastewater streams.* London: IWA Publising.

Galbraith, S., & Schneider, P. (2009). A review of struvite nucleation studies. In *International conference on nutrient recovery from wastewater streams.* London: IWA Publishing.

Gebremedhin-Vaile, T., Olguin, M., & Solache-Rios, M. (2003). Removal of mercury ions from mixed aqueous metal solutions by natural and modified minerals. *Water, Air, Soil Pollution, 148*(1-4), 179–200.

Goebel, K., & Stein, H. (2010). Phosphorus digestibility and energy concentration of enzyme-treated and conventional soybean meal fed to weanling pigs. *Journal of Animal Science, 89*(3), 764–772.

Gottardi, G., & Galli, E. (1985). *Natural Zeolites. Minerals and Rocks* (Vol. 18). Berlin: Springer.

Guest, J. S., Skerlos, S. J., Barnard, J. L., Beck, M. B., Daigger, G. T., Hilger, H., . . . Nancy, L. G. ((2009) "). A New Planning and Design Paradigm to Achieve Sustainable Resource Recovery from Wastewater. *Environmental Science & Technology, 43*(16), 6126-6130.

Haight, M. (2005). Assessing the enviromental burdens of anaerobic digestion in comparison to alternative options for managing the biodegradable fraction of municipal solid wastes. *Water Science and Technology, 52*(1-2), 553-559.

Hamilton, D. W., Luce, W. G., & Aimee, H. D. (n.d.). *Production and Characteristics of Swine Manure.* Oklahoma Cooperative Extension Service, Division of Agricultural Sciences and Natural Resources. Oaklahoma State University Extension Facts.

Hao, X., Wang, C., & van Loosdrecht, M. (2009). International conference on nutrient recovery from wastewater streams. London: IWA Publishing.

Hershey, D. R., Paul, J. L., & Carlson, R. M. (1980). Evaluation of Potassium-Enriched Clinoptilolite as a Potassium Source for Potting Media. *Horticulure Science, 15*, 87-89.

Higgins, M. R., & Olson, T. M. (2009). Life-cycle case study comparison of permeable reactive barrier versus pump-and-treat remediation. *Environmental Science and Technology*, 9432−9438.

Hill, B., Sutton, A., & Richert., B. (2009). Effects of low-phytic acid corn, low-phytic acid soybean meal, and phytase on nutrient digestibility and excretion in growing pigs. *Journal of Animal Science, 87*(4), 1518–1527.

Hospido, A., Moreira, M. T., Fernández-Couto, M., & Feijoo., G. (2004). Environmental Performance of a Municipal Wastewater Treatment Plant. *The International Journal of Life Cycle Assessment, 9*(4), 261-271.

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

ISO. (2006a). *Environmental management—Life cycle assessment: Principles and framework. ISO14040.* Geneva: International Standard Organisation.

ISO. (2006b). *Environmental management—Life cycle assessment: Requirements and Guidelines. ISO14044.* Geneva: International Standard Organisation.

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

Jeyanayagam, S. (2005). True Confessions of the Biological Nutrient Removal Process. *Florida Water Resources Journal*.

Johnston, A., & Richards, I. (2003). Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use Management, 19*, 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.

Jorgensen, S., Libor, O., Graber, K., & Barkacs, K. (1976). Ammonia removal by use of clinoptilolite. *Water Research, 10*, 213-224.

Karakashev, D., Schmidt, J., & Angelidaki, I. (2008). Innovative process scheme for removal of organic matter, phosphorus and nitrogen from pig manure. *Water Research, 41*(15), 4083-4090.

Kerr, B., Weber, T., Miller, P., & Southern., L. (2009). Effect of phytase on apparent total tract digestibility of phosphorus in corn-soybean meal diets fed to finishing pigs. *Journal of Animal Science, 88*(1), 238–247.

Kinyua, M. (2013). Effect of Solids Retention Time on the Denitrification Potential of Anaerobically. MS Thesis. Tampa, FL: University of South Florida.

Kinyua, M., Cunningham, J., & Ergas, S. (2014). Effect of Solids Retention Time on the Bioavailability of Organic Carbon in Anaerobically Digested Swine Waste. *Bioresource Technology*, Accepted.

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

Lahav, O., & Green, M. (1998). Ammonium Removal Using Ion Exchange and Biological Regeneration. *Water Research, 32*(7), 2019-2028.

Lahav, O., Schwarts, Y., Nativ, P., & Gendel, Y. (2013b). Sustainable Removal of Ammonia from Anaerobic-lagoon Swine Waste Effluents Using an Electrochemically-Regenerated Ion Exchange Process. *Chemical Engineering Journal, 218*, 214-222.

Lahav, O., Telzhensky, M., Zewuhn, A., Gendel, Y., Gerth, J., Calmano, W., & Birnhack, L. (2013a). Struvite recovery from municipal-wastewater sludge centrifuge supernatant using seawater NF concentrate as a cheap Mg(II) source. *Separation and Purification Processes, 108*, 103-110.

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

Le Corre, K. E.-J. (2009). Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology, 39*(6), 433-477.

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.

Leyva-Ramos, R., Monsivais-Rocha, J., Aragon-Piña, A., Berber-Mendoza, M., Guerrero-Coronado, R., Alonso-Davila, P., & Mendoza-Barron, J. (2010). Removal Of Ammonium From Aqueous Solution By Ion Exchange On Natural And Modified Chabazite. *Journal of Environmental Management, 91*(12), 2662-2668.

Lin, A. (2012). Precipitation of Phosphate Minerals from Effluent of Anaerobically Digested Swine Manure.MS Thesis. Tampa, FL.: University of South Florida.

Lind, B.-B., Ban, Z., & Bydén, S. (2000). Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. *Bioresource Technology, 73*(2), 169-174.

Linderholm, K., Tillman, A.-M., & Mattssona, J. E. (2012). Life Cycle Assessment of Phosphorus Alternatives for Swedish Agriculture. *Resources, Conservation and Recycling* , 27-39.

Liu, Y., Rahman, M., Kwag, J., Kim, J., & 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.

Lyberg, K., Lundh, T., Pedersen, C., & Lindberg., J. (2006). Influence of soaking, fermentation and phytase supplementation on nutrient digestibility in pigs offered a grower diet based on wheat and barley. *Journal of Animal Science*, 853–858.

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

Misaelides, P., Macasek, F., Pinnavaia, T., & Colella, C. (1999). *Natural microporous materials in environmental technology.* Dordrecht: Kluwer Academic Publishers.

Morris, J., Matthews, H., & Morawski, C. (2011). *Review of LCAs on Organics Management Methods & Development of an Environmental Hierarchy.* Edmonton, AB: Alberta Environment.

Morse, G. K., Lester, J. N., & Perry, H. (1993). *The economic impact of phosphorus removal from wastewater in the European community*. London, UK: Selper Publications.

Morse, G., Brett, S., Guy, J., & Lester, J. (1998). Review: Phosphorus Removal and Recovery Technologies. *The Science of The Total Environment, 212*(1), 69-81.

Moser, M. (n.d.). Anaerobic Digesters Control Odors, Reduce Pathogens, Improve Nutrient Manageability, Can be Cost Competitive with Lagoons, and Provide Energy Too. Retrieved from http://www.epa.gov/agstar/documents/lib-man_man.pdf

Mulder, A. ((2003)). The Quest for Sustainable Nitrogen Removal Technologies. *Water Science and Technology, 48*(1), 67-75.

Mumpton, F. A. (1999). La roca mágica: Uses of natural zeolites in agriculture and industry. *Proceedings of the National Academy of Science USA*, (pp. 3463–3470).

Murray, A., Horvath, A., & Nelson, K. (2008). Hybrid life-cycle environmental and cost inventory of sewage sludge treatment and end-use scenarios: a case study from China. *Environmental Science and Technology, 42,* 3163–3169.

Nasir, I. M., Ghazi, T. I., & Omar, R. (2012). Anaerobic Digestion Technology in Livestock Manure Treatment for Biogas Production: A Review. *Engineering Life Science, 12*(3), 258-269.

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.

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

Ohlinger, K., Young, T., & Schroeder, E. (2000). Post digestion struvite precipitation using a fluidized bed reactor. *Journal of Environmental Engineering., 126,* 361-368.

Pasqualino, J., Meneses, M., Abella, M., & Castells, F. (2009). LCA as a decision support tool for the environmental improvement of operation of a municipal wastewater treatment plant. *Environmental Science and Technology, 43*, 3300−3307.

Pecson, B., Barrios, J., Jimenez, B., & Nelson, K. (2007). The effects of temperature, pH, and ammonia concentration on the inactivation of Ascaris eggs in sewage sludge. *Water Research, 41*(13), 2893-2902.

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.

Pilchowski, K., & Chmielewska, E. (2003). Adsorptive separation of 1,2- dichloroethane from model waste water on natural clinoptilolite. *Acta Hydrochimica et Hydrobiologica, 31*(3), 249–252.

Polat, E., Karaca, M., Demir, H., & Onus, A. N. (2004). Use of natural zeolite (clinoptilolite) in agriculture. *Journal of Fruit Ornamental Plant Research, 12*(Special ed.), 183–189.

Ponizovskij, A., Dimoyanis, D., & Tsadilas, K. (2003). The use of zeolite for detoxication of lead-contamined soils. *Eurasian Soil Science, 36*(4), 439–443.

Poulsen, H., Blaabjerg, K., Strathe, A., Ader, P., & Feuerstein, D. (2010). Evaluation of different microbial phytases on phosphorus digestibility in pigs fed a wheat and barley based diet . *Livestock Sciences, 134*, 97–99.

Puschenreiter, M., & Horak, O. (2003). Slow-release zeolite-bound zinc and copper fertilizers affect cadmium concentration in wheat and spinach. *Communications in Soil Science and Plant Analysis , 34*(1-2), 31–40.

Rahman, M. M., Liu, Y. H., Kwag, J. H., & Ra., C. S. (2011). Recovery of struvite from animal wastewater and its nutrient leaching loss in soil. *Journal of Hazardous Materials, 186*, 2026-2030.

Randall, C. W. (2003). Potential Societal and Economic Impacts of Wastewater Nutrient Removal and Recycling. *Water Science and Technology, 48*(1), 11-17.

