

PROCESS DEVELOPMENT FOR RECOVERY OF NUTRIENTS AS STRUVITE AND
STRUVITE BASED PRODUCTS

By

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Dedicated to my beloved mother, brothers and late father

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TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS	4
LIST OF TABLES	9
LIST OF FIGURES	10
LIST OF ABBREVIATIONS.....	12
ABSTRACT.....	13
CHAPTER	
1 INTRODUCTION	15
1.1 Project Focus	15
1.1.1 Sources of Phosphorus in Water Streams	15
1.1.2 Industry	16
1.1.3 Livestock	16
1.1.4 Human Source.....	16
1.1.5 Fertilizers	17
1.2 Nutrient Removal in a Wastewater Treatment Plant.....	17
1.3 Phosphorus in Animal Manure.....	18
1.4 Current Phosphorus Removal Techniques from Wastewater	20
1.5 Hypothesis for the Present Research.....	24
1.6 Goals and Research Approach	24
1.7 Outline of Dissertation	25
1.7.1 Development and Experimental Validation of a Mathematical Model of Struvite Precipitation.....	25
1.7.2 Sequential Batch Reactor for Recovery of Nitrogen and Phosphorus as Struvite from Sewage Sludge Centrate and Dairy Wastewater	25
1.7.3 Development of Product Formulation Techniques Using Struvite Solids.....	26
1.7.4 Concept to Commercialization (C2C).....	26
1.7.5 Conclusions and Recommendations	26
2 DEVELOPMENT AND EXPERIMENTAL VALIDATION OF A MATHEMATICAL MODEL FOR STRUVITE PRECIPITATION	29
2.1 Struvite Modeling	29
2.2 Review of Struvite Precipitation Models	29
2.2.1 Struvite Modeling Approaches	29
2.2.2 Solution Approaches to Models.....	31
2.3 Model Formulation	33
2.3.1 Magnesium Phosphate Species	34
2.3.2 Calcium Phosphate Species	34

2.3.4	Other Salts	35
2.3.5	Equations	35
2.4	Results and Discussion	36
2.4.1	Model Validation	37
2.4.2	Effect of pH	41
2.4.3	Effect of Initial Magnesium, Phosphate, and Ammonium Ratio	43
2.4.4	Determining “Exion” Concentration for Real Wastewater	45
2.4.6	Effect of pH on Struvite Purity and Phosphorus Removal in Real Wastewater	46
2.5	Findings	48
3	SEQUENTIAL BATCH REACTOR FOR RECOVERY OF NITROGEN AND PHOSPHORUS AS STRUVITE FROM SEWAGE SLUDGE CENTRATE AND DAIRY WASTEWATER	60
3.1	Removal of Nutrients from Wastewater	60
3.1.1	Factors Affecting Struvite Formation: Concentration and Nature of Constituents	61
3.1.2	Effect of pH	62
3.1.3	Effect of Temperature	63
3.1.4	Hydraulic Retention Time (HRT)	64
3.2	Review of Reactor Designs for Struvite Production	64
3.2.1	Stirred Tank Reactors	66
3.2.2	Fluidized Bed Reactor (FBR)	67
3.3	Overview of Sequencing Batch Reactor (SBR) Technology	69
3.3.1	Introduction	69
3.3.2	Overview of Full-scale Applications of SBR Technology	69
3.3.3	Characteristics of SBR Technology	71
3.4	Objectives	72
3.5	Materials and Methods	72
3.6	Results and Discussion	75
3.6.1	Determination of Magnesium Needed for P Recovery as Struvite from Centrate	75
3.6.2	Struvite Precipitation from Synthetic Solution in the SBR	76
3.6.3	Phosphorus Recovery from Centrate	77
3.6.4	Experiments on Complete Nitrogen and Phosphorus Recovery from Centrate	78
3.6.5	Effect of Aeration on Centrate	79
3.6.6	Struvite Recovery from Dairy Manure	80
3.6.7	Settleability of Struvite in the SBR	82
3.7	Outcomes	84

4	DEVELOPMENT OF PRODUCT FORMULATION TECHNIQUES USING STRUVITE SOLIDS	93
4.1	Struvite as a Fertilizer	93
4.1.1	Recovery of Ammonia from Wastewater	95
4.1.2	Uses of Struvite	97
4.2	Objectives.....	99
4.2.1	Co-crystallization of Struvite with KMAG.....	99
4.2.2	Study Absorption of Ammonia in Acidic KMAG Solution	100
4.2.3	Investigate Use of Agglomerates to Make Struvite Pellets.....	100
4.3	Materials and Methods.....	101
4.3.1	Struvite Precipitation.....	101
4.3.2	Preparation of KMAG Solution	101
4.3.3	Agglomeration of Struvite	102
4.3.4	Crystallization of Struvite with KMAG.....	102
4.3.5	Ammonia Removal from Centrate and Synthetic Solution.....	103
4.4	Results and Discussion.....	103
4.4.1	Effect of the Polymer Addition on Struvite Filtration	103
4.4.2	Crystallization of Struvite with KMAG.....	104
4.4.2.1	Batch Crystallization	104
4.4.2.2	Semi-continuous Crystallization of KMAG with Stuvite.....	106
4.4.3	Absorption of Ammonia in KMAG	106
4.5	Outcomes	107
5	CONCEPT TO COMMERCIALIZATION (C2C)	129
5.1	Introduction.....	129
5.2	Materials and Methods.....	134
5.3	Results and Discussion.....	135
5.3.1	Trial 1	135
5.3.1.1	Treatment Step 1	136
5.3.1.2	Treatment Step 2.....	137
5.3.2	Trial 2.....	138
5.3.3	Comparison between Laboratory and the Pilot Scale Runs	139
5.4	Scale-up Considerations in Precipitation	140
5.5	Discussion of Feasibility on Full-scale	141
5.6	Economics of Struvite Recovery.....	141
5.7	Struvite Recovery as a Business	144
5.8	Outcomes	144
6	CONCLUSIONS AND FUTURE WORK.....	151
6.1	Overall Findings.....	151
6.1.1	Mathematical Model of Struvite Precipitation.....	151
6.1.2	Sequential Batch Reactor Operation for Recovery of Nitrogen and Phosphorus as Struvite from Sewage Sludge Centrate and Dairy Wastewater.....	152

6.1.3	Fertilizer Product Formulation Using Struvite Solids.....	152
6.1.4	Pilot Scale Study of the Sequential Batch Operation for Struvite Precipitation	153
6.2	Future Work	153
6.2.1	Automation of the Pilot Plant.....	153
6.2.2	Biological Struvite Formation with Existing Enhanced Biological Phosphorus Removal (EBPR) Processes	154
APPENDIX: POLYMATH MODEL FOR STRUVITE PRECIPITATION		156
LIST OF REFERENCES		159
BIOGRAPHICAL SKETCH		168

LIST OF TABLES

<u>Table</u>	<u>page</u>
2-1 List of solids included in the comprehensive model.....	50
2-2 Equilibrium expressions with equilibrium and solubility constants.....	51
2-3 Input parameters to the model for simulations on effect of pH.....	52
2-4 Validation of the chemical equilibrium mode	52
3-1 Optimum pH values used in struvite formation.....	87
3-2 Effect of magnesium concentration on nitrogen and phosphorus removal from the centrate.....	87
3-3 Phosphorus recovery from the centrate.....	86
3-4 Recovery of nitrogen and phosphorus from centrate.....	86
3-5 Sequential batch operation: Process details	89
3-6 Struvite recovery from dairy manure.....	887
4-1 KMAG chemical analysis.....	109
4-2 Solids considered in x-ray diffraction analysis as standards	110
4-3 Chemical added for struvite formation for polymer effect experiments.....	110
4-4 Effect of the polymer addition on filtration	111
4-5 Crystallization of synthetic struvite with the acidic solution of KMAG	111
4-6 X-ray diffraction results.....	111
4-7 Absorption of ammonia in KMAG.....	112
5-1 Details of equipment used in the pilot plant	146
5-2 Composition of struvite generated in the pilot scale runs.....	146
5-3 Chemical requirement for the pilot plant runs	146
5-4 Equipment cost of the SBR pilot plant	147
5-5 Capital cost of full-scale struvite plant; Capacity: 700,000 GPD.....	148

LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1-1 Secondary wastewater treatment plant at JEA.....	27
1-2 Proposed location for struvite production.....	28
2-1 Effect of pH on struvite purity for ammonium, magnesium, and phosphate ratios of 1:1:1 (at 10 mM and 100 mM) and 10 mM : 1.7 mM : 3.4 mM.....	55
2-2 Effect of molar ratio of magnesium: phosphate on % struvite and total solids for two different molar ratios of ammonium (A) and phosphate (P) at pH = 8.7	56
2-3 Titration curve for anaerobically digested wastewater from dairy operations	57
2-4 Effect of pH on struvite purity and phosphorus removal in centrate at an Mg:P ratio of 1:1	58
2-5 Effect of pH on struvite purity and phosphorus removal in centrate at an Mg:P ratio of 0.5:1	58
2-6 Effect of pH on struvite purity and phosphorus removal in dairy flushwater at an Mg:P ratio of 1:1	59
2-7 Effect of pH on struvite purity and phosphorus removal in dairy flushwater at an Mg:P ratio of 0.5:1	59
3-1 Sequencing batch reactor (SBR) process.....	88
3-2 Sequential batch reactor for struvite precipitation	88
3-3 X-ray diffraction patterns for struvite produced from the centrate.....	89
3-4 X-ray diffraction patterns for struvite produced	90
3-5 Settleability of solids in struvite formation.....	91
3-6 Solids settling in the SBR with dairy manure: Settling time = 15 min.....	91
3-7 Solids settling in the SBR with dairy manure: Settling time = 30 min.....	92
3-8 (A) Raw dairy manure; (B) Settled solids after struvite precipitation	92
4-1 Struvite recovered from experiments.....	113
4-2 Continuous crystallization of KMAG with struvite.....	114

4-3	Crystallization of KMAG with struvite	114
4-4	Absorption of ammonia in KMAG	115
4-5	KMAG with struvite: pH adjusted to 2.2 at commencement of crystallization.....	115
4-6	KMAG from saturated solution	116
4-7	X-ray diffraction results of solids from mixing KMAG with synthetic struvite	119
4-8	X-ray diffraction of raw KMAG with struvite from the pilot scale run	121
4-9	X-ray diffraction of solids from mixing KMAG solution with struvite from the pilot scale run	124
4-10	Change in potassium concentration in semi-continuous crystallization of KMAG with struvite	125
4-11	Change in phosphorus concentration in semi-continuous crystallization of KMAG with struvite	125
4-12	X-ray diffraction analysis of solids from the semi-continuous run	127
4-13	Recovery of nitrogen and phosphorus from centrate	128
5-1	Process layout	149
5-2	Process flow diagram.....	150

LIST OF ABBREVIATIONS

BNR	biological nutrient removal
C2C	concept to commercialization
DCP	monenite
EBPR	enhanced biological phosphorus removal
EPA	environmental protection agency
HAP	hydroxyapatite
HRT	hydraulic retention time
FBR	fluidized bed reactor
JEA	Jacksonville Electric Authority
KMAG	potassium magnesium sulphate
MAP	magnesium ammonium phosphate (struvite)
OCP	octacalcium phosphate
SBR	sequential batch reactor
XRD	x-ray diffraction

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Formation of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) in pipelines and inner surfaces of wastewater treatment processes has been found to make operation of the plant inefficient and costly. Struvite is also identified as a route to recover nitrogen and phosphorus as a marketable fertilizer. Controlled crystallization of struvite is possible to prevent its spontaneous precipitation. Existing struvite recovery techniques are found to have limitations such need for large reactor volumes, complicated designs, higher capital and operating & maintenance costs. The existing systems have been able to achieve only 90% removal of phosphate which does not necessarily meet strict EPA standards. In this study a novel struvite recovery process is developed which eliminates the limitations of existing phosphorus recovery techniques discussed above.

Struvite precipitation reaction was found to be rapid therefore if it was possible to decouple the precipitation process from agglomeration/crystallization process reactor volumes could be considerably reduced. The precipitation reaction was accomplished using a simple sequential batch reactor operation; this operation is similar to that currently employed by wastewater treatment plants thereby making it more operators friendly. A salable product

crystallized using potassium magnesium sulphate was produced in a separate unit operation using the reduced volume of settled sludge rather than entire wastewater.

Predicting struvite precipitation potential, yield and purity is important for designers and operators of reactors for struvite precipitation. In this study a mathematical model of struvite precipitation process was developed for a closed system using physicochemical equilibrium expressions, mass balance equations for nitrogen, phosphorus and magnesium, and charge balance. The model simulations were validated against our experimental data using synthetic wastewater and some data from literature. The model satisfactorily predicted all data.

Bench scale studies showed that the pH level 8.4 - 8.7 allow for rapid struvite nucleation which caused the precipitation of fines. Aeration of centrate was found to increase the pH to 8.4. This was useful for minimizing the caustic requirement for struvite formation and also to reduce carbonate concentration. This also improved quality of struvite by reducing solids with carbonate. Complete nitrogen and phosphorus removal was gained from centrate in a sequential batch reactor. Settling of precipitated struvite was found to be rapid with a settling time of 10 min. The recovery of phosphorus from dairy manure as a struvite containing precipitate was successfully demonstrated using the SBR mode of operation.

Pilot scale trials conducted in an SBR of 500 g trial were found to recover 93% of PO_4^{3-} -P from centrate in a single step. Successful ammonia recovery was found feasible by addition of phosphoric acid to centrate if additional nitrogen recovery is desired. It was found that the recovered struvite contained almost no hazardous materials and exhibited equivalent or better fertilizer effectiveness than conventional chemical fertilizers. Economic analysis of the process revealed that for a plant treating 750,000 gal per day of centrate, capital investment of \$1.5 million is needed and a net profit of \$ 452,000/year is predicted.

CHAPTER 1 INTRODUCTION

1.1 Project Focus

Removal and recovery of nutrients such as, phosphorus, nitrogen and potassium from different types of waste waters is of both ecological and economic importance. Currently mined phosphate represents the main source of phosphorus used by the fertilizer, detergent or insecticide industries (Steén, 2004). Recovery of phosphorus is of particular importance because of the rapid depletion of mineral phosphate deposits all over the world (Driver et al.,1999) Phosphorus recycling from wastewater effluents has also gained importance, due to stringent regulations of phosphorus levels in the effluents in wastewater discharged to sensible areas such as lakes, rivers and reservoirs (UWWTD, 1991). Therefore, as an alternative to traditional phosphorus removal techniques, recycling of phosphorus in the form of valuable and usable chemicals is gaining importance. Phosphorus can be recovered from effluents generated in a sewage treatment plant, animal wastes and agro processing industries. The studies presented in this thesis will focus on recovering phosphorus from sewage treatment plant effluents and dairy wastewater. A brief review of various sources of phosphorus is presented in next section.

1.1.1 Sources of Phosphorus in Water Streams

Phosphorus in municipal, industrial, and agricultural wastewater may come from a variety of sources listed below. The Southern Cooperative Series (1998) reports that phosphorus naturally enters the soil solution by the following means:

1. Dissolution of primary minerals,
2. Dissolution of secondary minerals,
3. Desorption of phosphorus from clays, oxides, and minerals, and
4. Biological conversion of phosphorus by mineralization.

In addition to these, other anthropogenic inputs to surface water are substantial and comprise the remaining balance of phosphorus inputs to surface waters. While many sources have been

decreased through managed use or treatment in past decades, livestock inputs have actually increased.

1.1.2 Industry

The application of phosphorus is wide in many aspects of industries. Phosphorus is used in some softened waters for stabilization of calcium carbonate to eliminate the need of recarbonation (Sawyer et al., 1994). Polyphosphates are also used in public water systems in order to control corrosion as well as in steam power plants to control scaling in the boilers. If phosphate complexes are used, these rapidly hydrolyze to orthophosphate at high temperatures in the power plants (Sawyer et al., 1994). Many industries release high phosphorus concentration wastewater, for example food and dairy processing, and other processes that use phosphorus, phosphoric acid or phosphates also contribute.

1.1.3 Livestock

Phosphorus is an essential element required for livestock. Animal feeding operations can provide a significant source of nutrients for crops through manure. The manure produced from the livestock is applied to the land, and often the ratio of nitrogen to phosphorus is unbalanced in a manure thus causing over-application of phosphorus to the land. However, supplying manure that is nutrient-balanced for nitrogen and phosphorus requires reducing the phosphorus content of manure, without compromising the performance of the livestock (ICM, 2000; Burns et al., 2002).

1.1.4 Human Source

After elimination of phosphate – based detergents in the 1980s, much of the inorganic phosphorus is now contributed by human wastes as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine. The amount of phosphorus released is a function of protein intake. An average person in United States releases 1.5 g/day of

phosphorus (CEEP, 2003). The per capita contribution from human populations, after sewage treatment, was estimated at 0.62 kg total phosphorus/person/year in Morse et al., 1998, whereas, the report presented by CEEP 2007 estimated 0.43 kg total phosphorus/person/year. In a wastewater treatment plant at Metamorphosis, Greece, the average total phosphorus influent value is 30.6 mg/L (Sotirakou et al., 1999). In 1992, Point Loma Wastewater Treatment Plant, City of San Diego discharged 954 metric tonnes of total phosphorus (SCCWRP, 1992).

1.1.5 Fertilizers

Phosphorus is applied to the land as a fertilizer providing nutrient to the crops. Phosphate is extracted from rocks containing apatite. Phosphate fertilizers are produced by adding sulfuric acid to the phosphate rock which is 16 – 21% as phosphorus pentoxide (Pollution Prevention and Abatement Handbook, 1998). Part of phosphorus applied to the land is taken up by the crops and is accumulated in them, whereas, the remaining fraction of phosphorus dissolves in the rain and can be transported to the nearby water body or infiltrates in to the groundwater (ICM, 2000).

1.2 Nutrient Removal in a Wastewater Treatment Plant

Point sources of anthropogenic phosphorus like municipal sewage can be treated before disposal. The objective of a secondary wastewater treatment plant for municipal sewage is to produce an effluent water and sludge stream suitable for discharge or reuse. A large amount of sludge is generated throughout the sewage treatment process. Primary sludge which is the material that settles out during primary treatment often has a strong odor and requires treatment prior to disposal. Secondary sludge is the excess microorganisms from the biological treatment processes. Untreated sludge is about 97% water. The goals of sludge treatment are to dewater, stabilize the sludge and reduce odors, decompose some of the organic matter, reduce volume, kill disease causing organisms and disinfect the sludge. Sludge treatment involves aerobic or anaerobic digestion followed by dewatering. Centrate or filtrate produced in dewatering

operations contains nutrients like ammonia and phosphate and can create discharge problems for treatment plant.

For example at Jacksonville Electric Authority's (JEA) Wastewater Treatment Plant, sludge from primary and secondary treatment as well as biosolids brought in by other waste management operators from around Duval and St. John' County is anaerobically digested and dewatered using centrifuges and gravity belt thickening. Operational stages of this wastewater treatment plant are depicted in Figure1-1. This produces centrate and filtrate streams containing 750-800 ppm of ammonia-N and 130-160 ppm of phosphate-P. Due to the nutrient content, environmental regulations prevent JEA from discharging these streams into St. Johns River. Therefore these streams are returned to the plant headworks where it adds to the wastewater burden.

1.3 Phosphorus in Animal Manure

Phosphorus is one of the vital elements needed for animal growth and milk production. The functions include in metabolic activities in soft tissues, the maintenance of appetite, optimal growth, fertility, bone development and the prevention of bone diseases. The daily nutritional requirements for dairy cattle and beef cattle have been stated as 86-95 g/day and 35-40 g/day respectively (CEEP, 2003). The mechanisms of phosphorus digestion and metabolism differ substantially between ruminant and monogastric animals. In many cases excess phosphorus is used in order to maximize the production of livestock. However, feeding excess phosphorus increases phosphorus levels in animal waste streams. Only 14% of phosphorus in corn and 31% of soybean meal phosphorus can be digested by cattle. Because a large percentage of phosphorus is unavailable, much of it is excreted (ICM, 2000). To overcome the limited availability excess phosphorus is fed to animals. The waste stream is therefore very rich in phosphorus.

Similar concerns with nutrients are observed in the animal manure treatment operations. The management, treatment and disposal of liquid and solid manure at dairy operations are receiving increased attention. In Florida, governmental regulation of waste disposal activities at dairies is cited as having a negative impact on dairy producers (Tefertiller et al., 1998). Florida dairies use large volumes of water for barn flushing, resulting in large amounts of dilute wastewater. The most common manure management system utilizes short-term holding ponds for flushed manure wastewater storage, with subsequent pumping to sprayfields to supply fertilizer nutrients and irrigation water for production of forage crops.

Generally, nutrients are conserved and recycled on individual farms. But, due to increased animal operations, the quantities of nutrients produced exceed the recommended agronomic application rates on the available land. Historically, anaerobic lagoons are commonly used for stabilization and storage of livestock wastes and wastewaters. Some nutrient removal is obtained by settling of solids and volatilization of ammonia. However, their use is declining because of issues with odors, groundwater contamination, overflow, and dike failures during heavy rainfall linked to tropical weather events. As the size of livestock operations increase, the quantities of nutrients in the waste or wastewater increases, and available cropland becomes limiting. Dairy farms in Florida have traditionally used flushing systems in milking parlors, feeding barns, and free stall barns (Reid and Horwath, 1980). It becomes increasingly difficult to apply the wastewater to available cropland at agronomic rates to prevent environmental problems from excess nutrients. A need exists for waste and wastewater management systems on production enterprises which capture, process and export nutrients from the farming business. Land area requirements would be minimized, odors and other gaseous emissions could be controlled, surface and groundwater pollution problems could be eliminated, and the nutrients

could be converted into value added products and exported from the farm. Although technologies exist for accomplishing these goals, it has been difficult to implement them in a manner which is economically viable and reliable. Drivers that could potentially provide positive economics for the recovery of phosphorus from animal waste in the United States include; 1) a dramatic increase in the cost of inorganic phosphorus, and 2) the implementation of enforceable regulations that require the land-application of animal manures on a phosphorus basis nationally.

1.4 Current Phosphorus Removal Techniques from Wastewater

Mainly, ammonia reduction techniques are well established and widely accepted. This is typically accomplished by nitrification and denitrification operations which biologically convert ammonia into nitrogen gas. Unlike nitrogen, the phosphorus contained in wastewater effluent is transformed into a solid form to be removed (Heinzmann, 2004). Traditional phosphorus removal processes work then by fixing the phosphorus into the sludge:

- either chemically by precipitation of soluble phosphorus with aluminum or iron salts into insoluble phosphate compounds. Separation of the precipitates is then achieved by sedimentation, filtration or flotation (Parsons and Berry, 2004)
- or biologically i.e. Biological Nutrient Removal (BNR), Enhanced Biological Phosphorus Removal (EBPR) using the ability of some micro-organisms to accumulate phosphates as polyphosphates for their own metabolism (Driver et al., 1999; Mulkerrins et al., 2004)

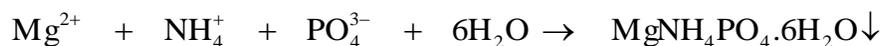
These processes are efficient in the sense that they can reduce phosphorus concentrations in wastewater treated to less than 1 ppm (Booker et al., 1999; Tebbut, 1998), but they present some disadvantages. Among them:

- the accumulation of nutrients (N and some P) in the resulting sludge [Parsons and Doyle, 2004)
- sludge production especially when using chemical processes where P is removed by the formation of P-rich sludge (*i.e.* iron phosphates and iron hydroxides precipitation) leading to significant increases in sludge management costs (Woods et al., 1999)

- phosphorus precipitates generated by these methods are not recyclable for reuse by the industry (de-Bashan and Bashan, 2004). Aluminum phosphates are toxic to human, animals and aquatic life. It is reported as a skin irritant (Berkowitz et al., 2005)

Another approach to remove phosphorus from wastewater effluents is through the crystallization of phosphate compounds such as calcium phosphate or struvite. Struvite is an ammonium magnesium phosphate mineral with the chemical formula $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. Struvite precipitation is accomplished by addition of magnesium and adjustment of pH. This approach has gained particular interest since both struvite and calcium phosphates have been identified as marketable fertilizers (Gaterell et al., 2000).

The general equation describing struvite formation is as follows:



Struvite is primarily known by wastewater companies as a hard scale occurring at points of high turbulence along the water treatment process and resulting in major breakdowns and pipe blockages. Struvite as a source of scale deposits in wastewater treatment plants was confirmed by Borgerding (1972) when it occurred on the walls of an anaerobic digestion system at the Hyperion treatment plant, Los-Angeles, 1963. Indeed struvite naturally occurs under favorable condition of pH and mixing energy in specific areas of wastewater treatment plants (e.g. pipes, heat exchangers) when concentrations in magnesium, phosphate and ammonium reach an equimolar ratio 1:1:1.

Struvite is frequently formed in recycle flush animal waste management systems. Formation of struvite in flushwater recycle pipes has been problematic in liquid manure handling systems because it creates blockages (Buchanan, 1994; Doyle and Parson, 2002). Most of the authors have considered struvite as a ‘problem’ to eliminate and not as a product which could be of economic interest. Until management strategies were developed, the problem of struvite

precipitation caused a serious setback to the recycle flush approach in confinement waste management (Safley et al., 1982). Therefore, a large portion of struvite research has been directed towards removal and prevention of struvite formation rather than towards its precipitation from solution for recovery and reuse.

But, studies by Bridger et al. (1962) have confirmed the excellent agronomic properties of struvite. While only slightly soluble in water and soil solutions, struvite is found to be a highly effective source of phosphorus, nitrogen and magnesium for plants through both foliar and soil application. The release of nutrients is enhanced by a biological nitrification mechanism, with the nutrients being released at a controlled rate over an extended period of time. When properly granulated, it can be applied to soil at rates greatly exceeding those of conventional fertilizers without danger of burning plant roots. Other than use as a premium grade slow releasing fertilizer, struvite also finds uses as a raw material in the phosphate industry, for making fire resistant panels and as a binding material in cements (Sarkar, 1990, Schuiling and Andrade, 1999).

Struvite precipitation can be adopted to:

1. Lower the phosphorus concentration of the effluent by reducing the phosphorus load of the return liquors from sludge treatment
2. Reduce the amount of Polyaluminium Chloride (PACl) and poly-ferric sulfate used, which in turn will reduce the volume of sludge produced
3. Produce a phosphorus rich material, which could be recycled by the fertilizer industry, providing extra revenue from the sale of struvite
4. Offer material, energy and transportation cost savings for the wastewater treatment plants resulting from reduced sludge transport
5. Save operational costs by preventing clogging of pipes from struvite crystals in the pipeline. For a typical wastewater treatment plant serving one million people, the annual cost of dealing with the struvite problem ranges from \$160,000 to \$800,000 (Parsons and Berry, 2004)

Several laboratory and pilot scale studies have been carried out to assess the potential of struvite recovery methods in removing and recovering phosphorus as a reusable product, and a few of them have been tested at full scale in The Netherlands (Giesen 1999) and Italy (Battistoni et al., 2005a; Battistoni et al., 2005b). In Europe and Japan, large municipal sewage-handling facilities have already embraced phosphorus recovery technology (Battistoni et al., 2001; Gaterell et al., 2000; Liberti et al., 2001; Piekema and Giesen, 2001; Ueno and Fujii, 2001). However Japan and Canada are the only countries where 90% P removal and recovery from anaerobically digested sludge liquors as struvite has been implemented and the resulting product sold to fertilizer companies (Gaterell et al., 2000; Ueno and Fujii 2001). A schematic diagram of wastewater treatment plant after the introduction of the struvite production facility is depicted in Figure 1-2. The centrate/filtrate recovered after sludge dewatering and supernatant liquor from gravity belt thickening, which are rich in nitrogen and phosphorus, can be subjected to struvite production. This will reduce the nutrient load on wastewater treatment plant because the water after struvite recover can be discharged as effluent after chlorination as shown in Figure 1-1.

The recovery technologies currently tested are based on the crystallization of phosphorus as hydroxyapatite (HAP) or struvite (MAP) and the majority uses sludge liquors generated from anaerobic digesters as their influent. The technologies can be classified in three main categories:

- Selective ion exchange (*i.e.* RIM-NUT[®] process, (Liberti et al., 1986))
- Precipitation in a stirred reactor (Laridi et al., 2005; Mangin and Klein 2004; Seco et al., 2004; Stratful et al., 2004)
- Precipitation in fluidized bed reactors or air-agitated reactors (Battistoni et al., 2005a; Battistoni et al., 2005b; Ueno and Fujii, 2001; Von Münch and Barr, 2001)
- Limitations of existing techniques are:

- It relies on in-situ crystallization and agglomeration which results in large reactor volumes to ensure appropriate residence times for successful agglomeration. Formation of crystals is favored as it reduces downstream processing cost to make salable product
- Overall reaction rate (consequently reactor volume) is controlled by crystallization process rather than precipitation
- Capital costs are high for these systems
- Reactors used in the commercial processes are fluidized bed or membrane reactors which incur high operating costs
- These systems have been able to achieve only 90% removal of phosphate

1.5 Hypothesis for the Present Research

There is a need to develop a struvite recovery process which eliminates the limitations of existing phosphorus recovery techniques discussed as follows.

- Struvite precipitation reaction is rapid therefore if it is possible to decouple the precipitation process from agglomeration/crystallization process reactor volumes can be considerably reduced
- The precipitation reaction can be accomplished in reactor designs similar to that currently employed by wastewater treatment plants thereby making it more operator friendly
- A salable product can be produced in a separate unit operation using the reduced volume of settled sludge rather than entire wastewater

1.6 Goals and Research Approach

The goal of this project is to develop and implement an efficient and cost effective process to recover N & P nutrients in wastewater as struvite. The nature of effluent from different wastewater unit operations is unique. The optimal conditions like pH and magnesium concentration for struvite precipitation should be determined for different streams (Uludag-Demirer et al., 2005). This approach is particularly important for struvite research because the complex chemical principles, which govern its precipitation, are readily altered by slight changes in the chemical composition. A novel approach of struvite precipitation in an sequential batch reactor (SBR) is developed and validated experimentally. A comprehensive model is utilized to

compute chemical quantities necessary for the reaction. It is also used to accurately predict the purity and amount of struvite sludge produced. Struvite produced in the process is utilized to develop different products with multiple nutrients. Struvite precipitation technique developed in the laboratory was validated in a pilot plant utilizing an SBR.

To summarize, the research approach included:

1. Development and validation of a mathematical model to calculate chemical requirements for struvite precipitation
2. Development and validation of an SBR mode of operation for struvite precipitation in a laboratory scale reactor
3. Development of product formulation techniques using settled struvite sludge for salable agglomerates
4. Pilot scale validation and implementation of the struvite precipitation and settling process

1.7 Outline of Dissertation

An outline of subsequent chapters in this thesis is given below.

1.7.1 Development and Experimental Validation of a Mathematical Model of Struvite Precipitation

This chapter describes the mathematical approach to modeling struvite precipitation. A review of existing equilibrium chemistry models is carried out. A detailed discussion of modeling approach and its validation along with simulation results is presented.

1.7.2 Sequential Batch Reactor for Recovery of Nitrogen and Phosphorus as Struvite from Sewage Sludge Centrate and Dairy Wastewater

This chapter describes results of sequential batch reactor experiments with synthetic wastewater, centrate and dairy manure. Experiments on struvite formation for chemical requirements with aeration of centrate are discussed. Effect of pH and concentration of struvite on settling of solids in the conical bottom reactor are provided in this chapter.

1.7.3 Development of Product Formulation Techniques Using Struvite Solids

Product formulation techniques using synthetic struvite as well as struvite from centrate are described in this chapter. It includes solids analysis using chemical methods, x-ray diffraction (XRD) and other physical parameters like yield strength, particle size distribution etc.

1.7.4 Concept to Commercialization (C2C)

Pilot plant testing details are provided for the sequential batch operation to recover phosphate, in the form of struvite, from centrate obtained from Buckman Wastewater Treatment Plant, City of Jacksonville, Florida. Study of the variations in concentration of soluble and dissolved species at various depths of pilot scale reactor as a function of settling time are discussed. An analysis of the plant design and operating procedures is provided to reduce costs and meet constraints, with an emphasis on improving efficiency and increasing profitability.

1.7.5 Conclusions and Recommendations

This chapter summarizes the outcomes of this research including results from laboratory, pilot scale and model simulations. It also lists recommendations for future research and process development for full scale operation.

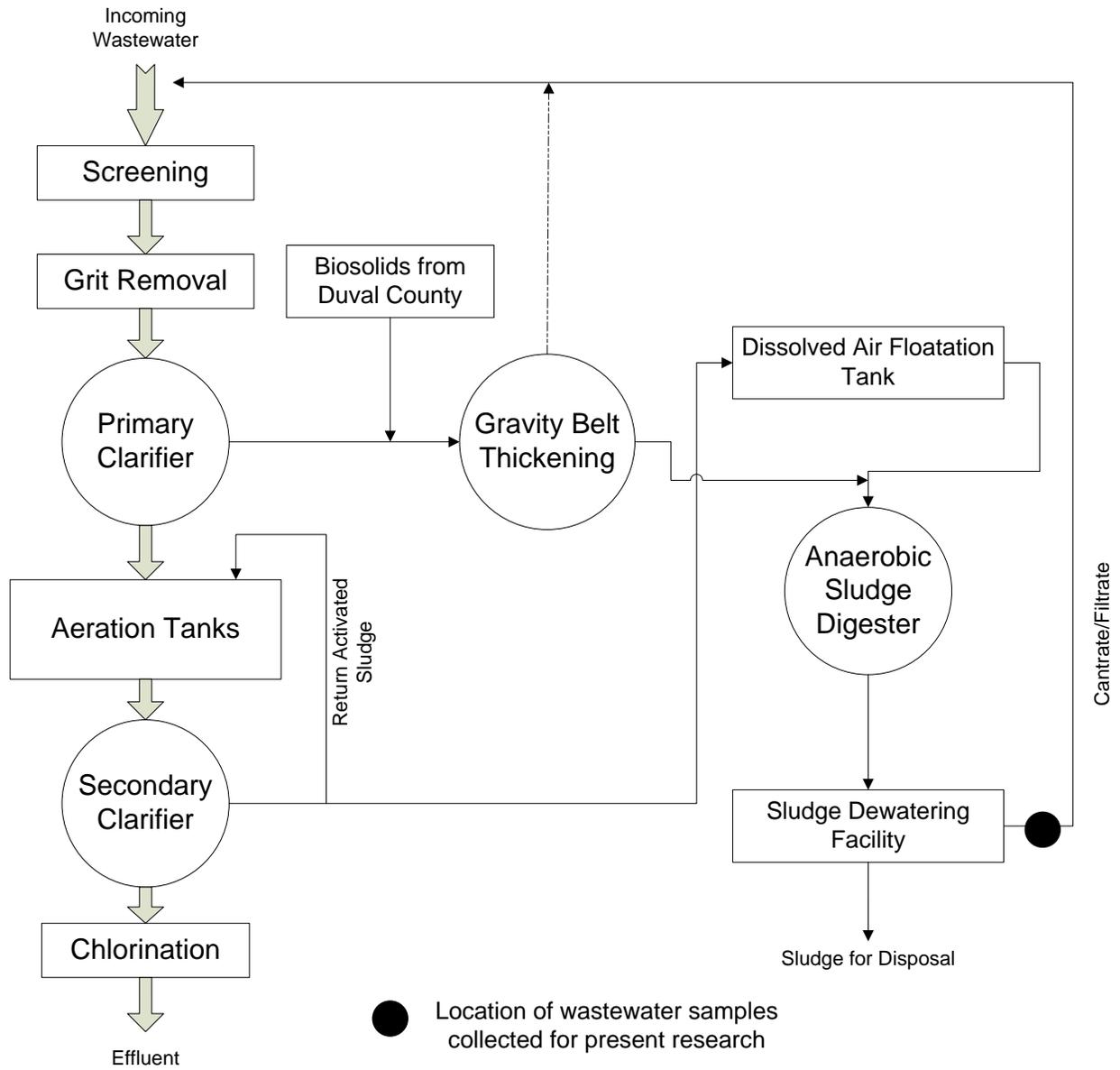


Figure 1-1. Secondary wastewater treatment plant at Jacksonville Electric Authority.

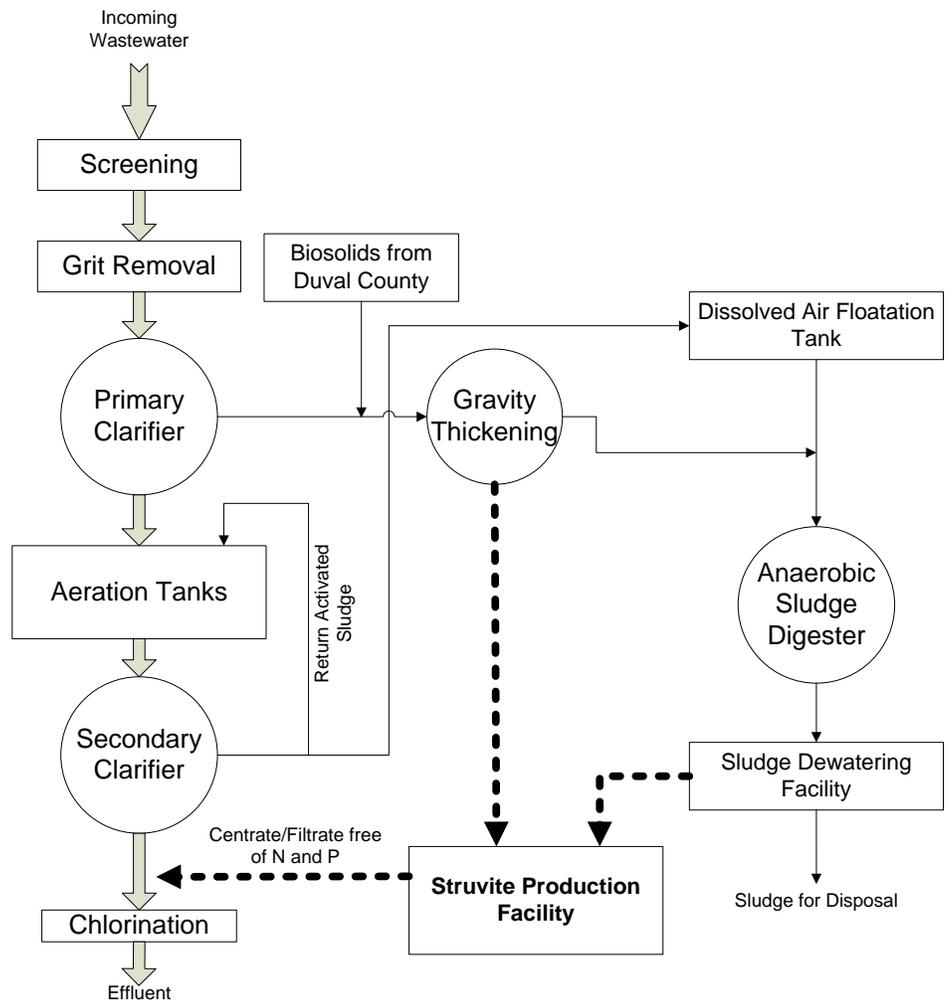


Figure 1-2. Proposed location for struvite production.

