

**NITROGEN RECOVERY FROM MUNICIPAL WASTEWATER THROUGH
NEWBERYITE TO STRUVITE CRYSTALLIZATION PROCESS**

by

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Abstract

The present study evaluated the feasibility of using newberyite ($\text{MgHPO}_4 \cdot 6\text{H}_2\text{O}$), a thermal decomposition product of struvite, as an inexpensive source of magnesium and phosphate to achieve high nitrogen removal efficiency from domestic wastewater, through struvite recrystallization.

Several bench scale and pilot scale experiments were performed with a different combination of synthetic wastewater, real centrate from the municipal post digestion wastewater stream, synthetic newberyite powder and actual newberyite pellets, derived from thermally decomposing struvite.

Ammonia removal efficiency as high as 94% was achieved in bench scale experiments for dewatering centrate from Annacis wastewater treatment plant at pH 8.5. Orthophosphate residual resulting from newberyite dissolution can be kept as low 23.8 mg/l. The recrystallized product was found to be a mixture of newberyite and struvite. Further experiments were carried out to solubilized newberyite, prior to providing a favorable condition for struvite formation. Although no struvite was formed at this stage, the orthophosphate release was lower, compared to model prediction. The reduction in orthophosphate dissolution is potentially due to low hydraulic retention time. The pilot scale experiment in the UBC fluidized bed reactor was inconclusive, due to an inability to continuously produce struvite pellets, instead of fines.

The present study illustrates the potential for newberyite to struvite recrystallization technology. However, it is recommended to carry out further research on newberyite solubilization and newberyite to struvite, pelletization kinetics.

Lay Summary

Nitrogen is one of the primary nutrients critical to the survival of all living beings. Nevertheless, this essential nutrient can become life-threatening when present in an excess amount in water. Municipal wastewater contains a high concentration ammonia nitrogen and requires proper treatment before discharging it into the water stream. Most conventional nitrogen removal techniques do not recover nitrogen in a usable form, instead it is oxidized back into inert nitrogen gas.

In this research, a novel treatment approach was applied to recover a higher percentage of nitrogen from domestic wastewater in the form of ‘struvite’ – a white crystalline substance which can be used as fertilizer. Several bench scale and pilot scale experiments were performed that compared different conditions and wastewater characteristics. The result obtained from this study shows the potential to recover up to 94% ammonia and can be used as a base for future research to optimize this technology.

Preface

This thesis is original, unpublished, independent work by the author, Afrina Zerín Disha.

The experimental setup configurations used in this research, described in Chapter 3, was adopted from a previous design developed by the Environmental Engineering Group, UBC.

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List of Abbreviations

AAS	Atomic Absorption Spectrophotometer
ANAMMOX	Anaerobic Ammonium Oxidation
AWC	Annacis Wastewater Centre
AWWTP	Annacis Wastewater Treatment Plant
BC	British Columbia
BNR	Biological Nutrient Removal
CI	Confidence Interval
CRT	Crystal Retention Time
CSTR	Continuously Stirred Tank Reactor
DO	Dissolved Oxygen (mg/L)
EC	Electric Conductivity (mS/cm)
FBR	Fluidized Bed Reactor
HRT	Hydraulic Residence Time (h)
LIWWTP	Lulu Island Waste Water Treatment Plant
MAP	Magnesium Ammonium Phosphate
RR	Recycle Ratio
RPM	Revolutions per Minute
SSR	Super Saturation Ratio
TSS	Total Suspended Solids (mg/L)
TP	Total Phosphorus (mg/L)
UBC	University of British Columbia
VFD	Variable Frequency Drive
VSS	Volatile Suspended Solids (mg/L)
WWTP	Waste Water Treatment Plant
XRD	X-ray Diffraction

List of Symbols

d	Day
gm	Grams
h	Hour
H ₂ SO ₄	Sulfuric Acid
kPa	Kilopascal
K _{sp}	Solubility Product
L	Litre
m	Metre
Mg	Magnesium
mg	Milligram
mL	Millilitre
mm	Millimeter
mS/cm	Millisiemens per centimeter
N	Nitrogen
N ₂	Nitrogen Gas
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NH ₄ -N	Ammonium Nitrogen
O ₂	Oxygen Gas
P	Phosphorus
pH	Power of Hydrogen
PO ₄ -P	Phosphate Phosphorus
Q	Flow rate
Re	Reynolds Number
s	Second
μm	Micrometre

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To my Husband and Sister

Whose unparalleled support and patience made this possible

Chapter 1: Introduction

1.1 Background

Nutrient recovery from wastewater in the form of an environment-friendly fertilizer, known as Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has gained wide attention, due to its sustainable nutrient management approach. A large percentage of essential nutrients to all form life, i.e. Nitrogen (N), Phosphorus (P) eventually end up in wastewater. While both nitrogen and phosphorus have very high demand for fertilizers, an excess of these nutrients in natural reservoirs adversely affects the aquatic life causing eutrophication (Britton, 2002; Randall and Tsui, 2002; Kahn and Ansari, 2005). Another problem associated to excess nutrients in the wastewater stream is that it causes the unwanted formation of struvite scaling, which has the potential to damage pumps and other equipment and significantly reduces the operational efficiency (Wilson, 2013; Lobanov et al., 2014; Kalam, 2015). The key solution to these problems is to consider wastewater as a resource, from which nutrients can be recovered and reused.

One technology that has been successfully used to recover nutrients from wastewater is the ‘controlled crystallization of struvite in a fluidized bed reactor’ also known as UBC struvite crystallizer - designed and developed by the Environmental Engineering Group at the University of British Columbia (Dastur, 2001; Britton, 2002; Adnan et al., 2003; Fattah, 2004; Bhuiyan et al., 2008). Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a white crystalline substance comprised of magnesium, ammonium, and phosphorus at equimolar concentrations with six molecules of water. The UBC struvite crystallizer is designed to provide a favorable condition for struvite pellet growth from the wastewater, which can then be used as fertilizer ‘as it is’, or blended with other products to have a

desired NPK ratio. By struvite precipitation, only 1 mole of nitrogen is recovered against 1mole of phosphorus based on struvite stoichiometry. Since municipal wastewater contains a relatively high amount of nitrogen compared to other nutrients, the amount of struvite that can be recovered is limited by the low magnesium and phosphate concentration (Wilson, 2013; Farhana, 2015). Although the UBC struvite crystallization process is proven to recover up to 99% phosphorus from the post-digestion stream, it can only recover 10% of the nitrogen (Britton, 2002; Fattah, 2004; Wilson, 2013; Farhana, 2015). This approach then requires the additional input of phosphorus and magnesium, in order to achieve higher nitrogen removal efficiency.

A possible inexpensive source of Mg and P can be obtained from the struvite itself (Lobanov et al. 2014; Wilson, 2013; Farhana, 2015). Several studies showed the possibility of the thermally decomposing struvite in order to form newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) – which contains no nitrogen and is expected to recrystallize as struvite, when added to the ammonia-rich wastewater. This presents the opportunity to efficiently recycle the struvite- newberyite – struvite, while recovering nitrogen.

Figure 1.1 illustrates the concept of struvite thermal decomposition, newberyite dissolution, and struvite recrystallization.

A bench scale study was conducted by Wilson (2013) to assess the potential for ammonia removal and recovery from municipal post-digestion waste streams via struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization using newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) as a source of magnesium and orthophosphate. Ammonia removal efficiencies as high as 87% were achieved with an optimum pH between 7~8, temperature between 10°C ~ 25°C and Mg:N:P molar ratio 1:1:1 (Wilson, 2013). This study was

limited to synthetic wastewater as process feed and synthetic newberyite powder. Several questions resulting from the bench scale study by Wilson (2013) encouraged this follow-up study, where the feasibility of recovering nitrogen from actual wastewater with the addition of actual newberyite pellets (derived from thermally decomposing original struvite pellets), was investigated.

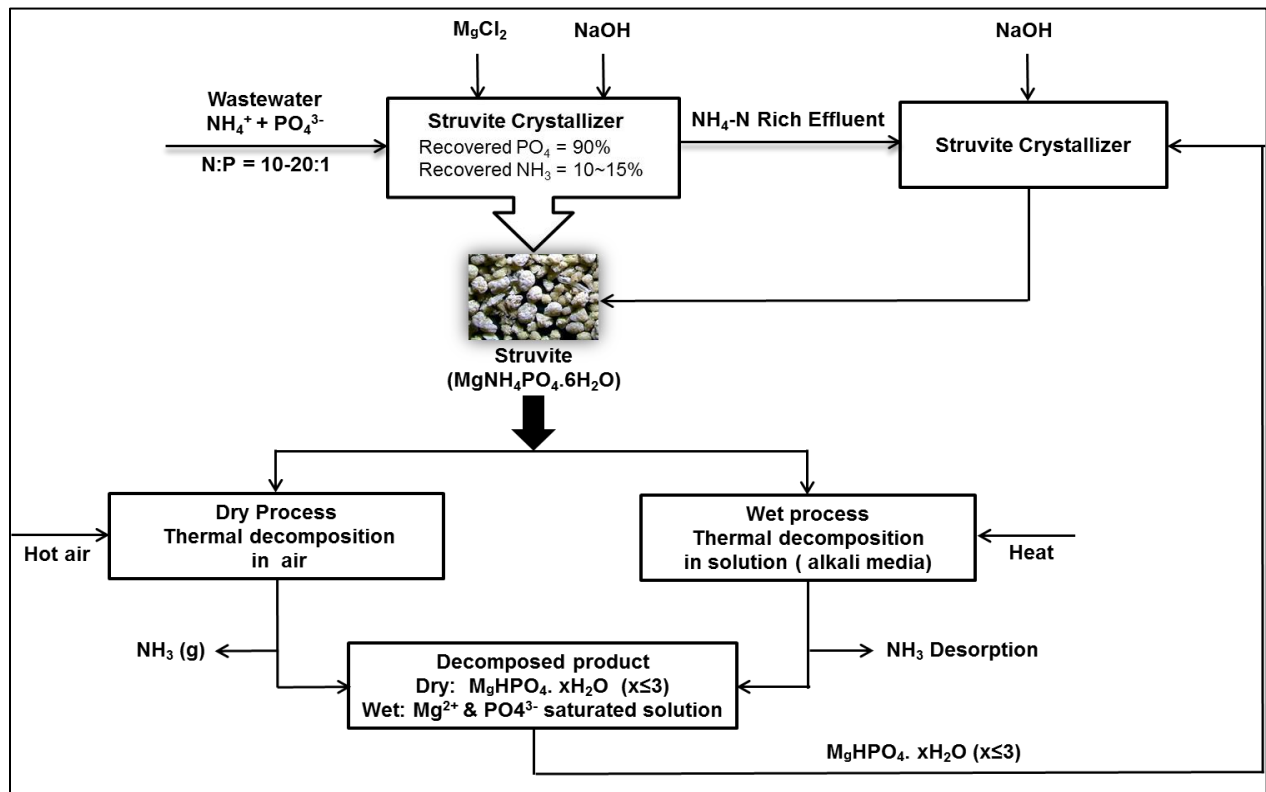


Figure 1.1 Process flow diagram of ammonia recovery using struvite decomposition product

(Farhana, 2015)

1.2 Research Objective

It was hypothesized that the newberyite-the decomposed struvite pellets can be used as a source of external magnesium and orthophosphate for recovering ammonium nitrogen, through struvite recrystallization from wastewater. This recrystallization process can be theoretically continued until maximum nitrogen recovering efficiency is achieved. (Lobanov et al., 2014; Farhana, 2015; Wilson, 2013). To explore this hypothesis, the present study employed a systematic approach to performing several bench scale and pilot scale experiments, with a combination of synthetic and real wastewater, through the addition of synthetic and actual newberyite. The overall objective of the study was to

- a. Assess the possibility and challenges to convert newberyite pellets to struvite pellets in a small-scale reactor
- b. Perform pilot-scale studies to better understand the fundamentals of struvite crystal agglomeration and pelletization in FBRs from newberyite
- c. To verify optimal conditions of the nitrogen recovery process through newberyite to struvite crystallization

1.3 Thesis Outline

This thesis is presented in 5 chapters. The content of the thesis is arranged in the following sequences-

Chapter 1 introduces the topic of nitrogen recovery from wastewater as struvite followed by the research objectives and thesis organization.

Chapter 2 presents the motivation behind studying on nitrogen recovering techniques from wastewater through struvite precipitation and up-to-date literature review on the subject.

Chapter 3 describes the detail experimental methods and related terminology employed in this research

Chapter 4 discuss the experimental results obtained in this study with relevant discussion.

Chapter 5 summarizes the conclusion from the research and provides a recommendation for future work.

Chapter 2: Literature Review

2.1 Importance of Nitrogen Management in Water Streams

Nitrogen is one of the primary nutrients critical to the survival of all living beings (CCME 2009; ThermoEnergy Corporation, 2007). Although the majority of earth's atmosphere is nitrogen (78% N_2), it is considered to be a limiting nutrient for plant growth as most plants cannot access nitrogen as dinitrogen gas (N_2) (Lobanov, 2013; Farhana, 2015). Plants can only take up nitrogen in 'fixed' form i.e. incorporated into compounds such as ammonium ions (NH_4^+), nitrate ions (NO_3^-) or organic nitrogen (NH_2CO) (Maurer et al., 2002). So, there is high demand of nitrogen fertilizer.

Nevertheless, this essential nutrient for life can become life-threatening when present in an excess amount in water. And as a matter of fact, a large portion of the nitrogen compound eventually ends up in wastewater. The source of the excess nitrates can usually be traced to agricultural activities, human wastes, or industrial pollution (Ansari, 2010).

Therefore, it is very important to effectively manage nitrogen compounds in the water stream in order to ensure proper nutrient supply for plant and prevent the adverse effect caused by excess nitrate ion in water.

2.2 Problems Associated with Excess Nitrogen in Water Streams

2.2.1 Eutrophication

Presence of excess phosphorus and nitrogen in water reservoirs is responsible for eutrophication- a widespread environmental concern. Eutrophication is characterized by enhanced algal bloom and can lead to the death of aquatic aerobic organisms by creating oxygen deficient zones i.e dead zones in water bodies (Kahn and Ansari, 2005; Ansari, 2010).

Oversupply of the two plant nutrients N and P induces the photosynthesis process and creates dense blooms of noxious, foul-smelling phytoplankton that reduce water clarity and harm water quality. Algal blooms limit light penetration, reducing growth and causing die-offs of plants in littoral zones while also decreasing the aesthetic value. When these dense algal blooms eventually die, microbial decomposition severely depletes dissolved oxygen, creating a hypoxic or anoxic ‘dead zone’ lacking sufficient oxygen to support most organisms (Conley et al., 2009).

Eutrophication in fresh water and salt water (lakes and oceans) increases un-ionized ammonia, which poses more threat due to its toxicity and rapid diffusion through biological membranes of aquatic organisms (Environment Canada, 2001). The annual cost of damage mediated by eutrophication in the U.S. alone is estimated to be approximately \$2.2 billion (Dodds et al., 2009).