Ras, C., & Blottnitz, H. v. (2012). A comparative life cycle assessment of process water treatment technologies at the Secunda industrial complex, South Africa. *Water SA, 38*(4), 549-554.

Rigamonti, L., Grosso, M., & Giugliano, M. (2010). Life cycle assessment of sub-units composing a MSW management system. *Journal of Cleaner Production, 18*(17), 1652-1662.

Rojas, O., & Stein., H. (2012). Digestibility of phosphorus by growing pigs of fermented and conventional soybean meal without and with microbial phytase. *Journal of Animal Science, 90*(5), 1506–1512.

Rosso, D., & Stenstrom, M. (2005). Comparative Economic Analysis of the Impacts of Mean Cell Retention Time and Denitrification on Aeration Systems. *Water Research, 39*(16), 3773-3780.

Sakar, S., Yetilmezsoy, K., & Kocak, E. (2009). Anaerobic digestion technology in poultry and livestock waste treatment—a literature review. *Waste Management Research, 27*, 3–18.

Sands, J., Ragland, D., Baxter, C., Joern, B., Sauber, T., & Adeola., O. (2001). Phosphorus bioavailability, growth performance, and nutrient balance in pigs fed high available phosphorus corn and phytase. *Journal of Animal Science, 78*, 2134–2142.

Song, Y., Qiu, G., Yuan, P., Cui, X., Peng, J., Zeng, P., . . . Qian, F. (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.

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.-H., Qiu, G.-L., Yuan, P., Cui, X.-Y., Peng, J.-F., Zeng, P., . . . Qian, F. (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.

Steen, I. (1998). Phosphorus availability in the 21st century: Management of a non-renewable resource. *Phosphorous & Potassium*(217), 25–31.

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

Sundqvist, J. (2005). *How should municipal solid waste be treated-a system study of incineration material recycling, anaerobic digestion and composting.IVL Report B 1547.* Stockholm: Swedish Enviromental Research Institute.

Suzuki, K. T. (2006). Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology, 98*(8).

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

Suzuki, K., Tanaka, Y., Osada, T., & Waki, M. (2002). Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Research, 36*(12), 2991-2998.

Tchobanoglous, G., & Burton, F. L. (2004). *Wastewater engineering: treatment, disposal, and reuse* (4 ed.). New York: McGraw-Hill.

Tian, W., & Wen, X. (2004). Using a zeolite medium biofilter to remove organic pollutant and ammonia simultaneously. *Journal of Environmental Science - China, 16*(1), 90–93.

Tomazovic, B., Ceranic, T., & Sijaric, G. (1996). The properties of the NH4-clinoptilolite. Parts 1 and 2. *Zeolites, 16*(4), 301-312.

USEPA. (2000). *Biosolids Technology Fact Sheet: Belt Filter Press.* Office of Water, Washington D.C.

USEPA. (2007). Revised National Pollutant Discharge Elimination System Permit Regulation and Effluent Limitations Guidelines for Concentrated Animal Feeding Operations in Response to the Waterkeeper Decision, EPA-823-R-07-002. Washington DC.

USEPA. (2008). Biological Nutrient Removal Processes and Costs, EPA-HQ-OW-2005-0037. Washington DC.

Van Bekkum, H., Flanigen, E., & Jansen, J. (2001). *Introduction to zeolite science and practice.* Amsterdam: Elsevier Science Publisher.

Van Vuuren, D., Bouwman, A., & Beusen, A. (n.d.). Phosphorus Demand for the 1970–2100 Period: A Scenario Analysis of Resource Depletion. *Global Environmental Change, 20*(3), 428-439.

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

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

Ward, A. J., Hobbs, P. J., Holliman, P. J., & Jones, D. L. (2008). Optimisation of the anaerobic digestion of agricultural resources. *Bioresource Technology*, 7928–7940.

Warmadewanthi, J. L. (2009). Recovery Of Phosphate And Ammonium As Struvite From Semiconductor Wastewater. *Separation and Purification Technology, 64*(3), 368-373.

Wenisch, S., & Monier, E. (2007). Life Cycle Assessment of different uses of biogas from anaerobic digestion of separately collected biodegradable waste in France. RDC-Environnement.

Westerman, P., Veal, M., Cheng, J., & Zering, K. (2008). Biogas anaerobic digester considerations for swine farms in North Carolina. Raleigh, NC: N.C. Cooperative Extension Service.

Wilsenach, J. A., Larsen, T. A., & Van Loosdrecht., M. (2003). From Waste Treatment to Integrated Resource Management. *Water Science and Technology, 48*(1), 1-9.

Woods, N. C., Sock, S. M., & Daigger., G. T. (1999). Phosphorus recovery technology modeling and feasibility evaluation for municipal wastewater treatment plants. *Environmental technology, 20*(7), 663-679.

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). Nutrient removal from anaerobically digested cattle manure by struvite precipitation. *Journal of Environmental Engineering Science, 5*, 285-294.

Zhang, Z., Kornegay, E., Radcliffe, J., Wilson, J., & Veit., H. (2000). Comparison of phytase from genetically engineered Aspergillus and canola in weanling pig diets. *Journal of Animal Science*, 2868–2878.

APPENDIX A: SUPPLEMENTAL INFORMATION

This appendix includes all supplementary images and data not provided in the text of the above thesis. These images are comprehensively included below, for reference.