CHAPTER 2

DEVELOPMENT AND EXPERIMENTAL VALIDATION OF A MATHEMATICAL MODEL FOR STRUVITE PRECIPITATION

2.1 Struvite Modeling

Predicting struvite precipitation potential is important to designers and operators for design, development, and operation of reactors for struvite precipitation. For process control, it is essential to know the conditions under which struvite precipitation is likely to occur. Upon mixing salts of magnesium, ammonium, and phosphate, several ionic and dissolved species are formed in addition to precipitates, including struvite. Modeling approaches used in struvite formation studies incorporate solution chemistry and thermodynamics, growth kinetics and process description of the recovery system.

2.2 Review of Struvite Precipitation Models

2.2.1 Struvite Modeling Approaches

Various researchers have developed equilibrium chemistry models for struvite precipitation (Harada et al., 2006; Loewenthal et al., 1994; Ohlinger et al., 1998). These models are based on the physico-chemical equilibrium of the various ionic, dissolved, and solid species. A struvite precipitation model at least requires the incorporation of concentrations of ionic species NH_4^+ , PO_4^{3-} , and Mg^{2+} , dissolved species NH_3 and H_3PO_4 , and solid species MgNH_4PO_4 . However, a number of other ionic species (e.g. HPO_4^{2-} , $\text{H}_2\text{PO}_4^{2-}$, MgOH^+ , MgPO_4^- , $\text{MgH}_2\text{PO}_4^+$, dissolved species (e.g., H_3PO_4 , $\text{MgHPO}_4(\text{dissolved})$) and solid species (e.g., $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{MgHPO}_4(\text{solid})$) exist in equilibrium. The complexity of models depends on the number of soluble and solid species considered.

Loewenthal et al. (1994) predicted struvite precipitation potential in synthetically prepared solutions that mimicked anaerobic digester effluents. This was a simple equilibrium

model that considered struvite as the only solid species; the ionic species considered were Mg^{2+} , NH_4^+ , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , and the dissolved species were NH_3 and H_3PO_4 . In addition to the previous H_2CO_3 , CH_3COO^- , CH_3COOH , carbonate and bicarbonate were also considered. Ohlinger et al. (1998) also considered only struvite as the solid species in their model. But, in addition to species modeled by Loewenthal et al. (1994), Ohlinger et al. (1998) also included $\text{MgH}_2\text{PO}_4^+$ and MgPO_4^- , as these complexes exert a strong influence on equilibrium conditions. The model also included ionic strength effects. Wang et al. (2006) included the formation of $\text{Mg}(\text{OH})_2$ precipitate in addition to struvite, and they also considered MgHPO_4 as an additional dissolved species. Scott et al. (1991) modeled five solid species: struvite, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, and MgHPO_4 and all the dissolved and ionic species considered by Wang et al. (2006). Harada et al. (2006) considered eight solid species: calcium precipitates: $\text{Ca}_3(\text{PO}_4)_2$, CaHPO_4 , $\text{Ca}(\text{OH})_2$, CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$ and precipitates containing Mg, namely, struvite, $\text{Mg}(\text{OH})_2$ and MgCO_3 . Wrigley (1999) developed a computer model to describe struvite solubility chemistry which included the mass balance and electro-neutrality equations in the input components. The model was improved by incorporating dissolved magnesium hydrogen phosphate and an activity coefficient.

Several researchers have employed MINTEQA2 and/or Visual Minteq to study struvite equilibrium chemistry. The MINTEQA2 is an aquatic chemistry equilibrium model. This program is the Windows version of MINTEQA2 originally developed by the U.S. Environmental Protection Agency. This model accepts inputs of magnesium, ammonium, and phosphate concentrations, pH, temperature, and ionic strength of a solution, and it computes the degree of saturation with respect to struvite. Visual Minteq is a chemical equilibrium computer program

with a thermodynamic database that allows for the calculation of speciation, solubility, and equilibrium of solid and dissolved phases of minerals in an aqueous solution.

Modeling work by Battistoni et al. (2002) was able to link pH with saturation on the precipitation with seed materials. This additional proposed model allows predictions on the precipitation efficiency of an FBR with a given concentration of constituents at a set pH, for example, at pH, 8.5 a precipitation efficiency of 70% can be achieved with a contact time of 0.2h. Though this is not the full story, the conversion of phosphorus to struvite is higher than the nucleation efficiency on the seed material, which implies the production of fines. This researcher concluded that to avoid the production of fines, a higher contact time within the reactor is needed.

2.2.2 Solution Approaches to Models

As the number of the considered solid and soluble species increases, the complexity of the model also increases, so analytical solutions are no longer possible, and a numerical solution is therefore needed. Lowenthal et al. (1994) and Ohlinger et al. (1998) employed an iterative technique to converge one concentration value to an experimentally measured value, while the other concentrations were calculated from equilibrium expressions. Scott et al. (1991) did not explicitly determine the concentrations of dissolved, ionic, and solid species, but they compiled operating curves that related pH with total concentrations of magnesium, nitrogen, and phosphorus in liquid under struvite recovery conditions. Only the mole fractions of the solids were computed. Harada et al. (2006) simplified the solution procedure by limiting the formation of solid mixtures to 14 patterns that were generated *a priori* by including or excluding various solid species. The concentrations of dissolved and ionic species were calculated for each pattern and the concentrations that gave reasonable values were chosen.

Scott and Venkitachalam (1996) used the symbolic codes to calculate the amount of struvite expected to precipitate in an inorganic system. They used the Maple program with the primary calculating variable of NH_4 . They used a quadratic expression with five constants, which produced the symbolic codes in the FORTRAN program. The calculations in this model proceeded, which included a method of convergence. They used checks to assure that the solution obeyed the mass and electroneutrality criteria. They also stated it is possible that the concentrations became too high for validity, or the iterations with activity coefficients calculated unreasonable values. They accepted the limitations of the codes and that the algorithm required that a solid phase be present; the lack of a solution implied no solid exists. They picked pH and pMg values that were close to the nearest values and also a weighted estimate (interpolated). This gave an estimate if the answer was within the selected set, and it was only useful during a single cycle. Also, they used the value from the quadratic fit (extrapolated); this was only effective when close to the correct value. The last was then an average of the last two estimates. In different nutrient or excess non-reactive ion concentrations, different estimates were found to be useful. Fast convergence occurred when close to a solution. They illustrated the convergence for the case when approximately equal molar quantities of P, Mg, and N were added at 0.01 molar (P = 310 mg/litre, M = 243 mg/litre, and N = 140 mg/litre), with no non-reactive ions.

Wrigley (1999) specified two input variables in the Maple file, which had the total molar concentration of magnesium in the liquid phase and pH . Maple gave an output, which was a series of FORTRAN codes that were algebraic equations with variables (ionic species with N, P, and Mg) and equilibrium constants. From the output data file, groups of variables were selected for graphical presentation. The amount of total solids or struvite precipitated was not reported here. Plots of variation of dissolved concentrations of Mg, P, and N with pH were presented.

The more complex models previously described are not easily amenable for developing dynamic models to predict struvite precipitation in dedicated reactors for the following reasons:

- Present models cannot be used to determine chemical requirement (magnesium and caustic) to operate a dedicated struvite precipitation reactor.
- Models cannot be used directly in the process control of a struvite reactor without modifications.
- Struvite is not included in the database of commercial software such as MINTEQA2 and Visual-Minteq.
- Total number of solids considered in the models is not complete. Some of the solids (calcium species), which are eliminated in the models previously discussed, may be formed in the system if the residence times are of the order of four to five days.
- Model reduction is done to solve it in the beginning by eliminating solid species, which may be formed under certain conditions.

In this chapter, a comprehensive model is developed and used to determine the concentrations of all species (dissolved, ionic, and solid) to enable investigation of the purity and yield of struvite for various operating conditions (pH and ratios of initial NH_4^+ , Mg^{2+} , and PO_4^{3-}). It uses mass and charge balances in addition to the physico-chemical equilibrium equations. The model described here considers 15 different solid species, which is the maximum number reported in the literature. The model was validated by comparing it to experimental data from the literature and data obtained from these experiments.

2.3 Model Formulation

The model describes the evolution of an open system in the presence of ionic species, such as ammonium (ammonium chloride), magnesium (magnesium chloride), and phosphate (potassium phosphate). A complete list of solids included in the model is presented in Table 2-1 and discussed as follows.

2.3.1 Magnesium Phosphate Species

Five possible magnesium phosphate species can crystallize in the presence of Mg^{2+} , NH_4^+ , PO_4^{3-} species: 1) magnesium ammonium phosphate or struvite ($MgNH_4PO_4 \cdot 6H_2O$); 2) magnesium hydrogen phosphate or newberyite, MHP ($MgHPO_4$); 3) $Mg_3(PO_4)_2 \cdot 22H_2O$, MP22; 4) bobierite, $Mg_3(PO_4)_2 \cdot 8H_2O$, MP8, and 5) magnesium hydroxide or Brucite ($Mg(OH)_2$). Struvite precipitates in the presence of Mg^{2+} , NH_4^+ , and PO_4^{3-} when the pH range is between 7 and 11 and at Mg/Ca molar ratios greater than 0.6. Newberyite precipitates at high concentrations of Mg^{2+} and P, but it precipitates at lower pH (< 6.0). Previous research demonstrated that $MgCl_2 \cdot 6H_2O$ could be added to the solution to force the precipitation of struvite (Munch and Barr, 2001).

2.3.2 Calcium Phosphate Species

Five calcium phosphate crystalline species can precipitate from solutions containing Ca and P: 1) hydroxyapatite [HAP, $Ca_5(PO_4)_3OH$], 2) tricalcium phosphate (whitlockite) [TCP, $Ca_3(PO_4)_2$], 3) octacalcium phosphate [OCP, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$], 4) monenite (DCP, $CaHPO_4$), and 5) dicalcium phosphate dihydrate (brushite) (DCPD, $CaHPO_4 \cdot 2H_2O$). Although formation of HAP and TCP are thermodynamically favored, the kinetics of this process is extremely slow (Ferguson and McCarty, 1971). It is also reported that the magnesium ion kinetically hinders the nucleation and subsequent growth of HAP and OCP (Salimi et al., 1985; Abbona, 1990;). Also OCP is formed by the hydrolysis of DCPD in solutions of pH 5-6. It is found that DCP is a thermodynamically stable species. Salimi et al. (1984) reported that the presence of Mg^{2+} has no detectable effect on the rate of DCPD crystallization. None of these species was removed from the model because the formation of these may be favored at high calcium concentrations (> 200 ppm) and higher residence times in the systems, such as pipes or recirculation lines.

2.3.4 Other Salts

Two forms of magnesium carbonates may also precipitate, magnesite (MgCO_3) and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). Both species were kept in the model. Two mixed carbonates of Ca^{2+} and Mg^{2+} were included in the model, dolomite [$\text{CaMg}(\text{CO}_3)_2$] and huntite [$\text{CaMg}_3(\text{CO}_3)_4$]. Calcium carbonate CaCO_3 was also added to the model.

The model was thus formulated based on the following assumptions:

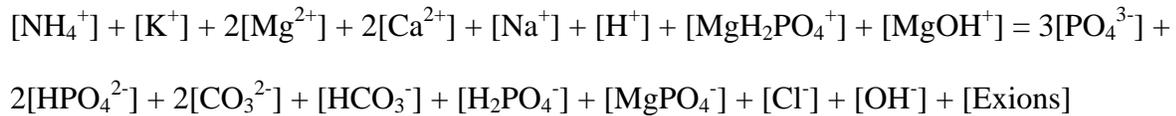
- a) Dissolved and ionic species present in the system are NH_3 , NH_4^+ , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4 , MgOH^+ , $\text{MgH}_2\text{PO}_4^+$, MgPO_4^- , MgHPO_4 (dissolved), CO_3^{2-} , HCO_3^{2-} , H_2CO_3 , Ca^{2+} , Na^+ , K^+ , Mg^{2+} , H^+ , Cl^- and OH^- .
- b) Fifteen different precipitates are produced, which are listed in Table 2-1, and are previously discussed.
- c) The pH was kept constant by addition of NaOH or HCl. This was simulated by adjusting the variable “exions,” which were set equal to $\Sigma[\text{cations modeled}] - \Sigma[\text{anions modeled}]$
- d) Reactions are at equilibrium.
- e) Reactions proceed in an open system or a batch reactor.
- f) Reactions occur at room temperature (25°C).
- g) Activity coefficients were assumed to be unity.
- h) Effect of ionic strength on activity was neglected.

2.3.5 Equations

The model includes overall mass balance for magnesium, nitrogen and phosphorus, electro-neutrality, and physico-chemical and solubility equilibrium equations to describe the system. Values of equilibrium constants and solubility products at 25°C are shown in Table 2-2 (Scott, 2001; Harada et al., 2006; Moon et al., 2007). Of particular importance is the solubility product for struvite. Various values have been reported ranging between 12.6 and 13.26 (Ohlinger et al., 1998). In the present model, a more commonly used value of 12.7 was used, unless stated otherwise.

Polymath Educational Version 6.1 was used to solve the model. Initial conditions, which include pH, total concentrations of nitrogen, magnesium, phosphorus, inorganic carbon, and calcium, were input along with all equilibrium constants. Initial guesses for Mg^{2+} , NH_4^+ , PO_4^{3-} , CO_3^{2-} and Ca^{2+} were provided. The Polymath program solved the expressions and gave concentrations of dissolved and ionic species and concentrations of solid components. These expressions were included as mass balance equations for total magnesium (Mg_t), calcium (Ca_t), ammonia-N (N_t), inorganic carbon (TIC), phosphorus (P_t), as shown in Appendix A. The expressions were written as functions of corresponding ionic species concentrations in molar quantities. Expressions for calculating residual concentration in the liquid form were expressed for nitrogen, phosphorus, and magnesium to get an idea of recovery of these species after struvite precipitation. Using the charge balance equation, the appropriate exion concentration was determined. This gave the acid or base requirement for the given pH. The concept of “exion” species is discussed in detail in a later section.

The following charge balance equation applies to the system:



$$Exions = \Sigma[\text{other cations}] - \Sigma[\text{other anions}].$$

2.4 Results and Discussion

The polymath program solves systems of nonlinear algebraic equations, which can be both nonlinear simultaneous (implicit) and auxiliary (explicit) equations. Only real roots (non-complex) are found. All equations are checked for correct syntax and other errors upon entry. An implicit nonlinear equation is entered in the form of a function $[f(x)]$. An explicit equation is

written in the form: $x =$ an expression where the expression may contain constants, implicit variables, and explicit variables.

The solution algorithms require specification of initial estimates for all the variables in the implicit nonlinear equations. Closer initial estimates have a better chance of converging to the desired solution. Multiple solutions may occur to a particular set of equations, which can be identified by starting at different sets of initial guesses. Solutions to the model equations in the present case are obtained by selecting “constrained” as the solution method.

Four algorithms are available in the Polymath program for solutions of nonlinear equations, and all of them are based on the Newton-Raphson (NR) method. This method uses a truncated Taylor series estimate of the function values to obtain better estimates of the unknowns. In each iteration, the function values and the matrix of partial derivatives are calculated. Numerical perturbation is used for calculating the matrix of partial derivatives. The iterative solution stops if either the sum of the magnitudes of the functions is less than 10^{-7} , or the sum of the absolute values of the corrections to the unknowns is less than 10^{-7} . The maximum number of iterations used in this all simulation was 300. For a system of equations containing constrained variables (some or all the variables must be positive throughout the solution process or only at the solution), an algorithm, which combines the step length restricted NR method with a continuation type method, is used. In the step length restricted NR method, the progress in the NR direction is restricted so that none of the constrained variables becomes zero or negative. In the continuation method, the original problem is converted into a sequence of easier to solve problems where the solution is closer to the initial estimate than in the original problem.

2.4.1 Model Validation

The model was validated by comparing its predictions to 12 struvite precipitation studies collected from literature that were carried out using synthetic and real wastewater at different pH

values and initial concentrations of magnesium, phosphate, and ammonium. The initial concentrations of these ions were equal to the total concentrations of magnesium (Mg_T), nitrogen (N_T), and phosphorus (P_T) species in the system. Data from model simulations are presented in Table 2-4. Solids containing magnesium are listed in Table 2-4, but the model considers a total of 15 solids, as mentioned earlier.

The model was found to satisfactorily predict struvite formation for all literature data. Five of these datasets marked by “*” in Table 2-4 need additional explanation. Closer inspection of experimental methods, as described in these references, revealed that the struvite concentration reported was actually total solids concentration. For example, Loewenthal et al. (1994) estimated struvite concentration from differences in average molar concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} between initial and final values in solution of these species. Since Mg^{2+} and PO_4^{3-} can form insoluble compounds other than struvite, for example, MP8, MP22, MHP, and $Mg(OH)_2$, differences in initial and final concentrations do not truly represent concentrations of struvite but represent concentration of solids. Using the experimental conditions of Loewenthal et al. (1994), the model predicted total solids concentration of 733 mg/L of which struvite was the only mg/L with MHP being the other dominant solid. Experimentally reported struvite was 601 mg/L, which in reality could be the total solids concentration, and was in agreement to the total solids predicted by the model. This researcher is reporting no data on calcium concentration.

Harada et al. (2006) reported that most phosphate in their experiments was precipitated in the form of struvite. Initial total calcium concentration reported was 1.21 mmol/L, which was input for validation. Experimental data indicated that 12.3 mM of PO_4^{3-} was precipitated as struvite (1685 mg/L). This value, however, was approximately equal to the total solids predicted

(1706.2 mg/L) by the model. Concentrations of NH_4^+ and Mg^{2+} used here were higher than concentration of phosphate. The model showed that other significant components, which could make up the solid phase, included MP8 (88 mg/L), MHP (222.9 mg/L), CaHPO_4 (15.6 mg/L), and $\text{CaHPO}_4 \cdot 5\text{H}_2\text{O}$ (7 mg/L). Hence, under phosphate limiting conditions, struvite is not the only component in the precipitate.

Tünay et al. (1997) used a 1:1:1 stoichiometric proportion of ammonia: magnesium phosphate for experiments. At the conclusion of the experiments, the solution was filtered and concentrations of total ammonia and phosphate were measured in the filtrate. The difference in the initial and final concentrations of ammonia was assumed to have been precipitated as struvite. In an experiment with initial pH of 9 and magnesium, total ammonia and phosphate concentrations of 14.26 mM each, 1714 mg/L struvite was precipitated. However, this concentration corresponded to the concentration of total solids predicted by the model. Struvite produced was only 1017.7 mg/L, about 59.37% of the total solids produced. Formation of two calcium-containing solids, $\text{Ca}_3(\text{PO}_4)_2$ (495.8 mg/L) and CaHPO_4 (384.4 mg/L), was observed. A 1:1:1 molar ratio of ammonia, phosphate, and magnesium does not yield a predominantly struvite precipitate. Similar observations are applicable to data from Stratful et al. (2001).

The error in solids concentration, which was predicted by the model and that measured in the experiments, was mostly less than 10%. But a comparison of model predictions to Tünay et al. (1997) and Lowenthal et al. (1994) gave the largest error, which was more than 10%. Given the complexity of real wastewaters, this researcher observed that the error in model prediction for the case of a mixture of landfill leachate and domestic wastewater was only 5%.

Depending on the experimental conditions, such as pH and initial ratios of magnesium, ammonium, and phosphate, the solid phase can consist of several components, not just struvite.

Therefore, equating total solids concentration to struvite can lead to erroneous results. The usual approach to accurately determining the struvite component in the solid phase involves redissolving the solid fraction after filtration by digesting in acid and measuring the ammonia concentration (Çelen et al., 2007; Munch and Barr 2001; Wilsenach et al., 2007; Yoshino et al., 2003). In this approach, it is assumed that ammonia is precipitated only as struvite, and the molar concentration of ammonia in solids is equal to the molar concentration of struvite. The model agreed well with experimental struvite data presented using this approach. The error in model predictions ranged from 1.6% to 9%. The error in the prediction of struvite was much less than the error in the prediction of total solids.

Experiments using defined solutions were also carried out in the research laboratory to validate the model. A solution of 10mM of PO_4^{3-} was prepared by dissolving 1320 mg of ammonium phosphate $(\text{NH}_4)_2\text{PO}_4$ in 1 liter of distilled water. The total ammonia concentration was made up to 50mM by adding 1605 mg of ammonium chloride. A 200 mM magnesium chloride $(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$ stock solution was used as a magnesium source. Precipitation experiments were carried out in 500 ml Erlenmeyer flask in which 475 ml of $(\text{NH}_4)_2\text{PO}_4$ and NH_4Cl solution were taken. To this solution 25 ml of magnesium chloride were added, giving an initial $\text{NH}_4^+:\text{Mg}^{2+}:\text{PO}_4^{3-}$ ratio of 48.6:5: 9.5 or $\sim 5:0.5:1$. A magnetic stirrer was used for mixing. The pH of the solution was continuously monitored with a pH probe. The pH of the solution was adjusted to 9.6 by adding 10 N NaOH. Precipitation was found to occur instantaneously after the addition of magnesium chloride solution, which increased with the addition of NaOH. After reaching a pH of 9.6, the solution was stirred for another 5 min. Then the entire 500 ml solution was filtered using 0.45 μm Whatman filter paper to recover the precipitate. The precipitate was dried overnight in an oven at 104°C and weighed. The

experiment was repeated three times. The average concentration of the precipitate measured in the experiments was 653 mg/L +/- 55 mg/L. The model predicted total solids of 682 mg/l. The error in the model prediction was about 4%, which was consistent with errors in the model predictions for data in Table 2-4. The model was then applied to study the effect of various experimental conditions on struvite concentration and purity.

2.4.2 Effect of pH

The pH is an important factor, which mainly determines the form in which ionic species exist in solutions. The model was used to investigate the effect of pH on the yield and purity of struvite (or struvite fraction of the precipitate). Chemically, since struvite contains 1 mole each of ammonium, magnesium, and phosphate, most of the struvite experiments reported in the literature have been carried out using approximately 1:1:1 initial molar ratio of magnesium, phosphate, and ammonia (Altinbas et al., 2002; Jaffer et al., 2002; Miles and Ellis, 2001; Stratful et al., 2001; Tünay et al., 1997; Uludag-Demirer et al., 2005; Yoshino et al., 2003). At the equimolar ratio, two simulations were performed first at 10 mM and a second one at 100 mM initial concentration of ammonium, magnesium, or phosphate, keeping all the other species concentrations zero. The maximum molar struvite yield in these experiments was assumed to be equal to the initial molar ammonium (or phosphate or magnesium) concentration used in the experiment. For the 10 mM solution, the maximum yield of struvite will be 10 millimole (i.e., 1370 mg/L).

The total precipitate produced increased from 613 mg/L to 1247 mg/L, as the pH increased from 5 to 10 and dropped to 1037 mg/L at pH 11. The mass fraction of struvite in this precipitate was only 0.6% at pH of 5, increasing to 89% at pH of 9.2, and then decreased thereafter. The concentration of struvite was the highest at pH 9.0 and was equal to 1122.3 mg/L. At pH of 9.2, the concentration of struvite was 1231 mg/L. The yield of struvite was

0.25% at pH 5, 79% at pH 9.0, and 57% at pH 11. At pH 9 and below, the primary precipitate produced was MHP, decreasing from 99.4% of solids at pH 5 to 21% of the solids at pH 9. The MHP decreased to 5.5% of the solids at pH 10. Above pH of 9, the predominant precipitate was MP8 and $\text{Mg}(\text{OH})_2$. The simulations were repeated at a higher initial concentration of 100 mM. The struvite fraction trend was similar. The optimum pH for maximum struvite fraction was 9.2, and its concentration at this pH was 12,670 mg/L. The total precipitate concentration increased with increasing pH up to pH 10 and then decreased. The total precipitate was 13,410 mg/L at pH 10.

The effect of pH on struvite purity follows a different trend when the molar ratios of ammonium, magnesium, and phosphate are set to values that yield struvite as the dominant precipitate. On such a condition is a molar ratio of 10:1.7:3.4 mM of ammonium, magnesium, and phosphate. For this mixture, the precipitate is made up of struvite and MHP, with small amounts of $\text{Mg}(\text{OH})_2$ appearing at pH above 9. The fraction of $\text{Mg}(\text{OH})_2$ is only 0.45%, even at pH 10. At pH 7, struvite is about 71% of the total precipitate, with MHP being the rest. At pH of 8, the struvite fraction is 82%, increases to 98.3% at pH 9.6, and then drops to 97.8% at pH 10. The total solids increased with increasing pH, peaking at pH of 9.8 and then dropping slightly. The effect of pH on the struvite fraction is plotted in Figure 2-1.

It has been generally reported that the optimum pH for struvite precipitation is between 8.1 and 9.6, without reference to the conditions of precipitation (Altinbas et al., 2002; Battistoni et al., 1998; Jaffer et al., 2002; Munch and Barr, 2001; Wang et al., 2006). The simulations here showed that the pH that maximizes the struvite fraction in the precipitate is dependent on the initial molar ratio of ammonia, magnesium, and phosphate. At the equimolar ratio, the optimum

pH is 9.2. However, the total precipitate concentration was highest at pH 10. For conditions at which ammonia is in excess, the optimum pH is 9.6 and the precipitate is predominantly struvite.

2.4.3 Effect of Initial Magnesium, Phosphate, and Ammonium Ratio

The effect of the initial ratio of ammonium, magnesium, and phosphate on struvite purity was then simulated. Figure 2-2 shows the effect of changing the magnesium-to-phosphate molar ratio at two different ammonia to phosphate molar ratios. The simulations were performed at a base concentration of 10 mM, that is, an equimolar mixture contained 10 mM each of ammonia, magnesium, and phosphate. A pH value of 8.7 was used for the simulations as it is close to typical pH values of wastewaters, which range from 7.5 to 8.5. Moreover, since pH 8.7 was below the optimum value determined in prior simulations, studies at this pH provided insight into manipulating the molar ratios to maximize struvite purity.

This researcher found that for a given ammonium to phosphate ratio, increasing magnesium decreases the fraction of struvite in the precipitate. The mass concentration of the total precipitate increases, reflecting the high magnesium dosage. For an equimolar concentration of ammonium and phosphate, extremely limiting concentrations of magnesium produced precipitate with about 89% struvite. This purity decreases rapidly as magnesium dosage is increased. The struvite purity is the lowest at 27% when magnesium is of the same concentration (i.e., 1:1:1 ratio). When magnesium is increased further, the struvite purity increases to 50% when the magnesium-to-phosphate ratio is 1.5, and then decreases slowly thereafter. At the pH value used, the other dominant compound in the precipitate was MHP when the magnesium-to phosphate-ratio is less than 1.0, decreasing from 70% to 13% as struvite fraction increases. At the magnesium to phosphate ratios greater than 1.0, MHP decreased from 27% to 16% and MP8 increased from 19% to 33%.

At conditions where ammonia is in excess compared to phosphate, for example, the ammonia-to-phosphate molar ratio of 2.94, the struvite purity decreased very slowly from 87% at magnesium limiting conditions to 75% when magnesium and ammonia were at equal concentration (i.e., magnesium to phosphate of 3). This researcher noted a slight dip occurred in the trend line at equimolar concentrations of ammonia, magnesium, and phosphate. The MHP was the other major component in the precipitate, increasing from 13% to 16% as the magnesium concentration increased. At high magnesium concentrations, MP_8 and $\text{Mg}(\text{OH})_2$ were also precipitated.

Struvite fraction in the precipitate is enhanced when magnesium is limiting, as compared to ammonia-N concentration. Struvite precipitation is enhanced by an increase in magnesium dosage, but it should not be in excess, as compared to the ammonia-N concentration. When the magnesium concentration was increased (still keeping ammonia-N concentration in excess), then the struvite precipitation reaction was favored, and it was driven toward right for solids formation. When the concentration of magnesium increases beyond a certain ratio of Mg:N, the formation of precipitates other than struvite is induced, which decreases struvite fraction in the solids. This ratio of Mg:N needs to be determined for a specific wastewater system by running simulations. Even at non-optimal pH values, struvite fraction can be increased by dosing magnesium at low concentrations. If ammonia is in excess, when compared to phosphate, as is the usual case, adding magnesium at a concentration equal to that of phosphate may produce a precipitate with at least 82% purity. This will ensure removal of most phosphate. Any remaining ammonia can be removed by further dosing with phosphate and magnesium.

2.4.4 Determining “Exion” Concentration for Real Wastewater

Typically, to determine wastewater’s acidity or alkalinity, a titration curve is generated, which is a necessary step in designing a pH-control system. The titration curve was used in the present study to determine exion concentration used in the model. Exion concentration is a measure of difference between cations and anions, which were not accounted for in the model simulations. Exion concentration is a necessary parameter for determining the amount of acid/base required to achieve a specific pH. An average value of exion concentration was determined using the model from the known amount of acid/base required for pH adjustment. The average exion concentration was then used to calculate the amount of acid/base required. In the present studies, the amount of base required was determined for increasing the initial pH of wastewater to a specific pH (8.7 in most of the cases) for struvite formation. This quantity of base was input to the model as a sodium concentration when sodium hydroxide is used for pH adjustment. The initial concentrations of total Mg, N, Ca, P, K and total inorganic carbon (TIC) were also input to the model. The value of TIC was taken from the literature (Lowenthal et al., 1994). The model solution computed equilibrium concentrations of ionic and solids species. It also determined the value of exion concentration. The exion concentration input to the model depended on the pH at which the struvite precipitation experiments were carried out. An average value of exion concentration was determined by performing simulations for different ranges of pH. Using the average value of exion, simulations were performed for determining the acid/base requirement; a titration curve was generated, as shown in Figure 2-3.

Experimentally, the titration curve was obtained by adding small amounts of 0.1M NaOH or 0.1M HCl to 50 ml of wastewater sample, and measuring the pH after each addition. The titration curve is presented and discussed here for anaerobically treated wastewater from dairy

which had initial pH of 7.25. A similar approach could be taken for validating exion determination for other wastewater. The titration curve had a typical S-shape, and it can be transformed into a buffer capacity profile with an appropriate mathematical algorithm. The S-shape curve suggested that the pH does not change at a constant rate with the addition of a strong base. The shape provided important information about the wastewater's response to the chemical reagent. The equivalent point was found to be at pH 6.5, which defined the level at which pH changed most dramatically per unit of acid added. This is the point where the curve's slope is the steepest.

This researcher assumed that in the titration curve measurements, each pH measurement was a result of a chemical equilibrium. The model determined an average concentration of exions as 0.002566 M with a standard deviation of 0.00059M. The values of exion concentration in this case ranged between 0.001776M and 0.002937M. A titration curve was generated using the model and was found to be close to the experimental titration curve, as shown in Figure 2-3. It is observed that for pH values between 2 and 6, the error in the model predictions of the amount of caustic needed for pH adjustment ranged from 2% to 11.3%. The model predicted more caustic requirements for pH values higher than 6, the error in model predictions being 4% to 12.3%.

2.4.6 Effect of pH on Struvite Purity and Phosphorus Removal in Real Wastewater

The effect of pH on struvite purity and phosphorus removal was simulated for real wastewater (centrate and dairy flushwater). The input concentration values to the model are shown in Table 2-3. Alkalinity values reported in the literature were used (Loewenthal et al., 1994; Battistoni et al., 2002). Alkalinity was reported in mg CaCO₃/L. Alkalinity was converted in the model to total inorganic carbon (TIC) by calculating corresponding carbonate and bicarbonate concentrations at a given pH. Simulations were carried out at two different

concentration ratios of Mg:P: 1:1 and 0.5:1. Ammonia-N was in excess in all the simulations. Total concentrations of nitrogen, phosphorus, calcium, and potassium were determined in the laboratory. Results of the simulations are shown in Figures 2-4, 2-5, 2-6, and 2-7.

When the Mg:P ratio of 1:1 was used for struvite formation in the centrate, 87% removal of phosphorus was observed at pH 8.5, as shown in Figure 2-3. At this ratio, total solids increased from 339.66 mg/L to 605.35 mg/L as pH increased from 5 to 8.4. The optimum pH of 8.4 was observed. Struvite purity at this pH was found to be 72.8% although the purity increases to 72.91 at pH 9. In acidic pH range, concentrations of CaHPO_4 and MHP were dominant. The concentration of CaHPO_4 was found to be maximum (70.14 mg/L) at pH 5 and decreases to 10.16 at pH 8.4. The concentration of CaMgCO_3 was found to increase from 65.56 mg/L at pH 5 to 145.36 mg/L at pH 8.4 and increase thereafter to 160 mg/L at pH 11. These two solid species were not included in the database of models by Çelen et al. (2007) and Harada et al. (2006) due to their slow rate of formation. By ignoring these solids in the present model, struvite purity could increase to 95%. This will be verified experimentally in Chapter 3. Simulations were also carried out using the Mg:P ratio of 1:1 on dairy flushwater, as shown in Figure 2-5. Initial concentrations of various ionic species were as shown in Table 2-3. Initial calcium concentration was found to be higher than that for centrate. Complete removal of phosphorus was observed in acidic pH range. Phosphorus was recovered in the form of CaHPO_4 . Struvite content in the solids was found to be negligible. A maximum struvite purity of 5.45% was observed at pH of 9.2. Phosphorus removal decreased with pH increase. Phosphorus removal decreased from 100% to 88.5% as pH increased from 5 to 9.2. The concentration of CaMgCO_3 was found to be maximum at pH 5 and decreased thereafter for basic pH. The CaMgCO_3 was the dominant solid species for all pH values.

Both types of wastewater streams were subject to simulations with the Mg:P ratio of 0.5:1 and compared as follows. This researcher observed that phosphorus removal from both types of wastewater was higher for 1:1 ratio of Mg:P, as compared to the Mg:P ratio of 0.5:1. Struvite purity was also found higher in the case of 1:1 ratio. Struvite purity was found highest at pH 8 for 0.5:1 ratio for centrate, as shown in Figure 2-4. In this case, total solids decreased as the Mg:P ratio was decreased to 0.5:1. At the Mg:P ratio of 0.5:1, prominent solid species were CaMgCO_3 and CaHPO_4 . Changes in these solids were similar, as explained for the case of the Mg:P ratio 1:1. Simulations with the Mg:P ratio of 0.5:1 showed similar changes in concentrations of CaMgCO_3 and CaHPO_4 . Struvite formation and purity were negligible for dairy flushwater, as well at the ratio of 0.5:1, as shown in Figure 2-6. It was therefore clear that with excess ammonia-N concentrations and an Mg:P ratio of 0.5:1, this was not suitable for struvite formation in both types of wastewater because precipitation resulted in mainly calcium phosphate species.

2.5 Findings

- A model was developed for predicting precipitation in closed systems containing solutions of ammonium, magnesium, and phosphate. The model incorporates 15 different precipitates and explicitly solves for precipitate, residual ion, and dissolved species concentrations using mass balance equations for magnesium, phosphorus, and nitrogen, along with chemical equilibrium and charge balance equations.
- Using the Polymath program and a solution procedure that involves converging the residual phosphate concentration to within tolerance limits, the concentration of the different precipitates, residual ion, and dissolved species concentrations was determined.
- The model was validated against data collected from literature for synthetic and real wastewaters. The model was able to predict struvite to within 1.6% to 9% and total precipitate prediction errors ranged from 1% to 24.5%.
- It found that for solutions containing Mg, NH_3 , and PO_4 , the optimal pH for struvite concentration depends on the initial ratio of ammonia, magnesium, and phosphate. A pH of 9.0 optimizes struvite concentration when the ratio is 1:1:1 and a higher pH of 9.8 when magnesium and phosphate are limiting.

- The equimolar stoichiometric ratio of magnesium, ammonium, and phosphate (i.e, the ratio of their occurrence in struvite) was not ideal for struvite precipitation. To obtain pure struvite, it was necessary to have excess ammonia in the solution, with magnesium being the limiting nutrient.
- A titration curve was generated by using the exions concentration and was validated using an experimental curve. The model determined an exion concentration of 0.002566 M in anaerobically treated wastewater from dairy operations. This species concentration should be considered while calculating the amount of caustic needed for pH adjustment.
- The model accurately predicted the amount of base needed for pH adjustment with an error less than 12.3%, as compared to the experimental quantities.
- A presence of calcium and carbonate species was found to decrease struvite purity.
- In the case of centrate, excess ammonia concentration and an Mg:P ratio of 1:1 were predicted to be suitable for struvite formation, considering the purity of struvite of 95% at this ratio.
- In the case of centrate and dairy flushwater, struvite precipitation was not suitable for the Mg:P ratio of 0.5:1 with excess ammonia because phosphate was mainly removed as calcium phosphate and calcium magnesium carbonate.