2.2.2 Health Concern

Nitrogen, if presents in high concentration in the form nitrate in water, may cause a life-threatening health concern. It can inhibit the ability of infants to incorporate oxygen into their blood and so results in a condition called the blue baby syndrome or methemoglobinemia. Some recent studies

have indicated a possible connection between elevated nitrate concentrations and cancer. (UNEP-6, 2016).

2.2.3 Environmental Regulation

To combat the environmental and health concern related to the disposal of nutrient-rich municipal sewage in water bodies, government and the regulatory organization have set different discharge criteria for the effluent.

According to Canadian Water Quality Guidelines (Canadian Council of Ministers of the Environment, 2010) for the protection of aquatic life in freshwater, un-ionized ammonia nitrogen value is .019 mg/l for freshwater. The relative percentages of un-ionized and ionized ammonia in aquatic environments are governed by the pH and temperature. Table 2.1 and Table 2.2 listed the guideline values for un-ionized and ionized ammonia respectively.

Nitrate concentration should not exceed 13mg/l for long-term exposure for freshwater species, while for marine water, the limiting value is 200 mg/l (Canadian Council of Ministers of the Environment, 2009).

Table 2.1 Water quality guideline for un-ionized ammonia for protection of aquatic life

(Canadian Council of Ministers of the Environment, 2010)

Aquatic life	Guideline value (mg·L)
Freshwater	0.019
Marine	NRG ¹

¹No recommended guideline

Table 2.2 Water quality guideline for ionized ammonia for protection of aquatic life

(Canadian Council of Ministers of the Environment, 2010)

Temp (°C)	pH							
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	10
0	231	73.0	23.1	7.32	2.33	0.749	0.250	0.042
5	153	48.3	15.3	4.84	1.54	0.502	0.172	0.034
10	102	32.4	10.3	3.26	1.04	0.343	0.121	0.029
15	69.7	22.0	6.98	2.22	0.715	0.239	0.089	0.026
20	48.0	15.2	4.82	1.54	0.499	0.171	0.067	0.024
25	33.5	10.6	3.37	1.08	0.354	0.125	0.053	0.022
30	23.7	7.50	2.39	0.767	0.256	0.094	0.043	0.021

* The guideline values and all reported total ammonia concentrations in this factsheet are reported in mg/L NH₃; measurements of total ammonia in the aquatic environment are often also expressed as mg/L total ammonia-N. The present guideline values (mg/L NH₃) can be converted to mg/L total ammonia-N by multiplying the corresponding guideline value by 0.8224.

** Values falling outside of shaded area should be used with caution.

*** No recommended guideline for marine waters.

2.2.4 Operational Problem in Wastewater Treatment Plant

2.2.4.1 Unintentional Struvite Encrustation

A common problem in many wastewater treatment plants is an accumulation of struvite. The centrate generated during digested sludge dewatering processes carry high ammonium and orthophosphate concentrations and, in the presence of magnesium, they may be supersaturated as magnesium ammonium phosphate (MgNH₄PO₄·6H₂O) or MAP, commonly known as struvite.

High turbulent areas (i.e. pump impellers, pipe bends etc.) and areas with high phosphate, magnesium, along with high pH (i.e. digested sludge liquor pipelines) are prone to struvite formation (Fattah, 2004; Hassan, 2013; Kalam, 2015).

Struvite scaling significantly reduces the pipe diameter, thereby resulting in low operational efficiency due to loss of hydraulic capacity (Wilson, 2013). Moreover, it can damage the pumps and other delicate equipment and cause a costly system shutdown. Struvite deposits are difficult to remove as it is sparingly soluble. Routine system cleaning includes the use of concentrated acid and use of hammer and chisel (Fattah et al., 2008). This problem not only increases the maintenance cost but also induces more process complexity. An additional remedial cost of over 100,000 USD is reported for a mid-size treatment plant (25 MGD) for struvite nuisance (Doyle and Parsons, 2002). Figure 2.1 shows struvite scale formed in some pipes in Lulu Island wastewater treatment plant (LLWWTP).



Figure 2.1 Struvite encrustation in a pipe at Lulu Island WWTP (Fattah, 2004)

2.2.4.2 Additional Nutrient Load

Typical wastewater treatment facilities result in a large amount of sludge and are generally treated by anaerobic digestion. A process flow diagram of conventional wastewater treatment plant is shown in Figure 2.2.

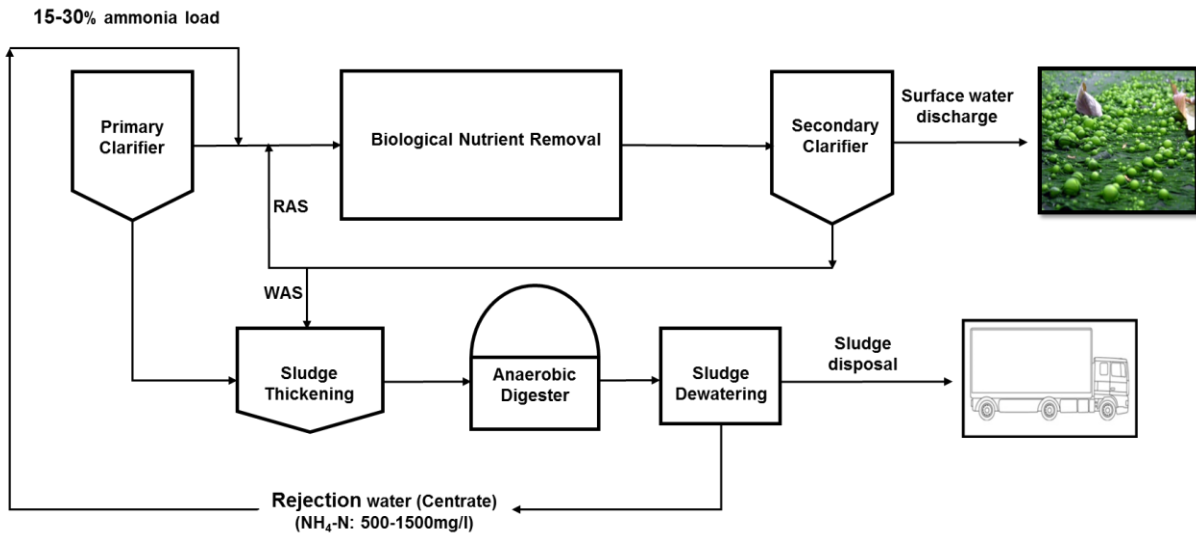


Figure 2.2 Schematic diagram of the conventional wastewater treatment process (Farhana, 2015)

The dewatered sludge liquor contains high ammonium nitrogen which is recycled back to the mainstream for further removal, to meet the ammonia discharge guideline (Hassan, 2013). This recycle can contribute to 15-30% of additional nitrogen loading, although total flow contribution might be as low as 1 % (Wilson, 2013). The process efficiency is significantly impacted due to side stream load addition and it is not cost effective to treat the additional nitrogen load in the

mainstream process. A separate sidestream treatment method is required alongside the mainstream treatment for centrate treatment and eventually, increase the operational cost.

2.3 Conventional Methods for Nitrogen Removal in Wastewater

Nitrogen removal from wastewater can be accomplished through physical, biological or chemical methods or combination of several techniques. The physical treatment methods include air stripping and microwave techniques. The frequently applied biological methods are nitrification-denitrification process, anaerobic ammonium oxidation (Anammox), while the chemical methods include breakpoint chlorination, selective ion exchange, and struvite precipitation.

2.4 Nitrogen Removal by Struvite Precipitation

Controlled struvite or MAP (Magnesium Ammonium Phosphate) precipitation is a popular technique to recover nutrients from anaerobically digested waste. Through a basic precipitation reaction, ammonium is combined with phosphate and magnesium ion of water in order to form a white crystalline odorless compound, struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and thereby recovering excess nitrogen and phosphorus from wastewater. Details of this technology are discussed in Section 2.6.

2.4.1 Advantages of Nutrient Recovery by Struvite Precipitation

Most conventional nitrogen removal techniques are associated with high capital and maintenance cost. Instead of recovering nitrogen in the form of ammonia, it is oxidized back to inert nitrogen gas. Struvite precipitation technique not only recovers nitrogen in a usable form, but also offers a solution to problems associated with the unintentional formation of struvite.

2.4.1.1 Struvite as Fertilizer - Turning a Problem into Solution

Struvite is proven to be a very effective fertilizer due to its slow release rate. The slow releasing nature ensures a prolonged and assured nutrient supply to the plants. It is non odorous, a non-sludgy crystal, which has low solubility in water, thereby avoiding any eutrophication problem that may arise from the runoff of other regular fertilizers (Zhang et al., 2009). The major advantage is it can be readily used after precipitation from the wastewater stream or can be blended with other fertilizers too (Lobanov et al., 2014). Struvite has been used for field crops, potted plants, and ornamental plants and found to be superior or equally effective as a chemical fertilizer. Some of the experimental results of using struvite fertilizers on various crops are summarized in Table 2.3.

Commercial struvite recovery units are operating in different countries, and commercial struvite is available in the marketplace. Japan has been running, full-scale MAP reactors to produce struvite and it is sold as ‘Green Map II’ fertilizer (Munch et al., 2001). In Canada, a struvite crystallizer technology was devolved by the UBC Environmental Engineering Group, which is commercially available by Ostara Nutrient Technologies. Ostara is successfully operating plants in Saskatoon, Saskatchewan and Edmonton, Alberta in Canada and several places in the USA and Europe. The recovered struvite is marketed under the commercial name of Crystal Green (Ostara, 2014).

Table 2.3 Effect of struvite as fertilizer on various plants (Kataki et al., 2016)

S. No.	Crop/plant	Struvite source	Type of experiment	Chemical fertilizer used	Soil type/growing media	Effect of struvite on crop/plant	Remark	Reference
1	Gram (<i>Cicer arietinum</i> L.)	Synthetic water	Pot	Single super-phosphate, Di ammonium phosphate, Ammonium polyphosphate	Typical acid	Variation of P uptake with level of P application	Superior or equally effective as chemical fertilizer	Ghosh et al. (1996)
2	Chinese flowering cabbage (<i>Brassica parachinensis</i>)	Municipal landfill leachate	Pot	Ammonium nitrate + calcium phosphate	Sandy clay (Red Earth) (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao (2003)
3	Water convolvulus (<i>Ipomea aquatica</i> , <i>I. reptans</i>)	Municipal landfill leachate	Pot	-	Sandy clay (Red Earth) (pH 6.2)	No significant difference in growth and no burning effect with increase in struvite dose	Higher dose of struvite does not affect plant	Li and Zhao (2003)
4	Water spinach (<i>Ipomoea aquatica</i>)	Municipal landfill leachate	Pot	Ammonium nitrate + calcium phosphate	Sandy clay (Red Earth) (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao (2003)
5	Chinese chard (<i>Brassica rapavar. chinensis</i>)	Municipal landfill leachate	Pot	Ammonium nitrate + calcium phosphate	Sandy clay (Red Earth) (pH 6.2)	Similar vegetable growth and more Mg, P uptake compared to chemical fertilizer	Comparable effect with chemical fertilizer	Li and Zhao (2003)
6	Maize	NR	Greenhouse pot	Diammonium phosphate	NR	P uptake is efficiency for struvite is 117% and residual P availability is 178%	Higher efficiency compared to chemical fertilizer	Barak and Stafford (2006)
		Swine wastewater	Pot	Superphosphate & urea	Sandy loam	Similar plant height, higher biomass, less N ₂ O emission as with chemical fertilizer	Equally effective with chemical fertilizer	Liu et al. (2011)
		Urine	Field	Triple super-phosphate	Sandy loam (Andosol)	No significant difference in dry yield compared to chemical fertilizer	Similar effect with chemical fertilizer, P in struvite is not limiting for plant	Gell et al. (2011)

2.4.1.2 Economic Consideration

Ammonia recovery by struvite precipitation has the potential for internal revenue generation and can minimize the overall operational costs of treatment plants. Nitrogen fertilizer has a very high demand, and an increasing trend has been observed for the market value of commercially-available nitrogen fertilizer, as shown in Figure 2.3.

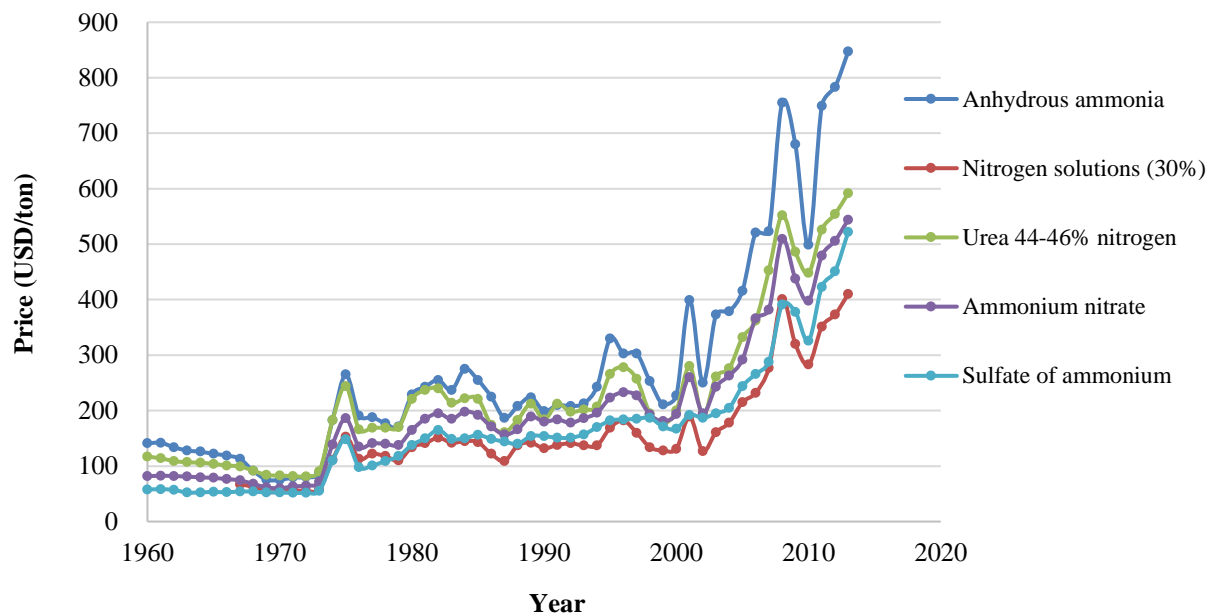


Figure 2.3 Price comparison of nitrogen fertilizers from 1960 to 2013 (Farhana, 2015)

A comparative economic evaluation was done to calculate the net present worth of Ostara's Pearl struvite recovery technology, compared to alternative side stream chemical treatment. (US patented Pearl technology was developed by UBC, made commercially available by Ostara Nutrient Recovery Technologies Inc.). The case study was based on the Nansemond wastewater treatment plant located in Suffolk, Virginia, USA which is designed to treat 30 million gallons of wastewater per day (MGD). The costs are shown in Table 2.4.