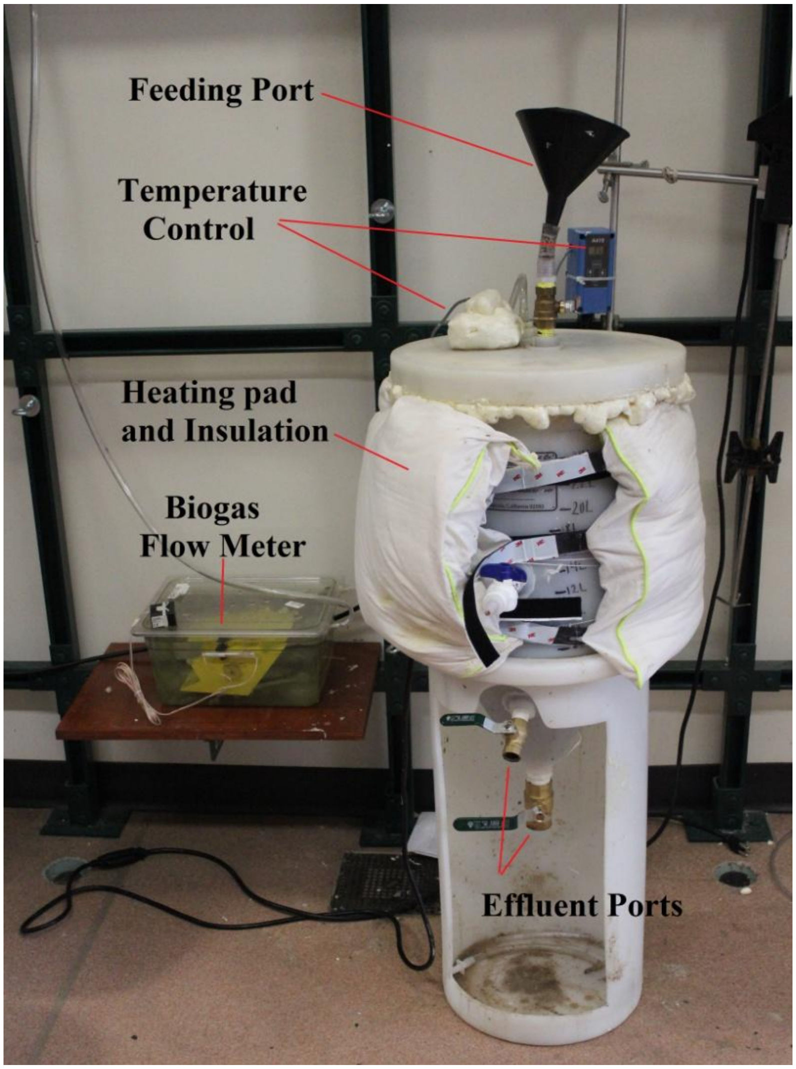


Figure A.1: AD Assembly, Custom-made from Homebrew Apparatus

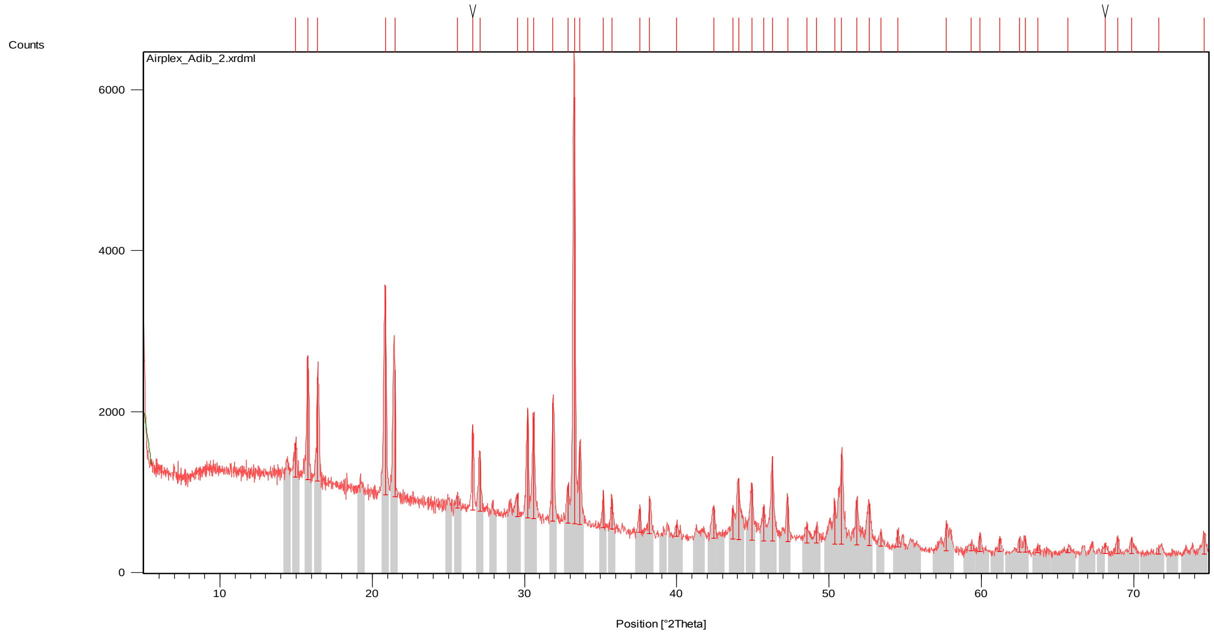


Figure A.2: Airprex XRD Scan with Struvite Match in Grey

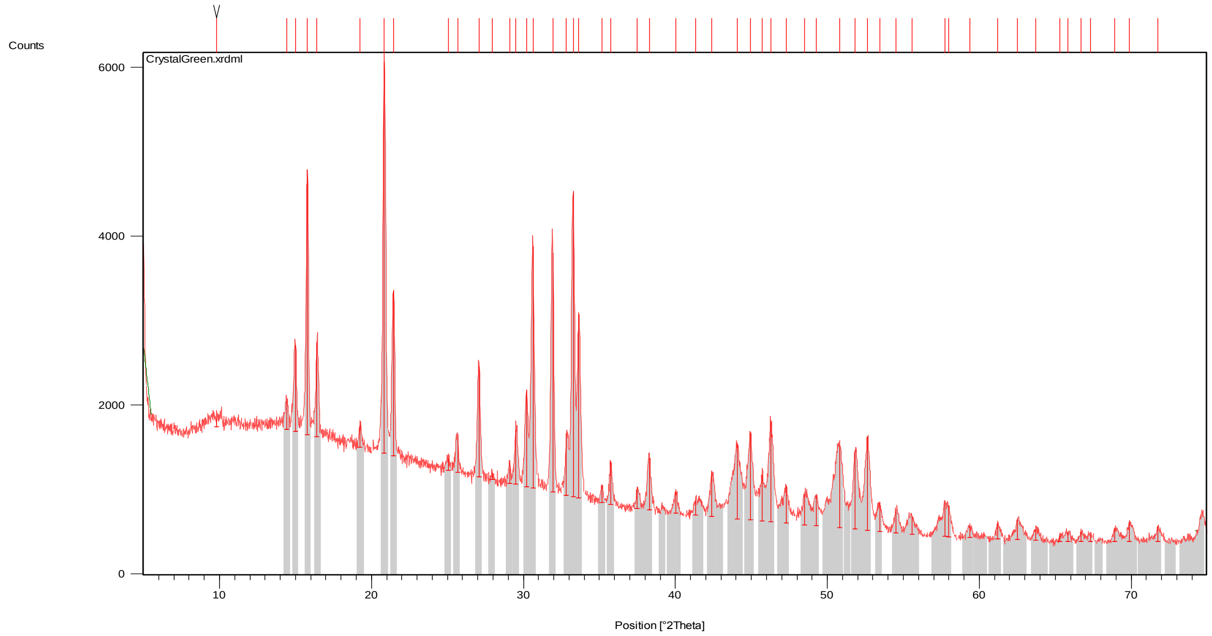


Figure A.3: CG Centrate XRD Scan with Struvite Match in Grey

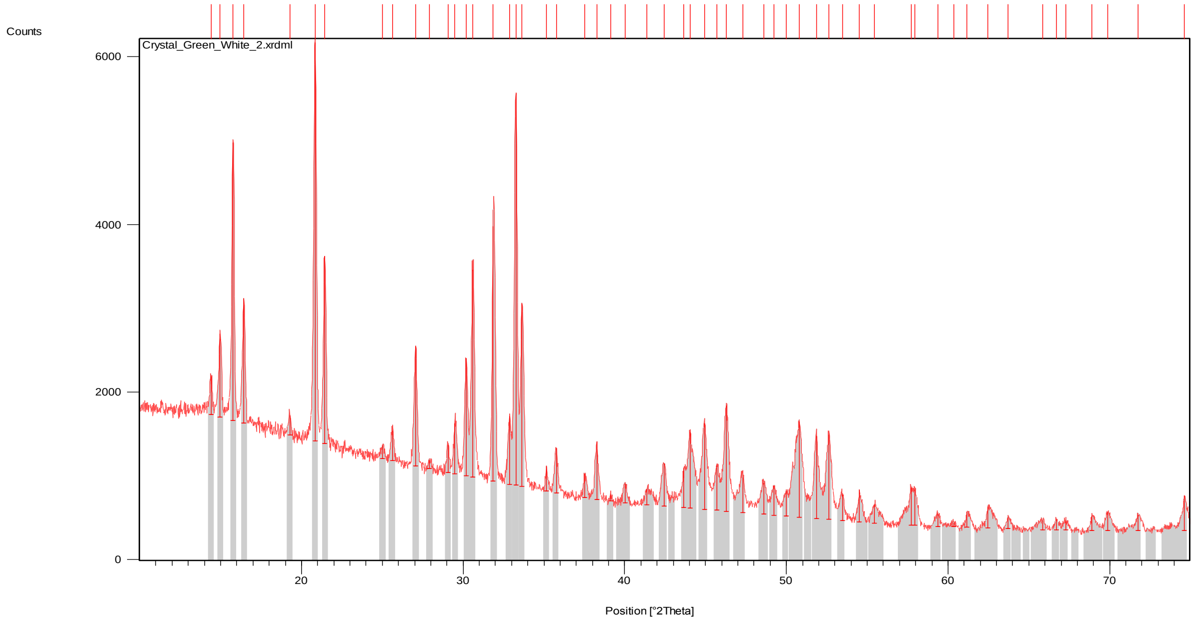


Figure A.4: CG Phosphate XRD Scan with Struvite Match in Grey

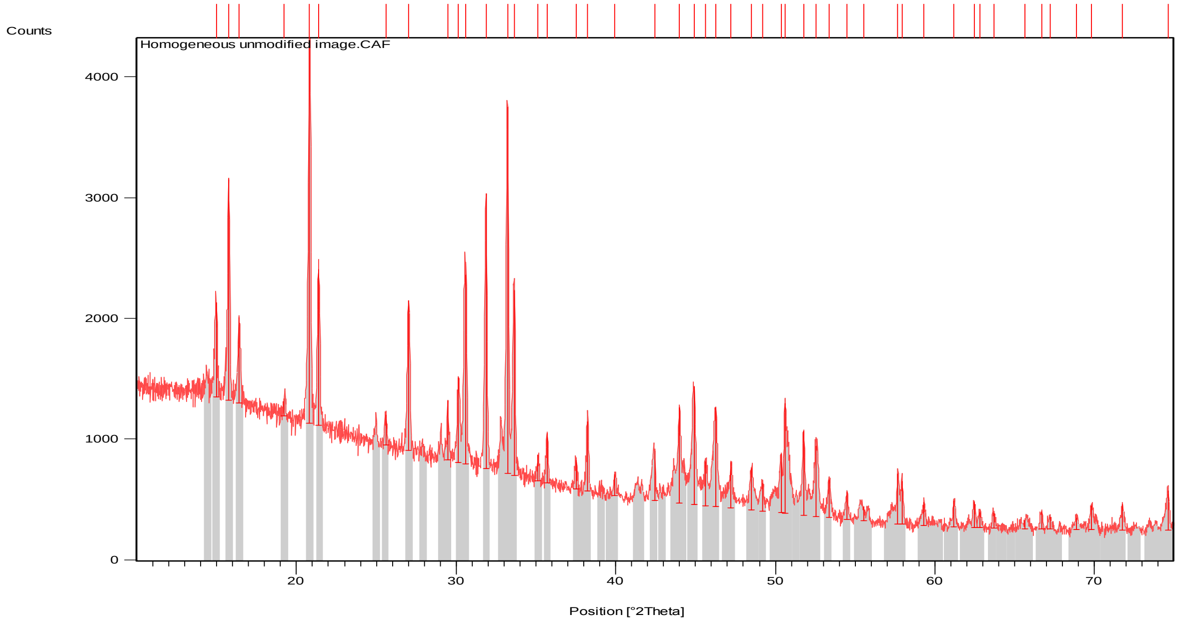


Figure A.5: Heterogeneous Lab Sample XRD Scan with Struvite Match in Grey

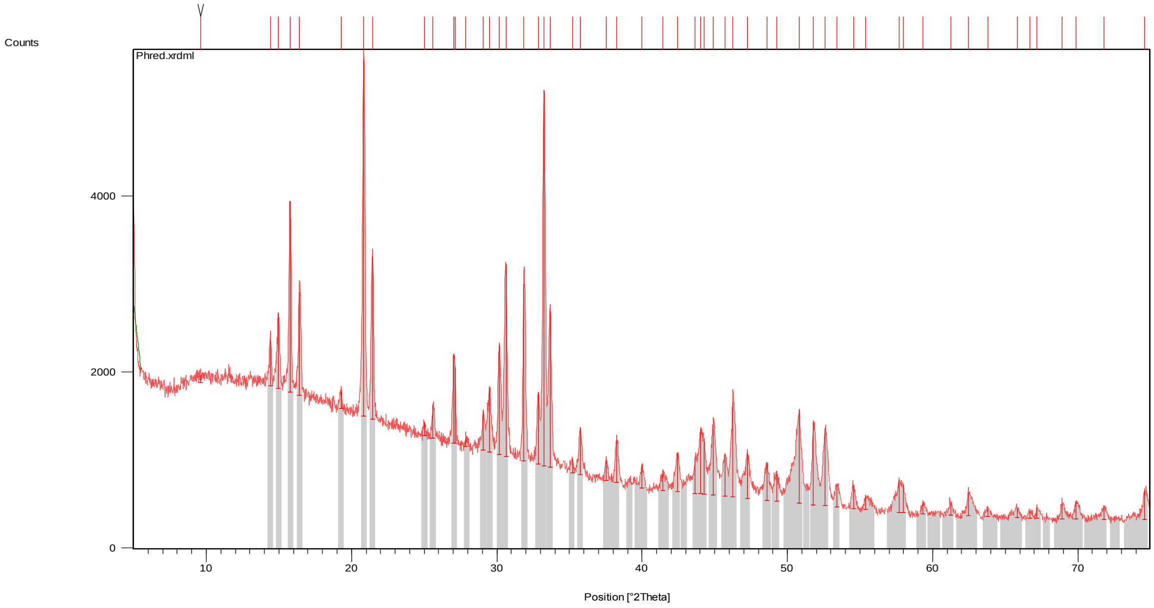


Figure A.6: Phred XRD Scan with Struvite Match in Grey

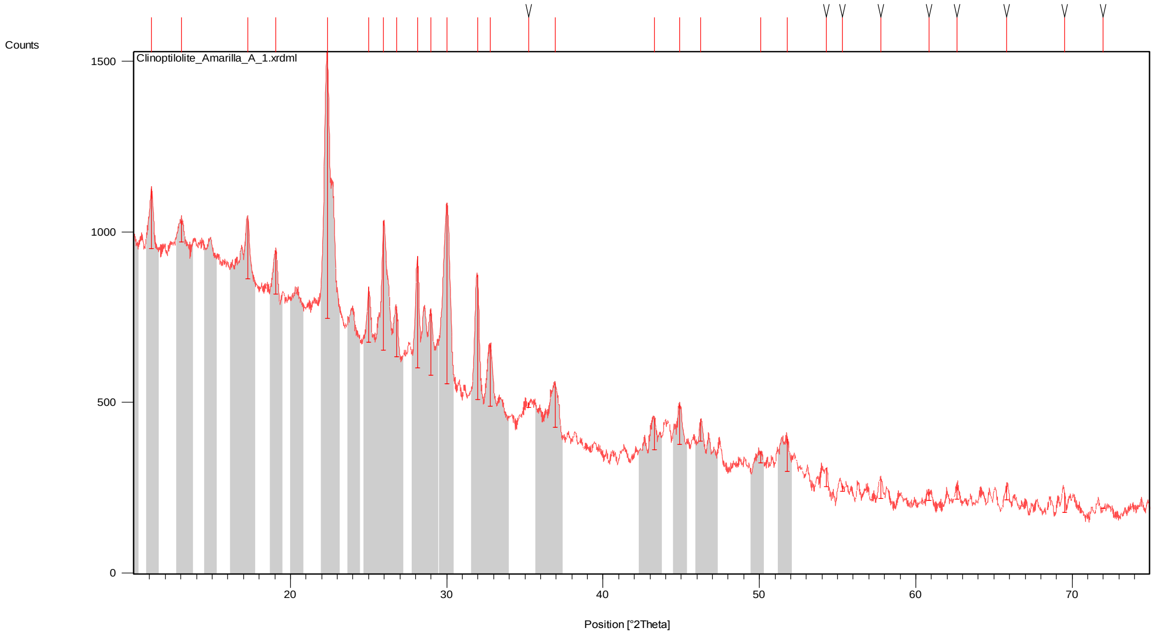