Table 2-1. List of solids included in the comprehensive model

Chemical Species	Commercial Name	Chemical Name	Chemical Formula
	1 Struvite	Magnesium Ammonium Phosphate	$MgNH_4PO_4 \cdot 6H_2O$
	2 Newberyte	Magnesium Hydrogen Phosphate	$MgHPO_4$
	3 Bobierite		$Mg_3(PO_4)_2 \cdot 8H_2O$
	4		$Mg_3(PO_4)_2 \cdot 22H_2O$
	5 Brucite	Magnesium Hydroxide	$Mg(OH)_2$
Calcium phosphate	6 Hydroxyapatite (HAP)		$Ca_5(PO_4)_3OH$
	7 whitlockite (TCP)	Tricalcium Phosphate	$Ca_3(PO_4)_2$
	8	Octacalcium Phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$
	9 Monenite (DCP)		$CaHPO_4$
	10 Brushite	Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \cdot 5H_2O$
Carbonate	11	Calcium Carbonate	$CaCO_3$
	12	Magnesium Carbonate	$MgCO_3$
	13 Nesquehonite		$MgCO_3 \cdot 3H_2O$
	14 Dolomite		$CaMg(CO_3)_2$
	15 Huntite		$CaMg_3(CO_3)_4$

Table 2-2. Equilibrium expressions with equilibrium and solubility constants

Equilibrium equation	pK
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	9.0
$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+$	12.3
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+$	7.2
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	2.14
$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$	6.3
$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	10.2
$\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+$	14.0
$\text{MgOH}^+ \leftrightarrow \text{Mg}^{2+} + \text{OH}^-$	2.56
$\text{MgPO}_4^- \leftrightarrow \text{Mg}^{2+} + \text{PO}_4^{3-}$	4.8
$\text{MgHPO}_4 \leftrightarrow \text{Mg}^{2+} + \text{HPO}_4^{2-}$	5.7
$\text{MgH}_2\text{PO}_4^+ \leftrightarrow \text{Mg}^{2+} + \text{H}_2\text{PO}_4^-$	0.45
$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \downarrow \leftrightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	23.98
$\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O} \downarrow \leftrightarrow 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 22\text{H}_2\text{O}$	22.89
$\text{MgHPO}_4 \downarrow \leftrightarrow \text{MgHPO}_4$	0.15
$\text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O} \downarrow \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^- + 6\text{H}_2\text{O}$	10.7
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} \downarrow \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$	12.7
$\text{Ca}_3(\text{PO}_4)_2 \downarrow \leftrightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	25
$\text{CaHPO}_4 \downarrow \leftrightarrow \text{Ca}^{2+} + \text{HPO}_4^{2-}$	6.57
$\text{CaCO}_3 \downarrow \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	16.7
$\text{MgCa}(\text{CO}_3)_2 \downarrow \leftrightarrow \text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{CO}_3^{2-}$	5.3
$\text{MgCO}_3 \downarrow \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-}$	5.0
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \downarrow \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}$	4.67
$\text{CaHPO}_4 \cdot 5\text{H}_2\text{O} \downarrow \leftrightarrow \text{Ca}^{2+} + \text{HPO}_4^{2-} + 5\text{H}_2\text{O}$	18.995
$\text{CaMg}_3(\text{CO}_3)_4 \downarrow \leftrightarrow 3\text{Mg}^{2+} + \text{Ca}^{2+} + 4\text{CO}_3^{2-}$	36.16
$\text{Ca}_5(\text{PO}_4)_3\text{OH} \downarrow \leftrightarrow 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$	36
$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \downarrow \leftrightarrow 8\text{Ca}^{2+} + 4\text{PO}_4^{3-} + 2\text{HPO}_4^{2-}$	46.97

Table 2-3. Input parameters to the model for simulations on the effect of pH

Component (mg/L)	Centrate	Dairy Flushwater
Nitrogen	750	740.88
Phosphorus	120	50.66
Calcium	35	140.5
Total Potassium	110	357.78
Alkalinity as mg/L of CaCO ₃	4750	1270

Table 2-4. Validation of the chemical equilibrium model

Ref.	Type of Wastewater	Initial Concentrations mM				Exptl Struvite (mg/L)	Model Predictions					Predicted Struvite fraction in solids (%)	Error ^s in Model Prediction of struvite (%)	
		pH	Mg _T	P _T	N _T		Struvite (mg/L)	MP8 (mg/L)	MP22 (mg/L)	Mg(OH) ₂ (mg/L)	MHP (mg/L)			Total solids (mg/L)
Lowenthal et al. (1994)	Solutions prepared by adding NH ₄ Cl, K ₂ HPO ₄ , MgCl ₂ , carbonate and acetate	6.8	8.23	12.9	21.43	601	300.2	0.001	0	0	432.9	733	40.95	18
Harada et al. (2006)	Synthetic urine containing PO ₄ , NH ₄ , Na, Mg, K, Ca, Cl, citrate, carbonate	8	20	13.45	20.18	1685	1317	88	11.54	17.72	222.9	1687.7	78	1.23
Wilsenach et al. (2007)	Synthetic urine containing PO ₄ , NH ₄ , Na, Mg, K, Ca, Cl, citrate, carbonate	9.4	7.415	14.83	18.7	1045	987.07	0.001	0	0.061	14.75	1001.89	98.52	5.87
Wilsenach et al. (2007)	Synthetic urine containing PO ₄ , NH ₄ , Na, Mg, K, Ca, Cl, citrate, carbonate	9.4	14.83	14.83	18.7	2011	1845.03	7.03	0.922	11.625	80.25	1944.86	94.87	9
Celen et al. (2007)	Liquid swine manure	8.5	2.39	5.51	80	338	322.2	0	0	0	2.7	324.9	99.17	4.9
Much and Barr (2001)	Supernatant from anaerobically digested sludge dewatering centrifuge	8.5	1.51	1.9677	43.88	195	200.86	0	0	0.003	3.08	203.95	98.49	2.92
Yoshono et al. (2003)	Anaerobic digester effluent supernatant	8.5	7.025	6.387	24.5	805	818.23	1.006	0.132	12.157	29.68	883.02	92.66	1.62
Tünay et al. (1997)	Synthetic samples prepared by using MgCl ₂ , NaH ₂ PO ₄ , NH ₄ Cl	9	14.26	14.26	14.26	1714	1017.7	44.44	5.82	284.9	4.75	2273	44.75	24.5

Table 2-4. Continued

Ref.	Type of Wastewater	Initial Concentrations mM				Exptl Struvite (mg/L)	Model Predictions					Predicted Struvite fraction in solids (%)	Error [§] in Model Prediction of struvite (%)	
		pH	Mg _T	P _T	N _T		Struvite (mg/L)	MP8 (mg/L)	MP22 (mg/L)	Mg(OH) ₂ (mg/L)	MHP (mg/L)			Total solids (mg/L)
* Altinbas et al. (2002)	Domestic Wastewater + 2% landfill leachate (DWL3 sample) Supernatant from	9.2	7.785	7.785	7.785	1420	1495	7.83	1.02	7.7	104.1	1616.1	92.5	5.01
Battistoni et al. (1998)	sludge centrifuges in a biological nutrient removal plant	8.12	1.54	2	44.5	210.98	198.21	0	0	0.001	6.56	204.77	96.79	6.44
Burns et al. (2001)	Swine Waste	9	9.736	6.085	12	758.6	705.47	44.963	5.896	161.05	54.53	971.91	72.59	7.53
* Stratful et al. (2001)	Deionized water with varying concentration of Mg ²⁺ , NH ₄ ⁺ and PO ₄ ³⁻	10	7.692	7.81	14.77	1629	1757	0.67	0.04	17.45	15	1790.5	98	7.2

[§] Error in struvite concentration predicted by the model and that measured experimentally

* For these data, the error between solids concentration, as predicted by the model and struvite reported in the experiments, was calculated.

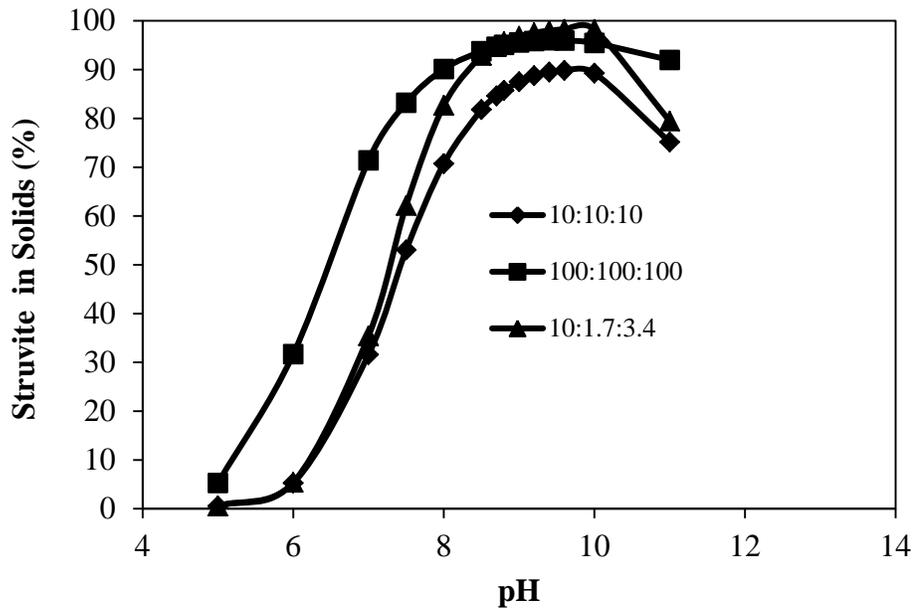


Figure 2-1. Effect of pH on struvite purity for ammonium, magnesium, and phosphate ratios of 1:1:1 (at 10 mM and 100 mM) and 10 mM : 1.7 mM : 3.4 mM.

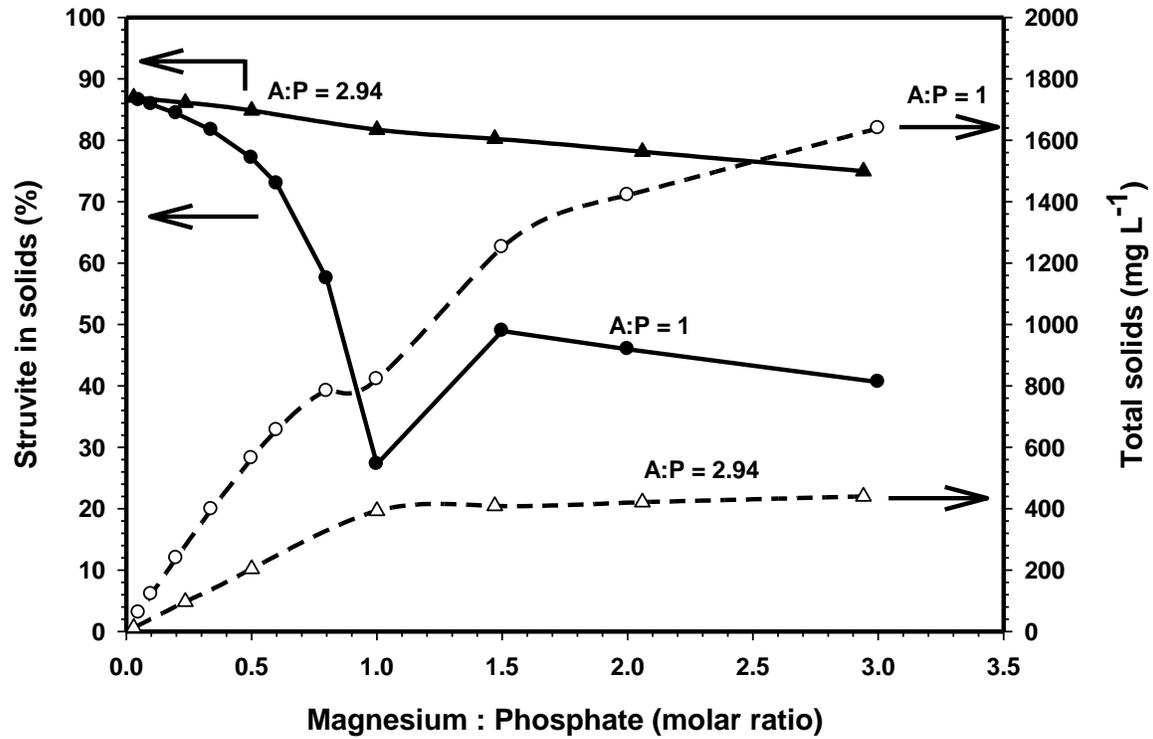


Figure 2-2. Effect of molar ratio of magnesium: phosphate on % struvite and total solids for two different molar ratios of ammonium (A) and phosphate (P) at pH = 8.7.

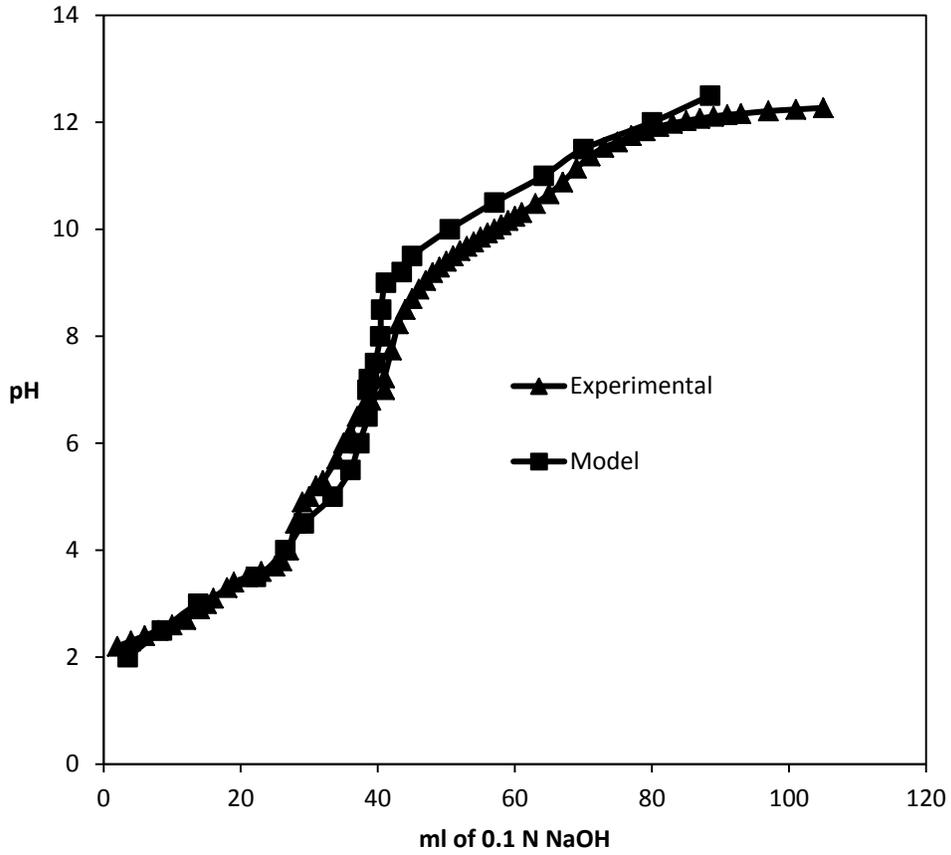


Figure 2-3. Titration curve for anaerobically digested wastewater from dairy operations.

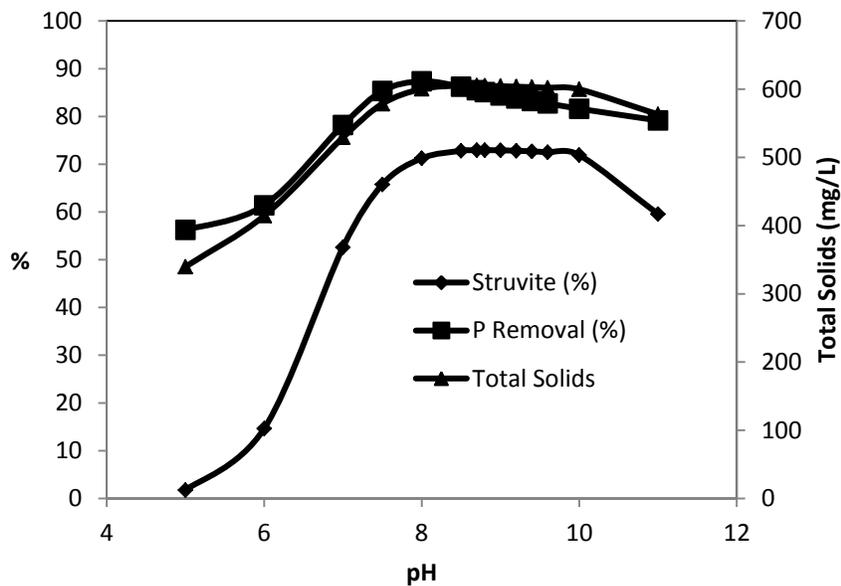


Figure 2-4. Effect of pH on struvite purity and phosphorus removal in centrate at an Mg:P ratio of 1:1.

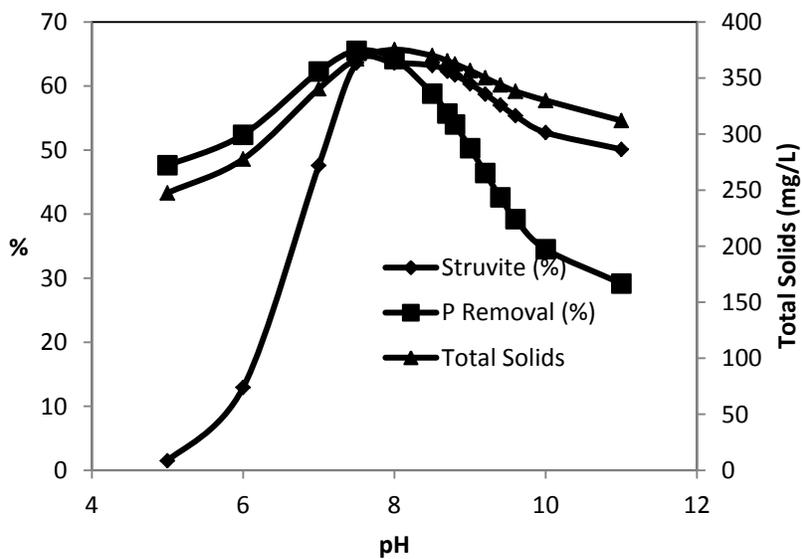


Figure 2-5. Effect of pH on struvite purity and phosphorus removal in centrate at an Mg:P ratio of 0.5:1.

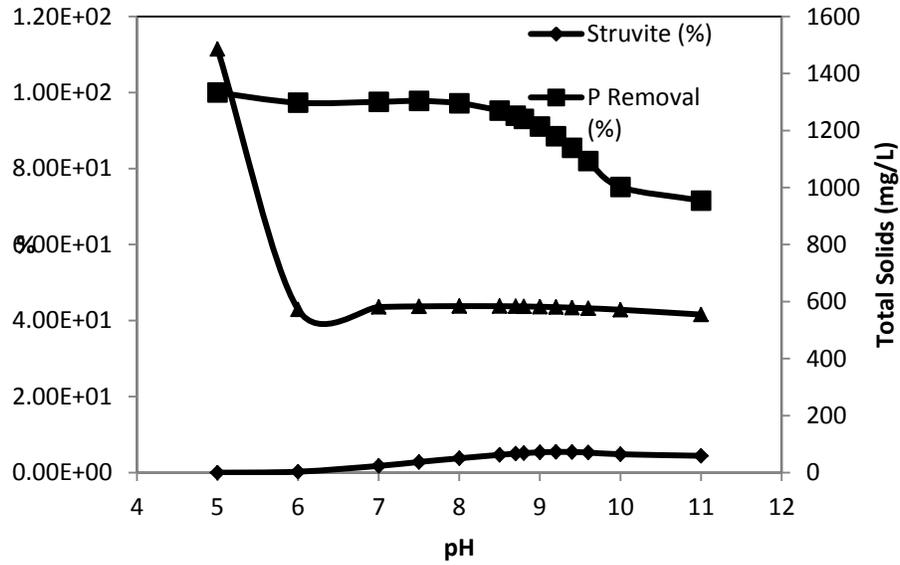


Figure 2-6. Effect of pH on struvite purity and phosphorus removal in dairy flushwater at an Mg:P ratio of 1:1.

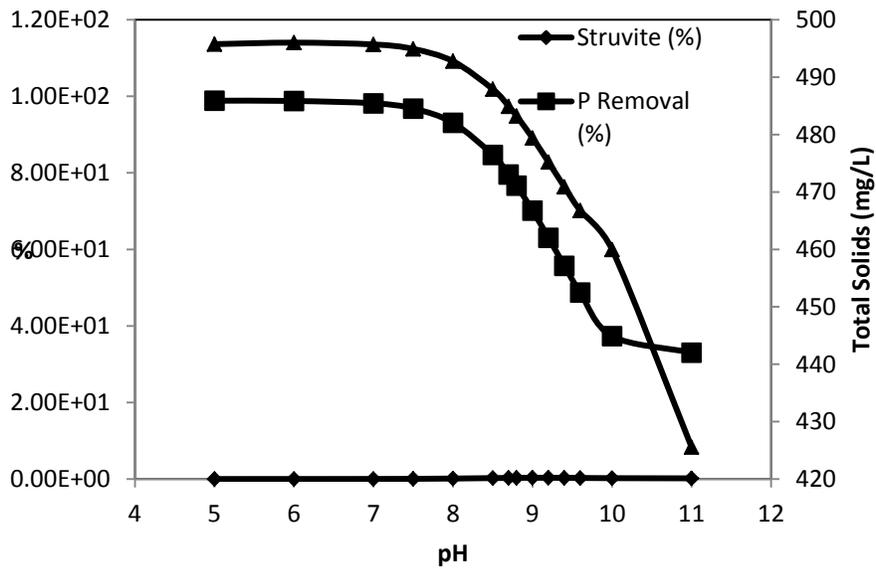


Figure 2-7. Effect of pH on struvite purity and phosphorus removal in dairy flushwater at an Mg:P ratio of 0.5:1.

CHAPTER 3
SEQUENTIAL BATCH REACTOR FOR RECOVERY OF NITROGEN AND PHOSPHORUS
AS STRUVITE FROM SEWAGE SLUDGE CENTRATE AND DAIRY WASTEWATER

3.1 Removal of Nutrients from Wastewater

The review presented in this chapter discusses the principles of struvite crystallization, and also examines the techniques and processes in experimentation to date by researchers. The experiments maximize phosphorus removal and reuse as struvite obtained from wastewater effluents.

Untreated, nutrient-rich wastewater is problematic and causes eutrophication of receiving waters. Removal of nutrients becomes challenging as regulatory authorities tighten discharge standards. Significant costs are associated with the extra treatment processes required to meet the discharge standards (Giesen, 1999). The most widely used technologies for nutrient removal, which are adopted by wastewater treatment plants, include biological nitrification/denitrification for nitrogen removal and metal salt precipitation or biological treatment for phosphorus removal. A significant amount of sludge is generated in the wastewater treatment plant, which is anaerobically digested and dewatered using centrifuges and gravity belt thickening. This produces centrate and filtrate streams containing 750 to 1000 ppm of ammonia-N and 100 to 200 ppm of phosphate-P. Most wastewater treatment plants return these streams to the plant headworks where it adds to the wastewater burden.

Currently, an approach to remove nitrogen and phosphorus from wastewater effluents, which is gaining attention, is through the crystallization of phosphate compounds such as calcium phosphate or struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Doyle and Parsons, 2002). This approach can be seen as resource recovery and may contribute positively to the economics of wastewater treatment.

3.1.1 Factors Affecting Struvite Formation: Concentration and Nature of Constituents

The concentration of constituents in the liquor must exceed the solubility product of struvite for crystal growth to begin (Taylor et al., 1963; Ohlinger et al., 1998). Usually magnesium is a limiting constituent for struvite precipitation. The amount of magnesium added to the influent is varied to achieve an appropriate ratio of magnesium to phosphate within the influent. Some reactors raise the magnesium concentration to achieve a 1:1 ratio with phosphate, for example, the Shimane and Osaka plants in Japan; others raise it above a 1:1 ratio. Burns et al. (2001) showed that the magnesium-to-phosphorus ratio of 1.6:1 is ideal because not all magnesium will be available for precipitation due to the formation of other complexes within the solution. Magnesium is also added to counteract the influence of calcium ions within the influent. The calcium-to-magnesium ratio cannot be greater than 1:1 due to the influence of calcium species on struvite precipitation. Generally, calcium is in excess of phosphate within liquors so a ratio of greater than 1:1 Mg:Ca should be set within a recovery operation to stop the detrimental effects of calcium on struvite precipitation. Two forms of magnesium are typically used. Magnesium chloride is the preferred choice within the literature though magnesium hydroxide has also been trialed (Munch and Barr, 2000; Ueno and Fujii, 2001; Miles and Ellis, 2001). Magnesium hydroxide is an attractive choice for reactors because it will raise the pH of the solution, which would lower the cost of raising the pH with the addition of a base, but the pH cannot be altered independently of magnesium addition. Ueno and Fujii (2001) used sodium hydroxide to alter the pH to offer finer control. Magnesium chloride is cheaper than magnesium hydroxide and is readily soluble in water. Due to these reasons, the use of magnesium chloride is more popular.

3.1.2 Effect of pH

The most important condition within a reactor is the pH of the liquor. The pH choice plays an extensive role in the speciation of reactants, the speed of reaction, and the nature of the product. By far, the easiest method to alter pH is by the addition of a base, such as sodium hydroxide. The addition of a base is an expensive process, and methods to avoid this procedure have been well researched. A brief review of pH values used in struvite precipitation is presented in Table 3-1. The Treviso and Geesterambacht treatment plants both employ an air stripping unit for the removal of carbon dioxide from the liquor. Carbon dioxide within the liquor reversibly forms carbonic acid (H_2CO_3), thereby lowering the pH. The removal of this CO_2 by injection of air into the liquor raises the pH without the addition of a base (Battistoni et al., 1997). This attractive method requires a substantial reactor volume for the removal of CO_2 from the liquor, which makes it an expensive investment. Ohlinger et al. (1999) showed that vigorous stirring of solutions raised the pH from 8 to 8.5, but this took a mixing speed of 500 rpm. The economics of such a reactor should be taken into account.

Chemical speciation within the liquor has been shown to depend on pH (Ohlinger et al., 1998). Phosphate and ammonia exist in different forms at different pH values. The solubility of struvite was linked by Ohlinger et al. (1998) to the speciation of these components. Ohlinger et al. (1998) showed that the presence of magnesium phosphates within the solution lowered the solubility of struvite by the removal of these vital components, with their presence prevailing at pH 8.5. The lowest point of struvite solubility had been shown to be at pH 9. A rise above pH 9 saw the stripping of ammonia from the liquor and an increase of phosphate concentration (Booker et al., 1999), which has been linked to the over-production of fines due to the stripping of ammonia from the liquors.

The rate of formation of struvite has been shown to be controlled by the pH. For a commercial recovery operation, this is important. It was showed that by increasing the pH to 9, nucleation could be achieved within a few minutes. One problem with such a high pH is the production of fines. Fines have been a problem for a number of authors (Mangin, 2004; Le Corre et al., 2006). Due to the production of fines at high pH levels, Battistoni et al. (2005) were able to show that by setting the pH to 8.5, the precipitation of struvite could be changed from a homogeneous to heterogeneous process with the use of seed material. The selection of the pH will be dependent on the conditions required within the reactor, that is, a seeded or non-seeded reactor.

3.1.3 Effect of Temperature

Literature on the effect of temperature on struvite formation gives a different explanation in every study. Borgerding (1972) studied the influence of temperature on struvite solubility in the anaerobic digestion of a wastewater treatment plant. He concluded that when the temperature increased from 0°C to 20°C, struvite solubility increased. However, above this temperature, solubility was found to decline steadily with an increase in temperature. Webb and Ho (1992) assumed 30°C to be the temperature of maximum struvite solubility in experiments designed to define thermodynamic parameters for its crystallization. On the other hand, Webb (1988) measured the solubility of struvite in various salt solutions at temperatures ranging from 0° to 80°C. Webb (1988) concluded that increasing temperature causes a rise in struvite solubility, especially for more concentrated solutions. Çelen and Türker (2001) reported that the reaction temperature did not have an influence on struvite solubility in an anaerobic digester effluent with temperatures 25° to 40°C. The effect of temperature on struvite formation is not studied here. All studies on struvite precipitation were carried out at room temperature (25°C) for typical wastewater temperatures.

3.1.4 Hydraulic Retention Time (HRT)

The hydraulic retention time (HRT) of a reactor is of particular importance to the design. Ohlinger et al. (2000) reported that struvite removal efficiency exceeded 80% when the HRT exceeded one hour. Munch and Barr (2001) found that after one to two hours, HRT had no effect on the effluent ortho-phosphate (OP) concentration. However, Çelen and Türker (2001) concluded that struvite precipitation is very fast and completed in minutes. Therefore, they assumed a 40-minute reaction time for process equilibrium.

To achieve larger crystal sizes, a high HRT (10 days) is coupled with a recycling unit in the Phosnix process. Mamais et al. (1994) found that an HRT of 14 days was most suitable and achieved a 91% removal of phosphate, though little information is available on product size or quality. Other authors have found that shorter HRTs have yielded good results. Suzuki et al. (2005) found that an HRT of 22 h was suitable for the accumulation reactor. Short HRTs are more attractive due to lower costs. Ways of achieving this should be further investigated. This is one of the important considerations of the present research.

3.2 Review of Reactor Designs for Struvite Production

Several laboratory and pilot scale studies have been carried out to assess the potential of struvite recovery methods in removing and recovering phosphorus as a reusable product. A few studies have been tested at full scale in The Netherlands (Giesen, 1999) and Italy (Battistoni et al., 2005a; Battistoni et al., 2005b). However, Japan and Canada are the only countries where 90% of the phosphorus removal and recovery from anaerobically digested sludge liquors as struvite have been implemented, with the resulting product sold to fertilizer companies (Gaterell et al., 2000; Ueno and Fujii, 2001).

Currently, five full-scale phosphorus recovery operations exist, three in Japan and two in Europe. All five operations share a similar design philosophy with the only differences being in

seed material used and the way the desired pH is achieved. The Shimane plant reactor has two internal compartments for the reaction and settling of struvite. The inner section of the reactor is the nucleation zone, and the outer section of the reactor is the separation zone. The separation zone allows the settling of struvite crystals with collection, happening about every 10 days by discharge from the bottom of the reactor. The smaller struvite crystals, which are called “fines,” are returned to the reactor to provide new seed material for the reactor to continue operating.

With the Crystalactor[®], a similar reactor design is seen but instead of recycled struvite acting as seed material for the growth of the product, quartz sand is used to grow HAP. The influent is pumped in an upward direction at high velocity (30-50 m/h) to enable a complete fluidization. Pellets of HAP-sand grow, and as their mass increases, there is not enough pressure to keep them fluidized and so they settle at the bottom of the reactor. Treviso’s reactor also has the same design as the Crystalactor[®] with pellets grown on sand and removed in the same manner. The design philosophy for an FBR reactor in the literature is quite standardized. Two main options exist which are varied in all the operations: how to achieve operation pH and collection of the product. Aeration has been demonstrated as a good method for the raising of the pH and has been successfully demonstrated at Treviso and Geesterambacht. The addition of a base, though, is the far easier method that does not require the installation and operation of a further unit. The NaOH is a relatively cheap chemical to purchase, but amounts required would vary depending on the alkalinity of the liquors. The other choice when designing a recovery operation is the method of recovering the product. Settling within the reactor is considered the easiest method available and is achieved by the use of seed material at Shimane, Treviso, and Geesterambacht. Two other options are available for the recovery of the final product: accumulation devices and coagulating polymers. Accumulation devices, such as steel mesh, as

reported by Suzuki et al. (2005) and Le Corre et al. (2006), have both shown great results for the collection of struvite, and initial results from this project have confirmed these results. One problem with this method, however, is how to transfer it to a full-scale operation. Unfortunately, it is difficult to set a machine to clean the mesh, and so it would need to be done by hand, adding costs to the operation.

Struvite crystallization is typically carried out using chemical additions. Three elements are typically altered within the reactor to aid precipitation of the desired product.

1. Chemical constituents are altered to achieve supersaturation or metastable conditions.
2. The influent pH is altered commonly by the addition of a base or the use of aeration to strip carbon dioxide so that the nucleation step can be made faster.
3. The addition of seed material allows for the growth of struvite crystals on the surface of seed material, which in turn allows for the growth of larger particles, which facilitates easier collection from the reactor.

Typical designs involve the use of stirred tank reactors and fluidized bed reactors, which are next reviewed.

3.2.1 Stirred Tank Reactors

Stirred tank reactors allow for even distribution of chemicals throughout the system, thus preventing any limitations on chemicals at crystal growth sites (Ali and Schneider, 2006). The nature of crystal growth requires a constant source of chemicals for continued growth (Ohlinger et al., 1999). Key unit operations can be varied using a continuously stirred tank to reach specified results, thus using the system for modeling. The stirring is generally carried out 1) by a mechanical paddle that operates at a constant speed, 2) by recirculation of the reactant through the reactor (Ali and Schneider, 2006), or 3) by the aeration of the solution with air.

Large-scale stirred reactors for the production of struvite are not widely reported in the literature. Burns et al. (2001) used a 140,000 liter tank for the production of struvite from animal

waste material with the addition of 2000 L of magnesium chloride; a 90% removal of phosphate was achieved. The recovered product was used as a fertilizer on nearby fields, but unfortunately, no results were given on how these crops were affected. At 13,000 L, the struvite reactor was trialed by Jaffer et al. (2001) at Slough Sewage Treatment Works in England with mixing achieved by aeration. With a relatively short residence time of one hour within the reactor, the addition of magnesium chloride and sodium hydroxide for pH elevation achieved a phosphate removal of 64%. Along with good phosphate removal, large quantities of struvite were produced, which were subsequently trialed successfully as a fertilizer when blended with a potassium source (Johnson et al., 2004).

Mangin et al. (2004) reported the effect of seeding a stirred reactor. The authors found that seeding the 21L reactor with sand had no effect on changing the precipitation of struvite from homogeneous primary nucleation to heterogeneous primary nucleation. The reactor produced a large quantity of fines, which was linked to the over-supersaturation of the solution. Le Corre et al. (2006) saw this lack of nucleation in atomic force microscopy (AFM) studies on different types of seed material. Le Corre et al. (2006) also observed that sand had the second lowest affinity to stick to struvite. Mangin et al. (2004) trialed struvite as seed material in additional experiments. Struvite was shown to be ineffective also as seed material for the stirred tank reactor due the production of a large amount of fines. Mangin et al. (2004) reported that even with dilution of the influent, over-production of fines still occurred within the reactor.

3.2.2 Fluidized Bed Reactor (FBR)

In the fluidized bed reactor (FBR), the liquor passes upward through a bed, generally made up of small particulate matter, at sufficient enough velocity to fluidize the media (Thomas, 2007). This process is used in all full scale phosphate recovery processes, that is, Geesterambacht, Treviso, and Shimane. At Treviso (Battistoni et al., 2000) and Geesterambacht

(Van Dijk and Wilms, 1991), the bed is quartz sand, and at Shimane (Phosnix process) (Ueno and Fujii, 2001), the process uses recycled struvite fines. The fluidization process increases the surface area of the particulate matter because all faces of the solid are now accessible as reaction sites [NIR] (Metcalf and Eddy, 2001). By using a high enough air inflow, the solid material is able to overcome any aerodynamic drag and gravity to become suspended within the liquid. The fluidization of the particles is used to achieve a greater level of mixing within the reactor, thus achieving a uniform mixing of reactants. A greater mixing of reactants increases the nucleation rate and lowers the chances of local supersaturation levels within the liquor which can lead to the over-production of fines (Ohlinger et al., 1999).

The FBR process for recovery of phosphate is generally divided into two phases: the air stripping phase and the reaction phase (Ueno and Fujii, 2001; Battistoni et al., 2005). The air stripping phase of the process is used to increase the pH of the solution by removal of carbon dioxide from the liquor. The air stripping phase can have a significant effect on the rate of precipitation where Battistoni et al. (1998) reported the reaction period can be reduced from 8 days to 100 min. Air stripping allows for the phosphate recovery process to proceed with a reduction in the amount of a base needed to raise the pH of the influent.

Though FBR reactors seem to be the most popular type, stirred reactors have been trialed at two sites along with many bench scale tests. Stirred reactors have their own problems, but one big advantage is that they are relatively simple to operate. The reactor design of Slough Sewage Treatment Works was designed with the same principles as that of the Phosnix process, that is, two zones within the reactor: one for nucleation and another for settling.

Limitations of existing struvite recovery techniques include:

- Reliance on in-situ crystallization and agglomeration, which results in large reactor volumes to ensure appropriate residence times for successful agglomeration. Formation of crystals is favored as it reduces downstream processing costs to make salable products.
- Overall reaction rate (consequently, reactor volume) controlled by the crystallization process rather than precipitation
- High capital costs for these systems
- Reactors used in the commercial processes are fluidized bed or membrane reactors, which incur high operating costs
- These systems achieving only 90% removal of phosphate

3.3 Overview of Sequencing Batch Reactor (SBR) Technology

3.3.1 Concept of Sequential Batch Reactors (SBR)

The sequential batch reactor (SBR) technology is considered to be an alternative to conventional processes, such as a stirred tank reactor for nutrient removal from wastewater. This configuration has a higher flexibility and controllability, allowing more rapid adjustment to changing influent characteristics (Baetens, 2000). Lower investment and a recurrent cost occur because secondary settling tanks and sludge return systems are not required (Novak and Lindtner, 2003). Furthermore, it is especially appropriate for places where there is significant flow and load variability (Metcalf and Eddy, 2003) or where space problems become a restriction. The SBRs are widely and commonly used in biological wastewater treatment (Mace and Mata-Alvarez, 2002). The SBR technology has been successfully applied in wastewater treatment plants that treat urban and industrial wastewater (Puig et al., 2005).

3.3.2 Overview of Full-scale Applications of SBR Technology

Alleman and Irvine (1980) demonstrated the potential of the SBR technology to maintain combined organic carbon oxidation and nitrification. Irvine et al. (1983) concluded that the SBR technology is a viable alternative to conventional, continuous, flow-activated sludge treatment of domestic wastewater, nitrification, denitrification, and chemical precipitation of phosphorus in

the first SBR demonstration site. Norcross (1992) considered the mechanical, process, and control aspects for the design of an SBR. Ketchum Jr. (1997) described the SBR physical system and explained approaches used to develop the bases of design needed to meet many different treatment objectives, especially for the feeding and reaction periods.

Arora et al. (1985) evaluated the SBR technology at several plants in the United States, suggesting that equalization, ideal settling, simple operation, compact layout, and cost savings are the major advantages of SBR systems versus continuous flow systems. Okada and Sudo (1985) studied the simultaneous removal of phosphorus in a lab-SBR. Rim et al. (1997) carried out successful full-scale tests for biological nutrient removal (BNR) purposes using the SBR technology, treating between 47.3 and 52.8 m³/day of sewage. Helmreich et al. (2000) investigated the performance of SBR plants in operation in Bavaria, Germany. The sizes of SBR plants in Bavaria range from 400 to 25,000 Population Equivalents (PE). Teichgraber et al. (2001) achieved complete biological nitrogen removal at full scale in a single tank SBR, treating 850 m³/d of domestic wastewater. Torrijos et al. (2001) concluded that SBR technology is, from a technical point of view, perfectly adapted to treating cheese production wastewater. Steinmetz et al. (2002) evaluated—in view of their effluent quality, treatment efficiency, and energy demand—four SBR wastewater treatment plants, which were designed for approximately 5,000, 8,000, 15,000, 25,000 PE. The study proved that the SBR technology is a good alternative for municipal sewage plants and can help to save investment costs. Two full-scale SBR plants in Australia processing between 2000 and 2500 m³/d of wastewater, which carried out enhanced nutrient removal. Demoulin (2006) reported on the world's largest non-conventional SBR plant, currently under construction in Malaysia for 1.2 million PE.

3.3.3 Characteristics of SBR Technology

Operational steps in a typical SBR are illustrated in Figure 3-1. The SBR technology is a fill-and-draw activated sludge system for wastewater treatment. While in continuous systems, the reaction and settling occur in different reactors. With the SBR technology, all the processes are conducted in a single reactor following a sequence of fill, reaction, settling, and draw phases. The cycle configuration depends on the wastewater characteristics and legal requirements.

The fill phase can be static, mixed, or aerated depending on treatment objectives. A static fill results in minimum energy input and high substrate concentration at the end of the fill phase. A mixed fill results in denitrification if nitrates are present, and provides anaerobic conditions required for biological phosphorus removal. An aerated fill results in the beginning of aerobic reactions, keeping substrate concentration low, which may be of importance if biodegradable constituents exist that are toxic at high concentrations (Ketchum Jr., 1997). The feeding phase could be single or multiple feeding depending on treatment objective.