It can be seen from the study that the struvite recovery by the Ostara Pearl process would eventually cover the capital cost of the installation, while other options would continue to be costly (Oleszkiewicz et al., 2015).

Table 2.4 Cost analysis of alternatives to struvite recover at Nansemond WWTP in Suffolk, Virginia in USA (Oleszkiewicz et al., 2015)

Cost Description	Do Nothing USD	Side Stream Chemical Treatment USD	Ostara Peral Technology USD
Total annual savings	0	0	528,000
Total annual operating costs	(392,000)	(492,000)	(91,000)
Net annual operating costs	(392,000)	(492,000)	437,000
Capital costs			3,926,000
Net present worth @ 10 years	(3,027,000)	(3,313,000)	(552,000)
Net present worth @ 20 years	(4,885,000)	(5,346,000)	(1,520,000)

2.5 Struvite Chemistry

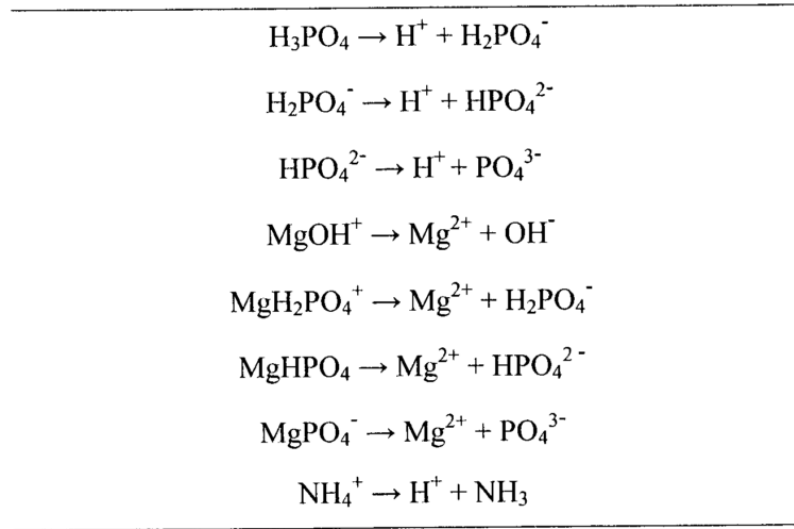
Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) also known as magnesium ammonium phosphate (MAP) is a white crystalline substance comprised of magnesium, ammonium, and phosphate at equimolar concentration, combined with six molecules of water.

General struvite formation reaction is represented by Equation 2.1



The above equation is a simplified representation as several side reactions occur during formation of struvite. The side reactions are listed in Table 2.5

Table 2.5 Side reaction involved in struvite formation (Fattah, 2004)



Struvite precipitation occurs in digester sludge lines in domestic wastewater treatment plants. Struvite can be formed in the human body as well- the most common mineral found in urinary tract stones is struvite (Suzuki et al., 2007)

2.6 UBC Struvite Crystallizer

Controlled crystallization of struvite from wastewater has become a promising technology, and several technologies are being used commercially. The US-patented, Pearl technology was developed by the Environmental Engineering Group of the University of British Columbia, Canada over the past fifteen years. This technology has been made commercially available by Ostara Nutrient Technology Inc. and was first implemented at a large pilot scale (20% flow) at the Gold Bar Wastewater Treatment Plant, Edmonton, AB in 2007. The first commercial, full-scale plant was established in 2009 at the Durham Advanced Wastewater Treatment Facility of Clean Water Service, Portland, USA.

The process is based on a fluidized bed reactor with multiple reactive zones of increasing diameter with height. A typical schematic diagram of the UBC struvite crystallizer is presented in Figure 2.4.

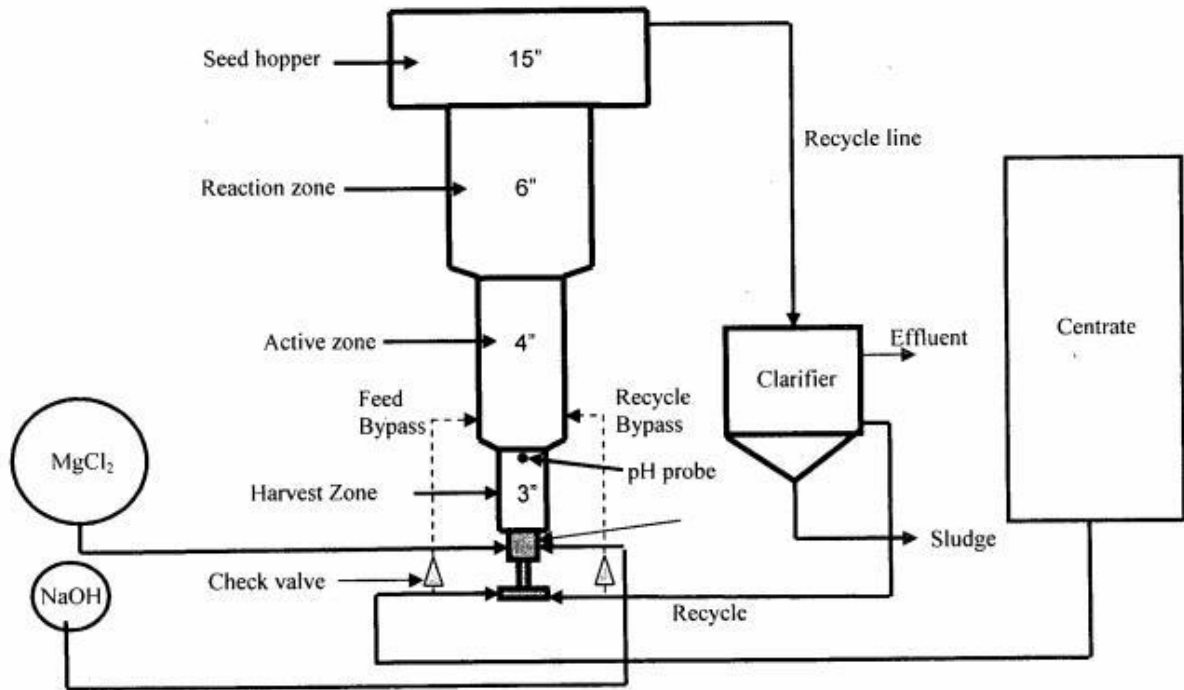


Figure 2.4 General Schematic of UBC struvite crystallization process (Fattah, 2004)

Ammonia and phosphate-rich wastewater are fed into the bottom, while external Mg is provided to maintain the Mg: N: P ratio of 1:1:1. With the addition of caustic, pH is maintained to optimum conditions. The variation in diameter ensures different up-flow velocity at different levels and therefore, provides an opportunity for growth for different particle size at different sections in the column (detail discussed in Section 3.3.1)

Phosphorus and ammonia recovering efficiencies of this process are reported to be 80%~99% and 15%~30%, respectively (Huang, 2003; Britton et al., 2005; Fattah, 2010; Kalam, 2015)

2.6.1 Factors Affecting Struvite Crystallization

Struvite crystallization is a complex process and influenced by several environmental and hydrodynamic factors. Some key parameters identified by the researchers, that affect the formation and growth of struvite crystal, are discussed here.

2.6.1.1 Solubility Product and Supersaturation Ratio

The rate at which struvite forms and dissolves can be described by the struvite solubility product. The solubility product (K_{sp}), more commonly referred as pK_{sp} ($-\log$ of K_{sp}) is defined as the constant of a reaction involving a precipitate and its constituent ion (Fattah, 2010). For struvite, when magnesium, ammonium, and phosphate ion in a solution exceeds the equilibrium solubility of struvite, struvite will form. The discrepancies in the value of struvite solubility product and reported values of pK_{sp} vary from 12.6~13.8 (Dastur, 2001). Some experimental values found from previous studies are listed in Table 2.6

Table 2.6 Reported pK_{sp} values for struvite at 25^o C (Wilson, 2013)

Solid Phase	$pK_{sp} = -\log_{10}K_{sp}$	Reference
Struvite	13.15	Taylor et al., 1963a
	13.26	Ohlinger et al., 1998
	13.36	Babić-Ivančić et al., 2002
	13.36	Bhuiyan et al., 2007
	13.68	Koutsoukos et al., 2007
	13.47	Lobanov et al., 2013

Another important parameter for struvite formation is the supersaturation ratio, commonly known as SSR. It is calculated based on the solubility product and constituent ion concentration. Struvite SSR can be calculated using Equation 2.2

$$SSR = \left[\frac{\{Mg^{2+}\}\{NH_4^+\}\{PO_4^{3-}\}}{K_{sp}} \right]^{\frac{1}{3}} \quad (2.2)$$

At equilibrium state, the SSR is 1. Struvite precipitation occurs when $SSR > 1$, while struvite ends to dissociate in under saturated condition ($SSR < 1$). An SSR of 1~5 is recommended for the UBC struvite crystallizer, for higher nutrient removal efficiency (Hassan, 2013; Kalam, 2015).

2.6.1.2 pH

pH is one of the critical factors affecting the struvite crystallization process. Struvite tends to dissolve in an acidic medium (lower pH) while the precipitation rate increase with the increase of pH. Previous studies showed that a pH value greater than 8.5 is suitable for struvite crystallization (Munch et al., 2001; Jaffer et al., 2002). However, if the pH goes above 9.8, ammonium ion is transferred into free ammonia gas, affecting the N: P ratio. As the N:P ratio drops below the requirement, a pH above 9.8 decreases struvite crystallization (Booker et al., 1999). The optimum pH value for struvite crystallization largely depends on the wastewater characteristics. An operational pH ranging from 7.5~9 have been reported to successfully achieve more than 80% phosphorus recovery through struvite precipitation (Munch et al., 2001; Adnan et al., 2003; Fattah et al., 2008; Rahaman et al., 2008; Hassan, 2013)

2.6.1.3 Temperature

Temperature affects the struvite solubility product, which is related to supersaturation ratio described in Section 2.6.1.1. Struvite solubility is observed to increase with the increase of temperature from 10°C to 50°C (Doyle and Parsons, 2002; Bhuiyan, 2007; Fattah, 2010). At higher temperatures struvite structure changes, reducing the solubility (Doyle and Parsons, 2002). Temperatures varying from 25 °C to 35 °C is considered to provide most desirable conditions for struvite formation (Hassan, 2013), although colder liquid temperatures are also acceptable (Mavinic, 2017).

2.6.1.4 Molar Ratio

Struvite is an equimolar substance of magnesium, ammonium, and orthophosphate. Municipal wastewater contains a higher molar concentration of ammonium compared to orthophosphate; studies showed that high N:P ratio forms relatively pure struvite (Munch et al., 2001; Hassan, 2013; Wilson, 2013).

Magnesium is the limiting factor in struvite formation and supplemental Mg is added to enhance struvite recovery. An Mg : P molar ratio of 1.05:1 to 1.3:1 is recommended to maximize phosphorus recovery from centrate (Huang 2003; Jaffer et al., 2002).

2.6.1.5 Hydrodynamics

The hydrodynamic condition plays an important role in struvite crystallization. An enhanced turbulence allows the particles to collide with each other, resulting in rapid accumulation of struvite (Ohlinger et al., 1999). Struvite particle shape is also dependent on the shear gradient of the turbulence provided inside the reactor. However, the excessive mixing rate may also result in

crystal breakage (Durrant et al., 1999). In the UBC struvite crystallizer, turbulence is achieved by adjusting the up-flow feed velocity (Adnan et al., 2003; Fattah 2010; Kalam, 2015).

2.7 Constraints in Nitrogen Recovery from Wastewater by Struvite Precipitation

Most struvite precipitation technology can successfully recover more than 90% of phosphorus whereas it is reported to recover only a small portion (15% ~20%) of nitrogen (Adnan et al., 2003; Fattah et al., 2008; Kalam, 2015). The main reason is that the nitrogen content in the wastewater stream is much higher than it is stoichiometrically required to precipitate struvite (Lobanov, 2013).

The N:P ratio in struvite is 1:1, whereas in municipal wastewater N:P ratios can be 10:1 (Kalam, 2015; Kataki et al., 2015). So, once all the phosphorous is recovered, the effluent is left with high residual ammonium concentrations. In order to recover a significant portion of ammonium through struvite precipitation, additional input of magnesium and phosphorus is required to maintain struvite stoichiometric ratio of Mg:N:P to 1:1:1. This approach raises the operating cost significantly, making large-scale use economically non-viable (Lobanov, 2013; Kataki et al., 2015). This constraint has prompted a search for alternative sources of P and Mg compounds.

2.8 Possible Nitrogen Recovery Options in The Form of Struvite Using Additional Source of Magnesium and Phosphorus to Wastewater

2.8.1 Using Commercial Reagents

Several researchers explored the possibility of recovering ammonium nitrogen from wastewater through struvite precipitation, adding chemical reagents as an external source of magnesium and phosphorus.

Yetilmezsoy & Sapci-Zengin (2009) investigated ammonium nitrogen recovering efficiency from poultry manure wastewater through struvite precipitation, in a lab scale batch study. Three different combinations of chemicals, including $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{KH}_2\text{PO}_4$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{MgO} + 85\% \text{H}_3\text{PO}_4$ were added to achieve the equimolar ratio of Mg:N:P of struvite. Highest NH_4^+ -N removal was achieved as 85.4% with the addition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{KH}_2\text{PO}_4$ at pH 9, whereas addition of $\text{MgO} + 85\% \text{H}_3\text{PO}_4$ showed the poorest performance (Yetilmezsoy and Sapci-Zengin, 2009). The experimental results are shown in Figure 2.5.

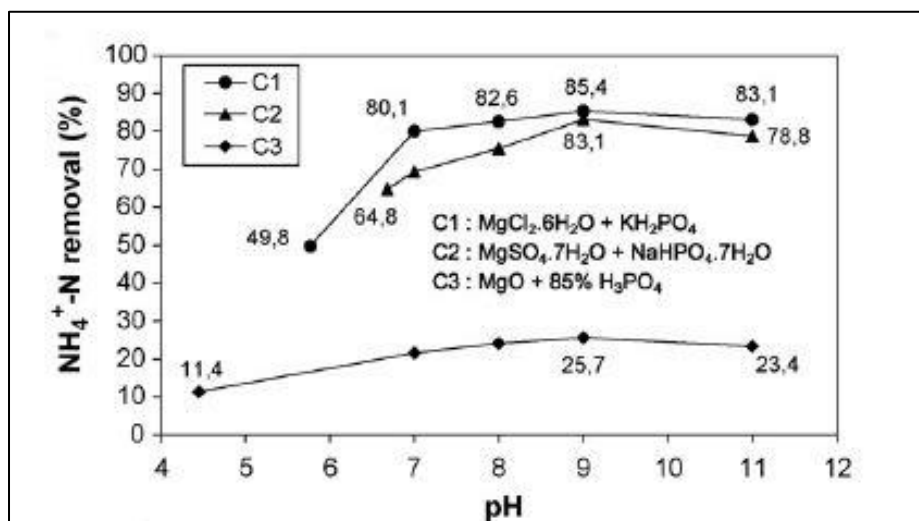


Figure 2.5 Ammonium nitrogen recovering efficiency adding different Mg and P source
(Yetilmezsoy and Sapci-Zengin, 2009)

Another study performed by Kim et al. (2007) used magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and potassium phosphate (KH_2PO_4) to recover ammonium nitrogen from landfill leachate. Around 90% NH_4^+ -N recover efficiency was found at Mg: NH_4 : PO_4 molar ratio of 1.2:1:1.2.