Figure A.7: C-Yellow XRD Scan with Na-Clinoptilolite Match in Grey

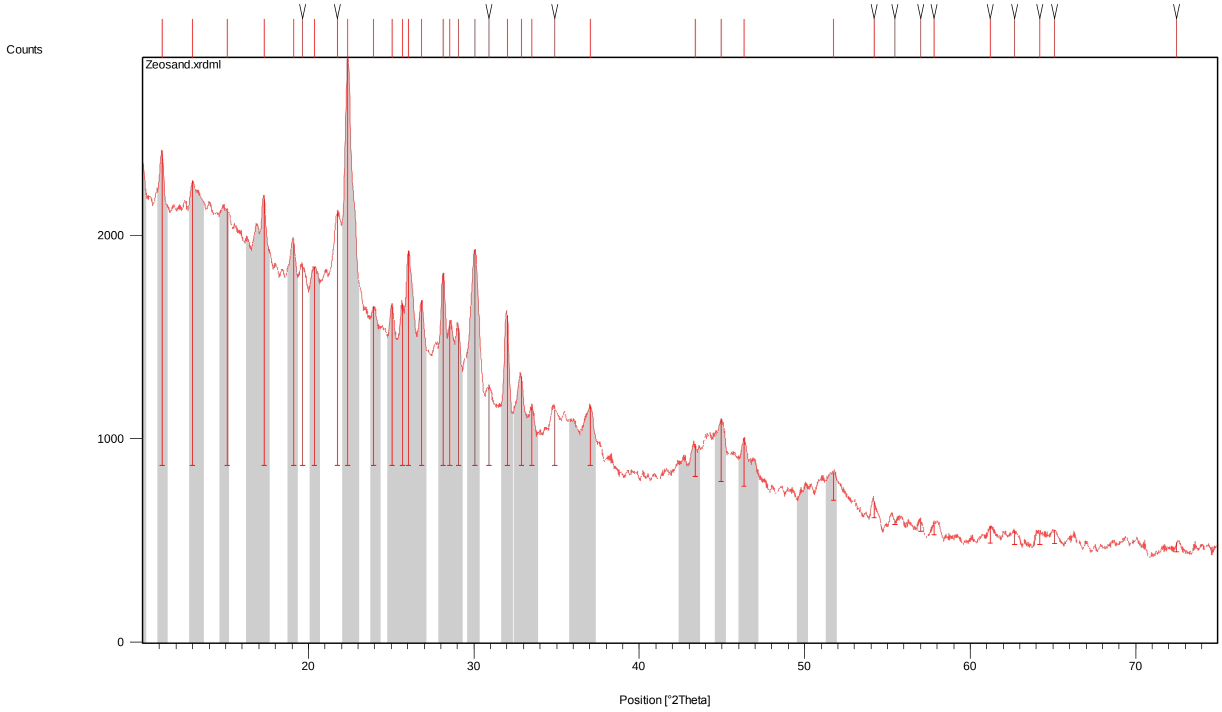


Figure A.8: Zeosand XRD Scan with Na-Clinoptilolite Match in Grey

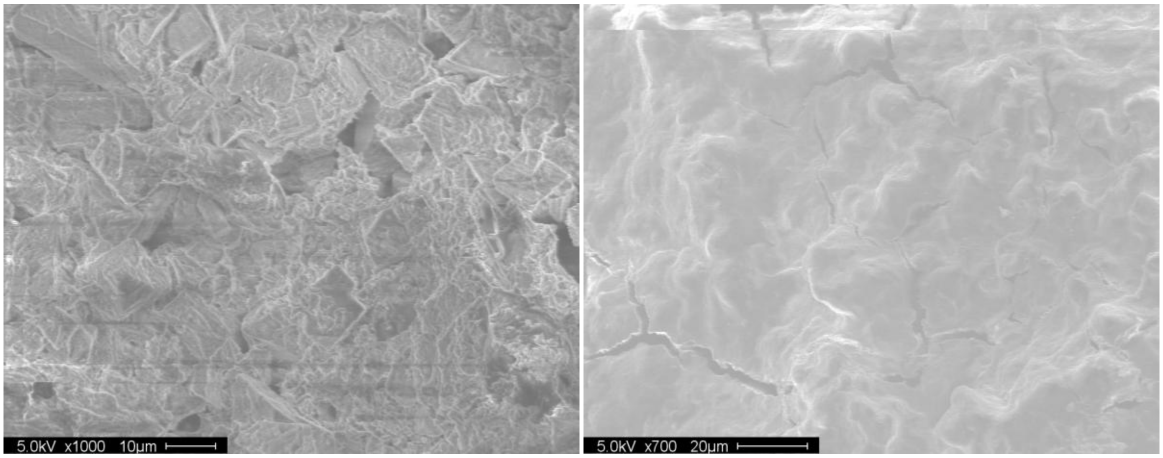


Figure A.9: SEM Images (1). Left: Lab Sample, Heterogeneous, Light Colored Surface (likely struvite); Right: Lab Sample, Heterogeneous, Dark Colored Surface (likely biosolids)

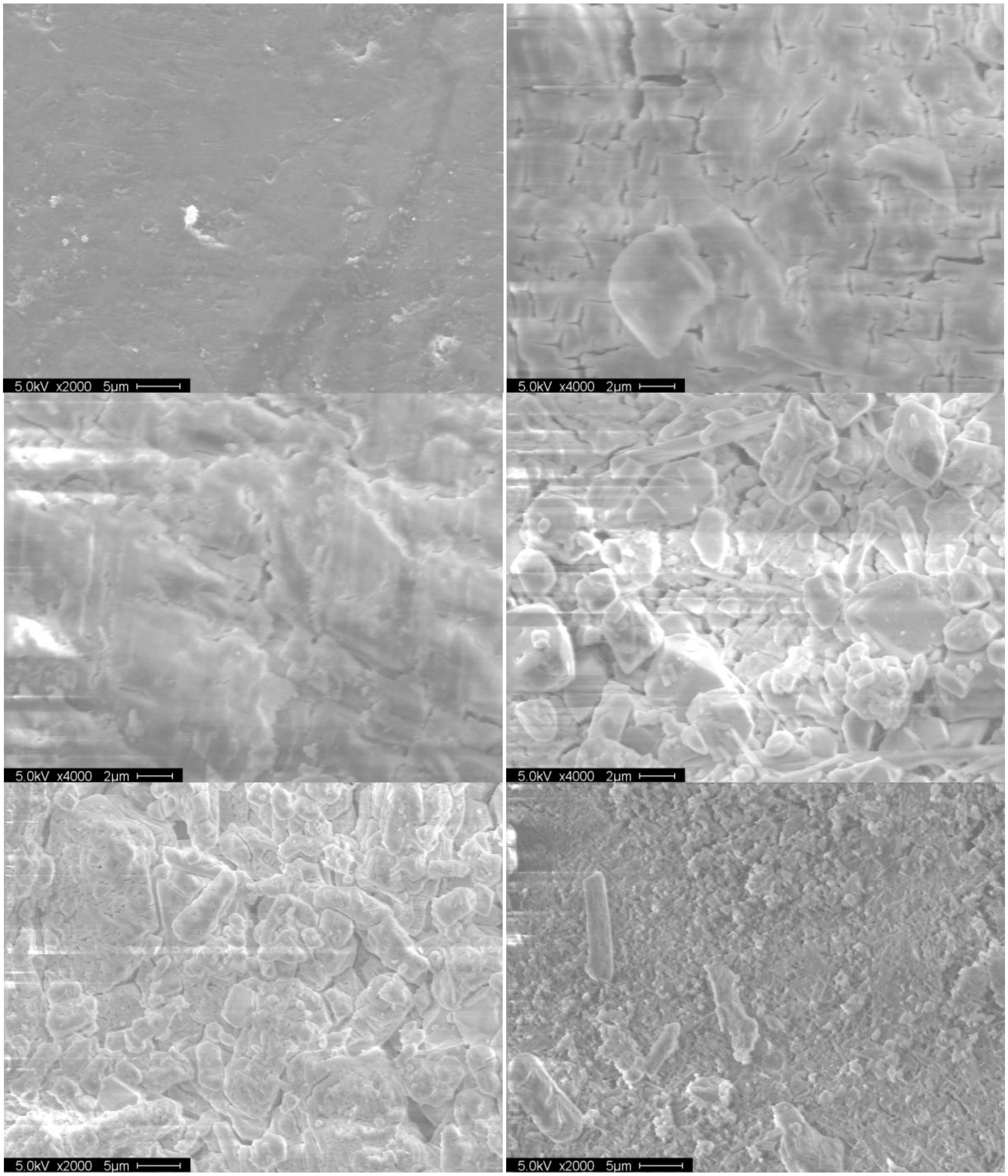


Figure A.10: SEM Images (2). Top Left: Airprex black flake; Top Right: CG Centrate, Inner Cross-section (Core); Middle Left: CG Centrate, Outer Cross-section; Middle Right; CG Centrate, Surface; Bottom Left: CG Phosphate, White Particle Surface; Bottom Right: CG Phosphate, White Particle Core