During the react phase, usually under mixing conditions, the biomass consumes the substrate under controlled environmental conditions (aerobic, anoxic, or anaerobic) depending on the wastewater treatment. In the aerobic react phases, the organic matter oxidation and nitrification take place. The classical heterotrophic denitrification process and the phosphorus uptake require anoxic conditions. During the anaerobic phase, phosphate is released into the liquid phase.

Sludge wasting is another important step in the SBR operation that greatly affects performance (Metcalf and Eddy, 2003). Its target is the regulation of the sludge solids concentration in the reactor. Sludge wasting could be done at the end of the reaction phase or during the settling phase.

In the present study, a sequential batch reactor (SBR) is utilized for producing struvite. As previously discussed, such a type of operation is becoming increasingly common in wastewater treatment plants. This operation can offer operating flexibility, better control, and cost-effectiveness. Operational details for an SBR are established by carrying out various experiments and pilot plant experience. Details of an SBR operation for struvite formation are presented in this chapter.

3.4 Objectives

The main purpose of this study was to test the effectiveness of the sequential batch reactor (SBR) operation to recover struvite. Experimental studies were carried out with the following five objectives:

- To determine quantity of magnesium chloride and sodium hydroxide required for struvite precipitation in synthetic and real wastewater
- To investigate operating details for complete nitrogen and phosphorus recovery in an SBR
- To test the possibility of using aeration as a method to increase pH for struvite precipitation
- To determine the nature of the precipitate obtained after struvite formation
- To study settling characteristics of the solid sludge generated after struvite precipitation

3.5 Materials and Methods

Experiments were performed on the following samples fresh from different wastewater streams: 1) centrate from Jacksonville Electric Authority's (JEA) Wastewater Treatment Plant, 2) synthetic solutions containing nitrogen and phosphorus, 3) dairy flushwater collected after grit removal, 4) dairy wastewater from an anaerobic lagoon, and 5) dairy effluent from an aerobic lagoon.

Dairy flushwater was collected after mechanical separation and sedimentation. Primary treatment (screening, sedimentation, or both) of flushed dairy manure is widely practiced in the

dairy industry since it is required to improve the operation of some wastewater irrigation systems. In addition, screening and sedimentation to remove solids are useful in reducing the organic loading rate to anaerobic lagoons to extend their capacity and reduce the frequency of sludge removal.

A conical bottom fluidized bed sequential batch reactor with a total volume 10.6 L was utilized (Figure 3-2). The dimensions and locations of ports on a conical bottom reactor were as follows:

- Diameter: 6"
- Height of cylindrical section: 1'7"
- Height of conical section: 1'
- Ports at following locations from top: 2@ 3"; 1@ 9"; 1@ 17.5", 1 on conical section @ 2', 1@ 29.5"
- Lid with four equidistant ports of 1/4" inside the diameter: 2 ports for exhaust, one for air inlet, and one for sampling

The volume of the cylindrical section and conical section were 2.5 L and 8 L, respectively. Centrate was fed from the top of the reactor. Magnesium chloride and sodium hydroxide were added to the reactor from the top. The reactor was fluidized by air through a sparger at the bottom. This provided mixing, which was required for the chemicals. The desired pH was set using 10 N NaOH. Magnesium was dosed to the reactor, in the form of magnesium chloride solution, to ensure the desired Mg:P molar ratio in the reactor. The reaction of struvite formation started instantly, and it was carried out for 30 min. The operation was carried out in a sequential batch mode in steps to remove the phosphorus completely. The struvite precipitate was allowed to settle for 30 min and then harvested at the end of the batch.

Ammonia-nitrogen and phosphorus were analyzed, according to Standard Methods (APHA, 1992). Potassium and calcium were analyzed using ion-selective electrodes purchased

from Hach. Standard methods were adopted, as suggested in the APHA manual titled *Standard Methods for the Examination of Water and Wastewater*. Solids were recovered by opening the ball valve at the bottom of the SBR. A part of these solids was dried to find the moisture content. The precipitate was dried overnight in an oven at 104°C and weighed. Solids were analyzed for nitrogen, phosphorus, calcium, and magnesium. Solids were also analyzed using x-ray diffraction (XRD), using a Philips x-ray diffractometer and Cu K α radiation, with an average scanning rate of 2.0° 2 θ min⁻¹. The struvite procured from Fisher Scientific was used as a standard for comparison.

For struvite precipitation, wastewater was filled in the reactor. After filling, the precipitation reaction was carried out by feeding appropriate amounts of caustic and magnesium chloride, calculated by a chemical equilibrium model described later. The reaction time was approximately 30 min. After the reaction precipitated, struvite was allowed to settle for about 5 min. Centrate was decanted from the top, and struvite was drawn from the bottom of the reactor. The settled struvite sludge was taken through other processing steps to make the final product.

Experiments were also carried out to study struvite settling characteristics. Anaerobically digested dairy manure was also subjected to struvite formation and settling. Solids present in the dairy manure were allowed to settle, and solid samples were taken at different heights of the reactor to quantify struvite accumulation at specific time. Samples were centrifuged at 5000 rpm for 15 min, then decanted, dried, and weighed to determine solid content. The sequential batch reactor was filled with anaerobically treated dairy manure with a total volume of 9.2 L. Mixing was provided with air fluidized from the bottom of the reactor. Samples were taken when the solids were uniformly distributed. Raw dairy manure was allowed to settle, and samples were taken at 15 min and 30 min after mixing was stopped. Samples were taken at four different

depths of the reactor (5', 17", 24" and 31"). A 100 ml of sample was centrifuged and decanted. A solid pellet in the centrifuge tube was resuspended in 20 ml deionized water, which was then dried at 105°C and weighed. The height of the liquid level from the top of the reactor was found to be at 5". The total height of the reactor including was 31". The dairy manure was subjected to struvite formation by adding 1.3 g/L of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at pH of 8.7. The experiments were carried out at room temperature (25°C). The reaction was carried out for 30 min in the sequential batch reactor.

3.6 Results and Discussion

3.6.1 Determination of Magnesium Needed for Phosphorus Recovery as Struvite from Centrate

The centrate was found to have the following species concentrations: NH_4^+ -N, 710 mg/L; PO_4^{3-} -P, 166 mg/L with pH, 7.4. The centrate was treated for phosphorus recovery in the form struvite using magnesium chloride. Different concentrations of magnesium were adjusted using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. As discussed in previous sections, magnesium hydroxide has been used by some researchers but magnesium chloride was found to be a better source of magnesium. Some authors have used magnesium oxide (MgO), which has the additional benefit of raising the solution pH and thus promoting struvite precipitation (Munch and Barr 2001; Schuiling and Andrade, 1999;. Çelen and Türker (2001) studied NH_3 removal as struvite from molasses-based industrial wastewater. They found that MgCl_2 was a better Mg^{2+} source than MgO. Using swine wastewater, Burns et al. (2001) and Beal et al. (1999) had the same results. Less NaOH was used for pH adjustment when MgO was used; however, less NH_3 was removed as struvite.

In the present experiments, pH was adjusted to 8.4 using 5N NaOH, and the samples were kept on a shaker for 24 hours in glass bottles with a volume of 500 mL. The pH value of

8.4 was chosen from model simulation results for the highest struvite purity of 98%. Final residual concentrations of NH_4^+ -N and PO_4^{3-} -P were analyzed.

Experimental results and model predictions are shown in Table 3-2. This researcher found that when magnesium was not added to the centrate and the pH adjusted to 8.4, reduction in phosphorus and ammonia nitrogen occurred. This indicated the presence of minerals, such as magnesium and calcium, in the original centrate, which caused precipitation. This researcher observed that 2.2 mM of ammonia-N and 2 mM of phosphorus could be precipitated without the addition of magnesium in the centrate. The concentration of calcium and magnesium in the centrate was reported to be in the range of 30 to 50 ppm and 50 to 100 ppm, respectively. Model simulations were carried out using the following concentrations of ionic species, which were input to the model: NH_4^+ -N, 710 mg/L; PO_4^{3-} -P, 166 mg/L; Ca, 30 ppm; pH, 8.4, with magnesium concentrations, as shown in Table 3-2, in addition to 35 ppm.

Experimentally, the optimum magnesium required was found to be 225 mg/L for centrate for the concentrations of NH_4^+ -N and PO_4^{3-} -P, as mentioned earlier. The residual NH_4^+ -N concentration was found to be very high, which can be recovered by adding more phosphate to form struvite or by ammonia stripping.

3.6.2 Struvite Precipitation from Synthetic Solution in the SBR

Experiments using defined solutions were carried out in the laboratory to study characteristics of the sequential batch reactor operation. The data obtained in the experiments were used to validate the model described in Chapter 2. A solution of 6 g/L of PO_4^{3-} was prepared by mixing 118.8 ml of 85% phosphoric acid in 9 L of distilled water. The total ammonia concentration was made to 3.8 g/L by adding 130.66 g of ammonium chloride. Model simulations were performed to get the highest struvite purity of 99%. The model predicted that a magnesium concentration of 4.5 g/L was suitable to get more than 99% purity. Magnesium

chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) of 338.7 g was used as a magnesium source. This gave an initial $\text{NH}_4^+:\text{Mg}^{2+}:\text{PO}_4^{3-}$ ratio of 27.14: 18.5: 0.1935.

In these experiments, a hydraulic retention time of 30 min was selected. In the sequential batch mode of the reactor operation, the settling of precipitated solids was studied against the mixing time (hydraulic retention time of the reaction). It was determined that a minimum of 30 min mixing was required for the solids to start to settle. In less than 30 min, the precipitation started, but solids formation was not observed, but the solution in the reactor became translucent in the initial 30 min of the reaction, which indicated commencement of struvite formation.

Precipitation was found to occur instantaneously after the addition of magnesium chloride solution, which increased with the addition of NaOH. After reaching a pH of 8.4, the solution was fluidized for 30 min. Precipitated struvite was allowed to settle in the reactor. This researcher noted that it takes about 10 min for the solids to settle. This researcher observed that the solids recovered had 80% moisture. Solids recovered from the SBR were filtered using 0.45 μm Whatman filter paper. The solids were dried, and this researcher observed that filtration could recover solids which had 63% moisture. Total dry solids of 218 g were recovered in the experiment. This is in good agreement with the model results, which predicted 225 g of solids.

3.6.3 Phosphorus Recovery from Centrate

Struvite formation was carried out in sequential batch mode in two steps. In every step, a hydraulic retention time of 30 min was used. In Step 1, the pH of centrate was adjusted to 8.7. Results are shown in Table 3-3. After pH adjustment, the phosphorus concentration was found to drop from 103 mg/L to 64 mg/L. In Step 2, 414 mg/L of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was added for further phosphorus recovery. This was found to recover 99.6% phosphorus in the form of struvite at a pH of 8.7. Experimental results were validated using the comprehensive model, as previously

explained. The model validation was also done for residual concentrations of nitrogen and phosphorus, as well as total solids. This is in agreement with the model predictions, as shown in Table 3-3. Model predictions on the caustic requirement do not match with the experiment because data on ionic species, other than Mg^{2+} , PO_4^{3-} and NH_4^+ were not available. The exion concentration was adjusted in the model to get accurate predictions on the caustic requirement. The exion concentration was found to be 0.003751M, which gave a close prediction to the experimental value.

3.6.4 Experiments on Complete Nitrogen and Phosphorus Recovery from Centrate

From known concentrations of ammonia and phosphate in centrate, the model was used to calculate the amount of magnesium chloride required. The reaction of struvite formation started instantly, and it was carried out for 30 min. This time was chosen for the solids to form completion of precipitation so that the solids could settle quickly. The reaction was carried out in a sequential batch mode in steps to remove nitrogen completely. Struvite precipitate was harvested at the end of the batch after all the steps. The precipitation reaction in every step was carried out at the pH of 8.4. Solids were harvested at the end of Step 4. In Step 1, the concentration of magnesium was adjusted to 1.1 g/L in the reactor. In this step, the phosphorus concentration was reduced from 88.97 mg/L to 2.8 mg/L, recovering 97% phosphorus in the solid form. In this step, ammonia decreased from 588.4 mg/L to 440 mg/L. Ammonia was further recovered by adding phosphorus in the form of phosphoric acid in Step 2. The model was run with 440 mg/L of ammonia and various concentrations of phosphorus and magnesium chloride to ensure the highest purity of struvite. As illustrated in Chapter 2, it is best to have ammonia in excess to get the higher struvite purity. As interpreted from the model simulation results, for Step 2, the concentration of phosphorus and magnesium were adjusted to 477.4 mg/L and 3.34 g/L, respectively. A similar chemical addition was carried out in Steps 3 and 4 to reduce

the ammonia concentration to 45 ppm. The amount of chemicals added is presented in Table 3-4. Solids collected were analyzed for nitrogen and phosphorus at the end of Step 4. Solids were found to contain: N, 5.03%; P, 23.14%, Ca, 0.55%; and Mg, 11.23%. Solids were also analyzed using x-ray diffraction (XRD) to ensure formation of struvite. Struvite procured from Fisher Scientific was used as a standard for comparison. The XRD results are shown in Figure 3-3. The intensity peaks match well with the standard struvite, suggesting formation of struvite as the only solid. This was also in agreement with the chemical analysis of the solids. Results from the experiments on struvite formation lead to the process details, as illustrated in Table 3-5.

3.6.5 Effect of Aeration on Centrate

The pH of wastewater increases with aeration because of CO₂ stripping (Battistoni et al. (1997) devised a phosphate removal technique by exclusively using the chemical physical properties of anaerobic supernatants without any addition of chemicals. This technique reached the operative pH only by aeration and obtaining a quantitative removal of phosphate through nucleation on sand quartz by CO₂ stripping with air. It was previously demonstrated that the wastewater pH increased by aeration, and the concentrations of total P and soluble PO₄-P were reduced by a struvite crystallization reaction induced under a high pH condition. Saidou et al. (2009) used the dissolved CO₂ degasification technique for struvite precipitation. They found that struvite precipitation occurred in alkaline solutions were pH > 8.1. Significant phosphorus removal efficiency through struvite precipitation was observed for experiments carried out with airflow rates between 10 and 25 L min⁻¹. Compared to traditional techniques of struvite precipitation, such as stirring and aeration, the dissolved CO₂ degasification technique is promising since a high amount of phosphorus could be removed in a relatively short experiment time.

In the present studies, the centrate was aerated at a rate of 3.5 L/min, using the same reactor to test the effect on the pH and precipitation. This researcher found that aeration increased the pH of centrate over a period of 30 min and then stabilized to a pH value of 8.5. Solids precipitation was detected when the centrate was aerated for a total of 60 min. The phosphorus concentration was found to decrease from 106.7 mg/L to 82 mg/L. This researcher thought that the centrate received from an anaerobic digester was rich in carbonate (~3500 ppm), and aeration removes carbonates in the form of carbon dioxide (Battistoni et al., 1997). The removal of carbonate improves struvite purity and decreases the caustic requirement for struvite formation.

3.6.6 Struvite Recovery from Dairy Manure

Struvite recovery experiments from dairy manure were performed in the SBR, as explained in an earlier section. The dairy manure sample volume of 7 L was treated for struvite recovery using magnesium chloride and 2 N sodium hydroxide. Struvite is recovered by gravity settling, decanting, and drying the resulting sludge-like material. Results from phosphorus recovery experiments on different streams of dairy wastewater are shown in Table 3-5.

The amount of magnesium and sodium hydroxide needed for struvite recovery were calculated from the model explained in Chapter 2. Concentrations of nitrogen, phosphorus, calcium, potassium, as well as pH, were input to the model. The magnesium requirement is determined from the model for the highest purity of struvite in the solids. Model simulations suggested that it was desirable to carry out the phosphate recovery in two steps.

Flushwater was found to contain 50.66 ppm of phosphorus and 740 ppm of ammonia, as well as 357.78 ppm of potassium and 140.5 ppm of calcium. After treating flushwater with 2 g/L of magnesium chloride, phosphorus concentration was found to drop to 22.35 ppm with some

precipitation of ammonia-N, potassium, and calcium. Phosphorus concentration in Step 2 of struvite precipitation was found to decrease to 5.7 ppm.

The experimental effluent phosphorus concentration on other types of dairy manure was reduced to less than 5 ppm, as shown in Table 3-6. This indicated more than 90% recovery of phosphorus. As presented in Table 3-5, this researcher inferred that complete recovery of phosphorus in a single step was not possible. Additional steps are required for more than 90% recovery of phosphorus. Model simulations suggest formation of precipitates other than struvite. This researcher also observed that a single step approach was not suitable for effective utilization of magnesium chloride. Experimental precipitation of other minerals, such as calcium and potassium, was minimized by selecting appropriate pH value (8.7) determined from model simulations.

Phosphorus precipitate recovered from cattle manure can be characterized by its physical and chemical properties. Chemical analysis of total nitrogen and total phosphorus indicated the recovered materials are valued as a fertilizer. Figures 3-4(A) and (B) show the results of an x-ray diffraction analysis performed on struvite recovered from cattle manure. Some of the definite struvite peaks indicate a presence of the mineral $\text{NH}_4\text{Mg}(\text{PO}_3)_3$. This shows that phosphorus precipitate, other than struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), formed that contained the same type of ionic species as in struvite. The presence of calcium carbonate was also detected by x-ray diffraction (XRD), as shown in Figure 3-4 (b). The precipitate contained N, 4.5%; P, 21.14%; Ca, 0.97%; and Mg, 12.3%. The phosphorus precipitate produced was not pure struvite, as the mass ratio of pure struvite is 1:0.74:3.9 and the molar ratio is 1:1:1, excluding the hexahydrate. The formed precipitate was enhanced with phosphorus from the formation of other phosphate-containing

compounds that may have been formed but not yet identified. Since the overall goal was to recover phosphorus—rather than produce pure struvite—this was a favorable result.

3.6.7 Settleability of Struvite in the SBR

This study aimed to create a model for computing suspended struvite behavior during batch settling. It also endeavored to better understand the settling process, as well as obtain a more accurate and convenient determination of struvite profiles in different types of wastewater. The method is built on the graphical approach, taking into account the effect of concentration of suspended solids and pH on the settling of the surface of suspension. The essential role of hydraulic settling time in the formation of struvite was studied in the sequencing batch reactor. The batch settling test was found to have four periods: free settling, zone settling, transition, and compression. Figure 3-5 shows a settling curve for explaining these four periods.

This researcher observed that struvite formation improved the settleability of solids in the dairy manure, and, at the same time, recover phosphorus. The settling of solids was studied for different concentrations of struvite formed. The settling curve was generated for synthetic struvite for concentrations of 31.2 mg/L and 6.24 g/L. Struvite was formed in the centrate sample, as described previously. The struvite concentration found, in this case, was 3.54 mg/L. The sludge formed was quantified by recovering settled solids from the bottom of the reactor. Precipitation experiments were carried out using methods discussed earlier. Solids formed were found to be struvite, as shown earlier. Struvite was dried overnight at 105°C and weighed. After 30 min of a struvite precipitation reaction, the solid layer was visually monitored in the reactor against the height of the height reactor. This researcher observed that settling time for solids was 10.32 min, 11.14 min, and 13.45 min for 31.2, 6.24, and 3.54 g/L of solid concentration respectively.

This researcher observed that the solids in raw manure do not settle completely in 30 min. Solids in fresh manure were found to be 0.29 g/L when uniformly mixed. In 30 min the solids content in raw manure decreased to 0.17 g/L. The struvite formation helps in solids settling, as shown in Figures 3-8(A) and (B). Solids measured in the top of the reactor were found to decrease considerably after struvite settling to 0.08 g/L. As shown in Figure 3-6, in 15 min of struvite settling, the solids content of 2.35 g/L was observed at a depth of 24" from top of the reactor which is a part of the conical section of the reactor. Complete settling of solids was observed in 30 min after the struvite formation, as shown in Figure 3-7. Formation of fines was not detected in the struvite formation.

This researcher observed that struvite formation improved settling of suspended solids in dairy manure, as shown in Figures 3-8(A) and (B). Settling of solids in struvite formation was similar to activated sludge settling. The zone settling period is approximated by a linear equation, while the compression period is approximated by the Roberts formula, as discussed below. In the zone settling period, flocs of solid interfere with each other while affected by coagulation and destruction, and the interface height, $H(t)$, declines at a constant velocity, A .

$$\frac{dH(t)}{dt} = -A \quad (3.1)$$

Integrating equation (3.2) gives:

$$H(t) = -At + B \quad (3.2)$$

where

$H(t)$ = ratio of the sludge interface height versus its initial height (%) at time t

A = initial settling velocity (%/min)

t = settling time (rain)

B = constant (%)

After the completion of zone settling, the sludge accumulated at the bottom of the settling cylinder began to dehydrate by the weight of the solids. Then the settling rate decreased slowly and the compression period was attained. Empirically, this compression period is expressed by the Roberts formula:

$$\frac{H(t) - H_{\infty}}{H_c - H_{\infty}} = \exp[-k_R(t - t_0)] \quad (3.3)$$

where

H_{∞} = ratio of the final sludge interface height (after about 30 min) versus its initial height (%)

k_R = Roberts constant (min^{-1}) for expressing compression velocity

t_0 = compression starting time (min)

H_c = ratio of the sludge interface height versus its initial height (%) at the compression point

3.7 Outcomes

- The pH level within the recovery processes varies from 8.2 to 9, depending on the strategy of the recovery process. Within the current work a pH of 8.4 to 8.7 was selected to allow for rapid struvite nucleation, being aware that this can cause the precipitation of fines.
- Aeration of the centrate was found to increase the pH to 8.4. This is useful for minimizing the caustic requirement for struvite formation and also to reduce carbonate concentration. This improves the quality of struvite by reducing solids with carbonate.
- The NaOH required to adjust the pH of centrate to 8.7 for complete phosphorus recovery was found to be 432 mg/L without aeration.
- Complete nitrogen and phosphorus removal is possible from centrate in a sequential batch reactor. Settling of precipitated struvite is rapid and it was found to settle in 10 min. Struvite, which was separated from bottom of the reactor, was found to have 80% moisture. Filtered struvite was found to have 65% moisture.
- The recovery of phosphorus from animal waste, as a struvite containing precipitate, has been successfully demonstrated using the SBR mode of operation. The next step in the growth of this technology is the development of a field-scale recovery unit at a commercial animal production unit. The operation of a field-scale recovery unit would supply the necessary data to complete a cost/benefit analysis to investigate the economics of the technology. A cost-effective magnesium source of magnesium chloride and a fast, low-cost method of pH adjustment using sodium hydroxide can be utilized to successfully implement this technology at the farm-scale.

Table 3-1. Optimum pH values used in struvite formation

Optimum pH	Wastewater Source	Reference
9.0	Anaerobic digester effluent used in a bench scale reactor	Jaffer et al., (2002)
8.5	Swine wastewater used in a bench scale reactor	Burns et al., (2002)
8.5-9.5	Wastewater and sludge	Schultze-Rettmer (1991)
9.0	Anaerobic digester effluent used in a pilot scale reactor	Munch and Barr (2001)
8.5-9.0	Anaerobic digester effluent used in a bench scale reactor	Çelen and Türker (2001)
9.0	Livestock waste	Buchanan et al., (1994)
9.0	Digester supernatant used in a lab and pilot scale reactor	Siegrist (1996)

Table 3-2. Effect of magnesium concentration on nitrogen and phosphorus removal from centrate

pH	Experimental			Model Predictions	
	Mg ²⁺ added, mg/L	Final NH ₄ ⁺ -N mg/L	Final PO ₄ ³⁻ -P mg/L	NH ₄ ⁺ -N mg/L	PO ₄ ³⁻ -P mg/L
8.4	0	679.45	100.88	710	166
	100	639.17	16.82	654.25	40.16
	150	619	10.17	637.50	2.24
	200	578	5.07	637.00	2.23
	225	550	1.05	637.00	2.24
	250	535	1.13	637.00	2.23

Table 3-3. Phosphorus recovery from the centrate

Parameters	Untreated Centrate	After pH adjusted to 8.7 (mg/L)	Model predictions after pH adjusted to 8.7 (mg/L)	After MgCl ₂ addition and adjusting pH to 8.7 (mg/L)	Model Predictions after MgCl ₂ addition and adjusting pH to 8.7 (mg/L)
N _t	710 mg/L	700	691.4 as NH ₄ ⁺ -N	680	651 as NH ₄ ⁺ -N
P _t	103 mg/L	64	27.32 as PO ₄ ³⁻ -P	0.5	0.83 as PO ₄ ³⁻ -P
Mg _t	35* mg/L	-	0.141 as Mg ²⁺	-	0.266 as Mg ²⁺
MgCl ₂ added	0	414	-	-	-
TIC	0.0125* M	-	-	-	-
C _{at}	50* mg/L	-	-	-	-
pH	7.7	8.7	-	8.7	-
NaOH added	0	360	745	72	1021
Total Solids			355.83		279
Struvite	-		181.2		277.3
MgCO ₃			0.0898		0.00
Mg(OH) ₂			0.00		0.46
MHPd			0.702		1.14
MHP			1		1.63
MP22			0		0.00
MP8			0		0.00
Ca ₃ PO ₄			0.02		0.00
Ca ₅ PO ₄ OH			0.00		0.00
Ca ₈ HPO ₄ H ₂ O			0.00		0.00
CaCO ₃			3.80		0.00
CaHPO ₄			150.97		0.00
CaMg ₃ CO ₃			0.00		0.00
CaMgCO ₃			18.75		0.00

* Values from Literature

Table 3-4. Recovery of nitrogen and phosphorus from the centrate

Parameters	Untreated Centrate	Step 1	After Step 1	After Step 2	After Step 2	Step 3	After Step 3	Step 4	After Step 4
NH ₄ ⁺ -N, mg/L	588.44		439.9	1	160		131.4		45
Phosphorus, mg/L	88.97		2.8	.4	46	100	14.69	84	4.5
MgCl ₂ .6H ₂ O added, g/L	0	1.1	-	4	-	1.05	-	1.5	-
pH	7.7		8.4	6.7	8.4		8.4	-	8.4

Table 3-5. Sequential batch operation: Process details

Parameter	Description
Raw Material	Centrate in a Secondary Wastewater Treatment Plant
Struvite Production Potential from Centrate	Depends on N and/or P Removal
Mode of Operation	Sequential Batch
Harvesting	Every Batch
Reactor Type	Conical Bottom Batch Reactor
Total Residence Time	60 min
Reaction Time	30 min
Settling Time	30 min
Phosphorus Recovery	99%
Ammonia Recovery	95%

Table 3-6. Struvite recovery from dairy manure

Sample	pH	NH ₄ ⁺ ppm	PO ₄ -P ppm	Ca ppm	K ppm	MgCl ₂ addition
Flushwater	7.21	740.88	50.66	140.5	357.78	
Step 1	8.7	513.25	22.35	113.3	322.1	2 g/L
Step 2	8.7	420.2	5.7	110.5	306.51	1.1 g/L

Sample	pH	NH ₄ ⁺ ppm	PO ₄ -P ppm	Ca ppm	K ppm	MgCl ₂ addition
Anaerobically Treated	6.8	1585.5	40.93	103.62	289.5	
Step 1	8.7	896	15.7	102.7	257.6	1.5 g/L
Step 2	8.7	782.6	4.5	94.56	242.57	1 g/L

Sample	pH	NH ₄ ⁺ ppm	PO ₄ -P ppm	Ca ppm	K ppm	MgCl ₂ addition
Aerobically Treated	7.55	497.7	30.51	106.22	303.89	
Step 1	8.7	385.6	9.74	90.47	257.6	1.3 g/L
Step 2	8.7	358.78	2.4	85.47	239.13	0.8 g/L

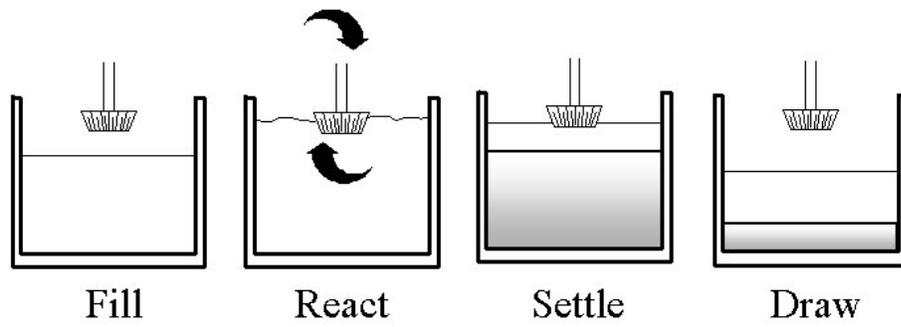


Figure 3-1. Sequencing batch reactor (SBR) process.

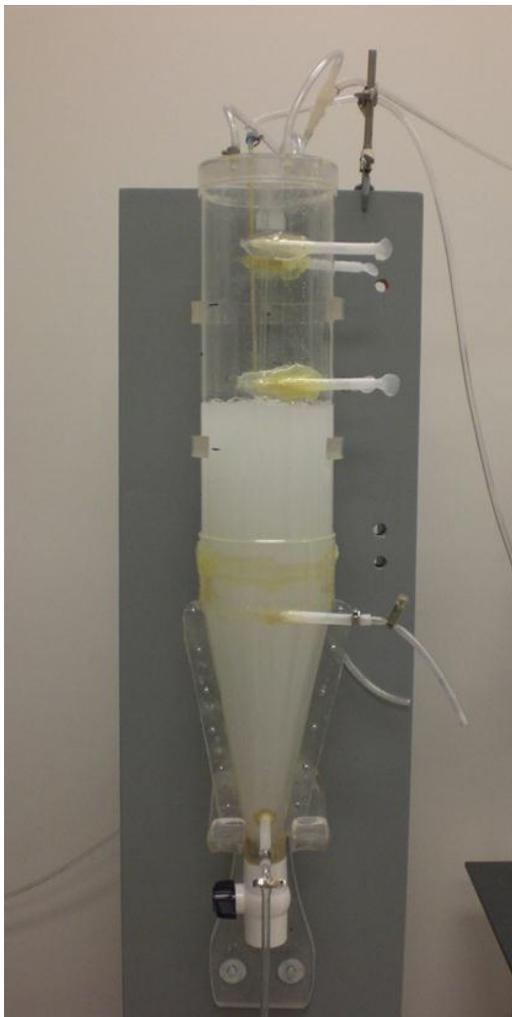


Figure 3-2. Sequential batch reactor for struvite precipitation.

XRD Struvite Samples

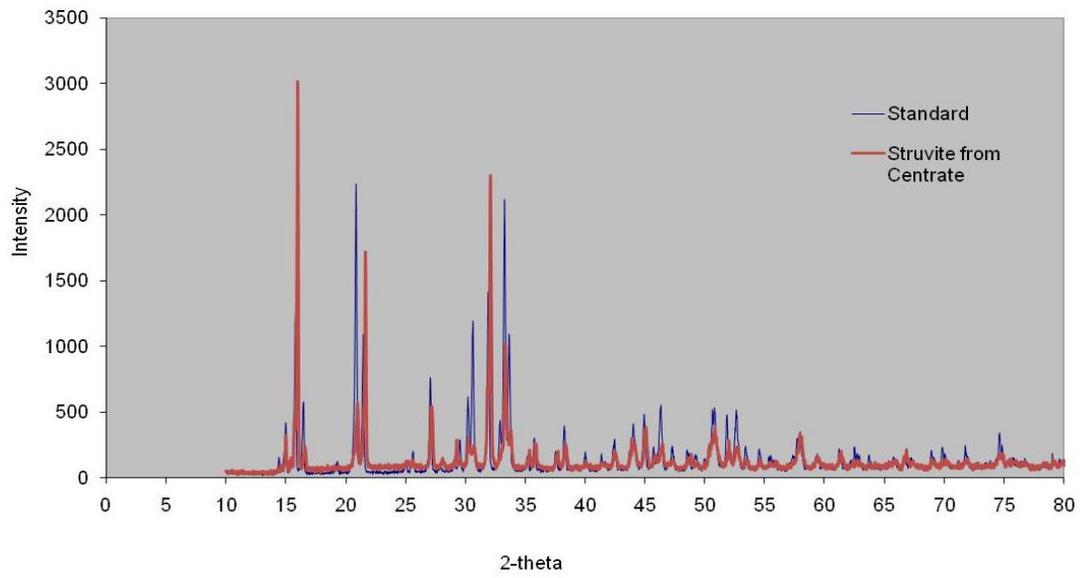


Figure 3-3. X-ray diffraction patterns for struvite produced from centrate.

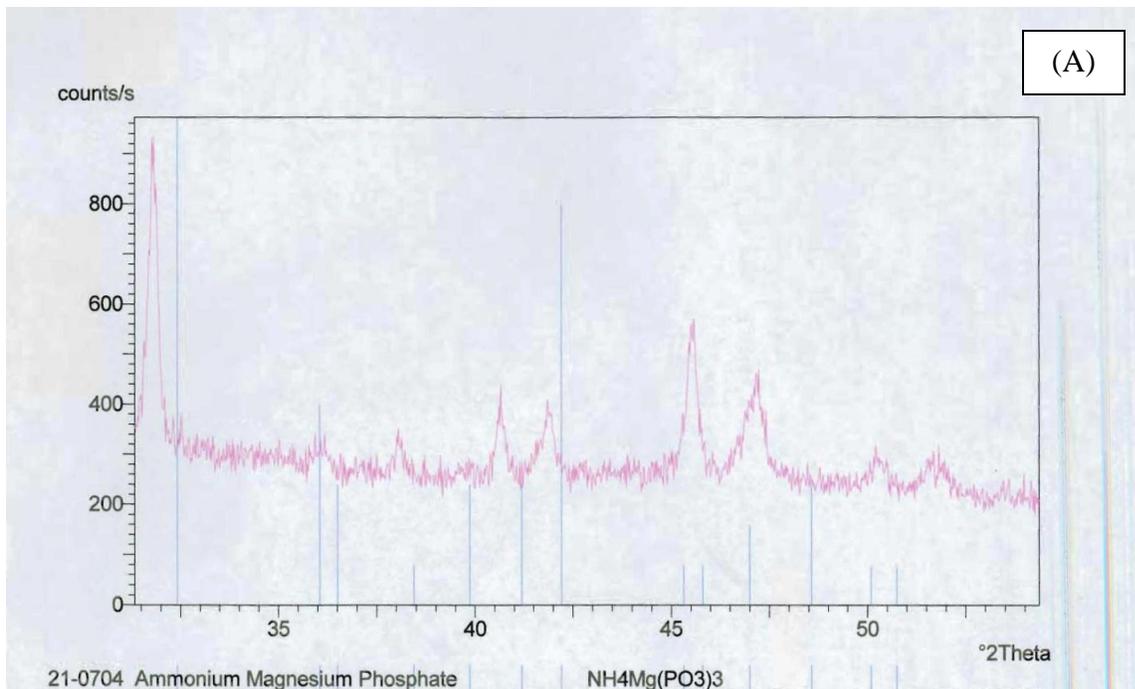


Figure 3-4. A). X-ray diffraction patterns for struvite from dairy manure

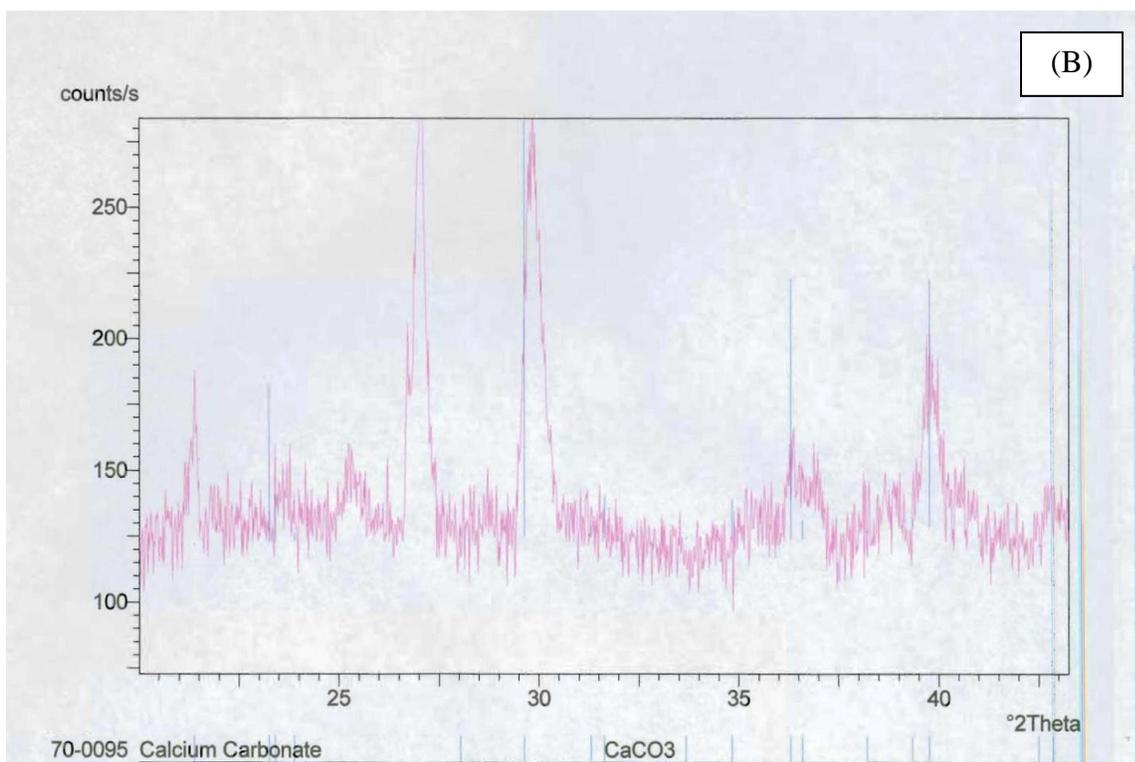


Figure 3-4. B) X-ray diffraction patterns for struvite from dairy manure showing presence of CaCO₃.

Figure 3-4. X-ray diffraction patterns for struvite. A) From dairy manure. B) Struvite from dairy manure showing presence of CaCO₃.