Some other study results, using different external source of magnesium and phosphate on ammonia removal efficiency through struvite precipitation, are summarized in Table 2.7

Table 2.7 Summary of ammonia removal studies through struvite precipitation using chemical reagents (collected by Farhana, 2015)

Type of Wastewater	pH	Initial NH ₄ -N Concentration (mg/l)	Removal % of NH ₄ -N	Sources of Mg ²⁺ and PO ₄ ³⁻ and Mg ²⁺ :NH ₄ ⁺ -N:PO ₄ ³⁻ -P	References
Industrial waste solutions	9.16-9.85	1000	100%	MgO and H ₃ PO ₄	Stefanowicz et al. (1992a)
Combined wastewater from bovine and leather tanning factories	9	200	82%	MgCl ₂ .2H ₂ O and Na ₂ HPO ₄ Mg:N:P = 1:1:1	Tünay et al. (1997)
Anaerobic digester effluents (Molasses Industry)	8.5-9	1400	> 90	MgCl ₂ and H ₃ PO ₄ Mg: N: P = 1.2:1:1.2	Çelen and Türker (2001)
Landfill leachate	9	2750	92%	MgCl ₂ .6H ₂ O and Na ₂ HPO ₄ .12H ₂ O Mg:N:P = 1:1:1	Li and Zhao (2002)
Landfill leachate	9	2750	36%	MgO and 85% H ₃ PO ₄ Mg:N:P = 1:1:1	Li and Zhao (2002)
Landfill leachate	9	2750	70%	MgSO ₄ .7H ₂ O and Ca(H ₂ PO ₄)H ₂ O	Li and Zhao (2002)
Leather tanning wastewater	9.5	6785	94%	MgCl ₂ .6H ₂ O and NaH ₂ PO ₄ .2H ₂ O Mg:N:P = 1:1:1.2	Zengin et al.(2002)
Synthetic wastewater	9.6	—	39%	Bittern as Mg ²⁺ Mg: N: P = 1.3:1.1:1.0	Lee et al.(2003)
Synthetic wastewater	10	—	54%	Seawater as Mg ²⁺ Mg: N: P = 1.3:1.1:1.0	Lee et al.(2003)
Synthetic wastewater	9.1	—	53%	MgCl ₂ as Mg ²⁺ Mg: N: P = 1.3:1.1:1.0	Lee et al. (2003)

Table 2.7 Continued

Type of Wastewater	pH	Initial NH ₄ -N Concentration (mg/l)	Removal % of NH ₄ -N	Sources of Mg ²⁺ and PO ₄ ³⁻ and Mg ²⁺ :NH ₄ ⁺ -N:PO ₄ ³⁻ -P	References
Slurry-type swine wastewater	8-10	2125	98%	MgO and H ₃ PO ₄ Mg: N: P = 3.0:1.0:1.5	Kim et al. (2004)
Anaerobically digested dairy manure	8.5	255	90%	MgCl ₂ ·6H ₂ O and Na ₂ HPO ₄ Mg: N: P = 1.3:1:4.8	Uludag Demirer et al. (2005)
Anaerobically digested dairy manure	8.5	480-520	90%	Mg(OH) ₂ and Na ₂ HPO ₄ Mg: N: P = 2.2:1:4.8	Uludag Demirer et al. (2005)
Simulated wastewater	8.5-10	2000	>95%	MgCl ₂ and Na ₂ HPO ₄	Lobanov and Poilov (2006)
Landfill leachate	8-11	1795	>98%	MgCl ₂ ·6H ₂ O, KH ₂ PO ₄ and struvite seed Mg: N: P = 1.2:1.0:1.2	Kim et al. (2007)
Landfill leachate	9	2132	98.3%	MgO (87%) and Na ₂ HPO ₄ ·12H ₂ O Mg:N:P = 1:1:1.2	Barnes et al. (2007)
Rare-earth smelting company wastewaters	11	1540	95%	MgSO ₄ and Na ₂ HPO ₄ Mg:N:P = 1.2:1:1.3	Li et al. (2007)
Landfill leachate	8.6-9	2700	91%	MgCO ₃ and H ₃ PO ₄ Mg: N: P = 1:1:1	Gunay et al. (2008)
Semiconductor wastewater	9.2	155	>89%	MgCl ₂ ·6H ₂ O and KH ₂ PO ₄ Mg: N: P = 1:1:1	Ryu et al. (2008)
Pre-treatment of Landfill leachate	9.5	2520	85%	MgCl ₂ ·6H ₂ O and Na ₂ HPO ₄ ·12H ₂ O Mg: N: P = 1.5:1:1	Zhang et al. (2009a)
Up-flow anaerobic sludge blanket (UASB) pretreated poultry manure wastewater effluent	9	1318	89.3%	MgCl ₂ ·6H ₂ O and KH ₂ PO ₄ Mg: N: P = 1.5:1:1	Yetilmezsoy and Sapci-Zengin (2009)

It is evident that additional input of Mg and P compounds largely increases the nitrogen recovering efficiency from the wastewater stream. But adding commercial-grade chemicals also contributes to higher operational and maintenance costs, which leads this researcher to look for further sustainable options.

2.8.2 Using Newberyite- A Struvite Decomposition Product

Several researchers have explored the idea of using struvite decomposition products as an alternate source of magnesium and phosphorus. Thermal decomposition of struvite results in a different combination of Mg and PO₄ compounds, which is illustrated in Figure 2.6. The decomposition can be done in air, often referred to as ‘dry process or in solution, commonly known as ‘wet process’ (Farhana, 2015).

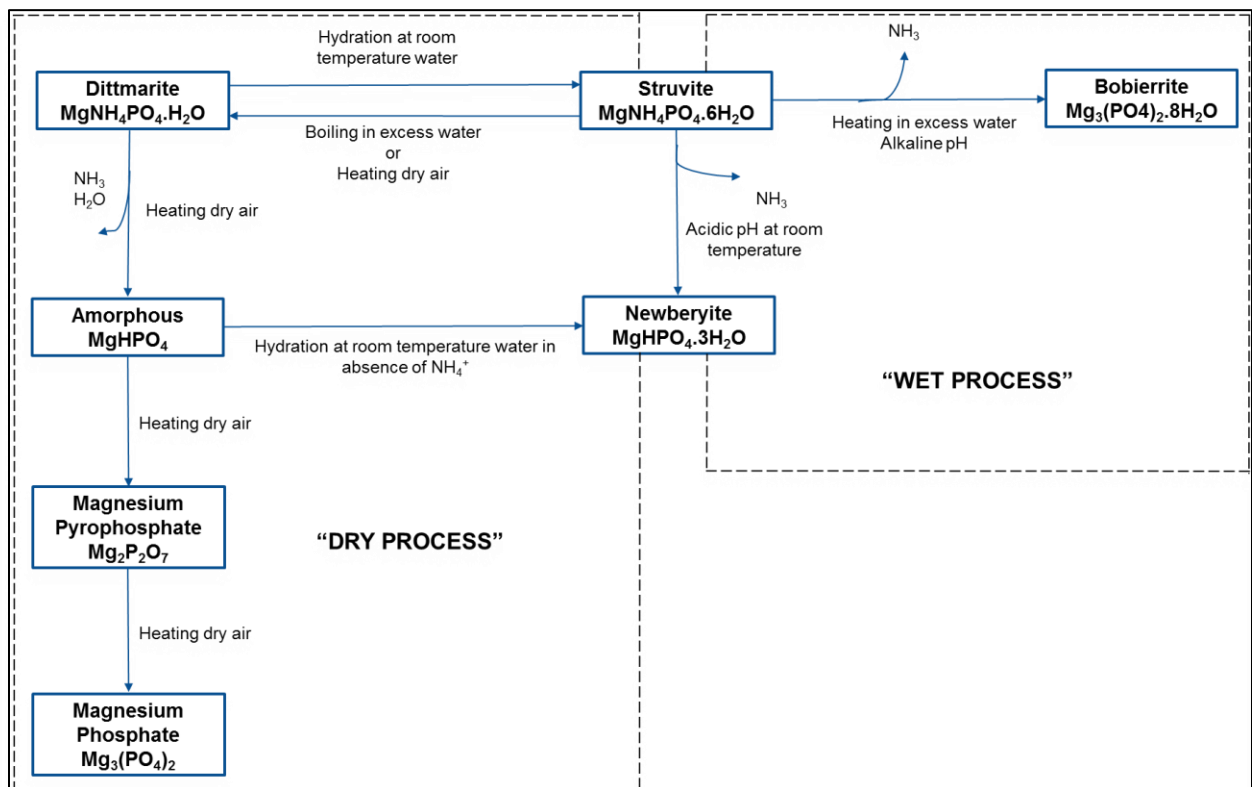


Figure 2.6 The possible transformation of struvite into various solid phases based on the decomposition method (Bhuiyan et al., 2008; Farhana, 2015)

Theoretically, the ideal form of struvite decomposition product which would be most suitable for recovering excess ammonia from wastewater, is found to be newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), since it contains no nitrogen and can release magnesium and orthophosphate to wastewater (Sugiyama et al., 2009; Wilson, 2013).

Newberyite is a white crystalline substance, composed of magnesium hydrogen phosphate with three molecules of water ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$). It can be synthesized by thermally decomposing struvite. It also is reported to be naturally found in the decomposed organic material, urinary tract of human and other animals. (Frost et al., 2005).

The potential of newberyite to recover ammonia was first demonstrated by Sugiyama et al. (2005). A series of experiments showed that newberyite would gradually transform into struvite in ammonia solution under favorable condition. 77% of ammonia was recovered in the first phase. The recovered struvite was decomposed in the air, and the resultant substance was used again in the struvite crystallization process, only to achieve a 41% ammonia removal. The same process was repeated, and 33% ammonia was recovered in the 3rd phase.

The authors further investigated the recycling potential of struvite decomposition product in 2009. A synthetic sheet of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ was developed using the sol-gel technique. When immersed in ammonia solution, 30 % ammonia was recovered within first 3 hours. The sheet was then heated to remove the ammonia and was re-immersed in the solution. 10% ammonia removal efficiency was achieved in the repeated process.

A similar study was conducted by Huang et al. (2011). The struvite decomposed product which was believed to be MgHPO_4 after 1~4 hour of heating struvite at 150°C was added to an ammonia solution. The 1-hour heating product resulted in a 53% ammonia removal in pH 9, whereas for 4-hour decomposed product, the ammonia recover efficiency was reported 47%. It was suspected that the presence of inactive $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Mg}_3(\text{PO}_4)_2$ resulting from prolonging heating, and contributed to less removal efficiency.

The idea was further explored by Wilson (2013) who used synthetic newberyite to assess the potential of ammonia recovery from post-digestion, synthetic wastewater stream via the struvite crystallization process. A maximum 87% ammonia recovery efficiency was achieved. Conditions approaching the optimum were reported to be pH – 7~8, Temperature 10°C ~ 25°C and Mg:N:P molar ratio 1:1:1

2.9 Integrated Approach to Recover Nutrient from Wastewater

In moving forward, if one looks at the bigger picture, different technologies can be combined to achieve the highest efficiency to recover the major nutrients (Mg, N & P) from wastewater.

The struvite crystallization technology can be used in the post-digestion stream to recover the maximum amount of phosphorus and a partial amount of nitrogen, which is already commercially available. Phosphorus and ammonia recovering efficiency of this process are reported to be 80%~99% and 15%~30% respectively (Huang, 2003; Britton et al., 2005; Fattah, 2010; Kalam, 2015).

The recovered struvite will be then decomposed to form newberyite. An extensive study done by Farhana (2015) explored the possibilities of transforming struvite to newberyite by a dry process. She was able to successfully transform particular size of struvite (size <1mm, hardness 300-500 g) into newberyite, in a pilot-scale reactor, within 1.5~2 hours at a humidity of 95%.

The ammonia gas released during struvite to newberyite transformation process can be further captured by acid absorption or a distillation process, and can be utilized as a valuable commercial product (Lei et al., 2007).

Finally, the remaining ammonia recovery from wastewater can be achieved by adding a struvite decomposition product (i.e. newberyite) to the struvite crystallizer effluent, to ensure the sufficient stoichiometric ratio of MG, N, and P for struvite precipitation. Figure 2.7 illustrates this approach.

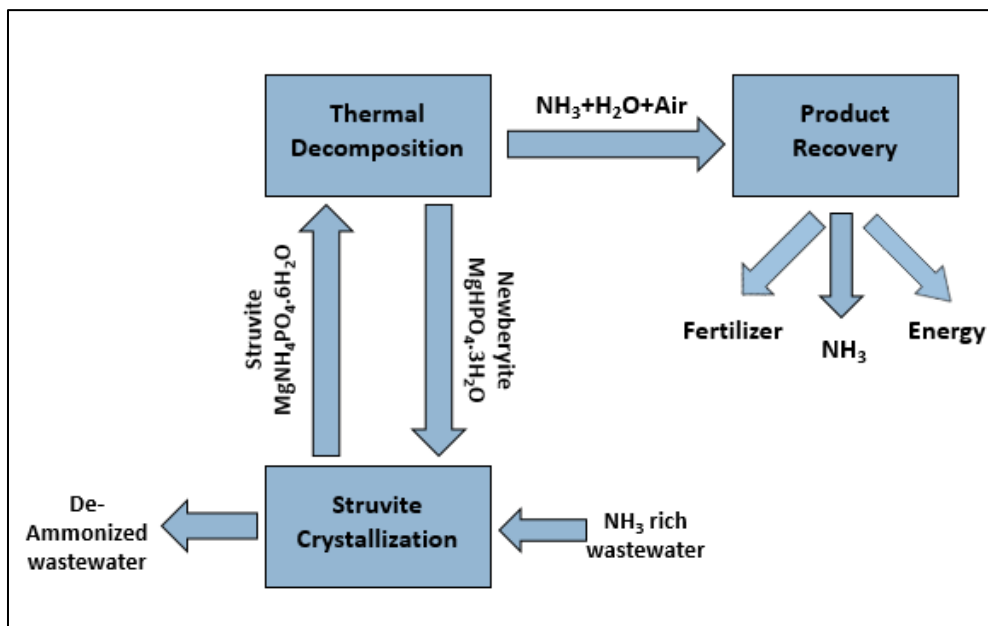


Figure 2.7 Conceptual schematic of an integrated approach to recovering nutrient from wastewater re-using struvite and newberyite (Adopted from Lobanov, 2014)

2.10 Conclusion for Development of the Present Study

Several knowledge gaps exist in the literature about the study of ammonia recovering technology using thermally-decomposed struvite, particularly newberyite. The little research that has been done to study the transformation of newberyite to struvite has mostly used synthetic newberyite (Wilson, 2013). Struvite crystallization is a complex process which would require optimization if real newberyite pellets were to be used, instead of synthetic powder. The present work included studying the ammonia recovering potential from wastewater using real newberyite pellets, in a post-digestion stream of a wastewater plant.