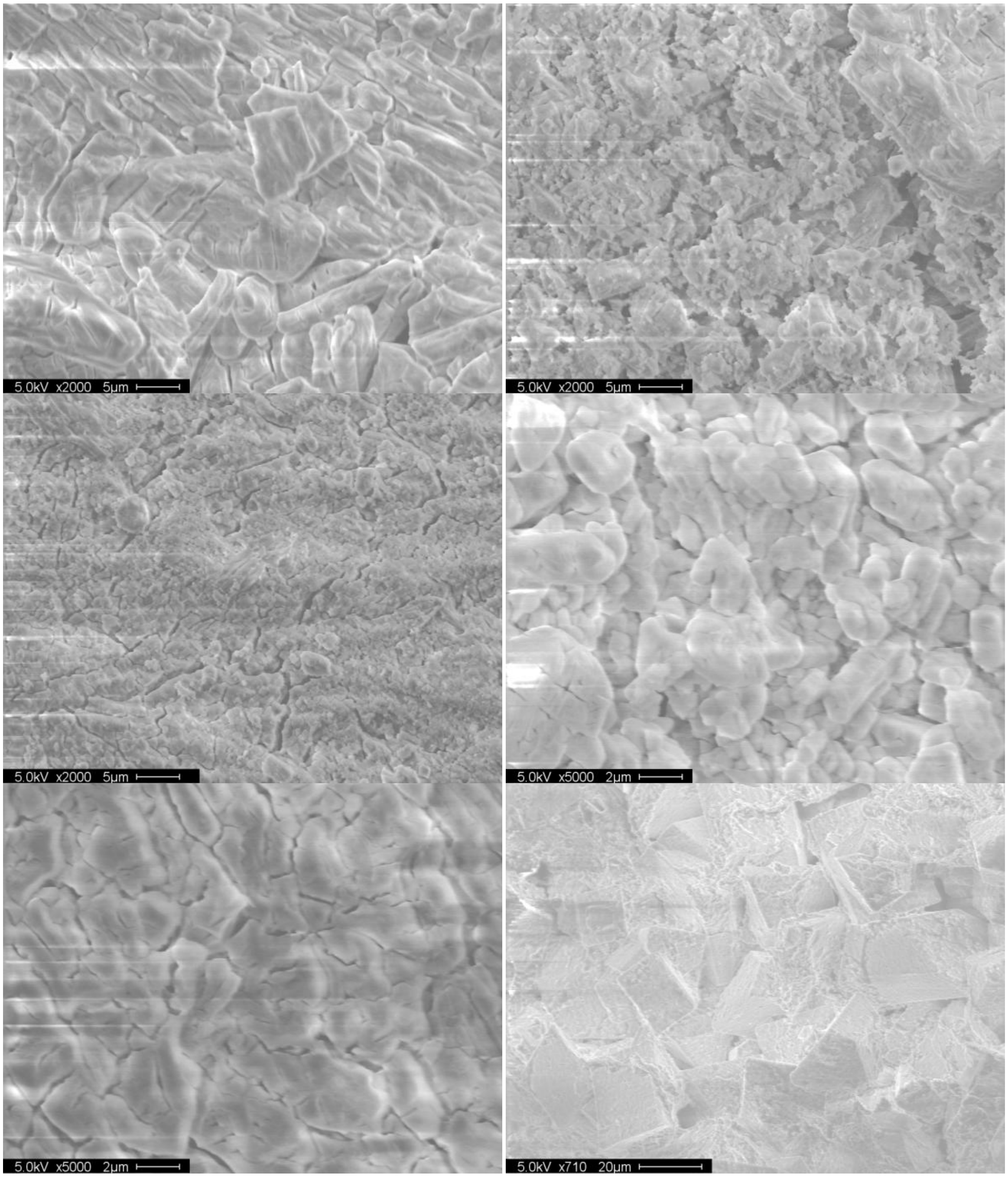


Figure A.11: SEM Images (3). Top Right: CG Phosphate, White Particle Cross-Section 1; Top Right: CG Phosphate, White Particle Cross-Section 2; Middle left: CG Phosphate, Brown Particle Surface; Middle Right: CG Phosphate, Brown Particle Cross-Section1; Bottom Left: CG Phosphate, Brown Particle Cross-Section 2; Bottom Right: Lab Sample, Homogeneous Cross-Section

Table A.1 Simpro Inputs for Construction LCI

AD Construction Input	Simapro Input	Simapro Processing Input
Volume of Digester Material (Concrete) (m^3)	Concrete, normal, at plant/CH S	
Mass of Cover Material (HDPE) (kg)	Polyethylene, HDPE, granulate, at plant/RER S	Calendering, rigid sheets/RER S
Insulation Material (Fiberglass) (kg)	Glass wool mat, at plant/CH S	
Volume of Storage Tank Material (Concrete) (m^3)	Concrete, normal, at plant/CH S	
Engine-Generator	Electric parts of Mini CHP plant/CH/I S	
Steel Pipe Mass (kg)	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
PVC Pipe Mass (kg)	PVC pipe E	
Excavation Volume (m^3)	Excavation, hydraulic digger/RER S	
Belt Filter Press x2 (kg)	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
Pump (x2)	Pump 40W, at plant/CH/I S	
Controls Parts (kg)	Electronics for control units/RER S	
Heater	Industrial furnace, natural gas/RER/I S	
Construction Materials Transport (tkm)	Transport, combination truck, average fuel mix/US	
Struvite Construction Input		
Steel mass (kg)	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
FBR Reactor (carbon steel) kg	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
Catwalk/Access Platform (carbon steel) kg	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
Stairs (carbon steel) kg	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
Foundation Concrete Volume (m^3)	Concrete, normal, at plant/CH S	
Pump	Pump 40W, at plant/CH/I S	
Construction Materials Transport (tkm)	Transport, combination truck, average fuel mix/US	
IX Construction Input		
Mass of Steel in Reactor (Steel) (kg)	Iron and steel, production mix/US	Steel product manufacturing, average metal working/RER S
Steel Transport (tkm)	Transport, combination truck, average fuel mix/US	

Table A.2: Simpro Input for Operation LCI

AD Operation Input	Simapro Input
Electricity Produced from Biogas (kWh/day)	Avoided Product: Electricity, high voltage (US)
Total Electricity Usage per day (kWh/day)	Electricity mix/US S
Pumps Electricity Usage (kWh/day)	Electricity mix/US S
Mixer electricity Usage (kWh/day)	Electricity mix/US S
Heater electricity usage(kWh/day)	Electricity mix/US S
Dewatering electricity (kWh/day)	Electricity mix/US S
Dewatering Polymer (kg/day)	Chemicals organic, at plant/GLO S
P2O5 equivalent Avoided (as DAP) by Biosolids Recovery	Avoided Product (296.4 kg DAP): Diammonium phosphate, as P2O5, at regional storehouse/RER S
Centrate discharged to Surface Water as N (kg/day)	Emissions to water
Centrate discharged to Surface Water as P (kg/day)	Emissions to water
Centrate discharged to Surface Water as K (kg/day)	Emissions to water
Polymer Transport (tkm/day)	Transport, combination truck, average fuel mix/US
Struvite Operation Input	
Electricity Usage (kWh/day)	Electricity mix/US S
Aerator Electricity Usage(kWh/day)	Electricity mix/US S
Pump Electricity Usage (kWh/day)	Electricity mix/US S
NaOH Usage (kg/day)	Sodium hydroxide, production mix, at plant/kg/RNA
P2O5 equivalent Avoided (as DAP) Avoided by Struvite Recovery (kg/day)	Avoided Product (29.5 kg DAP): Diammonium phosphate, as P2O5, at regional storehouse/RER S
Centrate discharged to Surface Water as N (kg/day)	Emissions to water
Centrate discharged to Surface Water as P (kg/day)	Emissions to water
Centrate discharged to Surface Water as K (kg/day)	Emissions to water
NaOH Transport (tkm/day)	Transport, combination truck, average fuel mix/US
Struvite Transport (tkm/day)	Transport, combination truck, average fuel mix/US
IX Operation Input	
K2O equivalent Avoided (as KNO3) by N and K Recovery (kg/day)	Avoided Product , Potassium nitrate, as K2O, at regional storehouse/RER S
Zeolite Usage Rate (as Bentonite) (kg/day)	Bentonite, at processing/DE S
HCl dry mass needed (kg/day)	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
Reclaimed water (L)	Avoided Product: Drinking water, water purification treatment, production mix, at plant, from surface water RER S
HCl Transport (tkm/day)	Transport, combination truck, average fuel mix/US
Zeolite Transport (tkm/day)	Transport, combination truck, average fuel mix/US