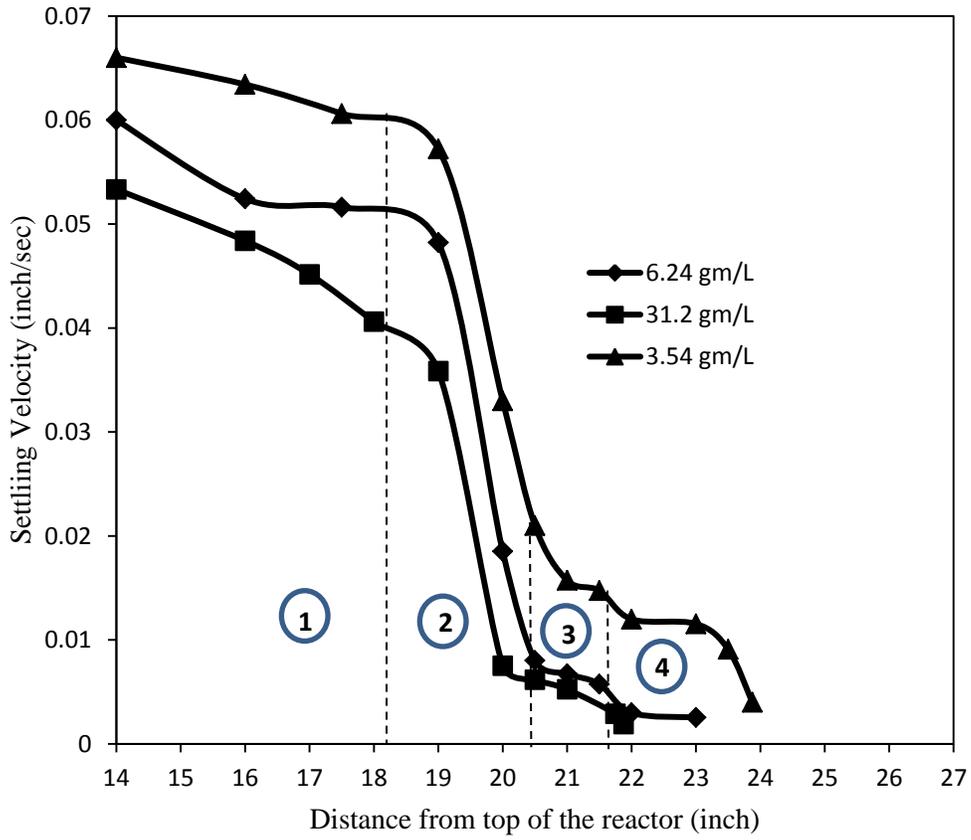


Figure 3-5. Settleability of solids in struvite formation.

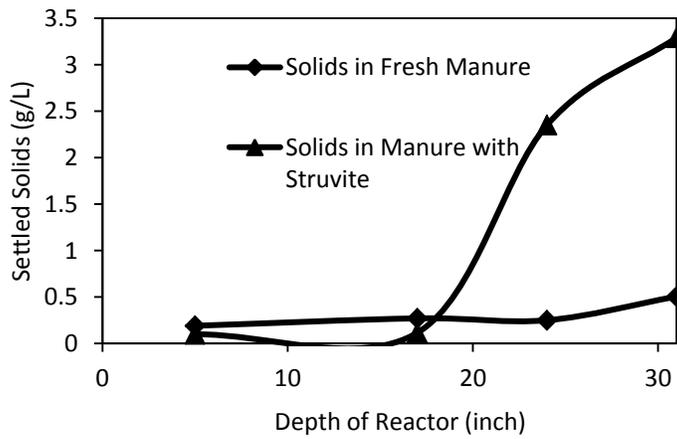


Figure 3-6. Solids settling in an SBR with dairy manure: settling time = 15 min.

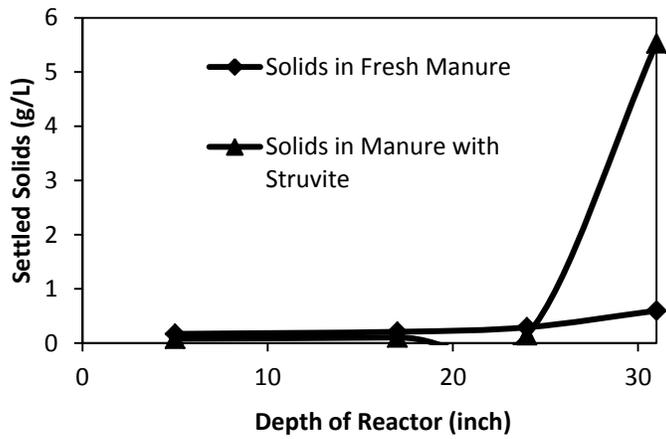


Figure 3-7. Solids settling in an SBR with dairy manure: settling time = 30 min.

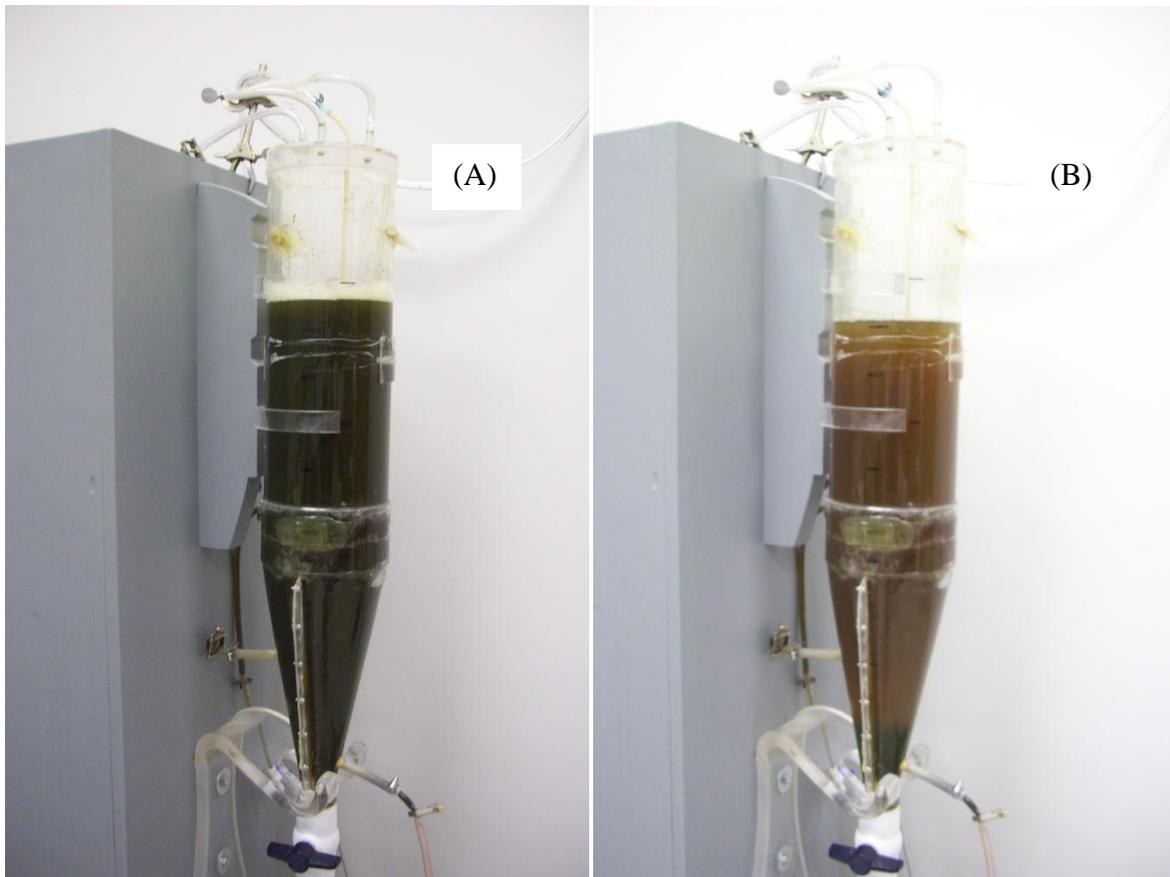


Figure 3-8. Struvite settling. A) Raw dairy manure. B) Settled solids after struvite precipitation.

CHAPTER 4 DEVELOPMENT OF PRODUCT FORMULATION TECHNIQUES USING STRUVITE SOLIDS

4.1 Struvite as a Fertilizer

The fertilizer industry has made a significant contribution to the agricultural sector by raising the fruitfulness of agricultural products by 50% and the efficiency on vegetal production. Research shows that the expenses for fertilizer result in 10.5 times more profit at harvest. The main reason for fertilizer application is to supply elementary needs of agricultural plants during their growth, for instance, nitrogen, phosphorus, potassium, calcium, magnesium, and sulphur. Therefore, the selection of an appropriate fertilizer should be based on the soil type and composition.

The potential hazards of fertilizers to the environment have results in stringent limitation to their use. About half of the applied fertilizers, depending on the method of application and soil condition, are lost to the environment, which results in the contamination of water (Salman, 1989; Salman et al., 1989). Use of conventional fertilizers may lead to concentration levels that are too high for effective action. A high concentration may produce undesirable side effects either in the targeted area, which could lead to crop damage, or in the surrounding environment (El-Refaie and Sakran, 1996). Slow-release fertilizers demonstrate many advantages over the conventional types: 1) decreased rate of removal of the fertilizers from the soil by rain or irrigation water; 2) sustained supply of minerals for a prolonged time; 3) increased efficiency of the fertilizer; 4) lower frequency of application in accordance with normal crop requirement; 5) minimized potential negative effects associated with over dosage; and 6) reduced toxicity (Byung-Su et al., (1996). Despite the advantages of slow and controlled release fertilizers, only about 0.15% of total fertilizer consumption is such products. This is mainly due to the high costs and lack of proper legislation in most parts of the world to restrict the use of soluble fertilizers.

Slow-release fertilizers may be more expensive than soluble types, but their benefits outweigh their disadvantages. Following advantages are identified with slow-release fertilizers:

1. Fertilizer burn is not a problem with slow-release fertilizers even at high rates of application.
2. Fertilizers are released at a slower rate throughout the season; plants are able to take up most of the fertilizers without waste by leaching.
3. Less frequent application is required.
4. Uniform particle size allows easier and precise mechanical distribution.
5. Flexibility of release periods last from 40 to 360 days at 25° C.
6. Reduced capital and labor outlay in horticultural crop production
7. Reduced nutrient loss via leaching and run-off.
8. Reduced seed or seedling damage from high local concentrations of salts.
9. Reduced leaf burn from heavy rates of surface-applied fertilizers.
10. Improved storage and handling properties of fertilizer materials.
11. Product differentiation resulting in improved market potential.

An augmentation has occurred worldwide on production of fertilizers containing phosphate, with an increasing demand for phosphate rock by 1.5% each year (Steén, 1998). About 85% of the phosphate is used for the production of fertilizer, with 7 billion tons of phosphate rocks as P_2O_5 remaining in reserves. Considering the 40 million tons of phosphorus as P_2O_5 consumption each year, the available resources of phosphorus are expected to be exhausted in 100 years. Therefore, finding a cheap method to obtain phosphate is critical. Considering the importance of fertilizer usage and existence of limited resources for its production, especially phosphorus with no substitute in nature, a technology, which has been developed for the recovery of the materials from waste, can provide a break through solution. One of the recent innovations is production and recovery of struvite ($MgNH_4PO_4 \cdot 6H_2O$) from waste. If the

formation of struvite is controlled, then it can be beneficial since its precipitation removes NH_4^+ -N and PO_4^{3-} -P from the water and the precipitate has the potential use as a fertilizer.

To date, struvite has been commercialized only in Japan as a fertilizer for growing rice and vegetables (Ueno and Fujii, 2001). Shu et al. (2006) presented the reasons why struvite is not widely applied as a fertilizer, why it has limited availability to farmers, and why its applicability and benefits are not known. At one point in time, W.R. Grace & Co., a fertilizer company, produced struvite from its individual components. However, this form of production was found to be too costly for the value of the product. Beal et al. (1999) estimated a value of \$206 per dry ton of struvite, based on the nutrient value. Typically, the following characteristics are desired for struvite or a struvite-blended product for it to sell to a wider range of fertilizer customers:

- High purity
- Multiple nutrient in a single pellet
- Lower weight and transportation cost
- Long shelf life
- Concentrated, granular, non-sludgy and non-odorous pellets
- Free of pathogens from wastewater
- Obtained from an organic source—not dependent on natural gas or open pit mining—and the raw material is free or government subsidized

4.1.1 Recovery of Ammonia from Wastewater

Ammonium removal from wastewater has become increasingly important for the worldwide emphasis on the eutrophication problem. Although many methods, such as biological nitrification/denitrification process, air stripping, and breakpoint reaction, have been successfully applied for removing ammonium from wastewater, treatment of wastewater containing medium

concentrations of ammonium (hundreds mg/l to thousands mg/l) has always been a big challenge.

Ammonia in industrial wastewater systems enters the plant. Additional ammonia is released in the aerobic or anaerobic digester as it reduces sludge volumes. This ammonia is concentrated in centrate or filtrate streams as the sludge is separated and consolidated in the filter press or centrifuge. Many industrial applications use ammonia as a part of the process chemistry, thus ammonia finds its way into the industrial wastewater as a contaminant. Typically, 40% to 50% of the total nitrogen in a municipal wastewater treatment plant is found as ammonia in centrate or filtrate streams. The ammonia removal and recovery process usually consists of a system that combines flash vacuum distillation with ion exchange to remove 90% of the ammonia in these streams at a much lower cost than traditional biological removal systems. Initially, the ammonia in industrial wastewater is conditioned so that neither suspended solids nor precipitates can reach the ammonia removal systems. Influent (with 300 ppm ammonia-nitrogen or less) is then input to an industrial grade ion exchange resin, which selectively adsorbs the ammonia. The adsorption columns are regenerated using either a brine or sulfuric acid. The regeneration solution is used repeatedly in which the ammonia concentration builds up to several thousand ppm. The spent ammonia-laden regeneration solution is stripped of ammonia to produce a commercial-grade (about 40%) solution of ammonium sulfate.

Ammonia stripping is possible both for full-scale wastewater treatment and nitrogen-rich liquids. Norway's largest wastewater treatment plant VEAS, located in Oslo, uses a closed loop ammonia stripping process on the filtrate from presses for sludge with great success. It then sells the ammonium-nitrate to a fertilizer manufacturer. Struvite can be re-utilized to remove ammonium from wastewater after ammonia gas is released from struvite in a heated alkali

solution. Struvite is transformed to MgHPO_4 by releasing ammonia under an acidic condition.

The reaction can be written as follows:



At a higher pH, however, MgHPO_4 reacts with ammonium ions to give struvite again.

Zhang et al. (2004) developed this process to solve the nitrogen removal problems by recovering ammonium, using acid and repeatedly using struvite residues. Ammonium was efficiently released from struvite with a low N/P ratio at a $\text{pH} < 5.0$ and temperature $> 40^\circ\text{C}$. Struvite was mainly transformed to $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ in acid solutions, which could be used for ammonium removal again. A novel approach to recover ammonia with potassium magnesium sulfate or langbeinite (commonly known as KMAG) was utilized in the present study. Experiments on additional ammonia recovery after struvite precipitation from synthetic solution are presented here in this section.

4.1.2 Uses of Struvite

The agronomic properties of struvite as a fertilizer have been widely discussed. It represents a highly effective source of nutrients (phosphorus, nitrogen, and magnesium) for plants (Li and Zhao, 2003). Struvite was also found to be as efficient as mono calcium phosphates (MCP) (Johnston and Richards, 2003). Struvite's low solubility in water, which is 0.018g/100ml at 25°C (Bridger et al., 1961), also presents the advantage to prolong the release of nutrients during the growing season (Gatterell et al., 2000) without danger of burning the roots of treated crops. In pure form, struvite crystals contain 5.7% elemental N, 12.6% elemental P, and 0% elemental K. Although the value of a natural 6-29-0 product is expected to be high, struvite is not currently a common commercial product that has a well-defined market value. Struvite is a nutritional soil supplement that prolongs the effectiveness of commercial fertilizers applied in

turf, horticultural or crop application. This quality saves time and labor costs in field application of nutrients. One application can last up to eight months.

The most obvious use of struvite is as a raw material for the fertilizer industry (Gaterell et al., 2000). Struvite can be used as a material in fire-resistant panels and in cement (Sarkar, 1990; Schuiling and Andrade, 1999). If cheap production methods are developed, it could be used in detergents, cosmetics, and animal feed, all of which use phosphates (Gaterell et al., 2000). The most promising application is as a slow-release fertilizer that can be applied in a single high dose without damage to growing plants. The plants suggested are ornamentals, vegetables, forest out-plantings, turf, orchard trees, and potted plants (Munch and Barr, 2001; Li and Zhao, 2003; Johnston and Richards, 2003). Highly soluble orthophosphate, serving as the initial phosphorus supply for establishing container plants, could be used together with struvite in a mixed fertilizer product. Struvite could also replace the major fertilizer diammonium phosphate, which is produced by neutralizing phosphoric acid with ammonia.

Mixing struvite with phosphoric acid might even yield a superior fertilizer: part slow-release $MgHPO_4$ and part fast release, highly soluble ammonium phosphate $(NH_4)_2HPO_4$. This might be considerably more cost-effective than commonly used diammonium phosphate fertilizers. Another possible product is untreated granular struvite that can be mixed with peat to serve as a lightweight potting mix (Gaterell et al., 2000). High solubility is not an asset in many fertilizer applications, as in grasslands and forests, where fertilizer is applied once in several years. The presence of magnesium in struvite makes it attractive as an alternative to contemporary fertilizers for crops, such as sugar beets that require magnesium (Gaterell et al., 2000). The phosphate industry uses rock phosphate for detergents, food, and cosmetics by applying a high-energy, high-temperature industrial process to purify the phosphate. Struvite will

not likely be used in the short term because struvite purification technology is unknown. Small amounts of phosphate is needed by these industries, as well as well-known rock phosphate purification technology. However, as high-quality rock phosphate increases in price, and the industry is forced to use low-quality rock phosphate, pressure will increase to develop purification methods for struvite.

Markets for struvite also include the natural foods and organic industry, as well as backyard gardeners interested in environmentally friendly products. The largest potential bulk market for struvite is the turf industry. Turf requires a tremendous amount of magnesium and supplemental zinc and copper in addition to nitrogen, phosphorus, and potassium. The turf grass industry is concentrated primarily in the metropolitan areas. Fertilizer companies use struvite as an additive, and it is mixed with other inorganic and organic materials to adjust the amount of nitrogen, phosphoric acid, and potassium. Two approaches generate revenue from the recovery of struvite. The first approach is to produce a relatively pure crystal and sell it to a fertilizer company or as a stand-alone product. The second approach is to blend struvite with harvested solid material and reap the benefit in terms of a higher price for the blended product.

4.2 Objectives

4.2.1 Co-crystallization of Struvite with KMAG

Potassium magnesium sulphate (KMAG) is an excellent source of potassium, magnesium, and sulfur for bulk-blended fertilizers. It is a naturally occurring mineral known as langbeinite, which has 22% K_2O , 11% Mg (18% MgO), and 22% S. Potassium magnesium sulphate is totally water soluble, providing potassium, magnesium, and sulfur in a form readily absorbed by plants. Because of its crystalline nature, KMAG dissolves gradually throughout the growing season, providing a continuous source of nutrients. Potassium, magnesium, and sulfur are basic nutrients essential for plant growth and vital to profitable crop production with nitrogen

and phosphorus. These nutrients are continually removed from the soil by high-yield crop production and, in the case of sulfur and magnesium, are not replaced by many of today's high-analysis fertilizers. Potassium is required for the uptake of nitrogen and synthesis of protein and starch. They also help activate more than 60 enzymes, making them available to stimulate other chemical processes within the plant. Adequate potassium is essential for fruit formation, optimum yields, and high quality. Sulfur activates a number of enzymes, is vital to the formation of amino acids, is crucial in the production of protein, and is especially important to plants with high oil content. Struvite was utilized in this study to produce a fertilizer product having multiple nutrients with a slow-release property using KMAG.

4.2.2 Study Absorption of Ammonia in Acidic KMAG Solution

This researcher explored the possibility of ammonia stripping and consequent absorption in acidic KMAG solution. This would give a product rich in nitrogen with other nutrients, such as potassium, magnesium, and sulfur, which can be further pelletized with struvite. This would help meet the nitrogen limits along with phosphorus in an integrated struvite process. With ammonia stripping, the wastewater treatment plant would not rely on an external source of phosphorus for additional nitrogen recovery as struvite.

4.2.3 Investigate Use of Agglomerates to Make Struvite Pellets

A commonly used cationic high molecular weight polymer used in wastewater treatment plant would help in struvite agglomeration to reduce moisture content in recovered solids, hence reducing the energy requirement for drying the product. The polymers are used to flocculate suspended solids, particularly for non-potable raw water clarification, primary and secondary effluent clarification, oily wastewater clarification, and so forth. Sodium alginate, which is the sodium salt of alginic acid, was also used for agglomeration of struvite solids. The effect of alginate was assessed on struvite agglomerative properties to produce strong pellets, which

withstand the rigors of storage, handling, packaging, and shipping. Sodium alginate was chosen for struvite agglomeration because of its water solubility. The calcium and magnesium salts of alginic acid do not dissolve in water. When dissolved in water, alginate has an ability to thicken the resulting solution by increasing the viscosity of aqueous solutions. They form gels as well as films of sodium or calcium alginate and fibers of calcium alginates.

4.3 Materials and Methods

4.3.1 Struvite Precipitation

An SBR was used for precipitation, as explained in Chapter 3. Struvite was allowed to settle for 30 min and then be recovered from the bottom of the reactor. The centrate or synthetic solution containing nitrogen, potassium, magnesium chloride, and sodium hydroxide were added from the top of the reactor. Mixing was provided by air using a sparger from the bottom of the SBR. The pH for struvite precipitation was adjusted using 10 N sodium hydroxide. Liquid samples were analyzed using calcium and magnesium probes. Struvite solids were filtered using “Ashless 41” micro-meter Whatman filter paper under vacuum. Struvite recovered from the pilot scale run, as shown in Figure 4-1(A), was also used in the crystallization experiments.

4.3.2 Preparation of KMAG Solution

Raw KMAG was obtained from “The Mosaic Company,” which suggested the chemical analysis of KMAG, as listed in Table 4-1. The fertilizer specification of KMAG was 0-0-22. The reddish brown granules of KMAG used in the present study are shown Figure 4-1 (b). For all experiments performed with KMAG, 1kg of KMAG was mixed in 1 L of deionized water. The mixing was carried out in a 2 L Erlenmeyer flask using an electric stirrer from the Arrow Engineering Co. The solution was stirred for 12 hours at room temperature. The solution was allowed to settle for 30 min and decanted. The decanted solution was filtered using Ashless 40 Whatman filter paper. The settled solids were filtered and dried at 105°C in an oven. This

researcher found that 40% of the weight of the raw KMAG was dissolved in water. Depending on the experimental need, KMAG was mixed multiple times in the same proportions, as mentioned earlier. The solution of KMAG was analyzed for potassium and calcium content. The concentration of potassium in the solution was found to be 64 g/L, with a standard deviation of 5.3 g/L. The calcium concentration was found to be 0.41 g/L, with a standard deviation of 0.13 g/L. Solids were analyzed by x-ray diffraction (XRD), as explained in Chapter 3. Solids under consideration as reference patterns for XRD analysis are listed in Table 4-2. These solids were chosen from the database for inorganic solids, which have a possibility of formation in the system of ionic species, which includes minerals such as magnesium, potassium, phosphorus, nitrogen, sulphur, and calcium.

4.3.3 Agglomeration of Struvite

The cationic polymer was mixed with the solution, which was subjected to struvite recovery in the SBR to study enhancement of struvite settling. Sodium alginate was used as an agglomerate for settled struvite. A dry weight of 1% of the sodium alginate was mixed with struvite in a 500 ml beaker, which formed a paste of struvite solids. The mixture was extruded in the form of strings using a clay pottery ceramics extruder. Extruded solids were dried at 105°C in an oven for 8 hours. Solids were crushed with size distribution carried out using an Octagon2000 shaker with USA Standard Sieves.

4.3.4 Crystallization of Struvite with KMAG

A conical bottom separator was used as a crystallizer as shown in Figure 4-2. A schematic of crystallization is shown in Figure 4-3. A thermometer was inserted from the top of the crystallizer. Struvite solids tend to settle at the conical bottom. Solids were fluidized by feeding recirculated liquid to the bottom of the crystallizer. The flow rate was maintained to make sure that solids are not carried in the feed to the recirculation line to the oil bath. The

temperature was maintained at 85°C unless otherwise mentioned using an oil bath. The supernatant solution was recirculated using a peristaltic pump through the oil bath. Air was allowed to flow on top of the crystallizer to enhance evaporation. Crystallization was carried out using evaporation, which concentrated the solution. Crystallization studies were performed with the following combinations of struvite and KMAG:

1. Struvite from the pilot plant and concentrated solution of KMAG
2. Struvite from the pilot plant and raw KMAG granules
3. Struvite produced from synthetic solutions and concentrated solution of KMAG
4. Synthetic struvite and concentrated solution of KMAG in acidic conditions

4.3.5 Ammonia Removal from Centrate and Synthetic Solution

Ammonia removal from solutions was carried out using a continuously stirred tank vessel. The ammonia stripped out was captured in an array of absorbers, as shown Figure 4-4. A pH of the solution was adjusted to 10.0, using 5N NaOH. Air was allowed to flow at the bottom of stirred tank through a sparger. In the first absorber, the acidic KMAG solution was used followed by another absorber with diluted sulphuric acid.

4.4 Results and Discussion

4.4.1 Effect of the Polymer Addition on Struvite Filtration

Polymers are widely used to remove fines in wastewater treatment operations. The polymer named polydiallyldimethylammoniumchloride (polyDADMAC) was used by Le Corre et al. (2007) specifically to remove struvite fines. This researcher thought that the polymer would agglomerate struvite and improve settling properties, as well as improve filtration. Experiments were carried in the laboratory to study the effect of the polymer. Struvite was produced by mixing chemicals listed in Table 4-3. The proportions of these chemicals were chosen from the model predictions to get about 220 g of struvite. The struvite produced was found to settle in 5 min after which it was separated and filtered. The time of filtration was kept for 10 min. As

shown in Table 4-4, this researcher found that the polymer improves settling. The polymer needs to be added after 30 min of struvite reaction to see the effect of the polymer. The polymer, when added after 5 and 10 min from commencement of the reaction, was not found to give an agglomeration effect. The solid content after vacuum filtration was found to be 35% consistently. The settling of struvite solids was improved by the polymer. After 30 min of settling, the solids content increased with the polymer addition, to 16% solids as compared to solids content without polymer addition which was 12% solids after settling.

4.4.2 Crystallization of Struvite with KMAG

4.4.2.1 Batch Crystallization

Crystallization under acidic conditions. Struvite produced from synthetic solutions was used in this experiment. In a 250 ml beaker, 6 g of wet struvite and 100 ml of KMAG solution were mixed under acidic conditions at a pH of 2.2, which completely dissolved struvite. Wet struvite solids were found to have 67% moisture before mixing with the KMAG solution. Crystallization was carried out at 55°C in the oven. Crystal formation was observed after 28 hr. The supernatant was collected by decantation and analyzed for NH_4^+ -N, phosphorus, potassium, and calcium concentrations.

Crystals were separated from the solution by decantation. A total of 41.13 g of crystals were recovered after 35 hours. A chemical analysis of the crystals was done by dissolving 5 g of air-dried crystals in 200 ml deionized water. This researcher observed that the crystals only partially dissolved. Therefore, 1 ml of 5N H_2SO_4 was added for dissolution of the remaining crystals for analysis. This solution was analyzed to estimate nitrogen and phosphorus content. Results are shown in the Table 4-5. This researcher found that crystals collected from mixing of struvite and KMAG were found to retain nitrogen and phosphorus.

Crystals were analyzed by x-ray diffraction and the results are shown in Figure 4-4. This researcher observed that formation of hannayite with Schoenite ($\text{MgK}_2(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_6$) occurred. Hannayite is $(\text{NH}_4)_2\text{Mg}_3\text{H}_4(\text{PO}_4)_4 \cdot 8(\text{H}_2\text{O})$, which contains the same minerals as in struvite. The rearrangement of minerals in struvite to hannayite could be due to the presence of higher concentrations of magnesium and hydrogen ions. Langbeinite is crystallized as schoenite in the presence of water, as shown in following equation:



Crystallization under neutral conditions. The same proportions of struvite and KMAG were used without any pH adjustment, as explained in the previous section. Mixing struvite and the KMAG solution gave a solution with a pH of 7.25. The x-ray diffraction results showed (Figure 4-6) that KMAG crystallized to schoenite ($\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), picromerite, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. This researcher found that crystallinity of KMAG was improved after crystallization. Transparent crystals of schoenite and picromerite produced from raw KMAG are shown in Figure 4-1(c). In all cases in which the KMAG solution and raw KMAG were mixed with struvite made synthetically from pilot scale run, the x-ray diffraction detected a presence of struvite and schoenite in the solids, which are listed in Table 4-6 and are shown in Figures 4-7, 4-8, and 4-9. Struvite was bound to schoenite after crystallization due to the presence of the magnesium species in the solution, which acted as a binder, Struvite from the pilot plant, before the addition to KMAG solution, was in the powder form, as shown in Figure 4-1(A). A picture of a combined schoenite and struvite is shown Figure 4-1(D). Raw KMAG and struvite were also found to bind together, as shown in Figure 4-1(E). When dried solids of raw KMAG and struvite were crushed, a powder formation was observed which can be recycled for re-crystallization.

4.4.2.2 Semi-continuous Crystallization of KMAG with Struvite

The crystallization was induced by evaporation of water using the system shown in Figure 4-2. This type of crystallization is usually referred to as “concentration crystallization” where a concentration of ionic species increases continuously to supersaturation and crystallization occurs. The rate of evaporation was found to be 15 ml/hr. After 21 hours, another batch of struvite slurry and KMAG solution was added to the crystallizer. The concentration of potassium in the solution decreased with time, as shown in Figure 4-10. This can be directly related to the rate of crystallization or potassium fixation in crystals, and it was found to be 4.64 g/L-hr. The phosphorus concentration in the solution increased initially and then decreased, as shown in Figure 4-11, due to a partial struvite dissolution and re-crystallization after 6 hours. The calcium concentration did not change substantially; it was found to decrease from 270.4 mg/L to 239 mg/L continuously over 33 hours. The crystal formation was not visually detected. Samples were taken at different times, as shown in Figures 4-10 and 4-11. To verify the crystal formation, solids were collected after a decrease in potassium concentration from 46 g/L to 10.45 g/L. This researcher found that nitrogen and phosphorus were retained in solids along with potassium. These solids can be used as 4.5 – 9 – 12 fertilizer. The x-ray diffraction confirmed the presence of potassium ammonium hydrogen phosphate, schoenite, picromerite, and ammonium sulphate, as shown in Figures 4-12(A), (B), and (C).

4.4.3 Absorption of Ammonia in KMAG

In the present study, ammonia was stripped out from the synthetic solution with an initial concentration of 650 mg/L, which resembled the concentration in the centrate. It was observed that under acidic conditions, stripped ammonia was completely absorbed in the first receiver. In the second receiver, the concentration of ammonia was found to be negligible. The rate of ammonia stripping was estimated to be 12.6 mg/L-hr. The results of this experiment are

presented in Table 4-7. This researcher observed that a total ammonia-N amount of 1296.72 mg was removed from the scrubber. The pH of the solution decreased with the ammonia removal, and the pH was adjusted to a value of 10, whenever necessary. The KMAG was found to crystallize in the first receiver over a period of 6 hours. Crystals were collected and analyzed for chemical content, and they were found to contain 4.5% nitrogen, which indicated ammonia immobilization with KMAG in the crystalline form. A process flow was suggested from this study for absorption of ammonia, as shown in Figure 4-13.

Experiments on ammonia stripping with high initial ammonia concentration were performed. The ammonia removal rate in the previous run was found to be slow. Ammonia concentration in the reactor was increased to observe the rate of ammonia removal. Experiments were performed with the following conditions:

Starting NH_4^+ -N in stripper = 15 g

NH_4^+ -N in stripper after 2 days = 6.21 g

Total NH_4 -N lost from stripper = 8.79 g

After about 2 hours, in the acidic KMAG, the concentration of ammonia-N was found to be 1.444 g/L. A total 3.61 gm of ammonia-N was recovered in the KMAG solution. Some ammonia was also carried to the second receiver with 150 ml of 0.1 M sulfuric acid. In the H_2SO_4 trap, the following concentrations were observed: 3.496 mg/L of NH_4^+ -N, pH of 2.2. The solids/crystals were collected from the KMAG column to investigate nitrogen content. After dissolution, the crystals gave a concentration of NH_4^+ -N as 161.5 mg/L.

4.5 Outcomes

- A cationic polymer can be used to remove fines (struvite crystals) from the reactor. The polymer should be added after 30 min of struvite.

- The settling of struvite solids was improved by a cationic polymer commonly used in wastewater treatment plants. With polymer usage, the solids content increased from 12% to 16%.
- The KMAG was crystallized to schoenite and picromerite in the presence of water.
- Struvite was found to recrystallize with saturated KMAG to give a product rich in nitrogen, phosphorus, potassium, and magnesium.. These crystals were found to be sparingly soluble in water at a neutral pH.
- The solution of KMAG and struvite under acidic condition was crystallized to hannayite and schoenite.
- The x-ray diffraction analysis confirmed that struvite was agglomerated to KMAG.
- Calcium precipitation was not detected in the crystallization of KMAG and struvite.
- Semi-continuous crystallization of struvite with KMAG was found to produce ammonium sulphate, potassium ammonium phosphate, schoenite, and picromerite.
- Saturated KMAG was found to absorb ammonia under acidic conditions to give a solid product rich in nitrogen. Crystals formed in the saturated KMAG solution after ammonia absorption were found to retain ammonia in solids.

Table 4-1. KMAG chemical analysis

Component	Symbol	Typical (%)	Guarantee (%)
Potassium Oxide	K ₂ O	22.1	22.0 min
Potassium	K	18.3	—
Calcium	Ca	0.2	—
Sodium	Na	0.3	—
Magnesium	Mg	11.3	10.8 min
Sulfur	S	22.4	22.0 min
Chloride	Cl	1.5	2.5 max
Water Insoluble	-	1	—
Moisture (105°C)	H ₂ O	0.05	—

Table 4-2. Solids considered in x-ray diffraction analysis as standards

Solid Name	Formula	Database reference Number
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	15-241
Ammonium magnesium phosphate	$\text{NH}_4\text{Mg}(\text{PO}_3)_3$	21-704
Ammonium magnesium phosphate hydrate	$\text{NH}_4\text{Mg}_2\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$	38-203
Struvite, syn	$\text{NH}_4\text{MgPO}_4\cdot 6\text{H}_2\text{O}$	15-0762
Schoenite	$\text{MgK}_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$	74-1064
Picromerite	$\text{K}_2\text{Mg}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$	21-1400
Periclase	MgO	71-1176
Ammonium magnesium sulphate	$(\text{NH}_4)_2\text{Mg}_2(\text{SO}_4)_3$	18-110
Ammonium potassium phosphate	NH_4KPO_4	1-925
Potassium hydrogen sulphate	$\text{K}_3\text{H}_3(\text{SO}_4)_4$	17-0597
Potassium magnesium sulphate	$\text{K}_2\text{Mg}(\text{SO}_4)_2$	36-1499
Potassium phosphate	K_3PO_4	27-435
Potassium phosphate sulfate	$\text{K}_2\text{P}_2\text{S}_2\text{O}_{13}$	22-846
Potassium ammonium hydrogen phosphate	$(\text{NH}_4\text{K})_3\text{HP}_2\text{O}_7\cdot \text{H}_2\text{O}$	28-82
Potassium ammonium hydrogen sulfate	$\text{KNH}_4\text{H}_2(\text{SO}_4)_2$	20-850
Hannayite	$\text{Mg}_3(\text{NH}_4)_2\text{H}_4(\text{PO}_4)_4\cdot 8\text{H}_2\text{O}$	16-0361
Struvite	$\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$	03-0240
Ammonium calcium phosphate	$(\text{NH}_4)_2\text{Ca}_3(\text{P}_2\text{O}_7)_2\cdot 6\text{H}_2\text{O}$	44-0758
Magnesium phosphate oxide	$\text{Mg}_2\text{P}_2\text{O}_7$	01-0866
Rustamite	$\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)\text{Cl}_2(\text{OH})_2$	84-0292
Calcium carbonate	CaCO_3	70-0095
Uranyl urea aqua iodide nitrate	$\text{C}_4\text{H}_{24}\text{IO}\cdot 36\text{N}_9\cdot 64\text{O}_{11}\cdot 92\text{U}$	28-1426
2,5 dichlorotropone	$\text{C}_7\text{H}_4\text{Cl}_2\text{O}$	20-1622
N-Hydroxysuccinimide	$\text{C}_4\text{H}_5\text{NO}_3$	36-1688
Potassium magnesium phosphate	KMgPO_4	20-0685

Table 4-3. Chemical added for struvite formation for polymer effect experiments

Chemicals	Concentrations(M)
Total Mg added using $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$	0.185
Total N as NH_4Cl	0.2714
Total P as 85% H_3PO_4	0.1935

Table 4-4. Effect of the polymer addition on filtration

Weight of Polymer added (g)	Wet Weight of Struvite (g)	Dry Weight of Solids (g)	% solids
0.02	630.9	221	35.03
0.12	620.4	218	35.14
0.22	714	216	30.25
0.44	540	195	36.11

Table 4-5. Crystallization of synthetic struvite with the acidic solution of KMAG

Parameter	Supernatant after crystallization	Solution of 5g of crystals dissolved in 200 ml DI water	Crystals collected after drying	Nutrients in crystals and supernatant
Amount recovered	19 ml	--	41.13 g	-
NH ₄ ⁺ -N, mg/L	242.29	80.79	-	-
P, mg/L	471.52	287.92	-	-
K, g/L	89.2	2.9	-	-
Ca, mg/L	763.5	35	-	-
pH	6.4	4.14	-	-
Total NH ₄ ⁺ -N, mg	4.6	-	129.71	134.31
Total P, mg	8.95	-	485.52	494.47
Total K, g	1.69	-	4.77	6.46
Total Ca, mg	14.5	-	57	71.5

Table 4-6. X-ray diffraction results

Sample	Solids detected in XRD
KMAG with synthetic struvite	Schoenite [MgK ₂ (SO ₄) ₂ ·6H ₂ O], Picromerite, K ₂ Mg(SO ₄) ₂ ·6H ₂ O, Periclase (MgO)
Raw KMAG with struvite from pilot scale run	Ammonium magnesium phosphate, schonite, and picromeite
KMAG with struvite: pH adjusted to 2.2 at commencement of crystallization	Hannayite [(NH ₄) ₂ Mg ₃ H ₄ (PO ₄) ₄ ·8(H ₂ O)], Schoenite
KMAG from saturated solution	Schoenite, Picromerite
KMAG with struvite from pilot scale run	Struvite, Schoenite, Ammonium Calcium Phosphate Hydrate [(NH ₄) ₂ Ca ₃ (P ₂ O ₇) ₂ ·6H ₂ O], Magnesium Phosphate Oxide [Mg ₂ P ₂ O ₇]

Table 4-7. Absorption of ammonia in KMAG

Ammonia Scrubber, Volume- 2L						First Receiver Volume - 2.7L	
Time (hrs)	NH ₄ ⁺ -N (mg/L)	pH	pH adjusted to 10	Total NH ₄ ⁺ -N in the reactor(mg)	NH ₄ ⁺ -N stripped out (mg)	NH ₄ ⁺ -N (mg/L)	NH ₄ ⁺ -N collected (mg)
0.0	650.00	10	yes	1300.00			
1.8	471.87	9.54	yes	943.75	356.25	0.00	0.00
7.9	446.68	10.5	No	893.36	406.64	--	-
22.5	396.30	10.5	No	792.60	507.40	--	-
46.5	312.33	9.84	yes	624.66	675.34	--	-
69.6	211.57	9.18	yes	423.13	876.87	354.32	956.65
73.5	161.18	8.92	yes	322.37	977.63	354.32	956.65
93.6	144.39	8.6	yes	288.78	1011.22	404.70	1092.68
97.6	135.99	11.1	No	271.99	1028.01	438.29	1183.37
118.6	1.64	9.58	No	3.28	1296.72	471.87	1274.06

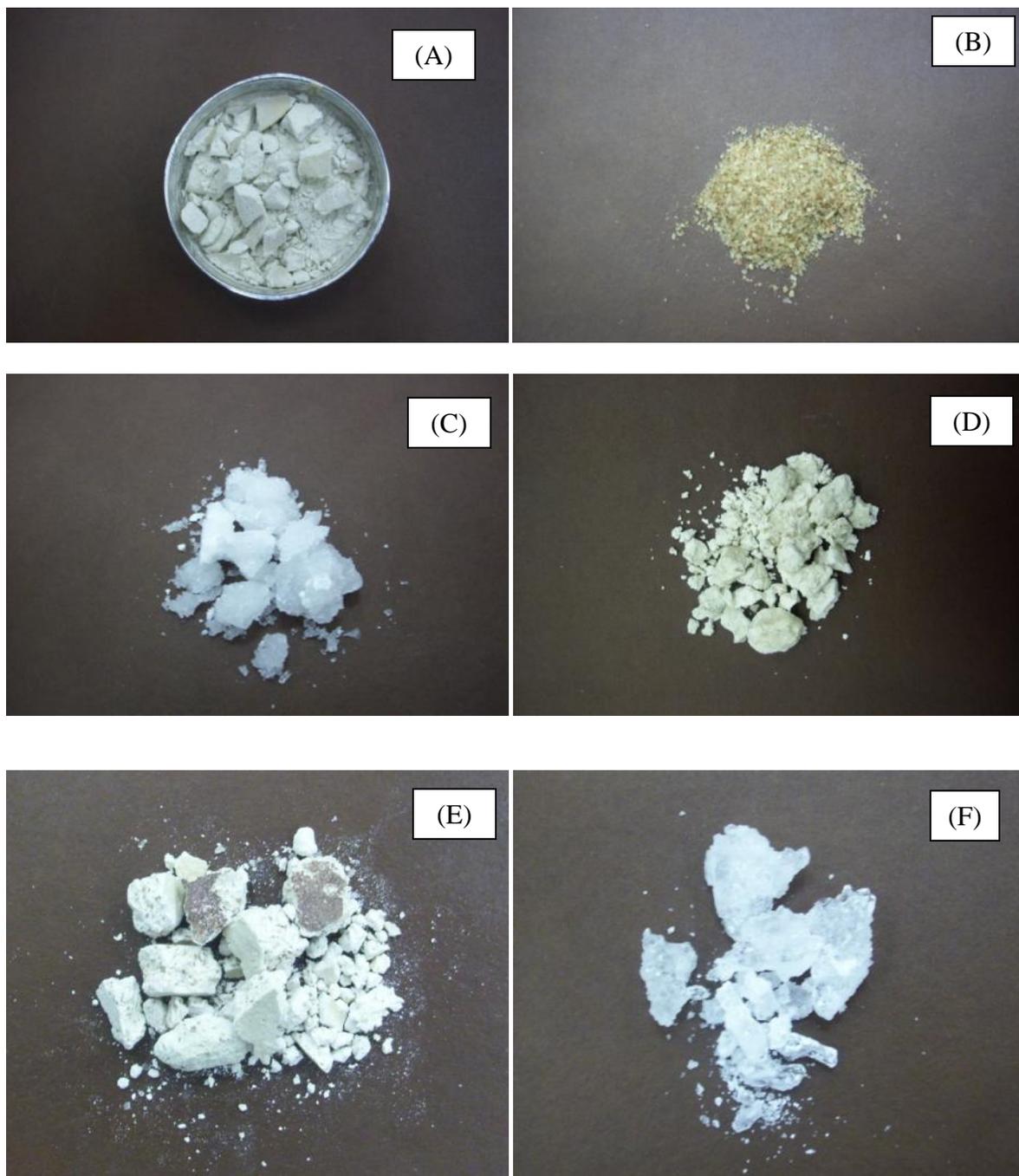


Figure 4-1. Struvite recovered from experiments. A) Struvite from the pilot plant. B) Raw KMAG. C) Crystals recovered from solution of langbeinite. D) Struvite from pilot plant crystallized in the solution of KMAG. E) Pellets from mixing struvite and raw KMAG. F) Struvite crystallized with the solution of KMAG in acidic conditions.