Chapter 3: Materials and Methodology

The main objective of this study was to examine the nitrogen removal capability from wastewater through the struvite crystallization process, by adding newberyite in process feed. A hypothetical configuration was proposed by Wilson (2013) where a different nutrient recovery process would be combined to achieve maximum nitrogen recover efficiency. Figure 3.1 illustrates a continuous or semi-continuous system, consisting of four main operating systems. A primary struvite crystallizer (A), struvite thermal decomposition to form newberyite (B), newberyite dissolution stage (C) and finally sending the newberyite solution to a secondary struvite crystallizer, to recover excess nitrogen (D).

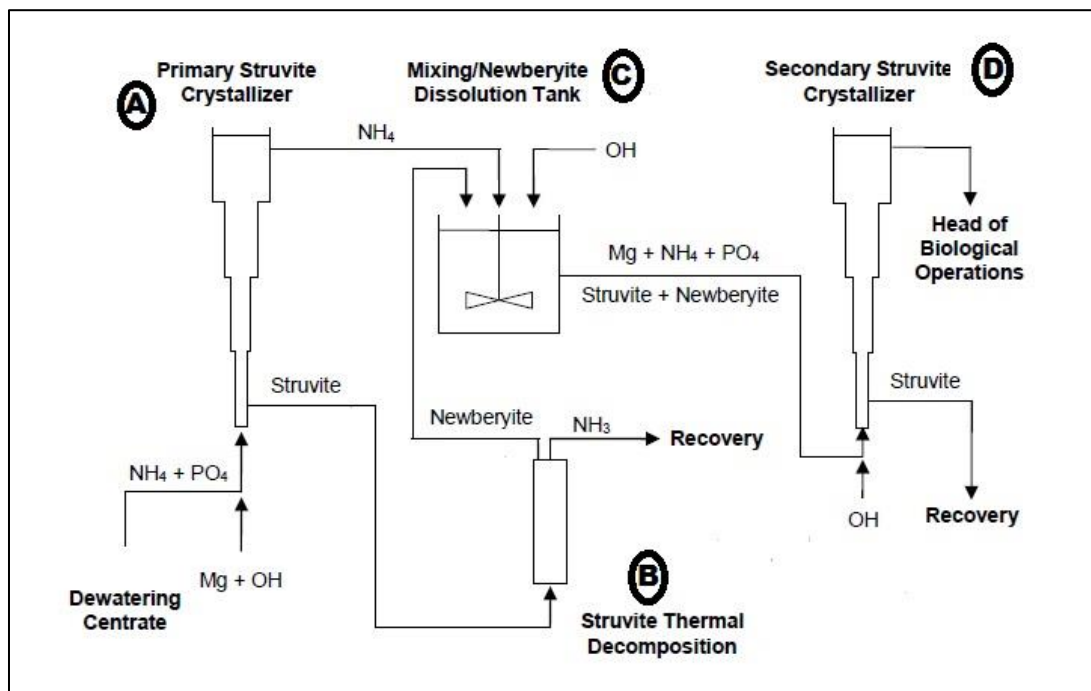


Figure 3.1 Schematic of a potential reactor configuration combining different process to recover ammonia from dewatering centrate (modified from Wilson, 2013)

Extensive research has been done on process A & B (Fattah, 2010; Huang et al., 2010; Wilson, 2013; Farhana, 2015). The present study focused on developing process C (newberyite solubilization technique) and D (using newberyite to recrystallize struvite in struvite crystallizer). The possibility of sending newberyite pellets into a struvite crystallizer, instead of adding external magnesium, was also explored by bench scale experiments.

So, the experimental methodology can be described in 3 different stages as follows:

- Bench-scale experiment for transforming newberyite pellets to struvite
- Newberyite Solubilization batch test
- Pilot-scale experiment on UBC struvite crystallizer to form struvite, by adding solubilized newberyite in the feed

3.1 Bench Scale Experiment for transforming newberyite pellets to struvite

Multiple sets of bench scale batch tests were performed to study the newberyite to struvite conversion mechanism, both in synthetic and real wastewater, with the addition of actual newberyite pellets. Based on the results from Wilson's (2013) study, the experimental conditions were narrowed down to an optimal pH range of 7~8.5 and temperature 10~25 °C. A newberyite dose that would result in Mg: N: P molar ratio 1:1:1 was selected in order to have a high newberyite to struvite conversion efficiency. Duplicate batch tests were performed for each combination of parameters. The experimental conditions are listed in Table 3.1

Table 3.1 Summary of the experimental parameters for duplicate batch tests

Solution	No. of Experiments	Duration (hour)	pH Control	Temperature (° C)	Mg:N:P Molar Ratio
Synthetic Crystallizer Effluent	4	4	7, 8	10, 25	1:1:1
Synthetic Centrate	4	4	7, 8	10, 25	1:1:1
Annacis Island Centrate	3	6	7.5, 8.0, 8.5	25	1:1:1

3.1.1 Batch Test Feed

3.1.1.1 Annacis Island WWTP Centrate

Centrate or dewatered sludge liquor from Annacis Island Waste Water Treatment Plant (WWTP) was used for 3 batch tests. The centrate generated from the plant operation was initially stored in a 5500L tank generally for 2 days, for solids settling, and then the supernatant transferred into a second storage tank. The centrate used in this study was collected from the top of the mentioned storage tank on Aug 28, 2014, and stored in a 10L plastic canister at room temperature in the Environmental Eng. Laboratory. The centrate was analyzed on the same day of collection and 2 months after the collection date. A slight change in ammonium concentration was observed, due to probable volatilization.

3.1.1.2 Synthetic Waste Water

3.1.1.2.1 Synthetic Centrate

A representative synthetic wastewater sample was prepared to contain the constituents' ions of struvite (ammonium and orthophosphate). The calculated amount of reagent grade chemical was mixed with distilled water in a large bucket, to achieve a similar composition of typical dewatering centrate from Annacis Island WWTP (Table 3.2). Monobasic ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$)

was used as orthophosphate (PO_4^{3-}) source and contributed to partial ammonium (NH_4^+) source, while the rest of ammonium (NH_4^+) concentration was achieved by using ammonium chloride (NH_4Cl). Since the Annacis Island centrate is characterized by high organic content, sodium bicarbonate (NaHCO_3) was used to provide the required alkalinity.

3.1.1.2.2 Synthetic Effluent

Synthetic crystallizer effluent was prepared to target the composition of a typical effluent of a pilot-scale, struvite crystallization process (Huang, 2003; Fattah, 2004). 0.5 M magnesium solution was prepared using magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). An equimolar quantity of magnesium solution (with respect to initial orthophosphate) was added to 4L of synthetic centrate. Proper mixing was ensured by motorized mixer rod while pH was maintained at 8.5, by adding the 2M caustic solution. The solution was allowed to settle for a couple of hours. The resulting supernatant was filtered by using Whatman 5 qualitative 12.5 cm diameter filter paper in a vacuum filtration apparatus.

All feed solution was stored in a plastic container at room temperature and was analyzed to record the actual concentration (Refer to Section 3.4 for analytical methods). Table 3.2 summarizes the feed solution concentration used in duplicate batch tests.

Table 3.2 Summary of wastewater composition

Feed	pH	Mg (mg/L)	NH ₄ -N (mg/L)	PO ₄ -P (mg/L)
Annacis Island Centrate (Tested on Aug 24, 2014)	8.0~8.5	4.77	1057	149
Annacis Island Centrate (Tested on Nov 04, 2014)	8.0	4.35	725	132
Synthetic centrate	8.0	0	948	150
Synthetic crystallizer effluent	7.5	13.81	879	8.71

3.1.2 Newberyite Pellets

3.1.2.1 Preparation of Newberyite Pellets

The newberyite pellets used in this study were prepared by thermally decomposing struvite pellets collected from Lulu Island (LIWWTP) and Penticton (COP AWWTP) in a fluidized bed reactor in a controlled environment (Farhana, 2015). An optimum 1.5~ 2-hour fluidization of 0.5~1.00 mm struvite pellets, in a controlled temperature of $80 \pm 2^{\circ}\text{C}$ and relative humidity of $95 \pm 7\%$, results in complete removal of nitrogen and thereby formed newberyite (Farhana, 2015). Each batch yielded approximately 10~12 g of newberyite after thermal decomposition of 20g struvite in the FBR. The newberyite pellets were collected in sealed sample bags and preserved in a vacuum desiccator, to prevent moisture absorption. (See Figure 3.2)



Figure 3.2 Newberyite pellets made by thermally decomposing struvite.

3.1.2.2 Analysis of Newberyite Pellets

The purity of all the newberyite samples was evaluated by chemical and XRD analysis (Refer to Section 3.4 for detail analytical methods). There was slight variation in molecular weight and the molar ratio of the constituents in a different batch of newberyite, since the controlling parameters during fluidization (temperature, humidity) were not identical in each batch.

3.1.3 Batch Test Apparatus Set Up

The batch test apparatus consisted of two, glass-jacketed containers (referred as Reactor A and Reactor B) sitting on top of a stir plate and connected to a heated water bath by 0.8cm (5/16 in) Fisher brand tubing. The water bath provided a continuous flow of heated water through the jackets and ensured controlled temperature. Prior to each set of experiments, the containers were properly cleaned using 5% hydrochloric solution, followed by a rinse with distilled water. An HCl solution helped to dissolve any residual solid particles that might stick to the inside wall during the previous experiment. 400 ml of wastewater feed was added to each reactor and a stirring rod with magnetic stirrer pill was placed inside the reactor. The heated water bath and stirring plates were then turned on for initial temperature adjustment. Once the feed reached the desired stable temperature, a premeasured dose of newberyite that ensures Mg:N:P molar ratio 1:1:1 was added to both reactors. Supplementary Mg was required for synthetic and Annacis centrate feed in order to precipitate struvite. 3~5 ml of 0.5M MgCl_2 solution was added to each reactor, based on the feed and newberyite composition. The time was recorded, and the mixing continued for 4~6 hour. As the reaction continued, the pH kept changing. pH was controlled by manually adding 2M caustic (NaOH) solution with a dropper throughout the duration of the experiment. For the 3 sets of the

experiments, a conductivity probe was connected to reactor A. Figure 3.3 shows the bench scale set up.

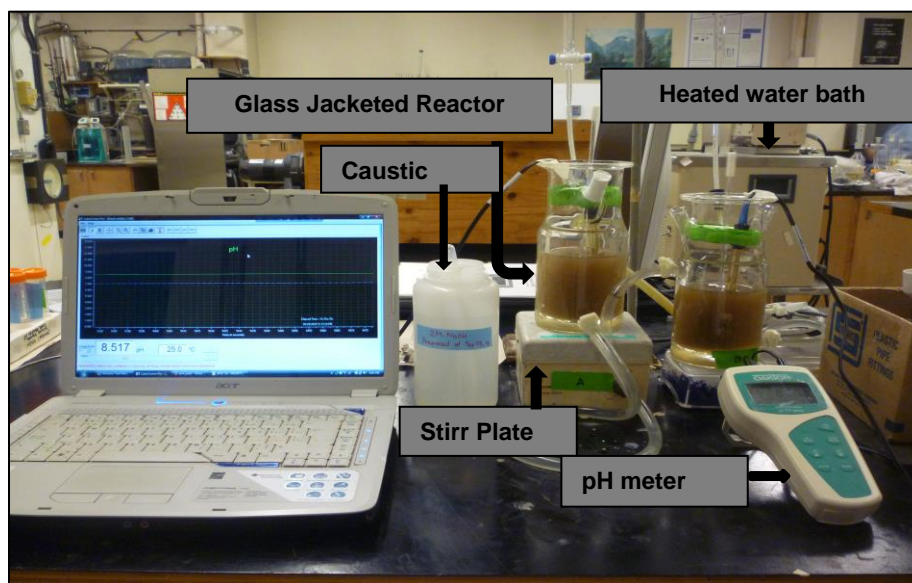


Figure 3.3 Bench scale experiment set up

3.1.3.1 pH Monitoring

An Oakton pH 11 series pH meter with ATC probe was used to monitor the pH of each reactor. The pH probes were submerged into the feed to a certain height through the opening of the top cover. A 3-point calibration was done using the standard buffer solution of pH 4, 7 and 10 prior to each set of experiments, to ensure accurate pH measurements.

3.1.3.2 Conductivity Monitoring

Conductivity was monitored in one of the two apparatuses in 3 sets of experiments with an ATC conductivity probe, along with an Oakton CON 110 meter. The meter was connected to a laptop via an analog-USB cord and conductivity data was recorded at 5-second intervals, using the software provided with the meter.

3.1.3.3 Temperature Monitoring

For one of the reactors, the temperature was monitored by the temperature sensor feature of ATC probe. For the other reactor, a simple thermometer was used to record the temperature.

3.1.4 Sample Collection and Preservation

Liquid samples were collected for every 10 min, 1, 2, 3 & 4 hours after initiation of each batch test by adding the newberyite pellets in the wastewater feed. For Annacis centrate two additional sample at 5 and 6 hours were collected. Two 60 ml syringe with tube extension attached at the top were used to collect samples from each reactor. A representative sample containing both liquids and solids was carefully collected so that the system equilibrium was not disturbed. Samples were then filtered through a 0.45 μm nylon membrane with help of vacuum filter apparatus. The filtrate was stored in a 50-ml centrifuge tube. The liquid sample was acidified with two drops of concentrated HCl, in order to prevent further formation of solid newberyite or struvite.

The solid particles that collected on top of the filter paper were washed with reagent alcohol and distilled water by using the same syringe and vacuum filter. The samples were kept in a small container to dry overnight at room temperature and were stored in individual sample bags. Although solid samples were collected in every hour, only the final hour (4 hours and 6 hours) were analyzed for chemical and XRD analysis. The pellets and powders were separated by a strainer and analyzed separately.

3.2 Newberyite Solubilization Batch Test

The second stage of the experimental methodology was to develop an experimental setup for complete newberyite solubilization without forming any struvite. Due to limited availability of actual newberyite pellets (thermally decomposed struvite), the solubilization experiment was initially done with synthetic newberyite. Later, the experimental set up was modified to a small-scale setup and further solubilization tests were performed with actual newberyite pellets.