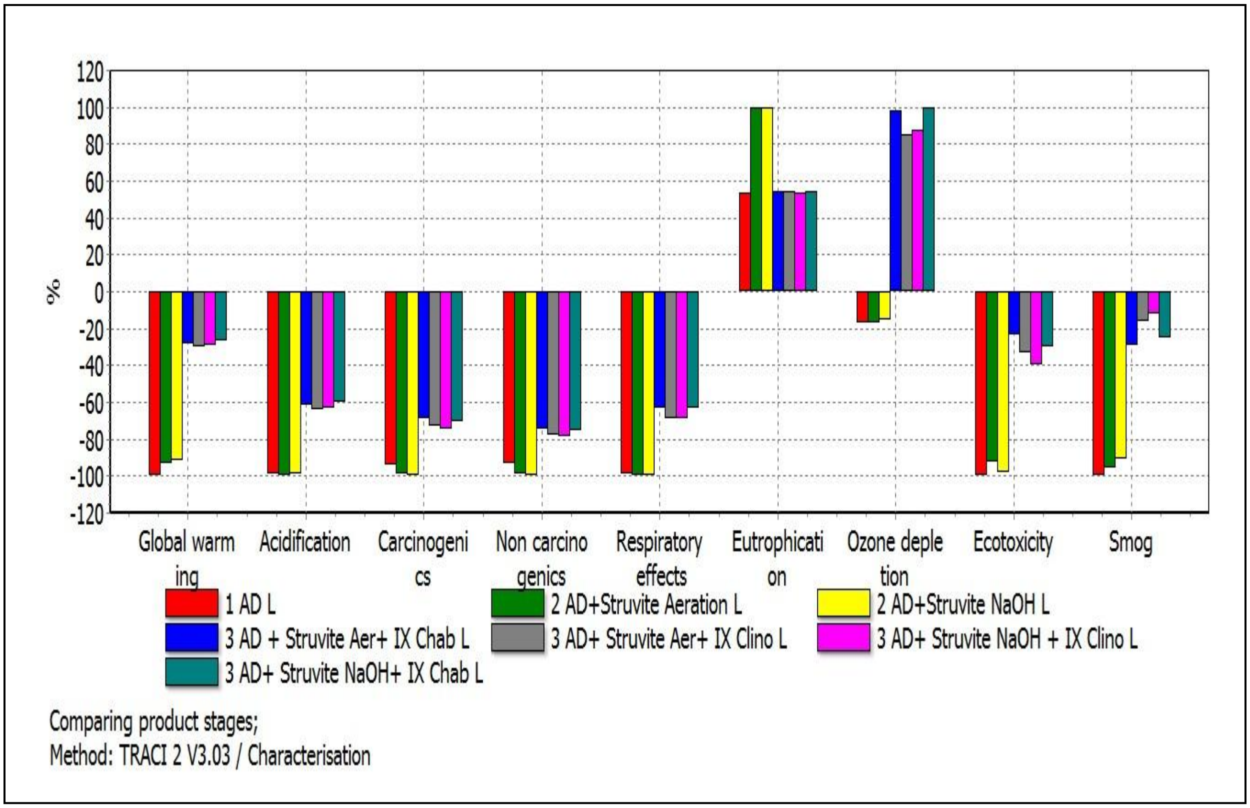


Figure A.12: Impact Assessment Comparing Additions to the Treatment Train for Large CAFO

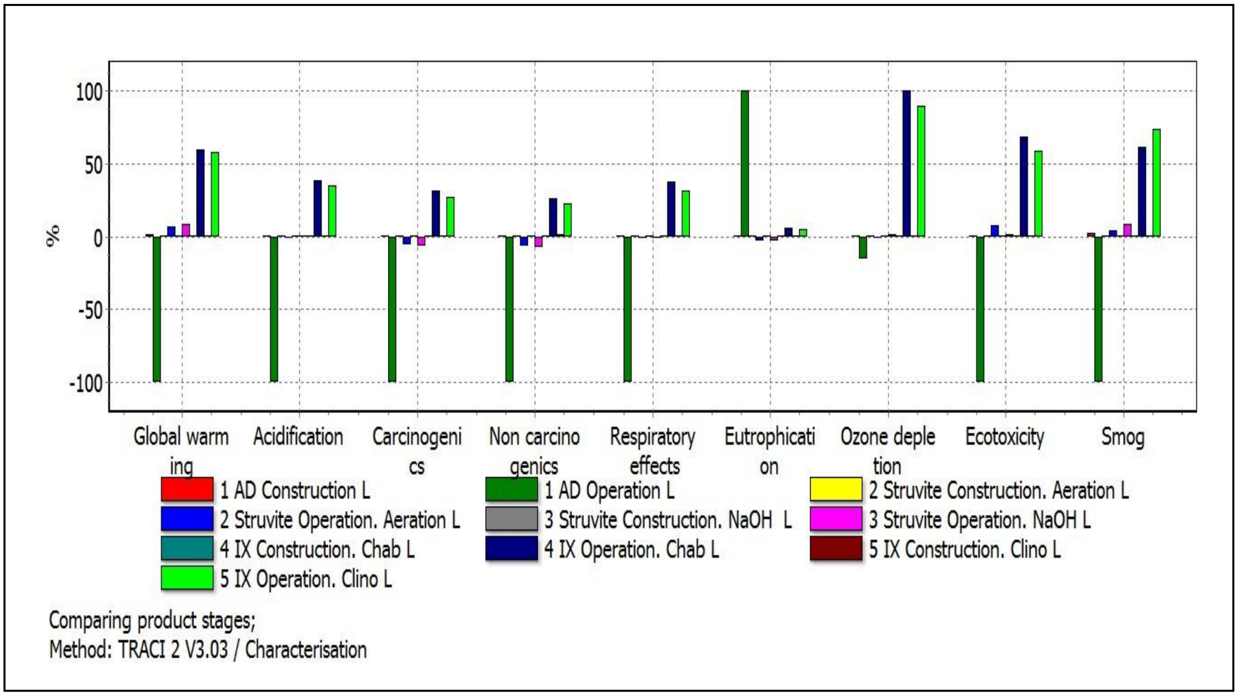


Figure A.13: Impact Assessment Comparing Construction vs. Operation for Large CAFO