Figure 4-2. Continuous crystallization of KMAG with struvite.

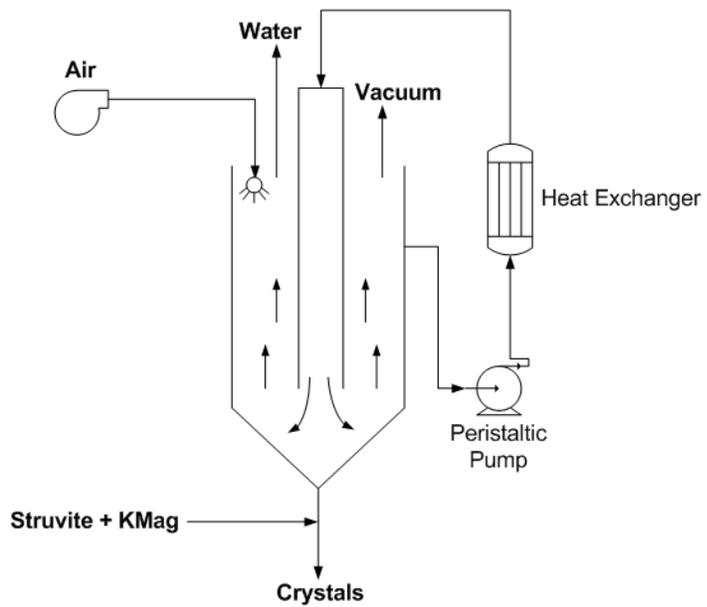


Figure 4-3. Crystallization of KMAG with struvite.



Figure 4-4. Absorption of ammonia in K MAG.

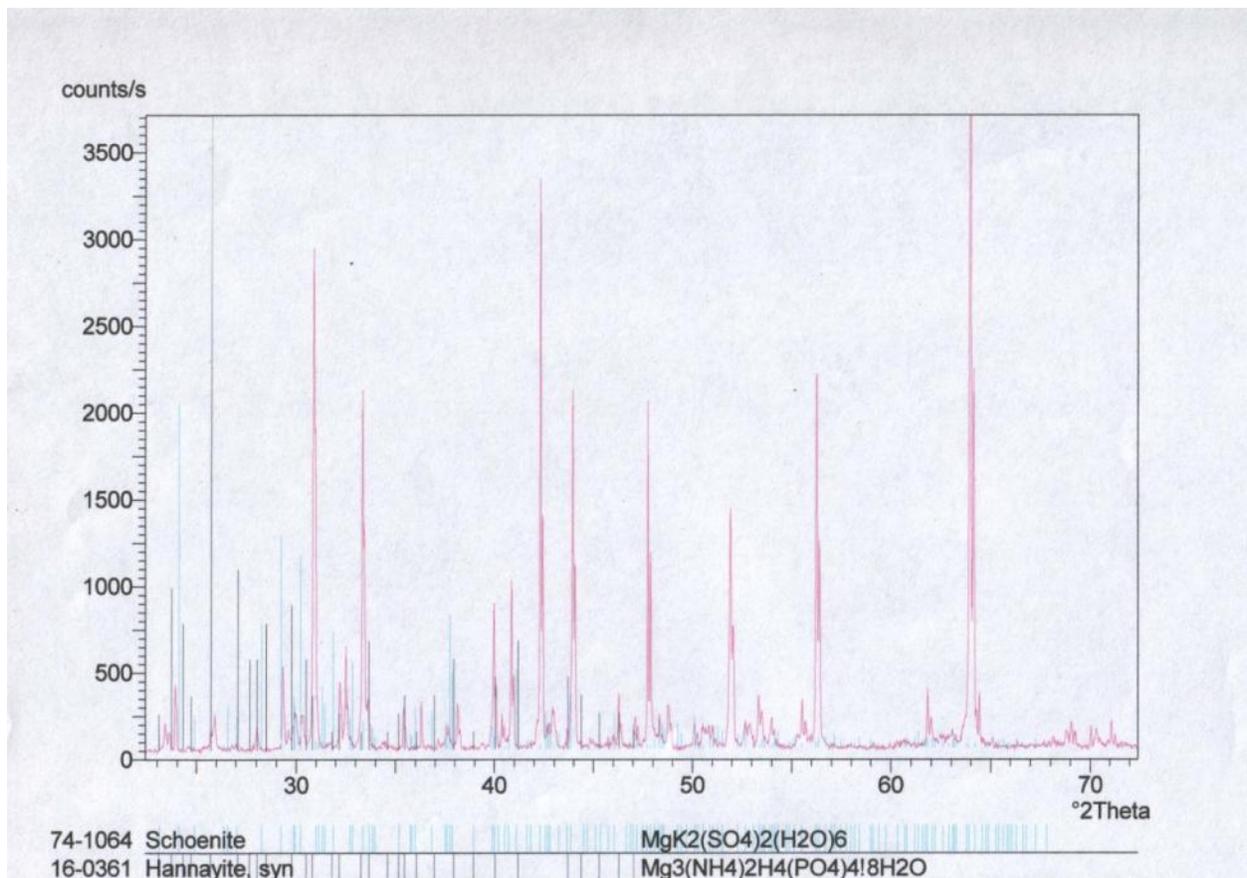


Figure 4-5. K MAG with struvite: pH adjusted to 2.2 at commencement of crystallization.

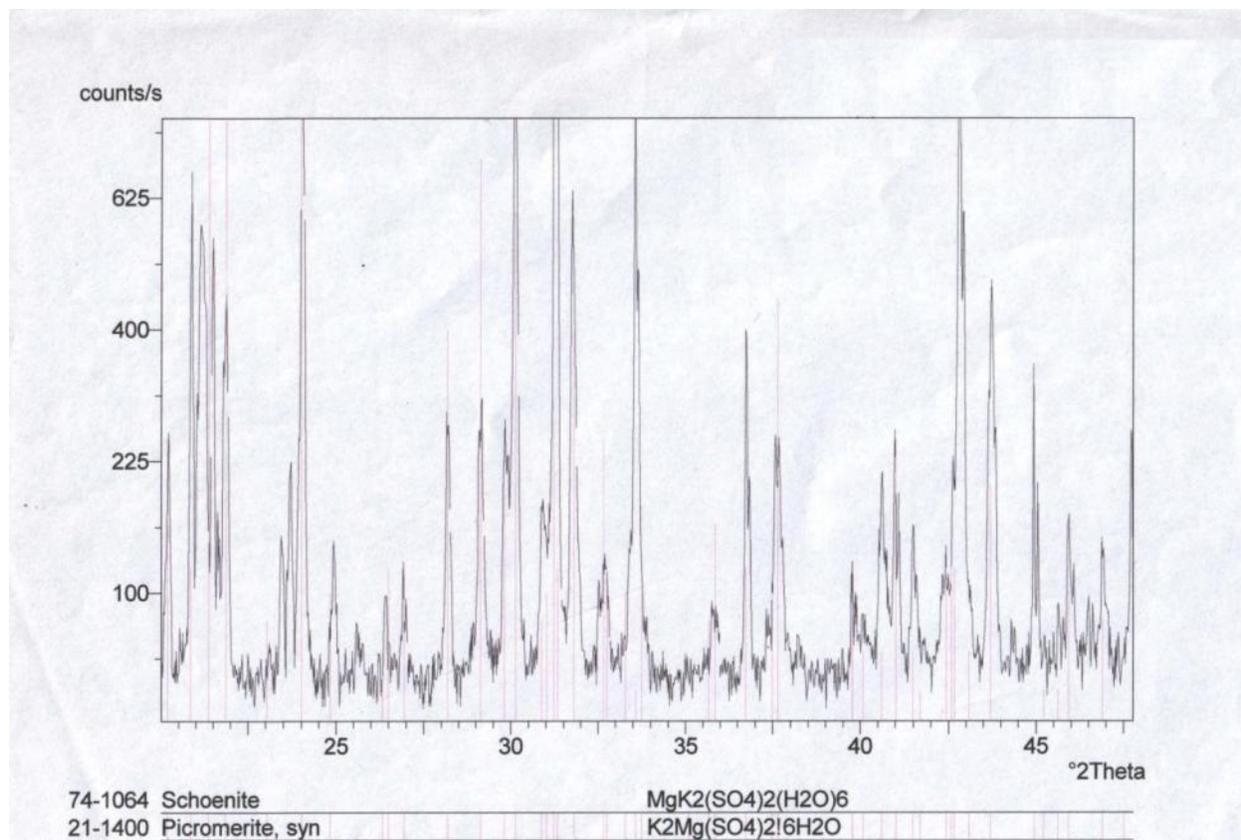
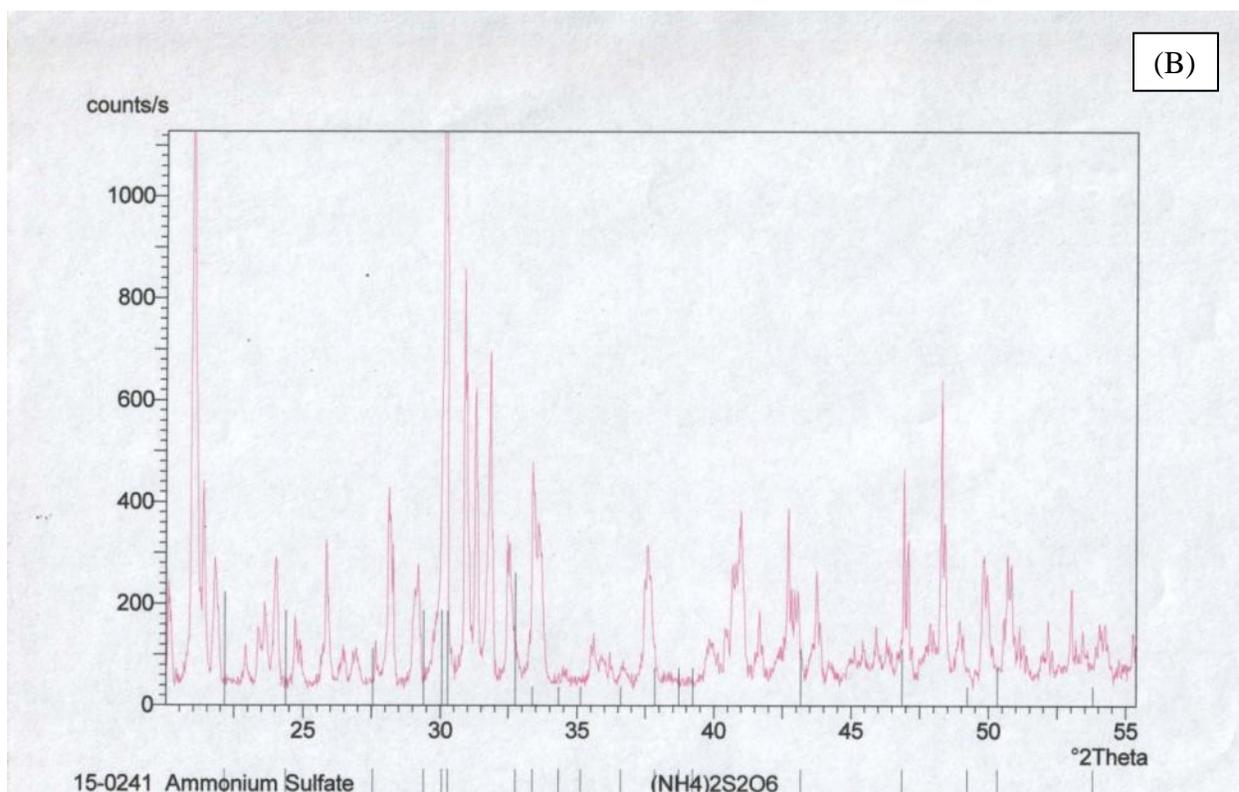
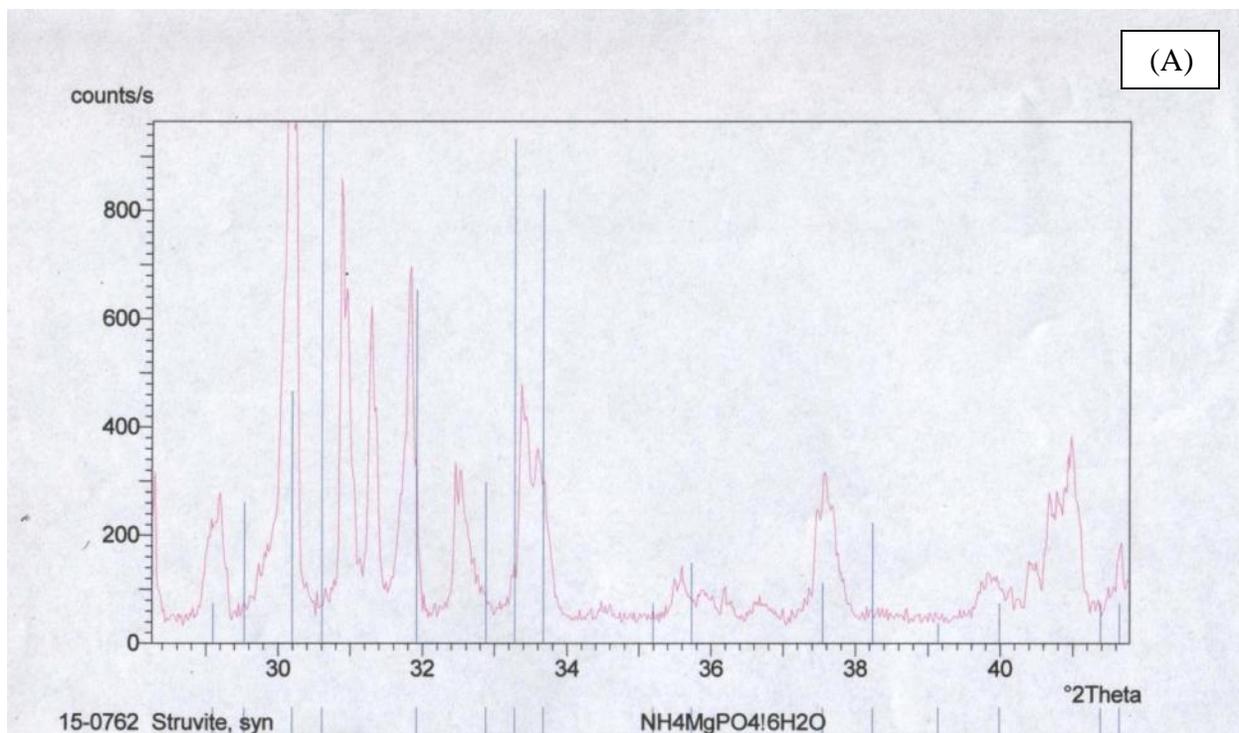
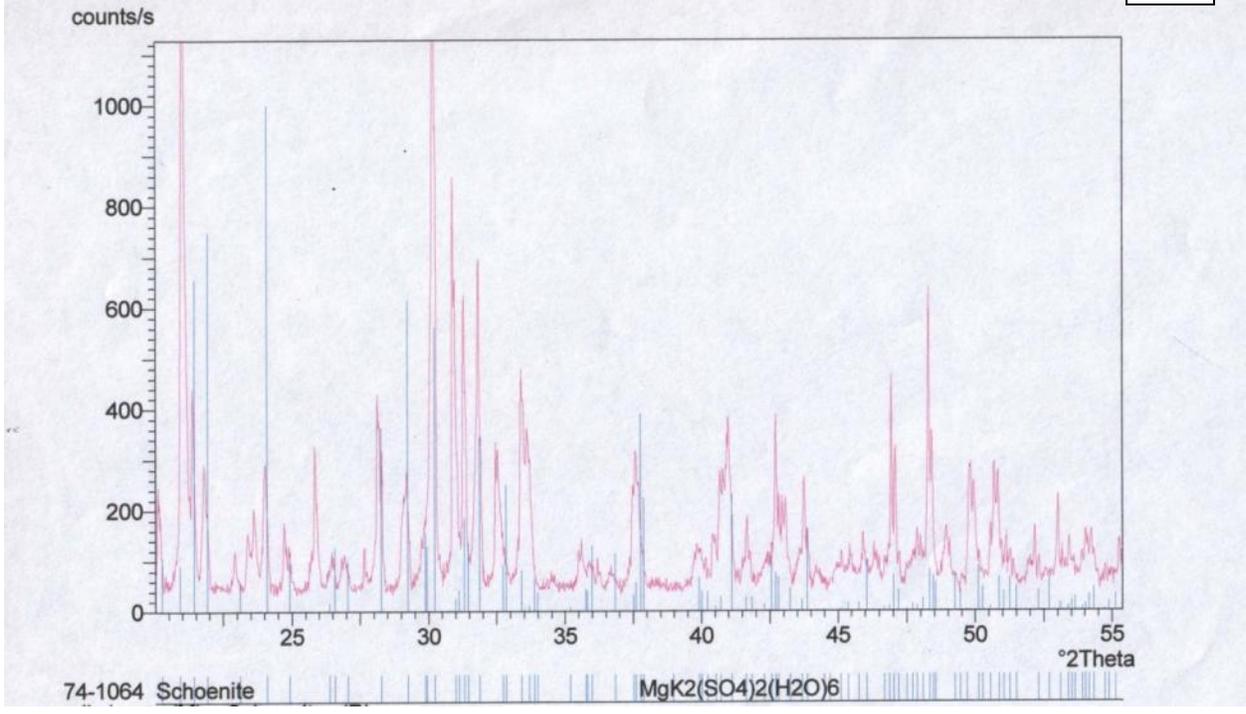


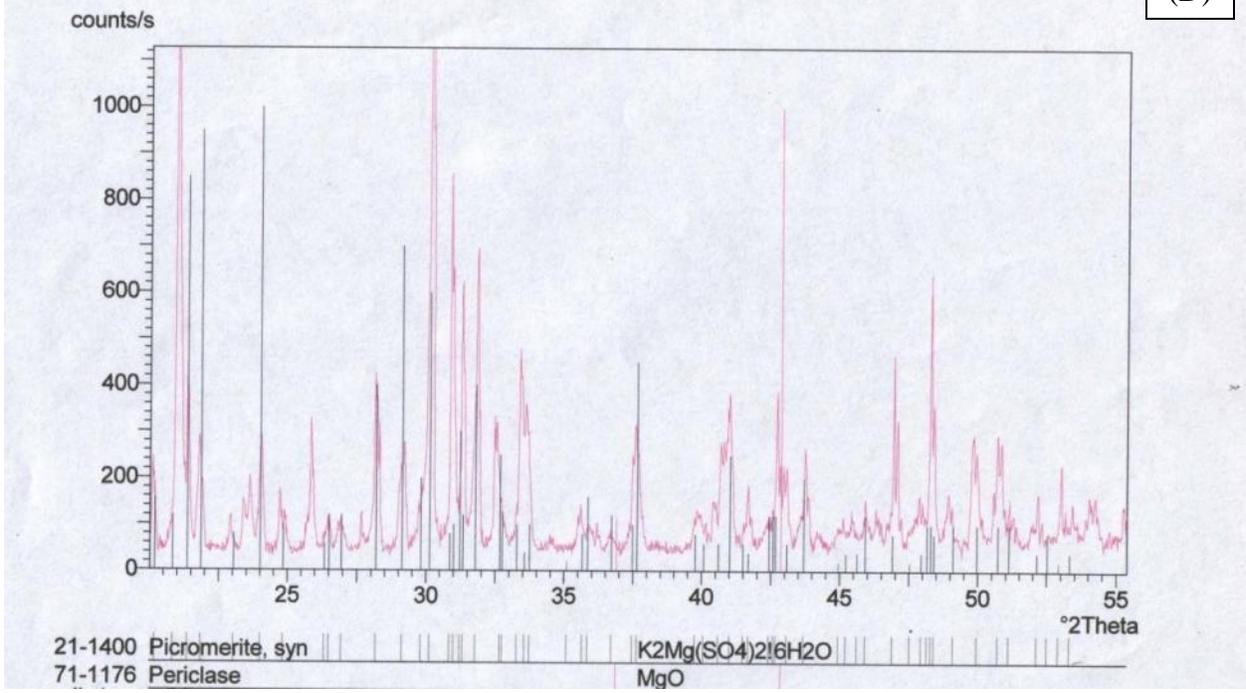
Figure 4-6. KMG from saturated solution.



(C)



(D)



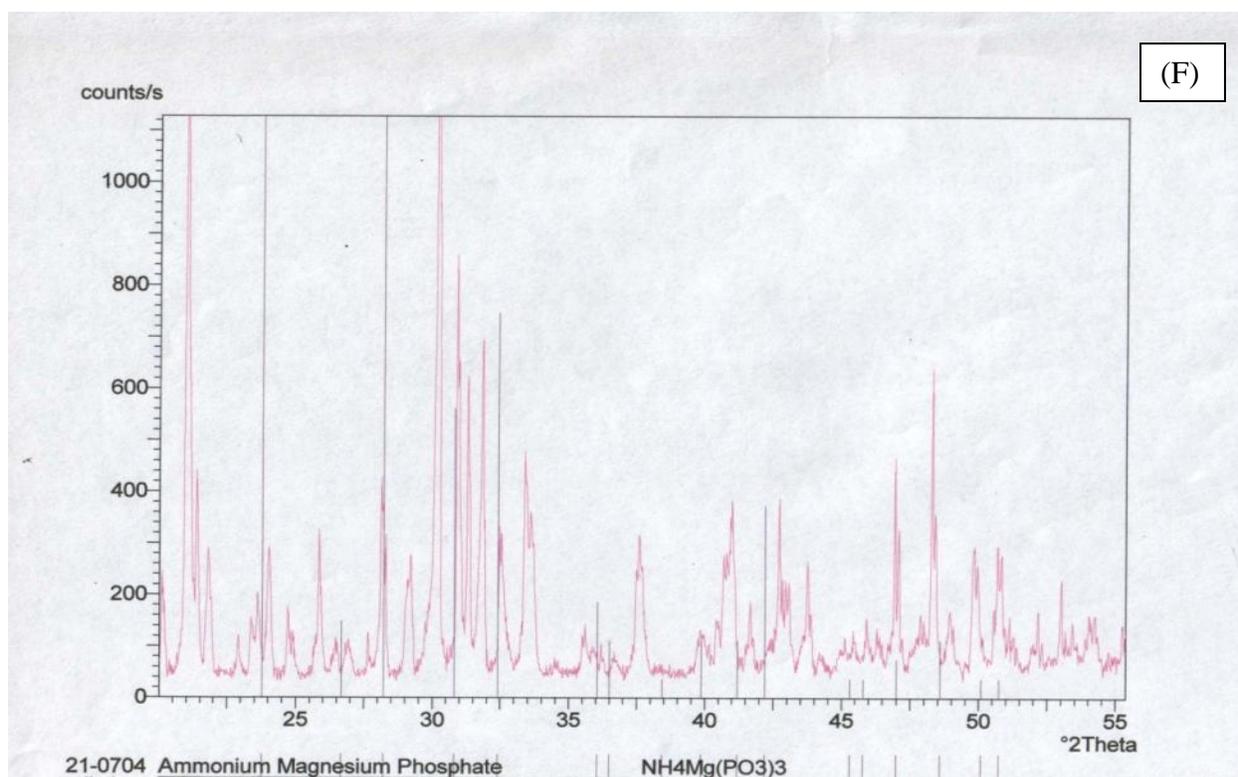
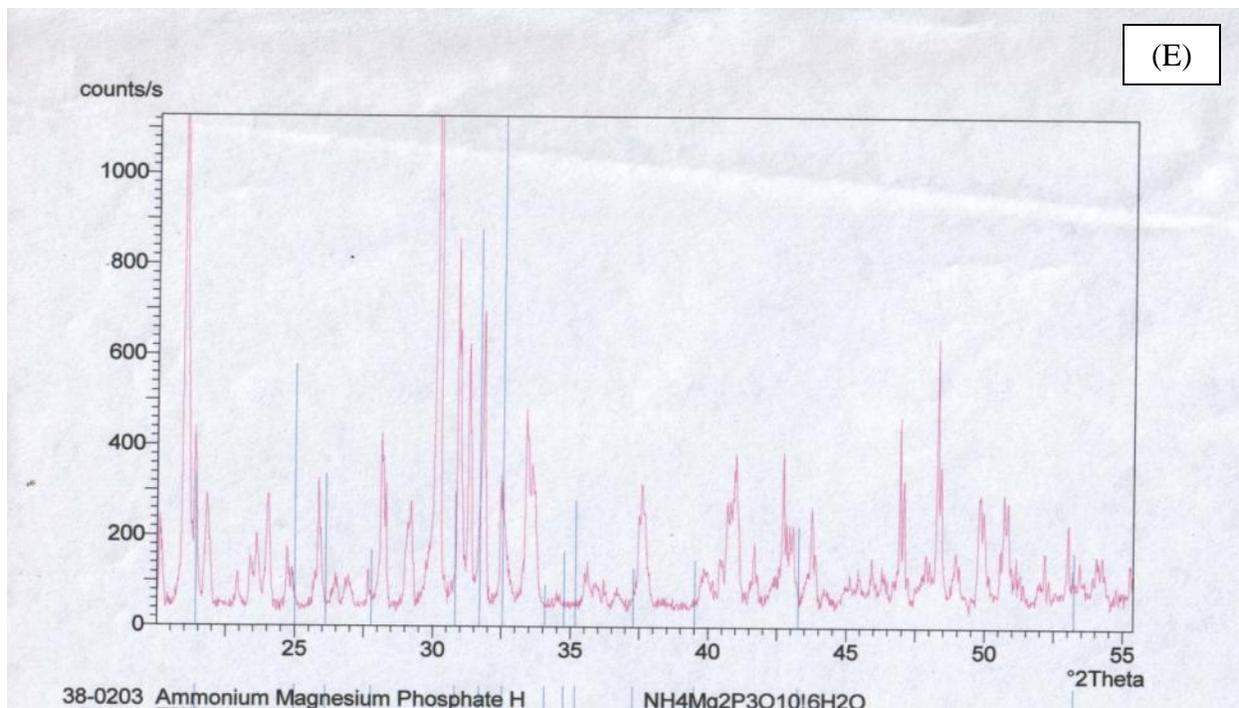
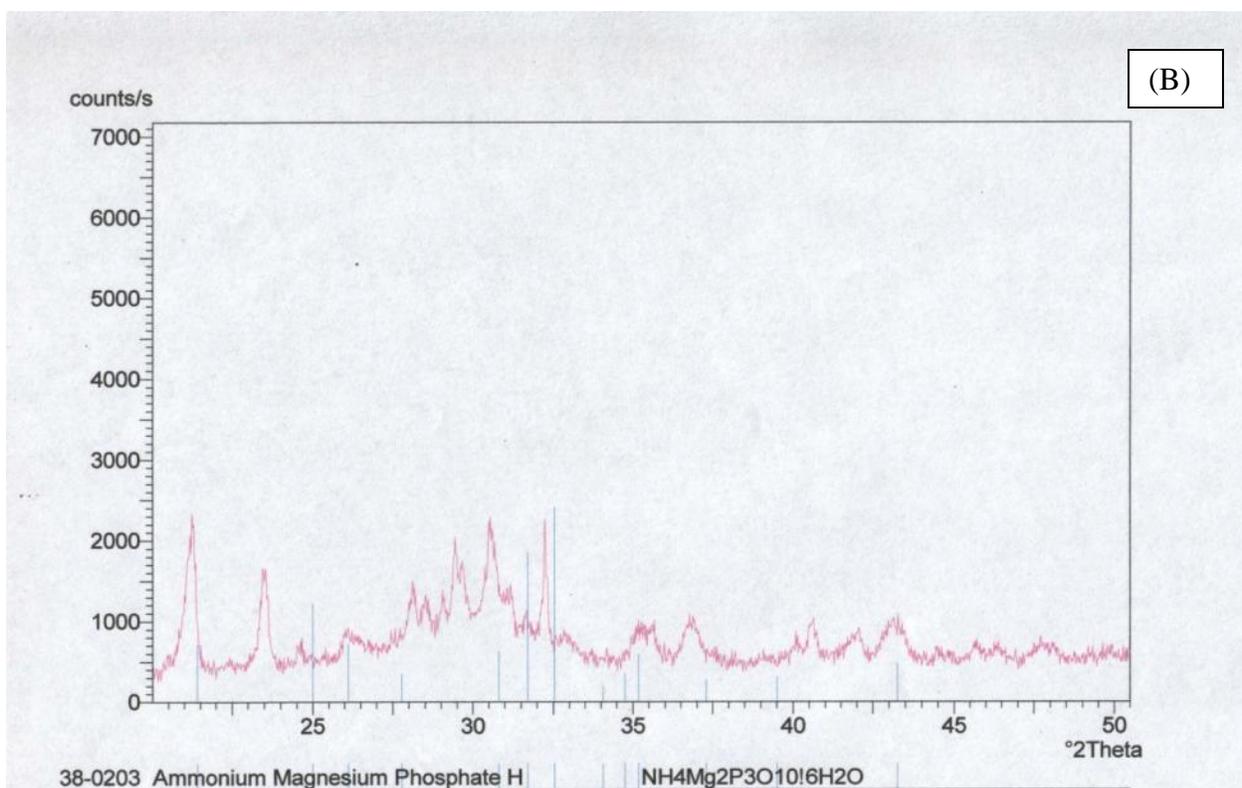
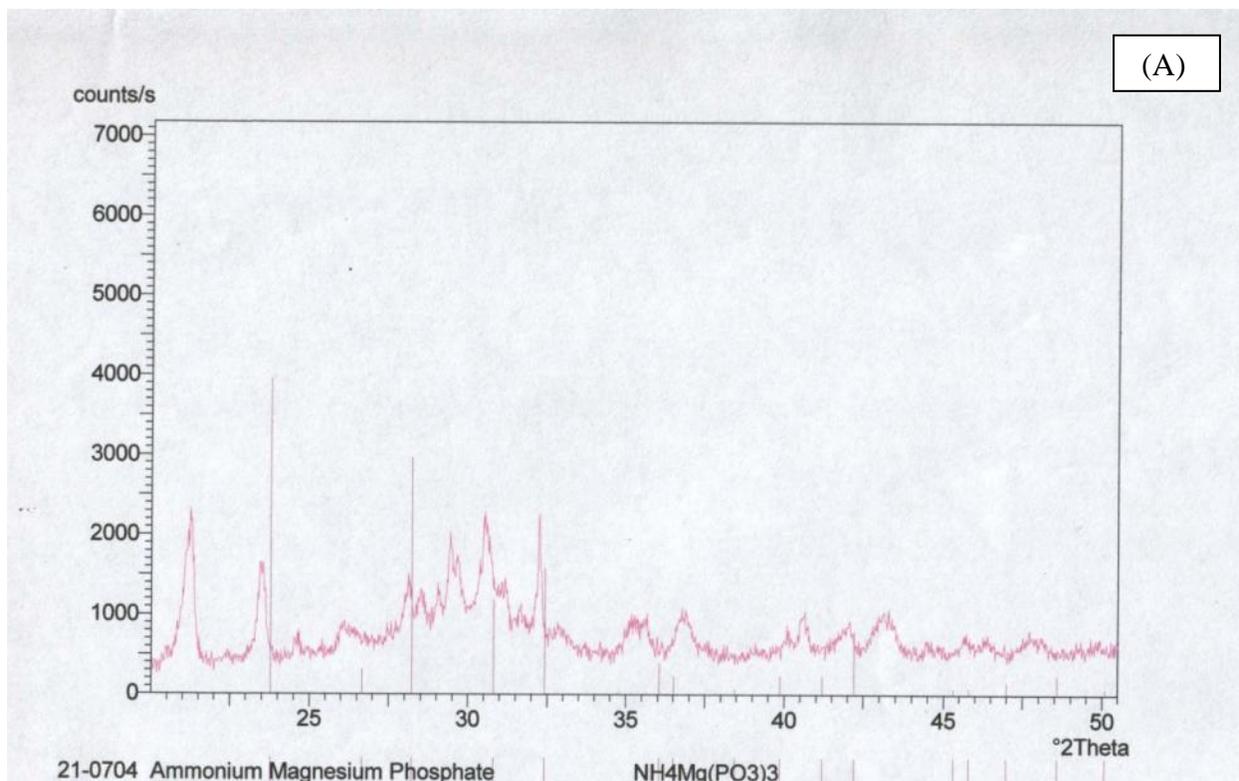


Figure 4-7. X-ray diffraction results of solids from mixing KMAG with synthetic struvite. A) Struvite. B) Ammonium sulphate. C) Schoenite. D) Picromerite and periclase. E) Ammonium magnesium phosphate hydrate. F) Ammonium magnesium phosphate