3.2.1 Newberyite Solubilization –Phase I

3.2.1.1 Preparation of Synthetic Newberyite

A chemical recipe was devolved based on the chemical composition of newberyite (Mg: P: H₂O ~ 1:1: 3), using the available commercial grade chemicals in the pilot plant. A 30-gallon tank was filled with warm water (25⁰C~30⁰C). 3.0 kg of try sodium phosphate (Na₃PO₄.12H₂O) and 1217 g of 75% H₃PO₄ was dissolved in the water with help of a motorized mixer. An ATC pH probe, connected to Okaton pH 11 series pH meter, was placed inside the tank to monitor the pH. Initially, the pH was less than 6.0. 3.5kg of hexahydrate magnesium chloride (MgCl₂.6H₂O) pellets were dissolved in a separate bucket with 10~15L of warm water. The magnesium solution was then added to the tank and properly mixed. 0.5 kg of Sodium Hydroxide powder (NaOH) was very carefully dissolved in a big plastic jar. The mixing continued in the tank, and pH was adjusted by the addition of NaOH solution and kept at pH 6.5~6.6. (See Figure 3.4 for set up)

After adequate mixing (around 30~45 min) the solution was allowed to settle overnight. Next day, the settled solid particles were collected through the bottom outlet and was filtered using Whatman 5 qualitative 12.5 cm diameter filters and a vacuum apparatus. The retained solids were washed

several times with reagent alcohol and distilled water. The synthetic newberyite was then dried in an oven at 100⁰C overnight, to remove any residual water or alcohol. The dried sample was then stored in a closed bucket and analyzed for Mg, N, and P, prior to use. This procedure yielded approximately 2 kg of synthetic newberyite.



Figure 3.4 Synthetic newberyite preparation tank (left), Settling of synthetic newberyite (top right), Filtered newberyite before drying (bottom right)

3.2.1.2 Preparation of Synthetic Crystallizer Effluent

Synthetic crystallizer effluent was used as wastewater feed for synthetic newberyite solubilization test. The required feed volume was found to be 144 liters for each set of an experiment, for a 6-hour test duration, with a continuous flow rate of 400ml/min. The synthetic feed was prepared in a large tank using reagent grade chemical $\text{NH}_4\text{H}_2\text{PO}_4$ (P and partial N source), NH_4Cl (N source), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Mg Source), NaHCO_3 (Alkalinity Source) and tap water. Ammonium, Magnesium,

and orthophosphate concentration were cross-checked by chemical analysis, prior to the experimental run.

3.2.1.3 Primary Experimental Set Up for Solubility Test

The experimental set up (Figure 3.5) includes a feed tank, a reactor with a mixer and a small clarifier. A pump was used to provide continuous feed supply from the feed tank to the reactor. The inlet feed tubing was connected to the bottom of the reactor, while another outlet tubing connected from the reactor top, was placed into the clarifier. The clarifier was placed at a lower height from the reactor, so that the excess fluid from the reactor passed into the clarifier by gravity flow.

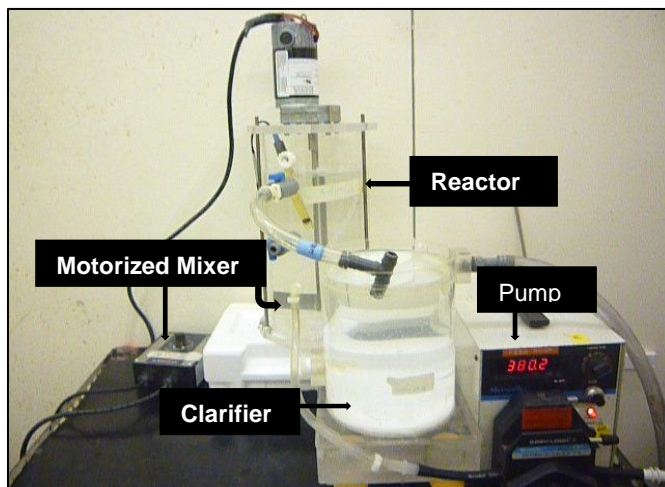


Figure 3.5 A part of the experimental setup for solubility test

Approximately 1.5kg to synthetic newberyite was added into the reactor to ensure 1:1:1 Mg: N: P molar ratio throughout the duration of the test. The pump was turned on to provide a continuous supply of feed to the reactor. An ATC pH probe was inserted into the reactor, and pH was

controlled by a pH controller, with the addition of 0.5 M HCl solution. The mixing speed was set up to an optimum level so that maximum mixing could occur without losing fines through the outlet tube. The solubilized feed was then collected in the clarifier and finally transferred to the drain via a connecting tube. The experimental conditions are summarized in Table 3.3.

Table 3.3 Experimental condition for Newberyite solubilization- Phase I

Newberyite Solubilization-Phase I	
No of Experiment	5
Test Duration	6 hours
Type of Newberyite	Synthetic
Feed Type	Synthetic Crystallizer Effluent
Flow rate of Feed	400ml/min
pH set point	4.1, 4.6, 5.0, 5.6, 5.9
Temperature	21 ⁰ C~23 ⁰ C (Room temperature)

3.2.1.4 Sample Collection

The liquid sample was collected from the clarifier at every 10 minutes, 1, 2,3,4,5 and 6 hours from the beginning of the experiment with the help of 60 ml syringe. For each sampling point, two sets of samples, filtered and unfiltered liquid, were stored in two separate 50 ml centrifuge tube. Samples were pushed through a Millipore 47 mm diameter 0.45µm nylon membrane filter for filtration. Both filtered and unfiltered samples were acidified with 2/3 drops of concentrated HCl, to prevent further formation of a solid phase, by creating undersaturation in the sample for both newberyite and struvite.

3.2.2 Newberyite Solubilization –Phase II

3.2.2.1 Experimental Set Up and Materials

For phase II, a smaller size reactor was used to reduce the required amount of newberyite and run the experiment with actual newberyite pellets. Synthetic centrate was used as wastewater feed. A detailed description for preparation of synthetic centrate and newberyite pellets can be found in Section 3.1.1.2.1 and 3.1.2.1, respectively. A summary of the experimental condition is given in Table 3.4

A calculated amount of newberyite pellets were placed in the reactor and continuous synthetic feed supply of 20 ml/min was ensured by a 1-100 rpm MasterflexTM L/S peristaltic pump. The pellets and liquid wastewater feed were slowly mixed with a magnetic stirrer. The effluent was first stored in a small clarifier for collecting samples before discarding it to the drain via an outlet tube. pH was controlled by adding 0.2M HCl with a HANNA instrument pH controller. The pH controller was connected to an Oakton pH probe and was placed inside the reactor to monitor the pH. The phase II newberyite solubilization tests were performed in 20⁰C. Temperature control was achieved by a cooled/heated water bath system.

Table 3.4 Experimental condition for Newberyite solubilization- Phase II

Newberyite Solubilization-Phase II	
No of Experiment	3
Test Duration	2.5 to 4.0 hour
Newberyite Type	Actual pellets made by thermally decomposing
Feed Type	Synthetic Crystallizer Effluent
Flow rate of Feed	20ml/min
Hydraulic Retention time	20 min
pH set point	4.5, 5.0, 6.0
Temperature	20 ⁰ C

3.2.2.2 Sample Collection

The liquid sample was collected in every 30 min by a 60ml syringe with extension tubing, and the filtered sample was stored in a 50ml centrifuge tube. Samples were acidified to prevent further formation of any solid particles.

3.3 Pilot Scale Experiment on UBC Struvite Crystallizer

2 sets of pilot-scale experiments were completed, to explore the possibility of recovering nitrogen in the form of struvite by the hypothetical addition of newberyite in wastewater. Due to limited availability of newberyite pellets and problems associated with synthetic newberyite powder, no newberyite was added into the system. Instead of adding the newberyite pellets or powder, a synthetic feed was used whose Mg, N and P concentration would be similar, if hypothetically, all the newberyite were dissolved in it.

The experimental setup systems consisted of a pilot-scale, fluidized bed reactor, storage tanks, and a pH control system. A simplified schematic diagram of the setup is shown in Figure 3.6

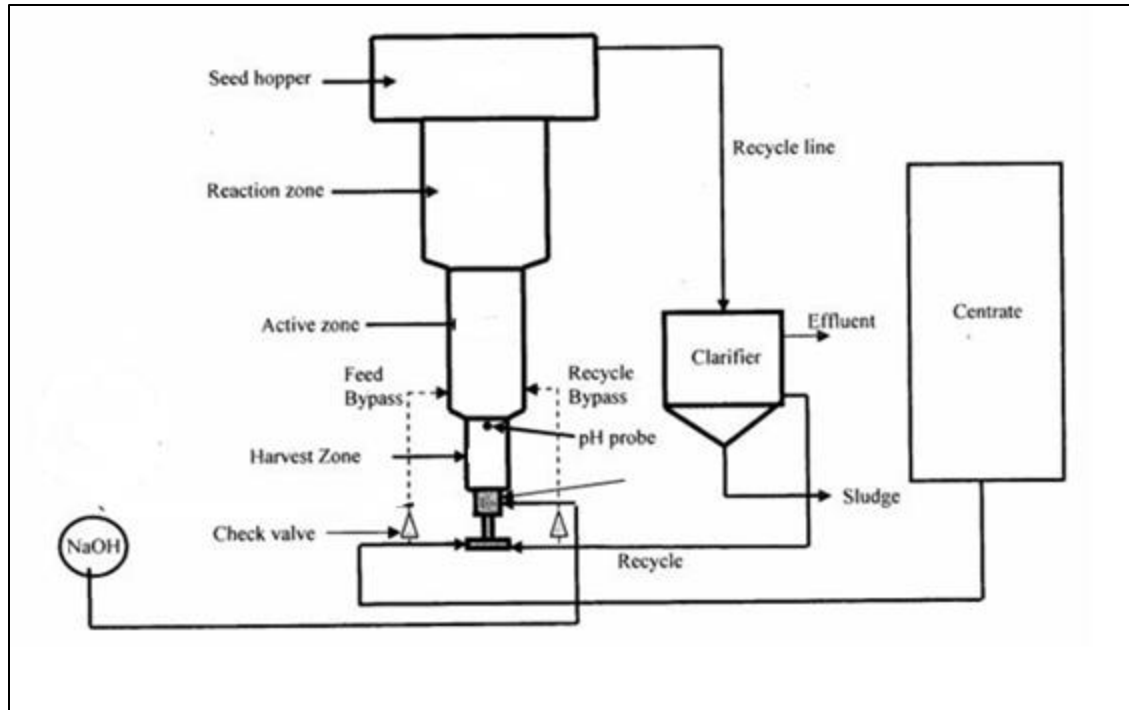


Figure 3.6 Schematic diagram of the pilot-scale experiment setup (modified form Fattah, 2004)

3.3.1 Struvite Crystallizer Reactor Design

A slightly modified version of the UBC struvite crystallizer (Fattah, 2004) was used to run the pilot scale experiments. Through continuous stimulation with the Dann Potts model (Kalam, 2015) and PHREEQC, the design parameters were set to achieve the most favorable condition for struvite crystal growth.

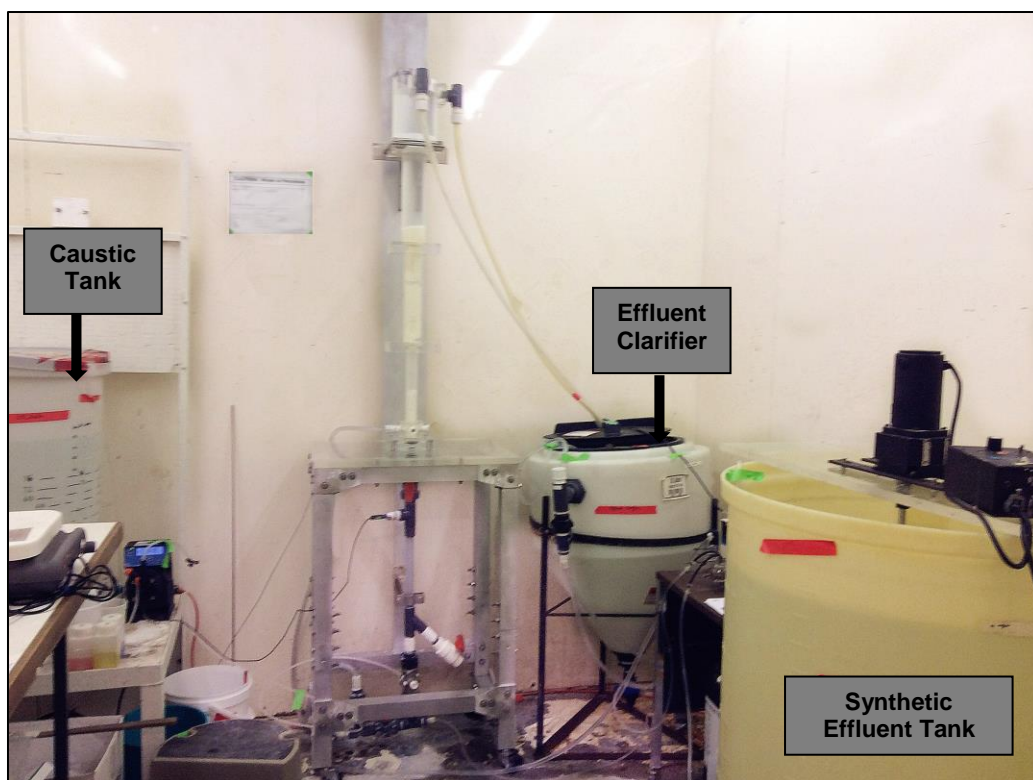


Figure 3.7 A partial view of the Pilot scale experimental set up

The reactor design is based on the concept of the fluidized bed (See Figure 3.7). It was made of 5 vertical columns of varying diameter, increasing from the bottom to top. The varying diameter facilitated the turbulent mixing which is a requirement for crystal formation (Rahaman, 2009). Due to decreasing up-flow velocity with increasing height, the fluidized particles were separated by size at a different section of the reactor (Adnan et al., 2003; Fattah, 2004; Rahaman et al., 2008). As the particles grew larger, they tend to move down and could be collected from the bottom through an outlet valve.

The reactor was made of transparent polyvinyl chloride plastic. The key sections of the fluidized bed crystallizer are listed:

Injection port

The bottom section of the reactor where all the process feed (synthetic influent, recycle feed returning from the external clarifier, caustic feed to maintain the desired pH) was injected into the reactor through a different pump at a certain specific rate. A high supersaturation ratio was expected to be achieved at this point (Fattah, 2010; Kalam, 2015)

Harvest Zone

Just on top of the injection port, a vertical section was separated by a ball valve from rest of the column section. An outlet valve was attached to this section to harvest solid particles.

Active zone

The two-vertical column section of 12inch height each, and diameter of 1inch and 2 inches respectively, above the harvesting zone, was referred as active zones. (See Figure 3.8 for crystal formation)



Figure 3.8 Struvite crystal forming in the active zone

Fine zones

The fine particles accumulated at the top of the active zone, since the up-flow velocity was low enough to keep them in this zone.