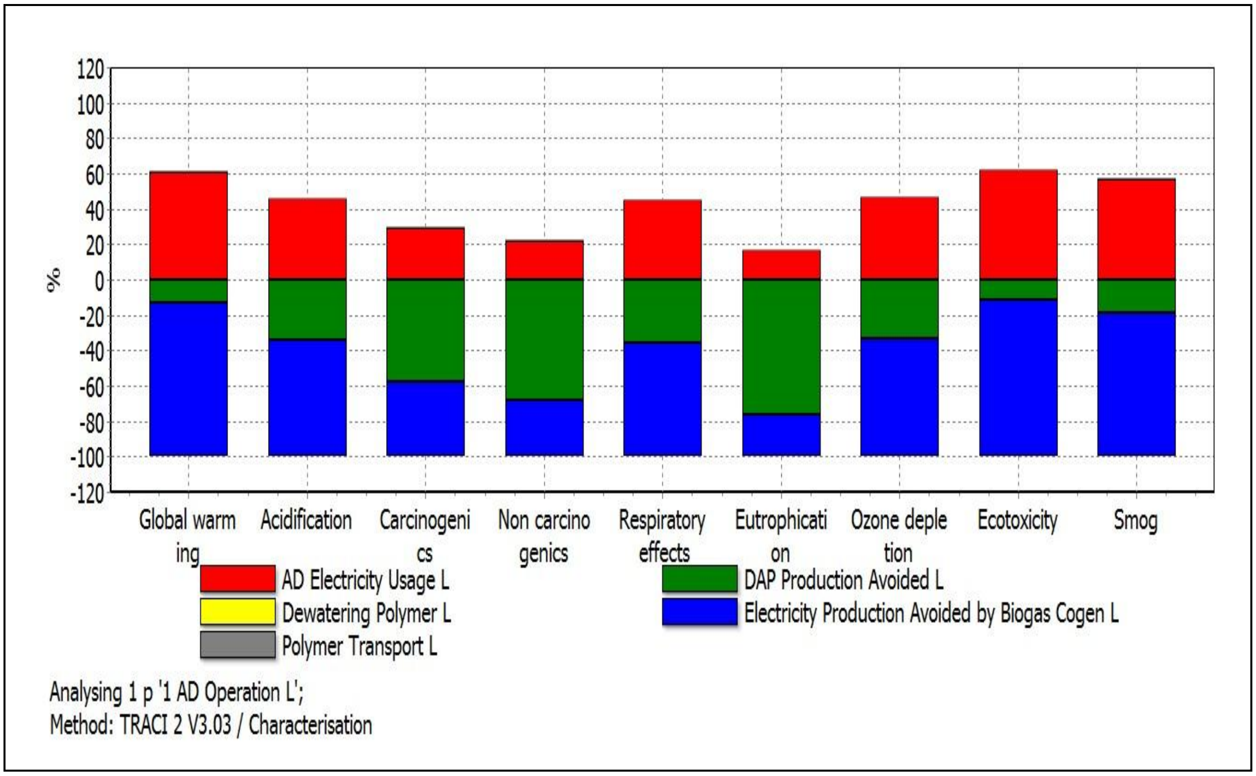


Figure A.14: Impact Analysis of AD for Large CAFO

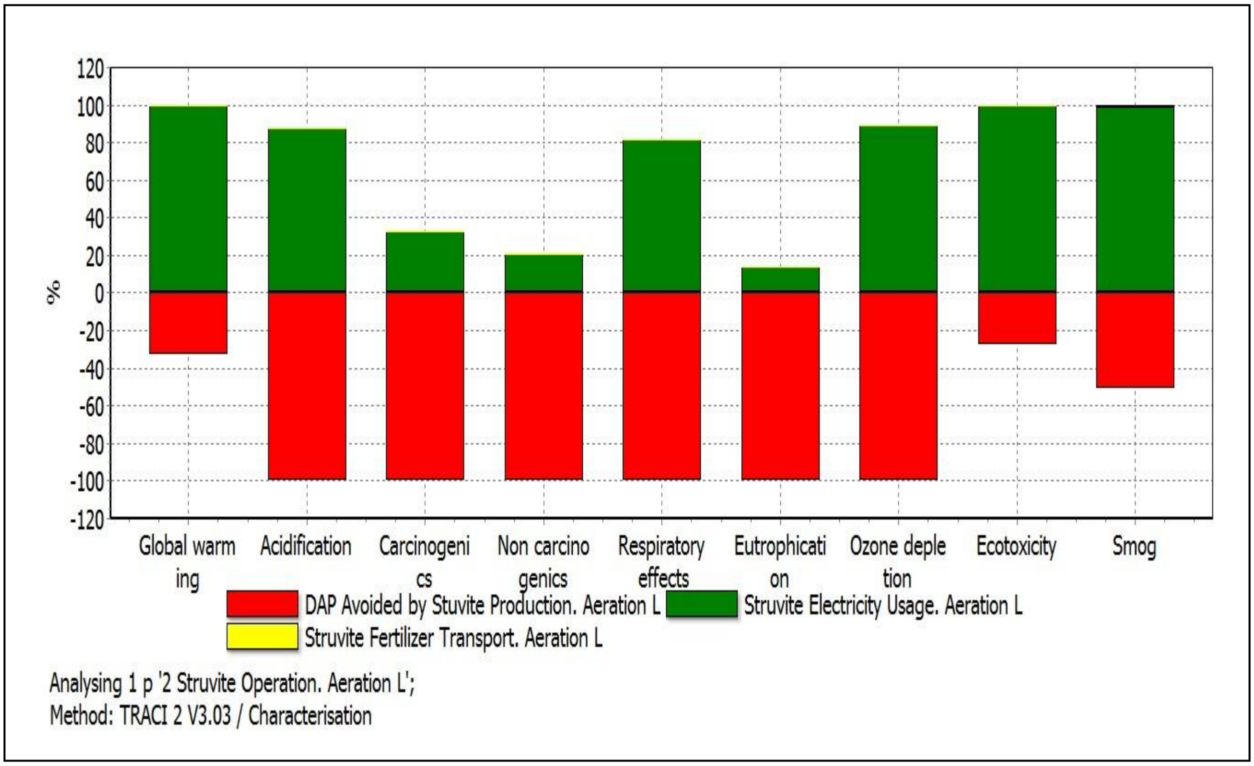


Figure A.15: Impact Analysis of Struvite Precipitation Using Aeration for Large CAFO