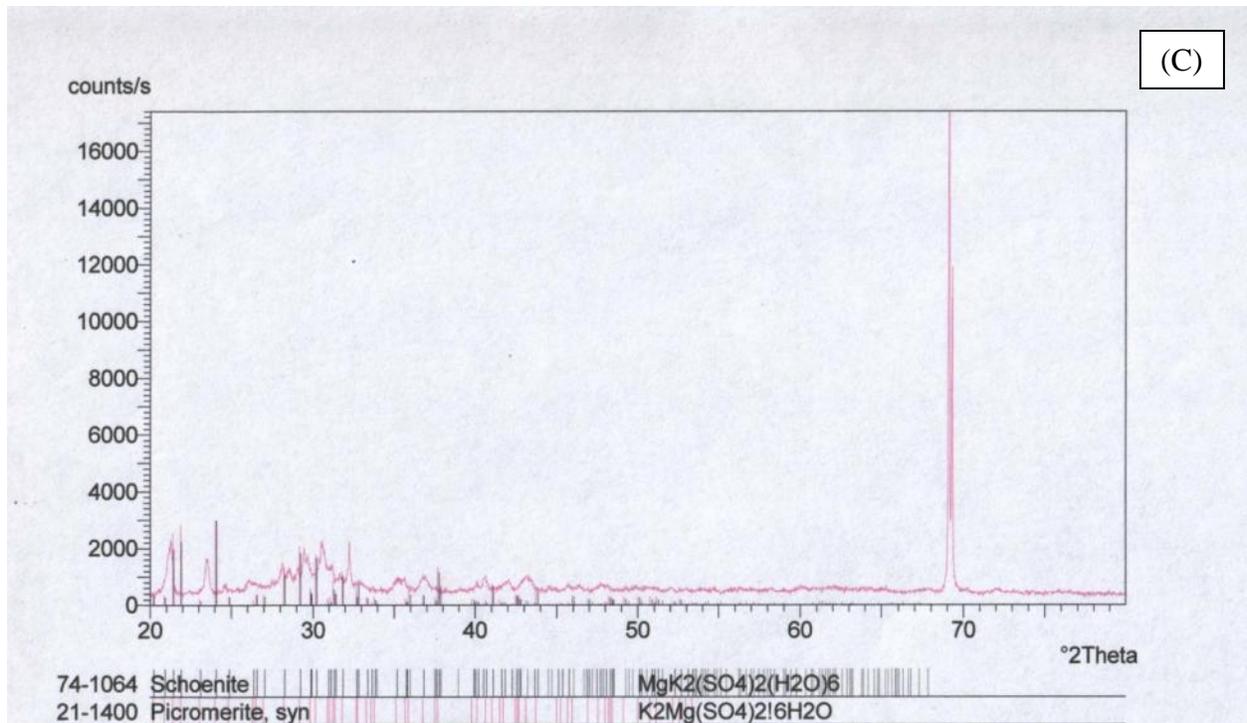
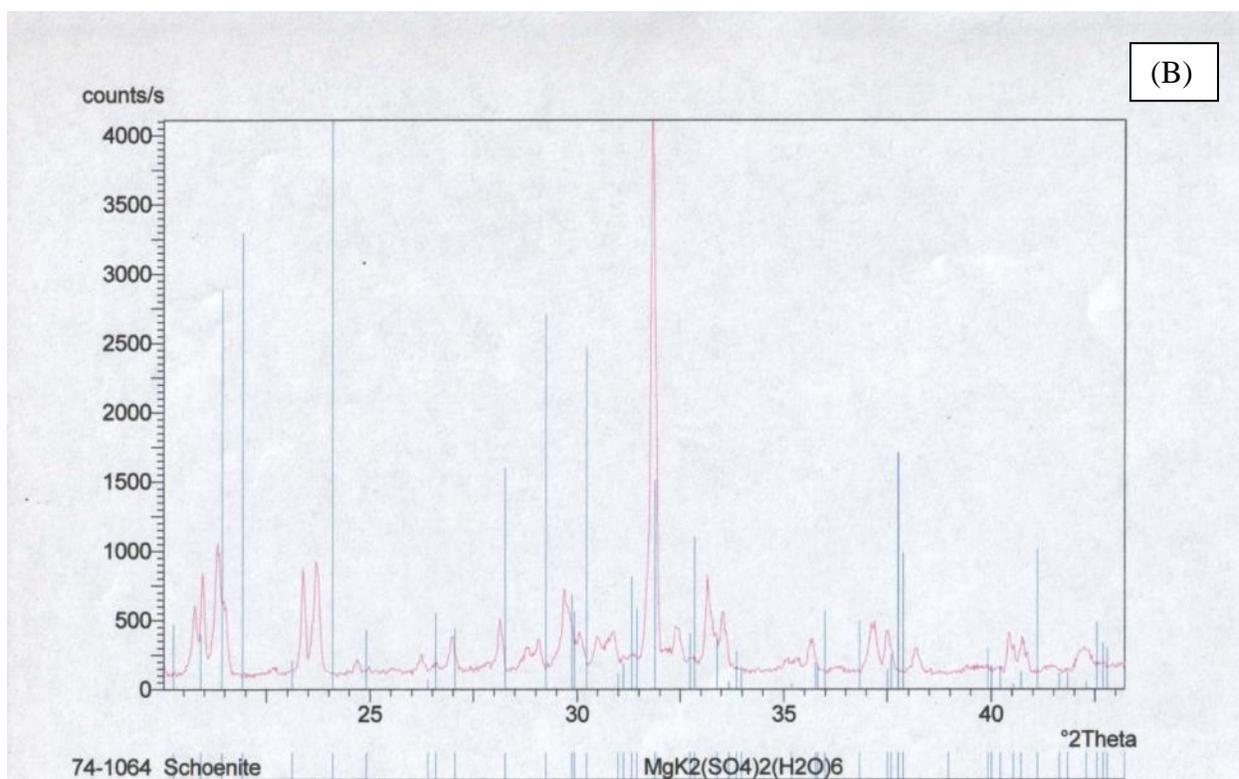
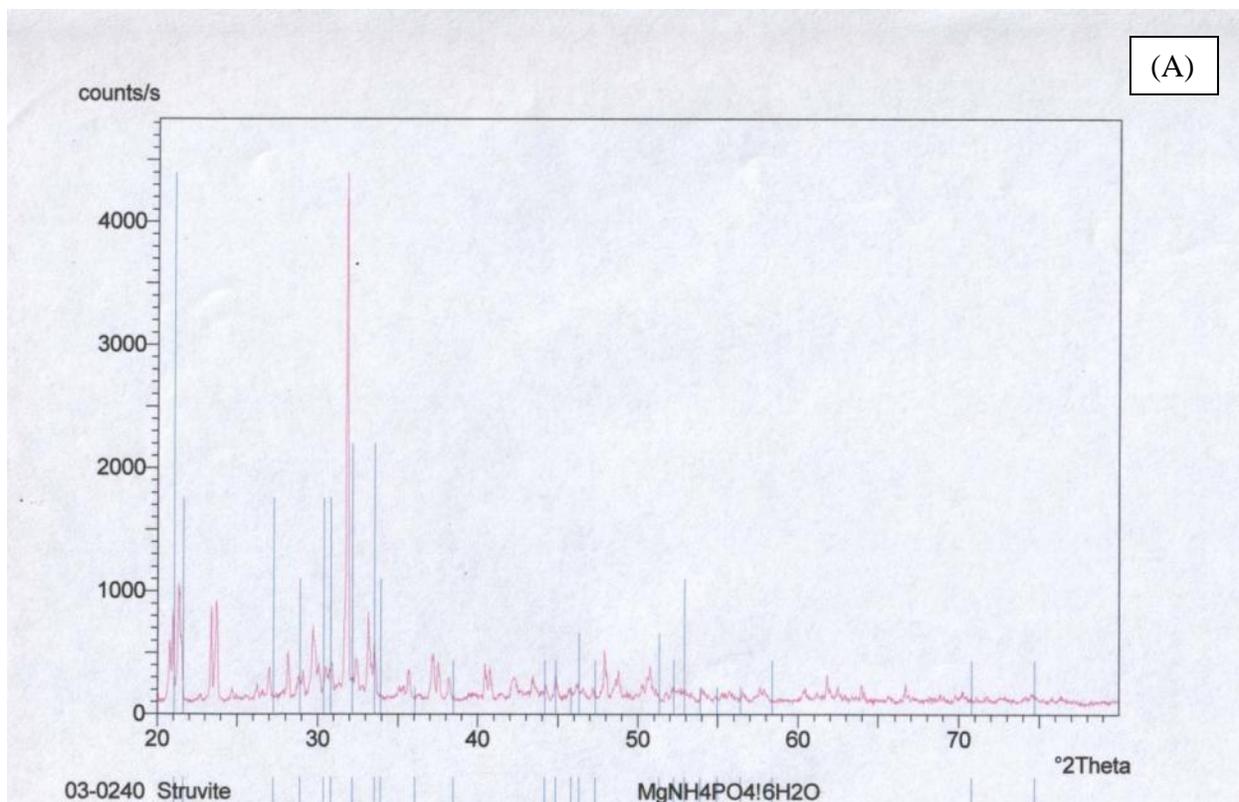
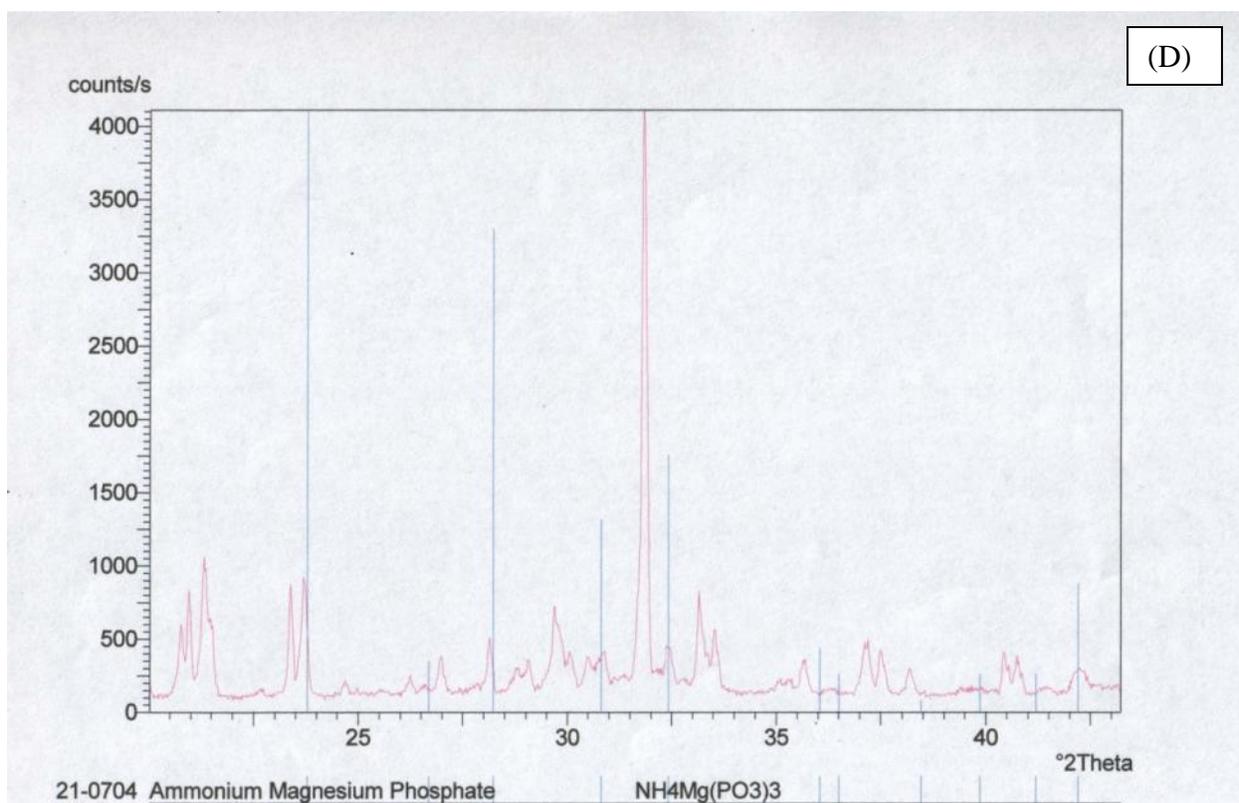
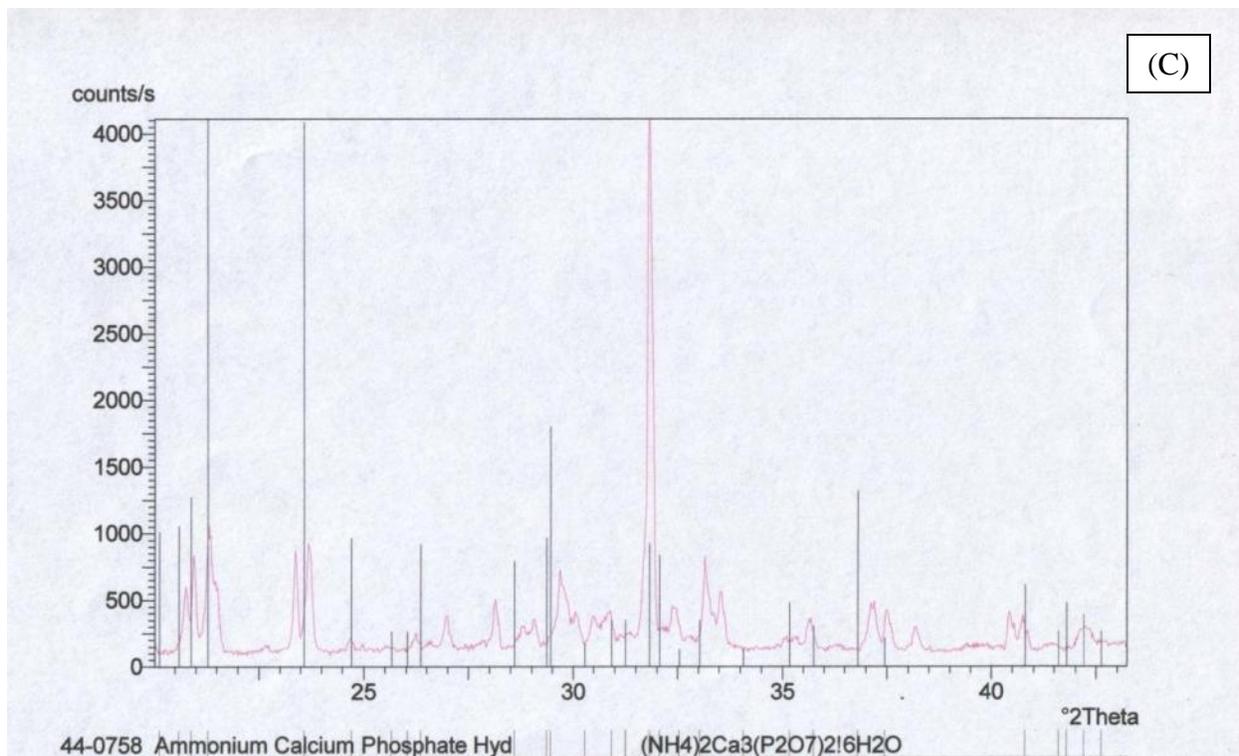


Figure 4-8. X-ray diffraction of raw KMAG with struvite from the pilot scale run. A) Ammonium magnesium phosphate. B) Ammonium magnesium phosphate hydrate. C) Schoenite and picromerite





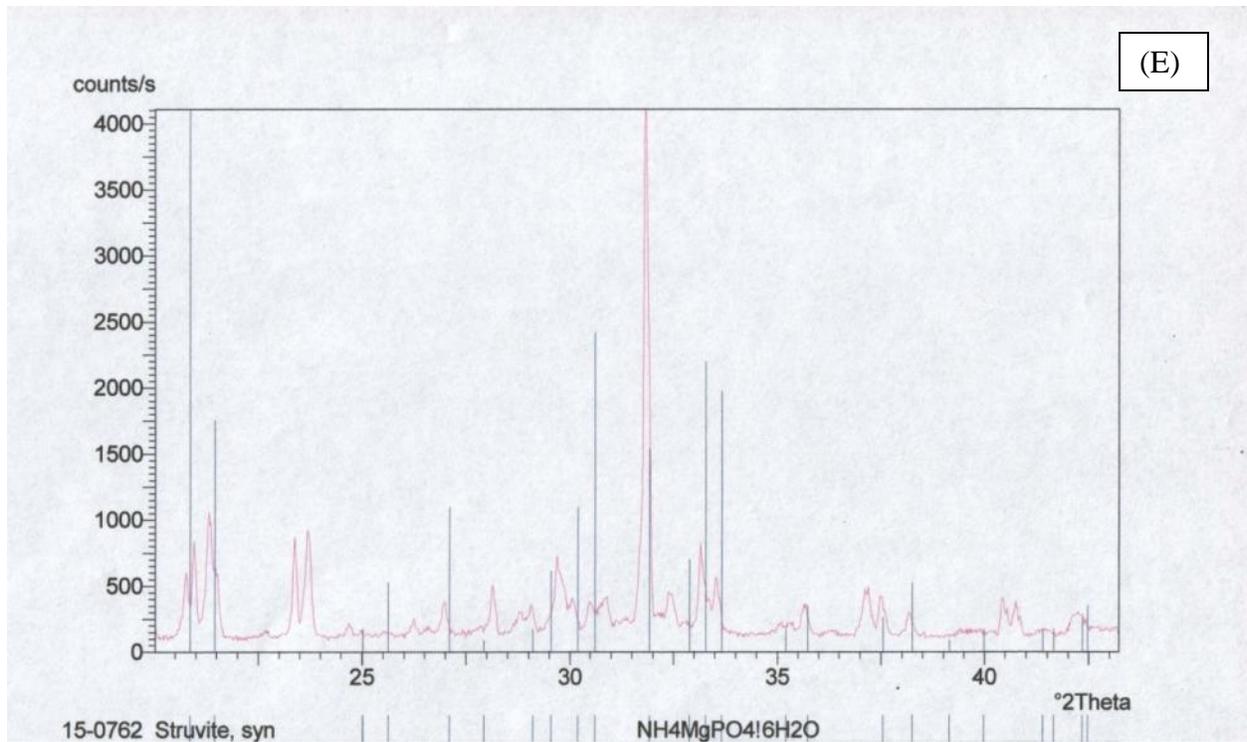


Figure 4-9. X-ray diffraction of solids from mixing KMAG solution with struvite from the pilot scale run. A) Struvite. B) Schoenite. C) Ammonium calcium phosphate. D) Ammonium magnesium phosphate. E) Synthetic struvite.

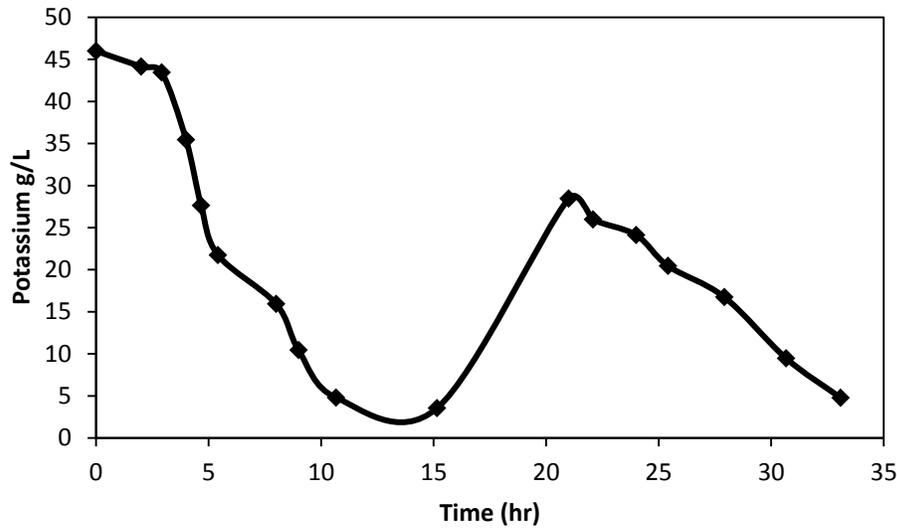


Figure 4-10. Change in the potassium concentration in the semi-continuous crystallization of KMAG with struvite.

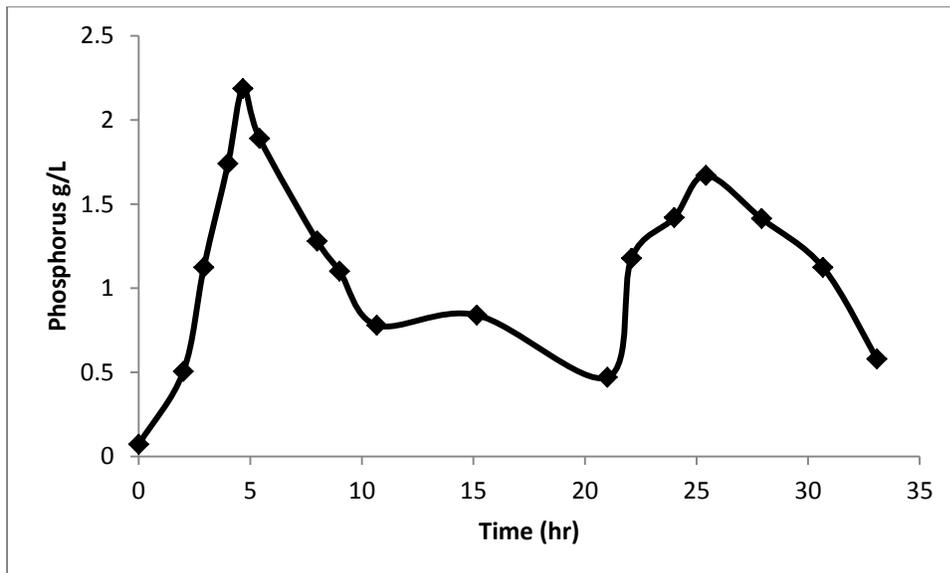
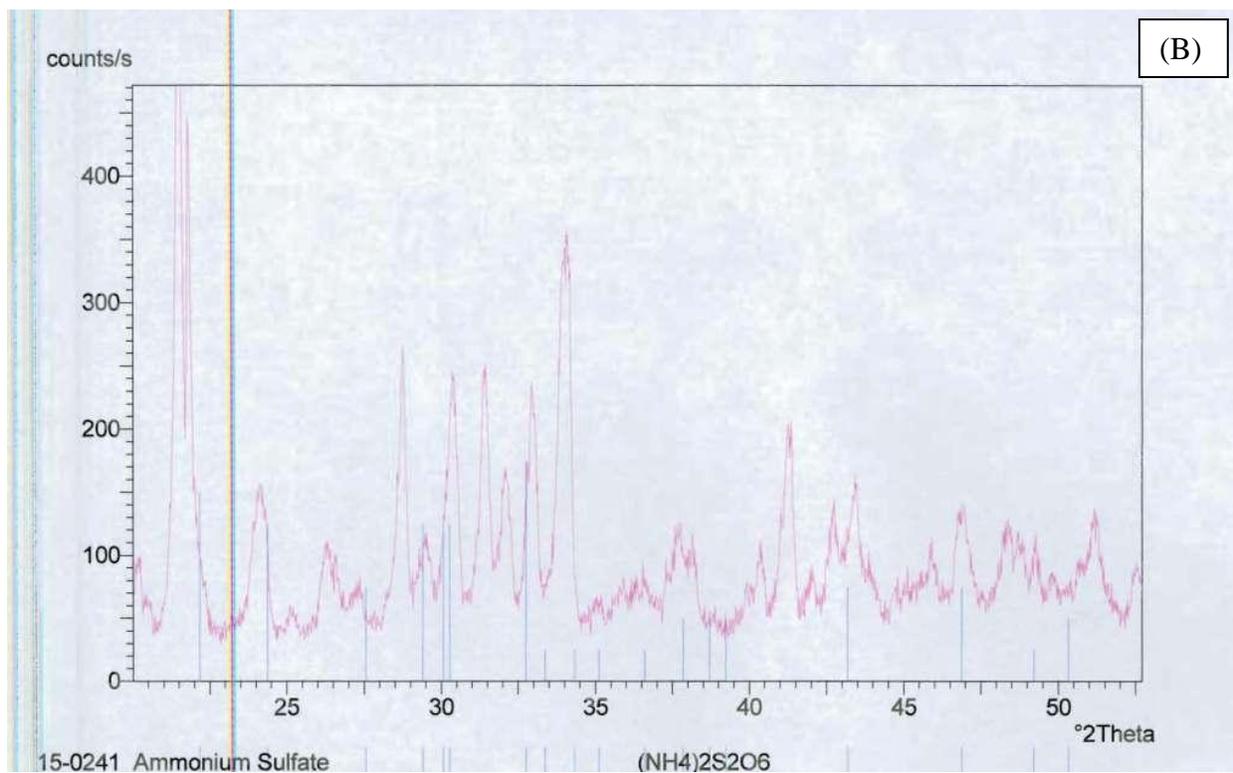
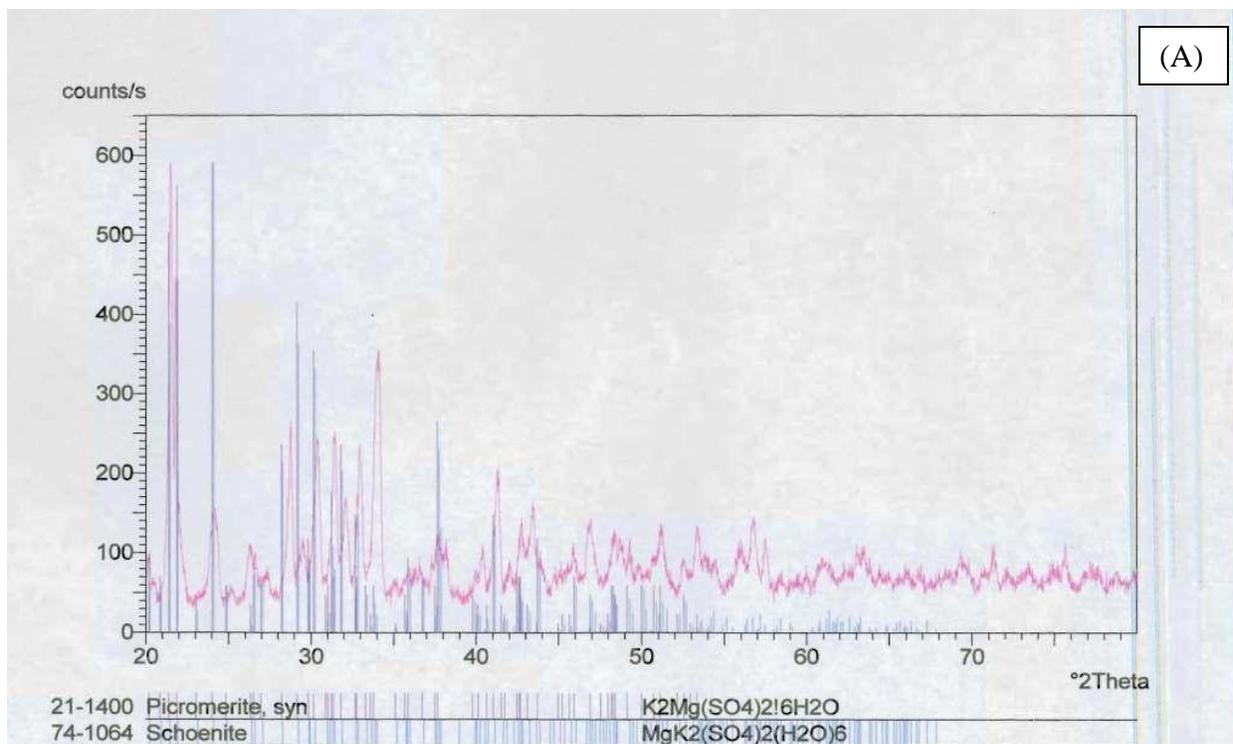


Figure 4-11. Change in the phosphorus concentration in the semi-continuous crystallization of KMAG with struvite.



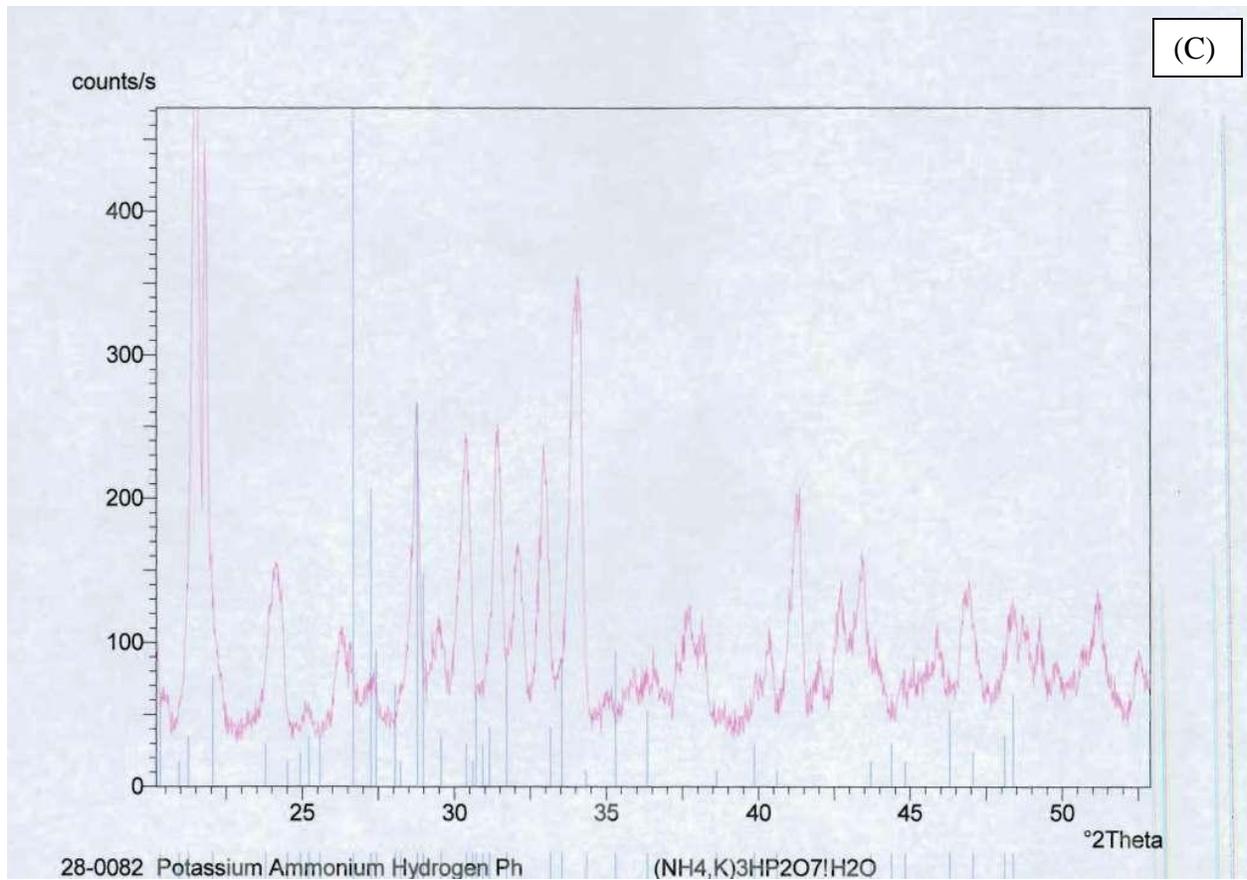


Figure 4-12. X-ray diffraction analysis of solids from the semi-continuous run. A) Picromerite and schoenite. B) Ammonium sulphate. C) Potassium ammonium hydrogen phosphate.

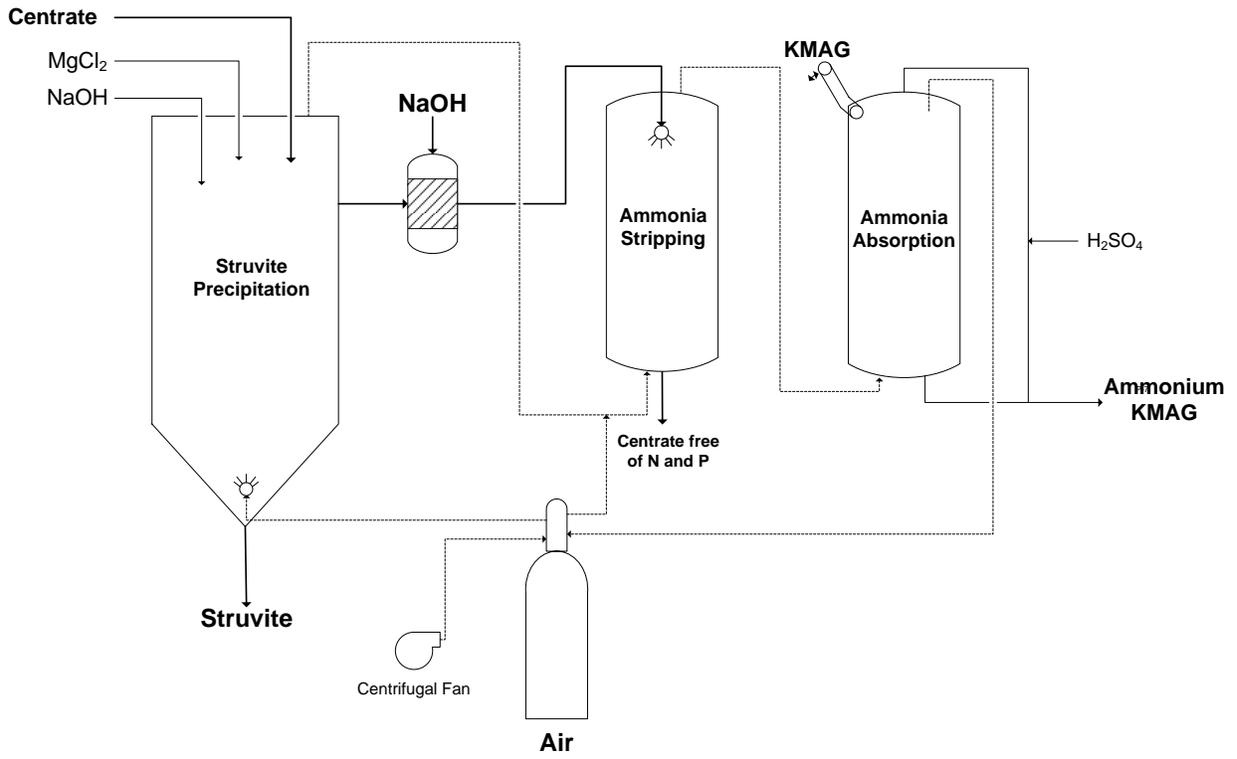


Figure 4-13. Recovery of nitrogen and phosphorus from centrate.

CHAPTER 5 CONCEPT TO COMMERCIALIZATION (C2C)

5.1 Commercializing Struvite

If conditions for struvite precipitation, which were predicted by chemical equilibrium model, can be duplicated and exploited in a practical engineering process, struvite may potentially be economical to extract from wastewater in commercial quantities. This might be done by precipitating struvite in a dedicated reactor instead of allowing spontaneous formation (Stratful et al., 2001; Munch and Barr, 2001; Hao and van Loosdrecht, 2003). This spontaneous formation fouls pipes and other inner surfaces of the treatment process, making operation of the plant inefficient and costly because the struvite must be dissolved with sulfuric acid or broken down manually with hammer and chisel (Durrant et al., 1999; Stratful et al., 2001; Williams, 1999). Another advantage of a dedicated reactor is that excess ammonium, which is a normal product of anaerobic wastewater digestion, might yield relatively pure struvite.

A growing interest has arisen of water utilities in preferential struvite crystallization as a way to control the problems of spontaneous deposition of struvite in post-digestion treatment lines and limiting phosphorus recycling in their wastes. However, the application of full-scale struvite crystallization processes in wastewater treatment plants is limited due to problems associated with quality control and quantity of the product generated.

One of the first points that water utilities should take into account, when considering struvite crystallization, concerns the selection of the most appropriate waste stream to precipitate and recover struvite. Anaerobically digested sludge liquors, where concentrations in phosphorus and ammonium are relatively high, seem the most suitable for this because in that type of liquor, magnesium and pH should remain the only factors to adjust to initiate struvite crystallization.

Step 2 is to precisely determine the chemical and physical characteristics of the liquors during the crystallization process. The key parameters, such as solution supersaturation, presence of foreign ions, pH, and mixing energy, could be responsible for dramatic changes in struvite crystal characteristics in terms of size, shape, and purity, as well as the quantity of the product generated. To illustrate, the purity of the formed crystals was found to be affected by the pH at which precipitation occurs and by the presence of calcium ions if the residence time for precipitation and crystallization is high. In this study, the optimum pH of precipitation was identified to be pH 8.7. Magnesium ions are commonly known to be the limiting ions that prevent struvite precipitation from real liquors. Moreover, they were found to be of great influence on struvite precipitation because increasing doses of magnesium could reduce significantly struvite impurity. This researcher concluded from the present study that the magnesium dosing should not be too excessive because this would result in excessive supersaturation ratios, which would cause rapid nucleation, hence, production of other magnesium precipitates. The operator would then have to determine the appropriate dose of magnesium (as $MgCl_2$) and the NaOH (for pH control) necessary to form struvite to ensure the selectivity of the process toward struvite and to control the quality of the product formed. This implies that application of full-scale struvite crystallization processes would require a regular and accurate monitoring of the liquors' chemical characteristics to regulate pH and chemically counterbalance Mg:N:P, when needed.

Phosphorus can be obtained from sludge only with biological processes because the commonly used chemical precipitation of phosphorus, which involves the addition of iron and aluminum salts, produces a product that cannot be recycled for industrial recovery of phosphorus (Donnert and Salecker, 1999). No common method can recover struvite from biological

processes. Equipment ranges from complex patented reactors employing ion exchangers to simple stirring tanks (Gaterell et al., 2000; Williams, 1999).

From the literature, this researcher found that struvite crystallization from digested sludge liquors, by means of fluidized bed reactors directly integrated in wastewater treatment plant lines, are the most common processes (Bhuiyana et al., 2008). However, if good phosphorus removals are always insured, these techniques still need improvement with regard to quality of the product formed to be applicable as an economically valuable route to recover phosphorus. The application of struvite crystallization processes at full scale is not widespread due to: 1) the unknown economical value of the process and the product, 2) the need of pH control, 3) the necessity of long operational times to ensure quality of the product, and 4) the formation of crystals.

Several laboratory and pilot scale studies have been carried out to assess the potential removing and recovering phosphorus as a reusable product, and a few of them have been tested at full scale in The Netherlands (Giesen, 1999) and Italy (Battistoni et al., 2005a, 2005b). However, Japan is the only country where complete phosphorus removal and recovery from anaerobically digested sludge liquors as struvite have been implemented, with the resulting production sold to fertilizer companies (Gaterell et al., 2000; Ueno and Fujii, 2001).

Struvite was produced in Japan from the filtrate of anaerobic sludge digestion by adding magnesium hydroxide and adjusting the pH from 8.2 to 8.8 with sodium hydroxide. A retention time of 10 days allowed the growth of pellets 0.5 to 1.0 mm in diameter. The recovered struvite was sold to fertilizer companies (Ueno and Fujii, 2001). Another experimental industrial process provided simultaneous removal of phosphate and ammonium ions by selective ion exchange and recovery of the product by chemical precipitation in the form of struvite (Liberti et al., 2001).

Usually, pilot plants are used to reduce the risk associated with construction of large process plants. It is done in following ways:

- Evaluating the results of laboratory studies and making product and process corrections and improvements
- Determining possible salable co-products
- Determining waste streams requiring treatment before discharge
- Identifying scale up issues
- Providing data that can be used in making a decision on whether or not to proceed to a full-scale production process. In the case of a positive decision, designing and constructing a full-size plant or modifying an existing plant
- They are substantially less expensive to build than full-scale plants. The business does not put as much capital at risk on a new project for testing. Further, design changes can be made more cheaply at the pilot scale and kinks in the process can be worked out before the large plant is constructed,
- They provide valuable data for design of the full-scale plant. Scientific data about reactions, material properties, and corrosiveness, for instance, may be available, but it is difficult to predict the behavior of a process of any complexity. Engineering data from other processes may be available, but this data cannot always be clearly applied to the process of interest. Designers use data from the pilot plant to refine their design of the production scale facility.