Seed hopper

A clarifying section referred as ‘seed hopper’ was located at the top of the reactor. This section trapped the fine particles from washing out. Two tubes were connected to overflow outlets of the seed hopper, to transfer the crystallizer effluent to the external clarifier.

Section dimensions are shown in Table 3.5, with an overall HRT =7 minutes.

Table 3.5 Design value of the struvite crystallizer column

Section	Length	Calculated Dia (maintaining the same ratio as UBC FBR)	Actual Dia	Area	Up-Flow Velocity to be maintained	Total Flow Rate	HRT
	inch	inch	inch	cm ²	cm/min	ml/min	min
Harvest Zone	18	0.75	0.75	2.85	287.70	820	7.0
Active Zone 1	12	0.97	1.0	4.82	170.23	820	
Active Zone 2	12	1.44	2.0	10.56	77.64	820	
Fine Zone	12	3.78	3.0	72.69	11.28	820	
Seed Hoper	15	7.50	7.5	285.02	2.88	820	

3.3.2 Process Feed

There were three feeds lines connected to the reactor, each accompanied by its own feed pump or controller.

3.3.2.1 Influent Feed

Synthetic feed with a high concentration of Mg (1306mg/l), N (950 mg/l) and P (1755mg/L) was used as influent for the pilot-scale experiments. (due to the small volume of newberyite being available to add in the feed). If all the newberyite were to be dissolved in regular crystallizer effluent, it would result in a highly concentrated solution of Mg, N, and P. Theoretically, these concentrations were calculated and based on that, the synthetic feed was prepared.

Each experiment required approx. 500 L of synthetic feed. Commercial grade magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), phosphoric acid (75% H_3PO_4), and ammonium chloride (NH_4Cl) were mixed with tap water, with a motor-shaft mixer in a large tank. The influent was pumped into the reactor using a MasterflexTM L/S peristaltic pump at a flow rate of 20 ml/min to the struvite reactor through a ½ inch (1.27 cm) tubing.

3.3.2.2 Caustic Feed

A continuous supply of caustic feed was provided to control the pH to a certain set point. This was achieved through the controlled addition of 1M caustic solution with a HANNA Instruments pH controller. The pH control unit allowed the pH to be controlled within ± 0.05 . The caustic solution was prepared by dissolving commercial grade sodium hydroxide pellets in 100L of tap water and stored in a 120L tank. An Oakton pH probe, connected to the pH controller, was inserted on top of the harvesting zone and regularly monitored.

3.3.2.3 Recycle Feed

Once the feed had passed through the controlled environment of the fluidized bed reactor, it was stored in an external clarifier. A recycle line from that clarifier was connected to the injection port of the reactor and was pumped by a Moyno 500 series progressing cavity pump, with a ½ HP motor and a digital VFD (variable frequency drive) controller. The recycle feed was controlled by a ball valve and occasionally redirected to the bypass line during harvesting or cleaning the injection port.

3.3.3 Process Operation

Wastewater was fed into the bottom of the reactor, along with the recycle feed. The pH set point and the up-flow velocity were set in such a way so that it resulted in the desired supersaturation ratio. In the beginning, some struvite pellets of 0.5mm ~1.00 mm were added in the reactor to initiate the crystallization process, known as ‘seeding’. Seeding is done to reduce the time required for nucleation. As the reaction continued in the fluidized bed reactor, the pH gradually decreased (Fattah, 2004). Once the pH dropped below the set point, the pH controller pumped in the caustic, until the set point was achieved. Struvite particles started to form within the controlled environment inside the reactor. As the particles increase in size, they moved towards lower section, overcoming the high up-flow velocity. The bottom section would enhance crystal growth because of high turbulence (Ohlinger et al., 1999). When enough particles were stored in the harvesting section, the main feed line was diverted through the bypass line. The valve on top of the harvesting zone was turned off to isolate that portion from the remaining reactor. Particles were collected in a bucket using the harvesting valve outlet. Once the harvesting was complete, the reactor was resumed its normal operation. This process was run for 14 days.

3.3.4 Reactor Operating Condition

The reactor operating condition was maintained as constant as possible throughout the duration of the experiment. However, due to reoccurring issues with the pH controller, the pH varied a bit. Additionally, after observing the pattern of struvite formation, the expected SSR was slightly varied to get more particles. The operational conditions are summarized in Table 3.6.

Table 3.6 Operational conditions for pilot scale experiments in struvite crystallizer

Pilot-scale experiment in struvite crystallizer	
No of Experiment	2
Test Duration	14 days
Feed Type	Synthetic Crystallizer Effluent (hypothetical solution of newberyite and synthetic effluent)
Flow rate of influent feed	20 ml/min
Recycle Ratio	40
Highest up flow velocity	288 cm/min
Expected SSR	1, 2
pH set point	8.6, 7.26
Temperature	20 ⁰ ~ 25 ⁰ C (room temperature)

3.3.5 Monitoring and Maintenance

Continuous monitoring and maintenance needed to be done during the experimental run. Influent and recycle feed flow were monitored twice a day, by observing the required time to fill up a certain level of the graduated cylinder. Inside temperature and pH of the reactor was monitored on top of the harvesting zone with an ATC Oakton probe connected to the pH controller. The external clarifier temperature and pH were also monitored by Oakton pH meter. pH was calibrated

at the beginning using the standard buffer solution of pH 4, pH 7 and pH 10. The deviation of the standard reading was recorded after the experiments, and the pH was adjusted accordingly.

Several operational problems were encountered during the run, and the experiments had to be shut down for a couple of days, before re-starting. Solids accumulation and plugging of the injection port caused pressure build-up inside the reactor, which displaced the recycle tube, and the experiment room was flooded overnight. The most probable cause of plugging was the low up-flow velocity.

To alleviate the difficulties of the stroke pumping of the Masterflex™ pump, two heads were used simultaneously in a special way and eventually smooth continuous pumping was achieved.

It was very difficult to achieve a consisted pH set point with the pH controller. There were abrupt changes in pH and it required continuous manual adjusting.

3.3.6 Sample Collection

Grab samples were collected from the seed hopper and the external clarifier with a syringe once a day, during the 2-week duration of each experiment. 2 sets of samples were collected from each sampling point. One set was filtered through a Millipore 0.45μm nylon membrane filter. Both filtered and unfiltered samples were acidified with strong HCl to dissolve particles and prevent further solids formation.

Solid samples were collected through the harvesting valve every 2nd or 3rd alternate day. The solids were then dried in open air and stored in airtight plastic bags for analysis.

3.4 Sample Analysis

All the wastewater feed, newberyite sample, liquid and solid samples collected during different experiments were analyzed for ammonia, magnesium, and orthophosphate. XRD analysis was also performed for selected solid samples, to confirm solid composition. Each sample was analyzed in triplicates to ensure satisfactory technical reproducibility. The chemical analysis was conducted at the Environmental Engineering Laboratory, UBC, Vancouver. The XRD analysis was performed in the Chemistry Department Laboratory, UBC.

3.4.1 Sample Preparation

3.4.1.1 Liquid Sample Preparation

The liquid sample was simply diluted to produce a good reading within the detection limit of the measuring instrument (refer to Section 3.4.2 and 3.4.3 for detailed procedure).

3.4.1.2 Solid Sample Preparation

All solid samples were crushed into powder using a ceramic mortar and pestle. A known amount of the finely crushed sample (approximately ~0.1g) was dissolved in distilled water with the help of a 100ml volumetric flask. Several drops of concentrated hydrochloric acid (HCl) were added to dissolve the particles. This stock solution was then diluted in different dilution ratios, for different analytical parameters.

3.4.2 Magnesium

Magnesium analysis was performed by flame atomic absorption spectrophotometry using a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer (AAS). (See Appendix

A for instrument operational settings). Samples and calibration standard were diluted in 1:10 ratio with 20g/l lanthanum solution (prepared from reagent grade Hexahydrate Lanthanum Nitrate or Lanthanum Chloride and de-ionized water) in a 25ml tube. The purpose of using lanthanum solution was to prevent the interference of carbonate or other ionic species in AAS. Some sample required a dilution factor of 20. One drop of concentrated nitric acid (HNO_3) was added to reduce the interference of any soluble organics. To ensure uniform mixing, each tube was agitated in a vortex mixer for minimum 10 seconds. An eight-point standard calibration curve (0, 0.25, 0.5, 1.0, 2.5, 5.0, 10.0, 15.0 and 25.0 mg/l Mg^{2+}) was developed to record the Mg concentration of the samples. Each sample was analyzed for three different angle positions, to improve accuracy.

3.4.3 Ammonia and Orthophosphate

Ammonia and orthophosphate of the samples were measured using the flow injection analysis method using Lachat QuickChem 8000 instrument. The standard method followed for ammonia and orthophosphate were 4500-NH₃ H and 4500-PG, respectively, adapted from Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 2012). Samples were diluted in the range of 1:50 to 1:100 with distilled water. The calibration standard was prepared from reagent grade potassium phosphate monobasic (KH_2PO_4) and ammonium chloride (NH_4Cl) with the addition of distilled water. (See Appendix A for instrument operational settings)

3.4.4 XRD Identification of Solid Phase

X-ray powder diffraction (XRD) analysis was performed for phase identification of the solid particles. The solid samples were grounded to a fine powder with a mortar and pastel. The fine powder was then placed into a sample holder assuring a flat upper surface. The samples were then

analyzed with a B Bruker D8 Advance X-ray diffractometer using $\text{CuK}\alpha$ radiation. The intensity of diffracted X-rays was continuously recorded as the sample and detector rotated through their respective angles. The XRD output peak patterns were matched with the standard peak of the known solid crystalline sample from a powder diffraction database file, provided by International Center for Diffraction Data. (See Appendix A for pattern database details and instrument settings).

3.4.5 Caustic (NaOH) Concentration

Standard acid titration method (ASTM, 2009) was used to determine the molarity of the caustic solution. A grab sample from the caustic tank was titrated with a known concentration of strong acid (HNO_3) and the end was determined with phenolphthalein indicator.

The concentration of base (NaOH) was calculated from the Equation 3.1.

$$C_b = (C_a \times V_a) / V_b \quad \dots\dots\dots (3.1)$$

Where, C_a = Concentration of acid, M

V_a = Volume of acid used in ml

C_b = Concentration of base, M

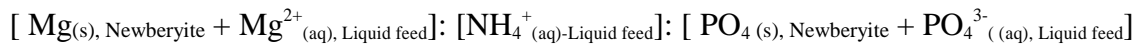
V_b = Volume of base used in ml

3.5 Terminology

For better understanding, several terms used to describe the material and methodology are defined here.

3.5.1 Molar Ratio

The molar ratio is defined as the proportion of each element in a balanced state of a chemical reaction. In the context of newberyite dosing, the molar amount of magnesium and phosphorus is contributed both from the solid newberyite and liquid wastewater feed. While nitrogen molar content is solely from the liquid feed as there is no nitrogen in newberyite. Mg: N: P molar ratio can be written as follows for our discussion case.



3.5.2 Supersaturation Ratio

Super saturation ratio is one of the most important parameters controlling the nucleation rate, and the growth rate of the crystals (Sazaki et al., 1994). It is a measure of the crystallization potential of the solution. It is the general understanding that a low initial supersaturation ratio is preferable for formation of larger size single particles; while a higher supersaturation ratio facilitates the formation of a large number of small crystals (Sazaki et al., 1994).

In case of struvite, if the supersaturation ratio in a solution for struvite is higher than 1, than struvite crystals will form, whereas as struvite will be dissolved when the supersaturation ratio is less than 1 (Wilson, 2013). In the current research, the supersaturation ratio of samples was assessed by the

elemental concentrations, model-generated parameters, activity coefficients and temperature-corrected solubility products.

3.5.3 Removal Efficiency

The removal efficiency of a particular component is calculated by using Equation 3.2.

$$X - \text{Removal (\%)} = \frac{X_{\text{influent}} - X_{\text{effluent}}}{X_{\text{influent}}} * 100 \dots\dots\dots (3.2)$$

Where, X = any parameter i.e Mg, N or P concentration

X_{influent} = initial concentration or concentration of the influent

X_{effluent} = Final concentration or concentration of the effluent

3.5.4 Up Flow Velocity

The upflow velocity is calculated from the reactor cross-sectional area and the combined feed flow rate using Equation 3.3.

$$\text{Up flow Velocity, } v = A_{x\text{-section}} / (Q_{\text{recycle}} + Q_{\text{influent}}) \dots\dots\dots (3.3)$$

Where,

$A_{x\text{-section}}$ = Cross sectional area of the section where up flow velocity is to be determined

Q_{recycle} = Recycle flow rate, ml/min or L/d

Q_{influent} = Influent flow rate, ml/min or L/d

3.5.5 Hydraulic Retention Time

Hydraulic retention time (HRT) is a measure of the average time span that a particle remains in the certain system (i.e reactor). It can be calculated by Equation 3.4.

$$\text{HRT (days or min)} = V_R / Q_{total} \dots\dots\dots (3.4)$$

Where, V_R = Volume of reactor, ml or L

$$Q_{total} = Q_{recycle} + Q_{influent} = \text{Total Flow rate, L/d or ml/min}$$

$$Q_{recycle} = \text{Recycle flow rate, ml/min or L/d}$$

$$Q_{influent} = \text{Influent flow rate, ml/min or L/d}$$

3.5.6 Recycle Ratio

Recycle ratio is described as the ratio of the recycle flow rate to influent flow rate, as in Equation 3.5

$$\text{Recycle Ratio (RR)} = Q_{recycle} / Q_{influent} \dots\dots\dots (3.5)$$

$$Q_{recycle} = \text{Recycle flow rate, ml/min or L/d}$$

$$Q_{influent} = \text{Influent flow rate, ml/min or L/d}$$

Chapter 4: Results and Discussion

4.1 Newberyite to Struvite Transformation Bench Scale Experiment Results

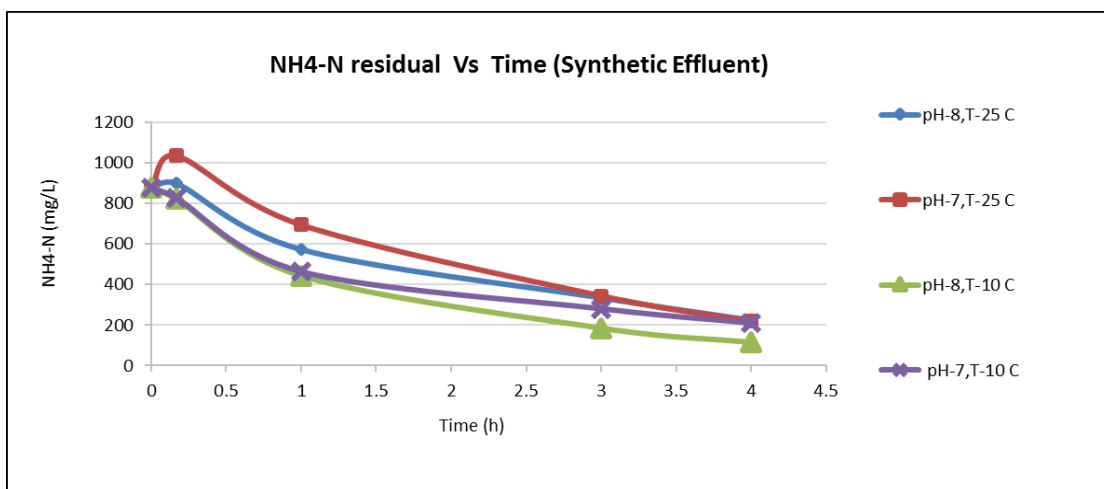
The first sets of experiments were performed to explore the possibility of using direct newberyite pellets in wastewater feed, to recover excess ammonia nitrogen by recrystallizing struvite. Three different types of process feed were used to gain a better understanding of the technique. The associated results are discussed in the following sections.