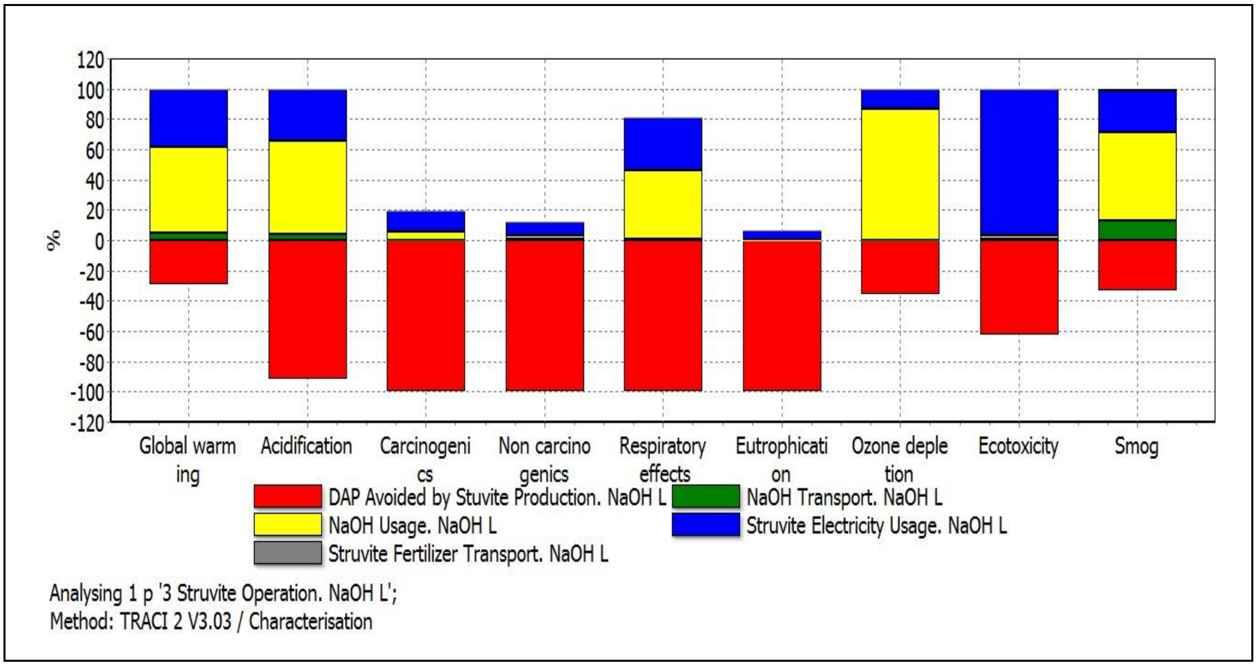


Figure A.16: Impact Analysis of Struvite Precipitation Using NaOH for Large CAFO

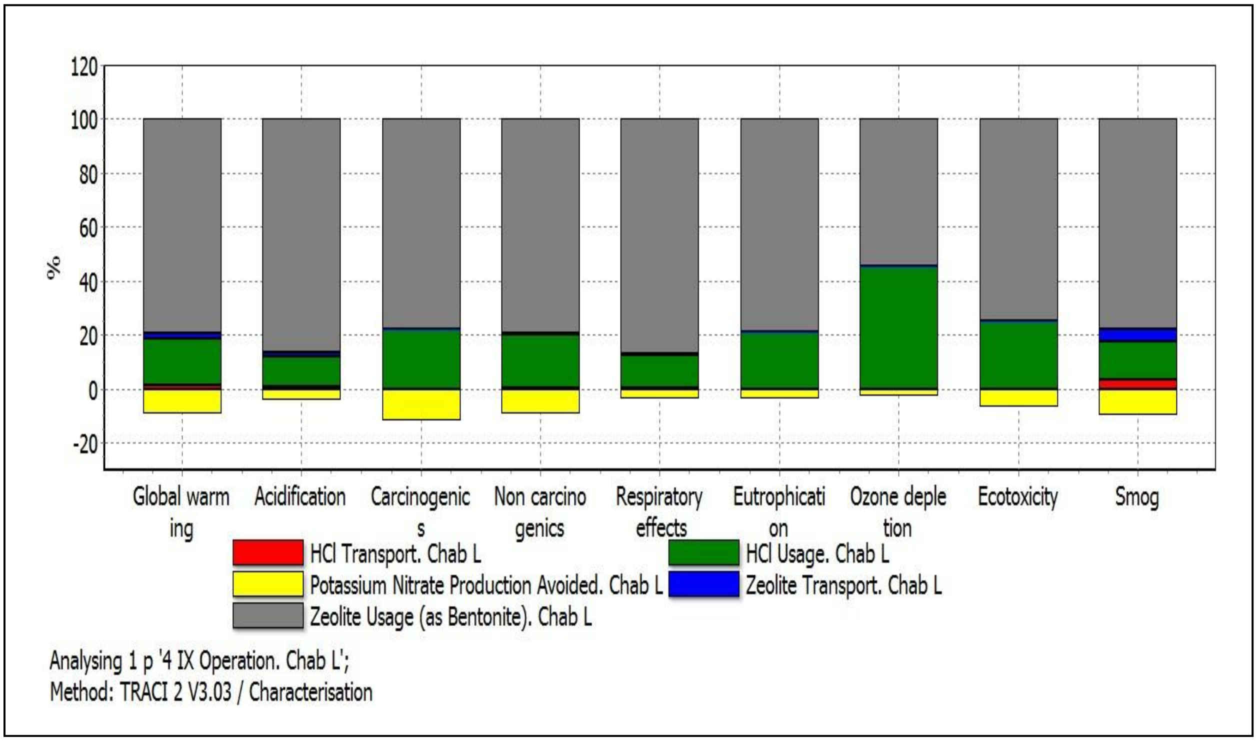


Figure A.17: Impact Analysis of IX using Chabazite for Large CAFO

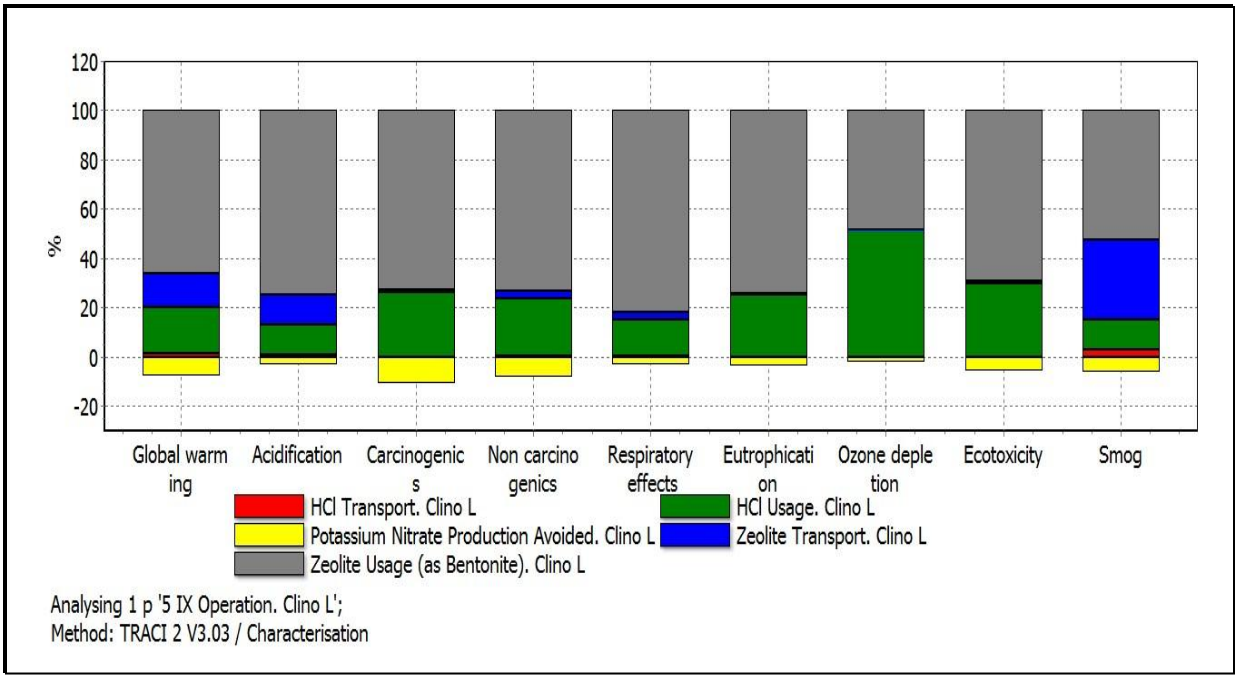


Figure A.18: Impact Analysis of IX using Clinoptilolite for Large CAFO

Table A.3: Detailed Construction Costs Breakdown for AD for Medium-Sized CAFO

Site Work		
Digester and Piping Excavation	$	46,950
Excavation and Piping for Digester and site Piping		
Digester Concrete Installation	$	51,777
Installation		
8.5mx9.8m Utility Building	$	34,020
Utility & Electrical	$	52,461
Total	**$**	**185,208**
Equipment		
Engine Generator - Martin Machinery	$	120,400
100kW MAN with Exhaust Heat Recovery		
GHU Skid and Accessories	$	116,830
Gas Skid, DG-Skid-Genset Tie-Ins		
H2S Scrubber - Designed for 2,500 PPM H2S Removal		
HW Skid and Accessories	$	45,713
Hot Water Skid, DG-Skid-Genset Tie-Ins		
Startup Propane		
Manure Pump	$	30,049
Chopper Pump		
Pump Control Panel		

Table A.3 (Continued)

Digester Mixers and Accessories	**$**	**65,562**
Bauer Mixer x3		
Mounting System x3		
Controls x3		
Utility Building Ventilation Equipment	$	2,505
MultiFan x1		
Modulating Temp Control x1		
Wall Shutter x2		
Wall Shutter Opener x2		
Digester Cover System	$	82,042
HDPE Cover 80 mil		
HDPE Imbed Strip		
Rainwater System		
Wall Insulation		
Cover Insulation		
Digester Startup Equipment	$	2,400
CO2 Test Kit x1		
pH Meter x1		
Manometer 36 inch (91cm) x1		
Infrared Temperature Sensor x1		
Compost Thermometer x1		
Fire Extinguisher x1		
Safety Signs x19		
Digester Control System	$	17,094
Digester Temperature Control System		
Hot Water Temp Sensors		
Digester Temperature Sensors		
Integrated Readout		
Flare System	$	23,581
Gas Flare		
Flame Arrestor		
PRV		
Witmer Automation Igniter		
Flare Data Logger		
Dewatering	$	70,000
Belt Filter Press - 0.5 meter. X2		
Site Pipe	$	122,480
DIGESTER PIPE & FITTINGS COST		
Digester Heating System Pipe		
Mounting System For Pipe		
PIPE CHASE PIPE & FITTINGS COST		
SITE PRIMARY HW PIPE & FITINGS COST		
Supply and return From Digester		
122m Between Points		
SECONDARY HW PIPE AND FITTINGS		

Table A.3 (Continued)

Supply and Return 30m Between Points		
SITE RADIATOR PIPE & FITTINGS COST		
Supply and Return For Radiator		
18 Between Points		
SITE GAS PIPE & FITTINGS COST		
Gas Pipe from Digester to Utility Building		
122m Between Points		
GAS PIPE & FITTINGS IN DG &PC COST		
SITE FLARE GAS PIPE & FITTINGS COST		
Site Flare Pipe		
Flare Mounting Pipe		
SITE MANURE PIPE & FITTINGS COSTS		
Pipe Between Manhole and Digester		
61m Between Points		
MANURE PIPE & FITTINGS @ PUMP COST		
Connections from Pump to Manure Pipe		
Vacuum Break		
SITE EFFLUENT PIPE & FITTINGS COST		
Pipe from Digester to Lagoon		
Total	**$**	**698,656**
<u>Engineering and Construction</u>		
RCM Design and Drafting		
Construction Management		
Total	**$**	**136,006**
<u>Total Project Cost</u>	**<u>$ 1,019,870</u>**	

Table A.4: Detailed Construction Costs Breakdown for AD for Large-Sized CAFO

<u>Site Work</u>		
Manure Transfer System Excavation and Pipe	$	117,312
Manure Pipe from Digester to Upper Farm	$	40,000
Digester System Excavation/Trenching/Stone	$	65,000
Concrete Digester	$	242,097
Generator/Separator Building/Precast Walls/Slab on Grade	$	92,679
Site Electrical Installation	$	69,000
Utility Interconnection	$	30,000
Total	**$**	**656,088**
<u>Equipment</u>		
Generator, Intertie, Controls, Chiller, Radiator	$	493,408
Gas Handling System	$	205,758
Gas Skid, DG Skid Genset Tie Ins		

Table A.4 (Continued)

Site Work		
H2S Scrubber and Control panel - 1,500 PPM H2S Removal		
Pipe chase piping to outside pipe chase wall		
Emergency Flare		
Flare mounting system		
Flame Arrestor		
Pressure Release valve		
Flare igniter		
Flare Data Logger		
Integrated Control Panels and Displays		
Digester Heating System	$	154,433
Digester Heat Exchange, mounting racks and fittings		
Hot Water Skid, DG Skid Genset Tie ins		
Hot water distribution manifolds		
Hot water supply and return lines between digester and utility building		
Pipe fusing machine rental		
Secondary hot water heat exchanger connection		
Digester Equipment	$	296,510
Digester Cover System		
HDPE Cover 80 mil		
HDPE imbed strip		
Rainwater collection pump		
wall insulation		
Cover Insulation - 2 layers		
Digester Mixers and Accessories		
Bauer Mixer x5		
Mounting System x5		
Controls x5		
Digester Temperature Monitoring System		
Digester Temperature Control System		
Hot Water Temp Sensors		
Digester Temperature Sensors		
Data Collection, Storage, readout panel		
Utility Building and Startup Equipment	$	7,630
Utility Building Ventilation Equipment		
MultiFan x 2		
Modulating Temp Control x1		
Wall Shutter x2		
Wall Shutter Opener x2		
Digester Startup Equipment		
CO2 Test Kit x1		
pH Meter x1		
Manometer 36" x1		
Infrared Temperature Sensor x1		
Compost thermometer x1		

Table A.4 (Continued)

Site Work		
Fire Extinguisher x1		
Safety Signs x19		
Manure Handling Equipment	$	171,063
Influent Pump (Long Distance)		
Long distance Pump x3		
Control Panel x3		
Doda Mixer x3		
Influent Pumps (Standard)		
Doda Chopper Pump x1		
Control Panel x1		
Effluent Pump		
Doda Chopper Pump or equivalent x1		
Control panel x1		
Dewatering		
Belt Filter Presses		
Site Piping	$	25,910
Site Manure Pipe		
Site Effluent		
Site Gas		
Total	**$**	**1,354,712**
Engineering Utility, Construction Management, Startup, Commissioning		
Engineering	$	279,709
Startup Fuel and Equipment	$	8,500
Total	**$**	**288,209**
Total Project Cost	**$**	**2,299,009**

Table A.5: List of Abbreviations

Abbreviations	Full Name	Abbreviations	Full Name
AD	Anaerobic Digestion	**LCI**	Life Cycle Inventory
AL	Anaerobic Lagoon	**Mg**	Magnesium
BOD	Biochemical Oxygen Demand	**N**	Nitrogen
Ca	Calcium	**P**	Phosphorus
COD	Chemical Oxygen Demand	**SEM-EDX**	Scanning Electron Microscope, Energy Dispersive X-Ray Spectroscopy
CP	Centrate Phosphorus (includes suspended solids)	**SF**	Sensitivity Factor
DAP	Diammonium Phosphate (fertilizer)	**SP**	Soluble Phosphorus (filtered)

Table A.5 (Continued)

Abbreviations	Full Name	Abbreviations	Full Name
FBR	Fluidized Bed Reactor	**SRP**	Soluble Reactive Phosphorus (filtered)
FU	**Functional Unit**	TN	**Total Nitrogen**
IC	Ion Chromatography	**TP**	Total Phosphorus (includes all solids)
IX	Ion Exchange	**TS**	Total Solids
K	Potassium	**TSS**	Total Suspended Solids
KNO3	Potassium Nitrate (fertilizer)	**VFA**	Volatile Fatty Acids
LCA	Life Cycle Assessment	**VS**	Volatile Solids
LCCA	Life Cycle Cost Assessment	**XRD**	X-Ray Diffraction

Table A.6: Values Used in LCI

Parameter	Value	Source
DAP Price	$369.88 per ton	(DAP - Index Mundi)
Aerator Electricity Requirement	2 kW	(Dongguan Modern Pump Factory)
Swine Waste Total Solids Production	0.80 lbs/pig/day	(Hamilton et al., n.d.)
Swine Waste N Production (Used to Calculate Biosolids Content)	0.053 lbs/pig/day	(Hamilton et al., n.d.)
Swine Waste P Production (Used to Calculate Biosolids Content)	0.02 lbs/pig/day	(Hamilton et al., n.d.)
Swine Waste K Production (Used to Calculate Biosolids Content)	0.028 lbs/pig/day	(Hamilton et al., n.d.)
Mixer Electricity Requirement	5.5 kW	(Submersible Motor Mixer, n.d.)
Pump Efficiency	30%	Estimated
Pump Motor Efficiency	30%	Estimated
Pump Average Dynamic Head (ft)	80	Estimated
Average Methane Generated	0.35 m^3/kg VS destroyed	(Speece, 1996)
National Average Electricity Cost	9.64 cents/kWh	(EIA, n.d.)
Biosolids Cost	$10 per yard	(AD manufacturer, personal communication, March 3, 2013; Goldstein and Block, 1997)
Dewatering Polymer Ruirements	2 g/kg biosolids	(USEPA, 2000)
Dewatering Polymer Costs	$24.38 per MGD treated (average value)	(USEPA, 2000)
Fertilizer Effectiveness of Struvite vs DAP	1.2 (most conservative estimate used)	(Barak and Stafford, 2006)