This chapter reports studies on the pilot scale carried out on centrate from the Jacksonville Electric Authority's Wastewater Treatment Plant. The City of Jacksonville's wastewater system collects and treats an average of 240 million gal of municipal sewage every month. The collection transports both storm water and sanitary flows. The wastewater is treated at a treatment plant located on the north side of Jacksonville. Once treated, the effluent flows into Mauvaisterre Creek. Most of Jacksonville's sewer system is constructed as a combined sewer. Street inlets are tied into it to convey storm water during storm events. The combined flow from customers and storm inlets is collected from service laterals into the over 90,000 linear

feet of sewer lines in Jacksonville. They tie into three main trunk lines that convey them to the wastewater treatment plant.

The Jacksonville plant is a secondary treatment system for wastewater. The processes include screening aerated grit removal, primary clarification with scum removal, activated sludge, secondary clarification, chlorination and dechlorination, and finally post-aeration before discharge into Mauvaisterre Creek. The plant also treats sewage and biosolids from surrounding communities. Biosolids are processed through mesophilic anaerobic digesters, followed by centrifuges, gravity belt thickeners and storage tanks with one year of biosolids storage capacity. Filtrate from the dewatering process is then returned to the head of the works. This present study illustrates the trial runs of operating a pilot plant with the sequential batch reactor (SBR) technology to produce and recover struvite. GreenTechnologies, LLC constructed a pilot plant in Starke, Florida, for processing 1,000 gal of centrate per batch for recovering nitrogen and phosphorus, using technology developed in this research project.

The primary goal of the pilot project was to prove that phosphorus recovery was possible using the SBR technology on real process fluids on a technical scale. The pilot plant was operated with the following specific objectives:

- Test the technology, on real process fluids which validate feasibility of struvite precipitation technique
- Find the amount of struvite and volume of the settled solid sludge
- Determine the quantity of chemicals needed for struvite recovery
- Carry out process economics and optimization for a large-scale struvite plant using the pilot scale operation experience
- Produce small quantities of struvite for chemical, x-ray diffraction evaluations, packaging, transportation, and storage stability studies
- Develop a business model of struvite recovery

5.2 Materials and Methods

The key unit operation in the SBR approach is the settling. A literature review found that a typical struvite particle has a 0.004 cm radius (Buchanan, 1993) and a 1.7 g/cm³ density (Sharp, 2002). Using Stokes law for particle settling, this researcher determined that the average settling velocity will be 0.0027 m/s, which is less than the liquid velocity in the tank. The liquid-solid separation is carried out in the SBR. The length of the conical bottom is based on the particle-settling velocity. The dimensions of struvite tanks are provided in Table 5-1. Dimensions of other equipment were not available at the time of the conducted trials. Tankage is required to store the MgCl₂·6H₂O and NaOH solutions. Details of the pilot plant layout and flow diagram are given in Figures 5-1 and 5-2, with details of equipment listed in Table 5-1.

Following standard operating procedure was developed for operating the pilot plant: Prepare 10 M solutions of magnesium chloride, sodium or potassium hydroxide (subject to availability), and 50% phosphoric acid, which are stored in chemical tanks CT1, CT2, and CT3, respectively.

- Transfer the centrate from the storage tank (ST), open ball valves BV1_{ST}, BV1_{P1}, BV2_{P2}, and start pump P1.
- Dose magnesium chloride and caustic, open BV1_{CT1}, BV1_{CT2}, BV1_{CP1}, and BV1_{CP2}. Adjust the flow of chemicals from CT1 and CT2, according to the flow of centrate from the storage tank, using dosing pumps DP1 and DP2.
- Transfer the reaction mixture to mixing tank (MT) by opening valve BV1_{MT}. Phosphoric acid from CT3 can be fed to the mixing tank, depending on the need for additional nitrogen removal.
- Open BV3_{MT}, which is in the overflow line from the mixing tank. The reaction of struvite formation starts in the static mixer and mixing tank. The effect of mixing either by using the static mixer and/or mixing tank is studied.
- Open BV1_{SR1} and FILL the struvite tank (SR1) with the centrate, already mixed with chemicals. About 500 gal of the reaction mixture is filled in the struvite tank by visually monitoring the liquid level.

- Allow the liquid mixture to REACT and/or SETTLE for 30 min in the struvite tank.
- Transfer the centrate with precipitated struvite to the struvite tank (SR2) by repeating the previous procedure.
- Thus, struvite precipitation is carried out in two steps for complete nitrogen/phosphorus recovery.
- Transfer the settled solids, open BV5_{SR2} and BV6_{SR2}, and feed the settled struvite slurry from SR2 to the filter press.
- Drain the centrate free of nitrogen and phosphorus using pump P1 and opening BV1_{Dr}.

5.3 Results and Discussion

The preliminary trial runs were conducted on the pilot scale using centrate from Jacksonville Electric Authority's Wastewater Treatment Plant. This run validated the model predictions for the caustic requirement, magnesium requirement, and residual concentrations of nitrogen and phosphorus in the centrate.

5.3.1 Trial 1

The centrate from JEA Wastewater Treatment Plant was found to have the following characteristics:

pH : 7.1
 NH₄⁺-N : 780 ppm
 PO₄³⁻-P : 135 ppm
 Ca²⁺ : 37 ppm
 K⁺ : 75 ppm

As observed in laboratory scale runs, complete phosphorus and nitrogen recovery from centrate was found to be successful in two steps, achieved for keeping struvite purity in the solids maximum (>99%). This concept was verified on the pilot scale, which is explained as follows.

5.3.1.1 Treatment Step 1

In Step 1, phosphorus originally present in centrate was recovered. The standard procedure, as explained earlier, was not followed completely because the complete pilot plant was not set up at the time of this trial. The struvite precipitation reaction was carried out by adding chemicals to 240 gal of centrate in the tote tank. A total of 687.54 gm of magnesium chloride hexahydrate was used for phosphorus recovery. The pH was adjusted to 8.7, which required 1.074 kg of KOH. The chemicals were mixed using an agitator in a tote tank. After the chemicals mixing, the centrate was transferred to a conical bottom 500 gal tank at a rate of 16 gal/min. The centrate was allowed to settle for 30 min, and a supernatant sample was taken. Nitrogen and phosphorus were recovered in the form of solids. The solids and liquid separation level was visible at the bottom of the struvite tank. The supernatant and the struvite sludge generated were stored in the conical bottom tank. The separation of solids was not done at the end of this step. In the supernatant sample, NH_4^+ -N was found to be 739.3 ppm and PO_4^{3-} -P to be 9.4 ppm. This gave 93% recovery of PO_4^{3-} -P. The calcium concentration in the centrate decreased from 37 ppm to 25 ppm. The potassium concentration in the centrate also decreased from 135 ppm to 108 ppm. Battistoni et al., (2000) demonstrated the operation of a full-scale fluidized bed reactor struvite formation from the belt press liquors using aeration to adjust the pH. They found only 61.7% to 89.6% removal of PO_4^{3-} in the process, as compared to 93% removal of PO_4^{3-} -P in the present study. Jaffer and Pearce (2004) also reported the operation of an air-agitated reactor on full scale for recovery of struvite from centrifuge liquors where they found only 60% to 80% recovery of phosphate. The Shimane Prefecture reactor removed 90% of ortho-phosphate from the treated supernatant.

5.3.1.2 Treatment Step 2

In this step, additional phosphorus in the form of phosphoric acid was used to recover residual NH_4^+ -N in the centrate previously treated. After about 22 hours of initial phosphorus recovery, NH_4^+ -N was found to decrease to 699.5 ppm from 739.3 ppm. This could be due to the increased pH (8.7) causing ammonia to volatilize.

The centrate was transferred to the tote tank, and the following chemicals were added to it:

- 85% Phosphoric Acid : 2.3 kg
- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$: 3.588 kg
- KOH : 2.5 kg
- pH adjusted to : 8.9

The centrate was transferred to the conical bottom struvite tank. The solids were allowed to settle for 30 min, and the supernatant sample was analyzed, which was found to contain 452 ppm of NH_4^+ -N and 157 ppm of PO_4^{3-} -P. The model predicted a supernatant ammonia concentration of 481 ppm, but the actual experimental residual concentration was less than 481 ppm, perhaps due to ammonia volatilization. The model predicted a residual PO_4^{3-} -P concentration of 105 ppm, which was less than an experimentally observed concentration of 157 ppm. The model predicted a formation of calcium phosphate precipitates in addition to struvite.

Step 2 was carried out to test the recovery of additional ammonia, but the centrate after this step can be treated further to recover PO_4^{3-} -P to recover more struvite. A total of 6.1 kg of dry solids were recovered from both treatment steps, which were close to the expected value of 5.9 kg computed by the model. Struvite solids were analyzed for chemical composition and x-ray diffraction (XRD), as explained in Chapter 3. The solids were utilized for struvite product development, as explained in Chapter 4. The composition of the struvite solids produced in the trial runs is shown in Table 5-1. The magnesium, ammonium, and phosphate content were

similar to the theoretical values of struvite. The solids recovered were found to be mainly struvite, which is also inferred from x-ray diffraction analysis, as shown in Figure 5-3. The solids produced were found to have a good match to the theoretical intensity values for struvite. The XRD analysis did not show the presence of other solids along with struvite, which indicated that calcium precipitation did not occur. This is also confirmed by chemical composition of solids where calcium content was only 0.0049%, as shown in Table 5-2.

5.3.2 Trial 2

The previous pilot plant run on struvite recovery incorporated two step operations. In Step 1, phosphorus, originally present in centrate, was recovered, along with some nitrogen. In Step 2, addition recovery of nitrogen was carried out by adding extra phosphorus in the form of phosphoric acid. Unlike this operation, Trial 2 was carried out by combining the two steps.

Initially, the pH of centrate was found to be 7.64, with ammonia-N concentration of 740 ppm. The model simulations suggested the addition of the following chemicals for 240 gal of centrate: 2.3 kg of 85% phosphoric acid and 3.5 kg of $MgCl_2 \cdot 6H_2O$. A total of 3.7 kg of potassium hydroxide was needed for pH adjustment.

These chemicals were added to 240 gal of centrate in the tote tank. The solution was mixed using an agitator. At the start of the experiment, the centrate pH was 7.64. The addition of phosphoric acid decreased pH to 6.0. Then 3.5 kg of magnesium chloride was added. Potassium hydroxide was added gradually. First, 2 kg of KOH was added and the mixture was recirculated for 15 min, which increased the pH to 6.7. An additional 1 kg of KOH was mixed in the solution, which increased the pH to 7.5. Another 0.7 kg of KOH was added slowly until the pH was set to 8.7. After pH adjustment, the centrate was transferred to a 500 gal conical bottom tank for settling and separation of the solids. The solids were found to settle in 10 min. A sample was taken to determine solids concentration in supernatant after 10 min and 30 min to study the

settling of the solids. The suspended solids concentration at both times in the supernatant was found to be 10 ppm, suggesting complete settling of the solids. Samples were taken for chemical analysis after 30 min after transfer. The final ammonia nitrogen was found to be 240 ppm and phosphorus of 85 ppm.

5.3.3 Comparison between Laboratory and the Pilot Scale Runs

The amount of chemical addition in the pilot scale runs was not calculated by scaling up the laboratory scale runs, but this researcher found to be proportionate to the laboratory runs. The chemical amounts used in the pilot scale runs were determined by model simulations. As discussed in Chapter 3, when 7 L centrate was subjected to struvite recovery, the amount of chemicals required to recover only phosphorus was as follows: 4.72 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 3.24 g of NaOH. The amount of sodium hydroxide is equivalent to 5.83 g of KOH for laboratory scale. This scaled up to 757.3 g of KOH required for 240 g. But this researcher observed that 1.074 kg of KOH was actually added in the pilot scale, as explained in treatment Step 1 of Trial 1, possibly due to the aeration provided for mixing in the laboratory scale, which enhanced the pH increase. The amount of magnesium chloride was found to be proportional to the pilot scale run conducted on 240 gal of centrate. The laboratory amount of magnesium chloride hexahydrate scaled up to 611.8 gm, whereas in the pilot scale, 687.54 gm were added. The solids were not separated from the centrate in the pilot scale run so a comparison with the laboratory scale run was not done. In the laboratory scale runs, 99.6% phosphorus recovery was observed, which was close to 93% removal of $\text{PO}_4^{3-}\text{-P}$ observed in Trial 1 treatment Step 1. In the laboratory scale experiments, magnesium chloride was dosed to the centrate in two steps in the SBR. In the pilot scale run, magnesium chloride was dosed in one step, as explained in treatment Step 1 of Trial 1.

When 7 L centrate was subjected to recovery of both nitrogen and phosphorus, the amount of chemicals required was as follows: 39.96 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; 4.29 g of 85% H_3PO_4 ,

which was proportionate to the chemicals added for 240 gal of centrate, as explained in Trial 2. Data on the caustic usage in the laboratory scale experiments were not available and not compared to the pilot scale run.

5.4 Scale-up Considerations in Precipitation

Processes for precipitation of solid products from dissolved reactants are almost always carried out in stirred reactors. The reactors are operated semi-batchwise or continuously. In both operation modes, one reactant is added to a stirred solution containing an excess of other reactants. The functions of a stirrer include: mixing of reactants, suspension of formed solid particles, and promotion of heat transfer to the wall.

The primary objective of the bench scale experiments is to find out which phenomena are important in the process. First, it is important to decide for the process whether primary or secondary nucleation prevails. When it follows from the lab experiments that meso-mixing (mixing of incoming stream with the reactor contents) has a strong influence on particle size, primary nucleation is probably essential. When particle size is related to slurry concentration, then secondary nucleation must be taking place. Second, it is important to find out whether or not growth of particles to their final size is mainly determined by the surface growth or by agglomeration. Struvite precipitation, carried out in the present study, takes place with primary nucleation with no agglomeration due to short hydraulic retention time. Therefore, the design of the reactor should be aimed at an effective control of meso-mixing and of the mass transfer of the growing crystals. The mass transfer of the growing crystals is mainly determined by specific power consumption of the impeller. At a given power input, meso-mixing is dependent on the way reactants are introduced into the reactor. However, secondary nucleation may occur on larger scales because the tip speed of the impeller increases with the scale (for constant specific

power input). Also, agglomeration may take place on a larger scale, even if does not on a lab scale since the longer circulation times may give agglomeration a better chance.

5.5 Discussion of Feasibility on Full-scale

For the purpose of estimating the cost of struvite precipitation from centrate, the treatment of 700,000 gal per day would be needed. For this operation, the same process-sequence explained for the pilot plant was used. Table 5-4 illustrates specifications of the equipment and related approximate cost. A low-pressure, high volume pump would transfer the centrate into the mixing tank through a static mixer. Within the static mixer, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH would be mixed with the centrate. An overflow at the top of the reactor would then direct the centrate to the struvite SBR tank. The supernatant from this tank would be supplied with chemicals for the second step, which would tank the centrate to the second struvite tank. Commercial tanks with this volume can be purchased with 45° conical bottoms and cylindrical sides. A mixing tank mentioned earlier is needed to allow the mixing of wastewater, magnesium, and a base, and it provides sufficient hydraulic retention time (HRT) for the precipitation reaction to occur. The present research has shown 30 min to be an appropriate HRT.

5.6 Economics of Struvite Recovery

An estimate of the chemical requirement for the pilot plant runs is shown in Table 5-3. The chemical requirement varies with the change in ammonia-N concentrations in the centrate. The ammonia-N concentration in the effluent centrate is targeted to 100 ppm. An economic analysis of the pilot plant is carried out, as shown in Table 5-4, with the following four assumptions:

- a. 1,000 gal of centrate processed per day (8 h of operation)
- b. 120 mg/L of $\text{PO}_4\text{-P}$ available for treatment from centrate
- c. Effluent concentration of $\text{NH}_4^+\text{-N}$ is allowed to be 100 mg/L
- d. Selling cost of struvite = \$500/ton

Since struvite contains phosphorus and nitrogen, removal will affect the content of both elements in the leftover sludge, which is used by farmers as a soil improvement agent and fertilizer. Struvite recovery from wastewater might have a marginal effect on the net content of nitrogen, but a greater impact on the concentration of phosphorus in the sludge. Gaterell et al. (2000) calculated—because sewage has a typical N:P ratio of 8:1 and struvite 1:1—that a theoretical maximum of 12.5% of the nitrogen load could be removed as struvite. The practical limit is lower because not all phosphorus can be recovered as struvite with today's technologies. Struvite removal leaves less phosphorus in the sludge. This is beneficial from two perspectives:

1. Sludge applied to fields usually has phosphorus in excess of the needs of plants. Subsequent eutrophication of water bodies from leached phosphorus compounds would be reduced.
2. Struvite recovery would help to meet legal requirements imposed on sludge disposal and reduce the area needed for disposal.

The struvite recovery technique offers material, energy, and transportation cost savings for the wastewater treatment plants. The transportation savings is a result of the reduced sludge transport. Operation cost savings will be in the prevention of clogged pipes from struvite crystals in the pipeline. This unintentional struvite deposition leads to additional pumping and cleaning costs that can be avoided by the intentional formation and recovery in the reactor. For a typical wastewater treatment plant serving 1 million people, the annual cost of dealing with the struvite problem ranges from \$160,000 to \$800,000.

The total nitrogen and phosphorus market for the United States and Puerto Rico is more than 21 million tons. In terms of struvite, 19 million tons annually would be needed to fulfill that demand. However, slow-release fertilizers, such as struvite, account for only 4% of the total fertilizer market or roughly 791,000 tons/yr.

Because 84% of the product's raw materials are derived from waste recovered in the reactors, struvite has low production costs compared with fertilizers produced from mined phosphorus. A strong demand and higher input costs are rapidly pushing prices for phosphate end-products to record highs. Global companies that import phosphate rock are faced with costs nearly five times higher than a year ago, necessitating high end-product prices. PotashCorp is the world's third largest producer of phosphates and second largest seller of phosphoric acid, and with high-quality, low-cost phosphate rock, this company is well positioned in these unprecedented phosphate market conditions. PotashCorp expects a combined gross margin for nitrogen and phosphate to exceed 2007 levels by 20-25% (Agri-Marketing E-Newsletter, 1/25/08. PotashCorp Issues 2008 Outlook).

The economics of struvite recovery also become important in final product marketing. The value of the recovered phosphorus, in the form of struvite, tends to be higher than that of phosphate ore, due to higher quality (in terms of purity), as well as low heavy metal contamination. The intrinsic value of struvite is also important because it was identified as a non-burning, slow-release fertilizer as early as the 1960s. The disadvantage is that struvite is more costly to produce, that is, USD \$140 to \$460 per ton, compared to the USD \$40 to \$50 per ton that is required for phosphate ore. This cost differential is offset by the suggested market value of USD \$198 to \$1885 per ton (Ueno and Fujii 2001; Jaffer et al. 2002). Several fluidized bed reactors have been in full-scale production in Japan, and the recovered struvite has been sold as a fertilizer (Shimamura et al. 2003) at a price of approximately USD \$250 per ton in 2001 dollars (Ueno and Fujii 2001). This market analysis demonstrates, if distributed successfully, that wastewater treatment plants can generate revenue to offset operational costs through struvite recovery processes. Concurrently, these processes are becoming more sustainable.

5.7 Struvite Recovery as a Business

Results from the pilot scale runs helped in the demonstration of the commercial potential of the struvite process. An approximate capital cost of a full-scale plant of 700,000 gal per day (GPD) capacity is presented in Table 5-5. With a selling price of \$500 per ton, the payback period of the plant of 700,000 GPD is about six years. This will decrease if the struvite selling price is increased to up to \$750 per ton. The market price of struvite is flexible, and this researcher found that some of the companies sell struvite at a price of \$1,200 per ton. The economic analysis in the present study is carried out with conservative estimates. The struvite produced gave a clear idea of the amount of the product recovered as well as quality. The pilot plant is used to reduce the investment risks which are usually encountered in unproven production methods. The pilot plant continues to operate to test ideas for new products, new feedstocks, and different operating conditions. Alternatively, it is operated as a production facility, augmenting production from the main plant. A struvite recovery business, using the developed technology, can offer design, consulting, and construction management services for wastewater nutrient recovery systems for primary customers, such as local governments and agricultural operations. In addition to these services, the recovery process can distribute a superior slow-release fertilizer additive in the form of struvite crystals to fertilizer blenders,.

5.8 Outcomes

- The pilot scale trial recovered 93% of $\text{PO}_4^{3-}\text{-P}$ from the centrate in a single step.
- Ammonia recovery was possible by the addition of phosphoric acid to the centrate, if additional nitrogen recovery is desired,
- The amount of magnesium chloride added in the pilot scale was proportionate to the amount needed in the laboratory scale for phosphorus and nitrogen recovery. The amount of caustic needed for pH adjustment in the pilot scale was more than the laboratory scale.
- The recovered struvite contains almost no hazardous materials, and exhibits an equivalent or better fertilizer effectiveness than conventional chemical fertilizers.

- For a plant treating 750,000 gal per day of centrate, a capital investment of \$1.5 million is needed; a net profit of \$452,000/year is possible.

Table 5-1. Details of equipment used in the pilot plant

Equipment	Capacity
Storage tank (ST)	5000 gal
Flushwater tank (FT)	1000 gal
Chemical tanks (CT1, CT2 and CT3)	50 gal
Mixing tank (MT)	50 gal
Struvite tanks (SR1 and SR2) with outside diameter of 50', Height of cone, 34' and height of cylinder 53'.	500 gal
Major pipes of PVC (i.e., all except pipes from chemical tanks, CT1, CT2, CT3)	3" schedule 40
All ball valves (BV) manually operated.	

Table 5-2. Composition of struvite generated in the pilot scale runs

Component	Theoretical Value (%)	Struvite from Trial 1 (%)	Struvite from Trial 2 (%)
magnesium (Mg)	9.8	9.7	9.7
nitrogen (N)	5.7	5.9	5.7
phosphorus (P)	12.7	12.9	12.8
calcium (Ca)	-	0.049	0.018
potassium (K)	-	0.6	0.51

Table 5-3. Chemical requirement for the pilot plant runs

NH ₄ -N in Centrate (mg/L)	NH ₄ -N removed (mg/L)	Total N removed per day (kg)	Total P needed (Kg)	85% H ₃ PO ₄ needed per day (L)	MgCl ₂ .6H ₂ O needed (Kg)	NaOH needed (kg)	Struvite Produced per day (kg)
1000	900	3.41	3.91	8.61	23.19	142.36	33.34
950	850	3.22	3.49	7.69	21.90	134.45	31.48
900	800	3.03	3.07	6.77	20.61	126.55	29.63
850	750	2.84	2.66	5.84	19.33	118.64	27.78
800	700	2.65	2.24	4.92	18.04	110.73	25.93
750	650	2.46	1.82	4.00	16.75	102.82	24.08
700	600	2.27	1.40	3.08	15.46	94.91	22.22
650	550	2.08	0.98	2.16	14.17	87.00	20.37

Table 5-4. Equipment cost of the SBR pilot plant

Unit	Number of units	Capacity	Unit Cost \$	Total Cost \$
Storage Tank	1	5000 gal		5000
Flushwater Tank	1	1000 gal		1000
Chemical Tanks	3	250 gal		250
Mixing Tank	1	50 gal		50
Struvite Tanks	2	500 gal		500
Major Pipes	100 ft	PVC 3" schedule 40	4.31/foot	431
Small connection pipes for chemical tanks	50 ft	PVC 2" schedule 80	2.87/foot	143.5
PVC Fittings	30	--	--	200
Ball Valves	20	PVC 3"	56.85	1177
Ball Valves	10	PVC 2"	9.95	99.5
Static Mixer	1	PVC 3"	100	100
Centrifugal Pump	1			1000
Dosing Pumps	3		450	1350
Blower	1			450
Instrumentation				4000
Estimated Total = \$15,751				

Table 5-5. Capital cost of a full-scale struvite plant; capacity: 700,000 GPD

Equipment	Capacity	Approximate Cost
2 x Struvite Tanks	20,000 gal	\$100,000
Filter Press	2,000 gal	\$100,000
3 x Fiber Glass Chemical Tanks	6,500 gal	\$150,000
2 X Pumps	500 gal/min	\$10,000
3 X Dosing Pumps	10/min	\$45,000
Storage Tank	50,000 gal	\$50,000
Mixing Tank	2,000 gal	\$2,500
Instrumentation and Controls	--	\$35,000
Piping and Fitting	500 ft	\$5,000
Valves: 15 automatic		\$7,500
Building	3,000 sq. ft	\$250,000
Engineering Fees	--	\$100,000
Contractor Fees	--	\$300,000
Drier	40 tons	\$300,000
Packaging Equipment	1	\$50,000
Total		\$1,505,000

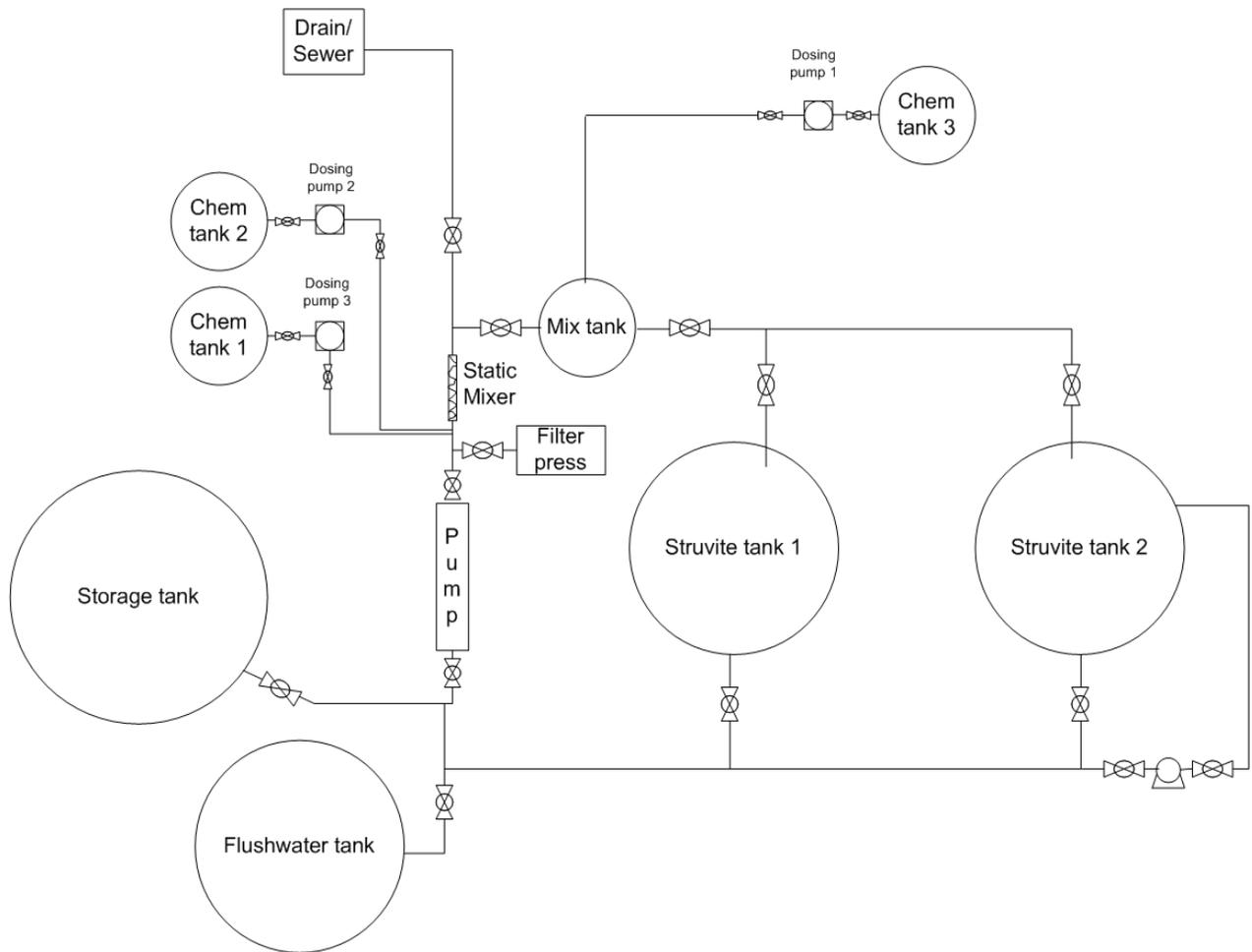


Figure 5-1. Process layout.

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

6.1 Overall Findings

The critical findings in the process development study are as follows:

6.1.1 Mathematical Model of Struvite Precipitation

- A model was developed for predicting precipitation in closed systems containing solutions of ammonium, magnesium, and phosphate. The model incorporates 15 precipitates and explicitly solves for precipitate, residual ion, and dissolved species concentrations using mass balance equations for magnesium, phosphorus, and nitrogen, along with chemical equilibrium and charge balance equations.
- Using the polymath program and a solution procedure that involves converging the residual phosphate concentration to within tolerance limits, the concentration of the different precipitates and residual ion and dissolved species concentrations were determined.
- The model was validated against data collected from literature for synthetic and real wastewaters. The model was able to predict struvite to within 1.6% to 9% ,and the total precipitate prediction errors ranged from 1% to 24.5%.
- This researcher found that for solutions containing Mg, NH₃, and PO₄, the optimal pH for struvite concentration depends on the initial ratio of ammonia, magnesium, and phosphate. A pH of 9.0 optimizes the struvite concentration when the ratio is 1:1:1 and a higher pH of 9.8 when magnesium and phosphate are limiting.
- The equimolar stoichiometric ratio of magnesium, ammonium, and phosphate (i.e., the ratio of their occurrence in struvite) was not ideal for struvite precipitation. To obtain pure struvite, it was necessary to have excess ammonia in the solution with magnesium being the limiting nutrient.
- A titration curve was generated by using the exions concentration and was validated using an experimental curve. The model determined an exion concentration of 0.002566 M in anaerobically treated wastewater from dairy operations. This species concentration should be considered while calculating the amount of caustic needed for pH adjustment.
- The model accurately predicted the amount of a base needed for pH adjustment with an error less than 12.3%, as compared to the experimental quantities.
- The presence of calcium and carbonate species was found to decrease struvite purity.
- In the case of centrate, an excess ammonia concentration and an Mg:P ratio of 1:1 was predicted to be suitable for struvite formation considering the purity of struvite of 95% at this ratio.

- In the case of centrate and dairy flushwater, struvite precipitation was not suitable for an Mg:P ratio of 0.5:1 with excess ammonia because phosphate was removed mainly as calcium phosphate and calcium magnesium carbonate.

6.1.2 Sequential Batch Reactor Operation for Recovery of Nitrogen and Phosphorus as Struvite from Sewage Sludge Centrate and Dairy Wastewater

- The pH level within the recovery processes varies from 8.2 to 9, depending on the strategy of the recovery process. Within the current work a pH of 8.4 to 8.7 was selected to allow for rapid struvite nucleation, being aware that this can cause the precipitation of fines.
- The aeration of centrate was found to increase the pH to 8.4. This is useful for minimizing the caustic requirement for struvite formation and also for reducing carbonate concentration. This improves the quality of struvite by reducing solids with carbonate.
- The NaOH required to adjust the pH of centrate to 8.7 for complete phosphorus recovery was found to be 432 mg/L without aeration.
- The complete nitrogen and phosphorus removal is possible from centrate in a sequential batch reactor. The settling of precipitated struvite is rapid and it was found to settle in 10 min. The struvite separated from the bottom of the reactor was found to have 80% moisture. Filtered struvite was found to have 65% moisture.
- The recovery of phosphorus from animal waste, as a struvite containing precipitate, has been successfully demonstrated using an SBR mode of operation. The next step in the growth of this technology is the development of a field-scale recovery unit at a commercial animal production unit. The operation of a field-scale recovery unit would supply the necessary data to complete a cost/benefit analysis to investigate the economics of the technology. A cost-effective magnesium source of magnesium chloride and a fast, low-cost method of pH adjustment using sodium hydroxide can be utilized to successfully implement this technology at the farm-scale.

6.1.3 Fertilizer Product Formulation Using Struvite Solids

- A cationic polymer can be used to remove fines (struvite crystals) from the reactor. The polymer should be added after 30 min of struvite.
- The settling of struvite solids was improved by a cationic polymer commonly used in wastewater treatment plants. With the polymer usage, the solids content increased from 12% to 16%.
- The KMAG was crystallized to schoenite and picromerite in the presence of water.
- Struvite was found to recrystallize with saturated KMAG to give a product rich in nitrogen, phosphorus, potassium, and magnesium. These crystals were found to be sparingly soluble in water at a neutral pH.

- The solution of KMAG and struvite under acidic condition was crystallized to hannayite and schoenite.
- The x-ray diffraction analysis confirmed that struvite was agglomerated to KMAG.
- Calcium precipitation was not detected in the crystallization of KMAG and struvite.
- Semi-continuous crystallization of struvite with KMAG was found to produce ammonium sulphate, potassium ammonium phosphate, schoenite and picromerite.
- Saturated KMAG was found to absorb ammonia under acidic conditions to give a solid product rich in nitrogen. Crystals formed in the saturated KMAG solution after ammonia absorption were found to retain ammonia in solids.

6.1.4 Pilot Scale Study of the Sequential Batch Operation for Struvite Precipitation

- The pilot scale trial was found to recover 93% of $\text{PO}_4^{3-}\text{-P}$ from the centrate in a single step.
- Ammonia recovery was possible by the addition of phosphoric acid to the centrate if additional nitrogen recovery is desired.
- The amount of magnesium chloride added in the pilot scale was proportionate to the amount needed in the laboratory scale for phosphorus and nitrogen recovery. The amount of caustic needed for pH adjustment in the pilot scale was more than the laboratory scale.
- The recovered struvite contains almost no hazardous materials, and exhibits the equivalent or better fertilizer effectiveness than conventional chemical fertilizers.
- For a plant treating 750,000 gal per day of centrate, a capital investment of \$1.5 million is needed and a net profit of \$452,000/year is possible.

6.2 Future Work

6.2.1 Automation of the Pilot Plant

The pilot plant in this study was run by manually feeding centrate and other chemicals. A model-based control system can be developed using the model described in Chapter 2. The model can calculate the chemicals required for a recovery of nitrogen and phosphorus, and the model can be used to dose appropriate amounts in the reactor. Thus, control algorithms can be developed. The main gap in instrumentation is an online phosphorus probe, which is not available in the market for commercial application. A number of sensors can measure the total or individual chemical species, such as ammonia-N, alkalinity and pH. Overall, a quantum advance

in application and sophistication of instrumentation and controls has occurred, and it is an effective option for an improved process loading rate and conversion efficiency. Automation of the pilot plant can be used to test feasibility of the model application with real-time controls.

6.2.2 Biological Struvite Formation with Existing Enhanced Biological Phosphorus Removal (EBPR) Processes

The formation of extracellular struvite crystals by bacteria was first described by Robinson (1989). Crystal formation is induced by the microorganisms by the combination of NH_4^+ --released by the metabolism of nitrogenous organic substances—with magnesium and phosphate that are present in the medium with concomitant precipitation of struvite. Struvite formation is also achieved by the physical-chemical process when ammonium, magnesium, and phosphate are present in sufficient quantities (Momborg, 1992). *Myxococcus xanthus* can be utilized for the biological formation of struvite. This technique is useful in achieving a supersaturation ratio for the struvite formation other than stoichiometric proportions, as considered in chemical precipitation. The cell membranes are useful for attracting magnesium, phosphate and ammonium ions on them so that supersaturation conditions for the struvite formation are achieved in the bulk around the cell debris. This increases the specificity of the struvite formation, also minimizing the chances of formation of other solids, so it increases the struvite purity. The cell debris can be useful to achieve proper fluidization velocities in the reactor. Conditions under which biological struvite crystallization occur are similar to that of a chemical formation in terms of pH, temperature, supersaturation ratio, and so forth. This researcher looks forward to achieving better, faster struvite crystallization using a biological technique. The following scope of the research is identified:

1. To study induction time (nucleation) and crystal growth of struvite using biological surfaces

2. To model struvite crystallization incorporating the surface energy of seed material, induction time, and so forth
3. To study bacterial surfaces forming struvite and characterize them plus contribute knowledge to the medical field
4. To run a continuous crystallizer on biological formation of struvite
5. To study different stoichiometric proportions of different ionic species in the biological struvite formation
6. To develop a kinetics model on the bacterial struvite formation

$$\text{Total_solids} = \text{Struvite} + \text{MP8s} + \text{MP22s} + \text{MgOH2s} + \text{MHPs} + \text{CaCO3_s} + \text{CaMgCO3_s} +$$

$$\text{CaMg3CO3_s} + \text{Ca5PO4OH_s} + \text{Ca3PO4_s} + \text{Ca8HPO4_H2O} +$$

$$\text{CaHPO4_s} + \text{MgCO3_s} + \text{CaHPO4_5H2Os} + \text{MgCO3_3H2Os} \text{ \#in mg/L}$$

$$\text{Struvite_purity} = 100 * \text{Struvite} / \text{Total_solids} \text{ \#in \%}$$

$$\text{Na} = 2 * \text{Mg} + 363.1082062 * \text{Mg} * \text{OH} + 2.818489290 * \text{Mg} * \text{H} * \text{H} * \text{PO4} / (5.011 * 10^{-13}) / (6.34 * 10^{-8}) + \text{K} + \text{H} + \text{NH4} - 63131.31313 * \text{Mg} * \text{PO4} - \text{Ac} - \text{Cl} - \text{OH} - \text{H} * \text{H} * \text{PO4} / 0.5011000000e-12 / 0.6340000000e-7 - 2 * \text{H} * \text{PO4} / 5.011 * 10^{-13} - 3 * \text{PO4} - 2 * \text{CO3} - \text{H} * \text{CO3} / 0.4688133821e-10 \text{ \#}$$

Charge Balance Equation

$$\text{NaOH} = 40000 * \text{Na} \text{ \# mg/L}$$

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BIOGRAPHICAL SKETCH

Sachin Gadekar was born in Maharashtra (India). He received his Bachelor of Technology in chemical engineering from Laxminarayan Institute of Technology, Nagpur (India). Gadekar is a chemical and bioprocess engineer with understanding and practical knowledge of industrial processes in biofuels, waste-to-energy, and nutrient recovery. He is professionally trained and experienced working in U.S., India and Canada. He has proven ability to use applied research and problem-solving skills to support personal and professional development. In October 2005, he came to University of Florida to pursue his Ph.D. degree in the Agricultural and Biological Engineering Department under the supervision of Dr. Pratap Pullammanappallil. He has received prestigious fellowships and awards for development of sustainable technologies. Till date, Gadekar has more than 9 years of experience working in the chemical and biological engineering fields. He has worked on multiple international projects that bring process and product development expertise. He has given several seminars and technical presentations in national and international conferences. He has written several research articles, and grant proposals.