4.1.1 Nutrient Recovery from Synthetic Crystallizer Effluent and Synthetic Centrate

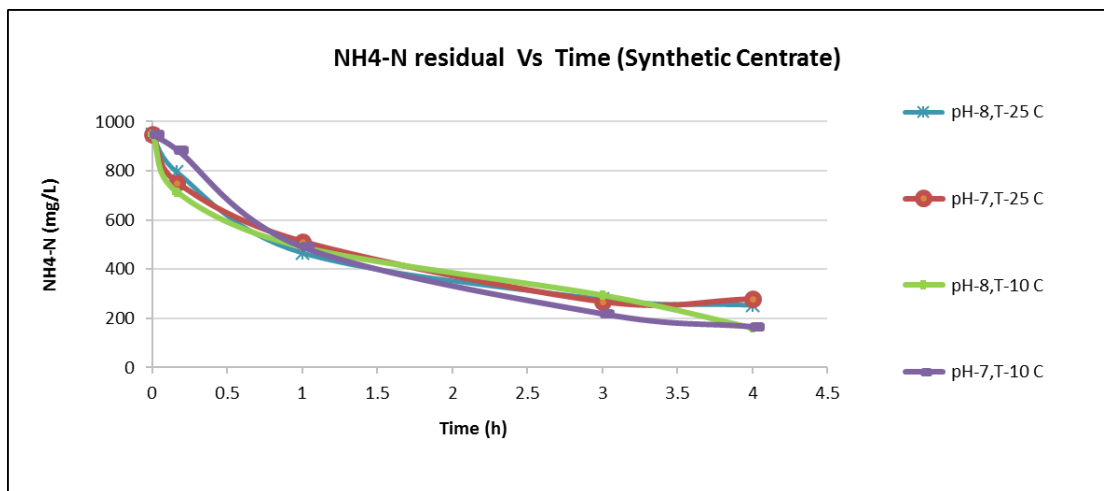
4.1.1.1 Ammonia Removal

The rate of ammonia removal in synthetic crystallizer effluent and synthetic centrate was observed over 4 hours, for four different sets of pH and temperature conditions. From a previous study by Wilson (2013), that used synthetic newberyite powder on similar feed, a pH range of 7 to 8 and temperature of 10⁰C and 25⁰C were selected as near optimal experimental conditions. The experimental parameters are listed in Table 3.1 while a summary of wastewater composition is given in Table 3.2. Newberyite dose was selected in such a way so that 1:1:1 Mg:N:P ratio was obtained, when the newberyite pellets dissolved in the feed solution. In all cases, ammonia tended to decrease significantly which is illustrated in Figure 4.1 a & b.

As the newberyite dissolved into the solution, it released phosphate and magnesium ion. In presence of ammonium from wastewater and favorable pH, temperature and hydrodynamic conditions, these ions crystallized into struvite and thus, the ammonium from wastewater was partially recovered.



(a)



(b)

Figure 4.1 Ammonia removal in (a) synthetic crystallizer effluent (b) synthetic centrate in bench scale reactor

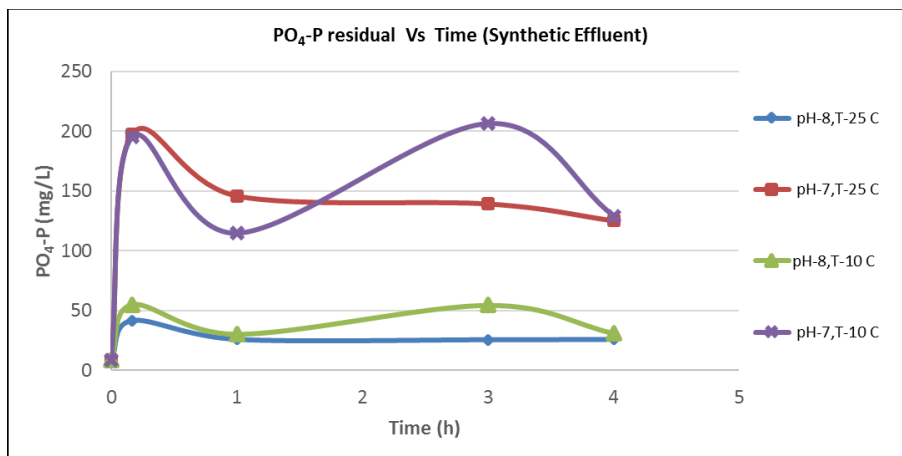
For synthetic effluent, the residual ammonia was found to be as low as 113.2 mg/l, compared to the initial concentration of 878.9 mg/l, after 4 hours. Average ammonia removal ranged from 74% ~87%. These results compare well to that observed by Wilson (2013), using synthetic newberyite powder. He reported mean ammonia removals of 73%~87%. In Wilson's study, residual ammonia appeared to be leveling after 3 hours, whereas the present study showed a decreasing trend, even after 4 hours (as illustrated in Figure 4.1). It is believed that if the reaction were to continue for a longer duration, more ammonia could be recovered.

A slight increase of ammonium concentration was observed for one of the experiments (pH-8, T-25°C) after 10 min of reaction. The newberyite pellets used in this study were produced by thermally decomposing actual struvite and tested for chemical compositions. There might be a trace amount of impurities (i.e Dittmarite) present in that particular batch, which contributed to the slight elevation.

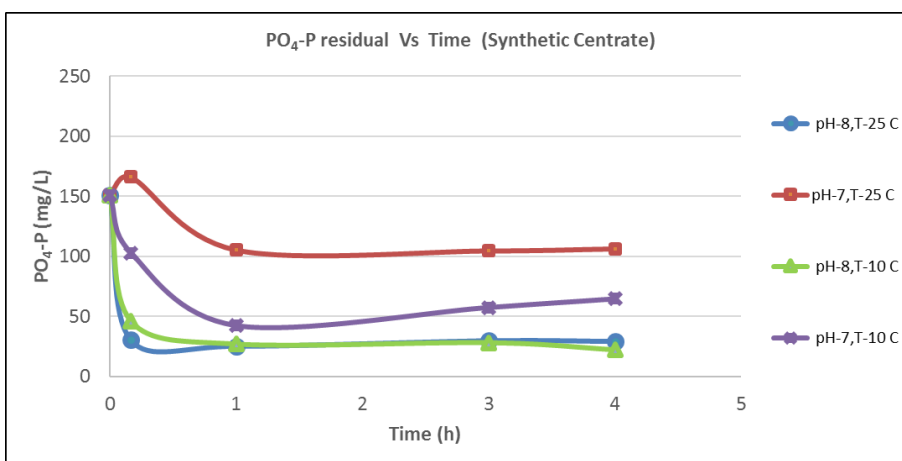
Ammonia removal for **synthetic centrate** followed a similar trend to that of synthetic crystallizer effluent. The average ammonia recovering efficiency in synthetic centrate was found to be 71% ~84%, which falls exactly within the range reported by Wilson (2013). As illustrated in Figure 4.1 (b) residual ammonia appears to be approaching an equilibrium value after 4 hours. So, using newberyite pellets, instead of synthetic powder, resulted in similar ammonia recovery efficiencies.

4.1.1.2 Orthophosphate Residual

Although the main objective of this study is to recover as much as nitrogen possible, it is also important to have low residual phosphate; otherwise, it would increase the nutrient load within the secondary treatment phase. Figure 4.2 plots the orthophosphate residuals with time for both the synthetic effluent and synthetic centrate process feeds.



(a)



(b)

Figure 4.2 Residual Ortho-Phosphate in (a) synthetic crystallizer effluent (b) synthetic centrate in bench scale reactor

In **synthetic effluent**, the initial orthophosphate was very low (8.7mg/l), as it passed through a primary treatment phase. Orthophosphate residual was primarily generated from the dissolution of newberyite pellets. The newberyite pellets dissolved within a few minutes, after starting the test, resulting in a sharp elevation of orthophosphate concentration at 10 minutes (as shown in Figure 4.2(a)). The final orthophosphate residual appeared to be significantly higher in pH 7 test at around 130mg/l, for both sets of temperatures, compared to pH 8 (at around 30mg/l). This was expected and can be explained in relation to supersaturation of struvite (S_s). pH 8~9 will allow effective struvite crystallization due to increased S_s (Abbona et al., 1982) and the enhanced struvite formation corresponds to the reduction of orthophosphate residuals.

The **synthetic centrate** contained higher initial orthophosphate levels compared to synthetic effluent. Residual orthophosphate tended to decrease with time and appeared to approach a state of equilibrium by 3 hours (Figure 4.2 (b)). The highest final orthophosphate residual was found to be 106.3 mg/l at pH 7 at 25⁰C, whereas at pH 8 (T~10⁰C), the lowest residual of 22.1 mg/l occurred. The presence of high alkalinity did not affect equilibrium residuals, as it followed a similar trend to that of synthetic effluent and no statistical difference was observed between the results of this two-different feeds. These results suggest that a simultaneous 85% orthophosphate and 83% ammonia removal could be possible, as a single struvite crystallizer process, using newberyite as an additional reagent.

4.1.2 Nutrient Recovery from Annacis WWTP Centrate

Ammonia recovery from centrate or dewatered sludge liquor from the Annacis Island Waste Water Treatment Plant (WWTP), was examined to study the feasibility of using this method at conditions

which represent a real wastewater stream. Based on the results of synthetic feed, the test duration was increased to 6 hours, since the reaction equilibrium was not achieved within 4 hours for some of the previous experiments. Operational pH was further revised to a narrow, optimal range of 7.5, 8.0 and 8.5. System temperature was selected to be 25⁰C. (Effect of pH and temperature is discussed in Section 4.1.4)

4.1.2.1 Ammonia Removal

The average ammonia removal followed a familiar decreasing trend, as illustrated in Figure 4.3. Mean ammonia removal ranged from 78%~95% after 6 hours. The ANNACIS centrate is characterized by high alkalinity (average ~3000mg/l as CaCO₃) accompanied by total suspended solids (TSS) and other impurities ((Kalam, 2015). These additional constituents did not appear to affect ammonia recovering performance. The results also compared well to that observed for the synthetic centrate (discussed in Section 4.1.1.1).

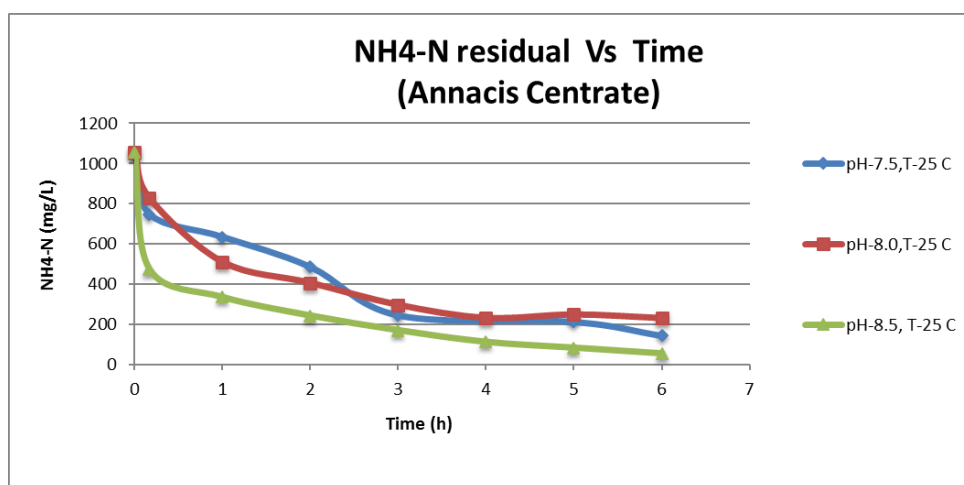


Figure 4.3 Ammonia concentration with time for Annacis Centrate

4.1.2.2 Orthophosphate Residual

Figure 4.4 plots orthophosphate residual over time, for batch tests transforming newberyite pellets into struvite, in Annacis island WWTP centrate. The highest residual orthophosphate was found to be 109 mg/l for pH~7.5, whereas the lowest 36.7mg/l was observed for pH~8.0. The tests above pH 7.5 showed significantly lower phosphate residual, due to the increased supersaturation ratio of struvite. A Maximum 75% phosphate could be recovered in this process for the tested operational conditions.

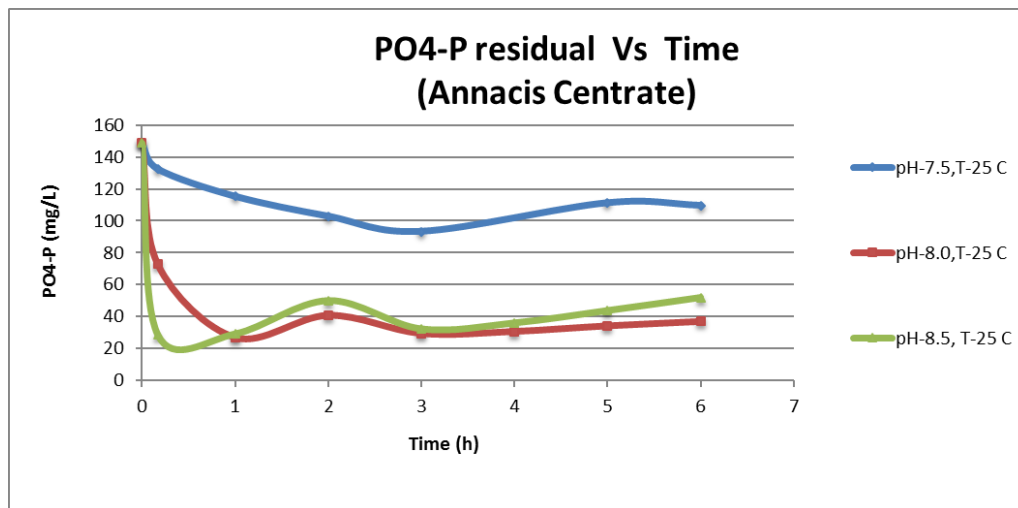
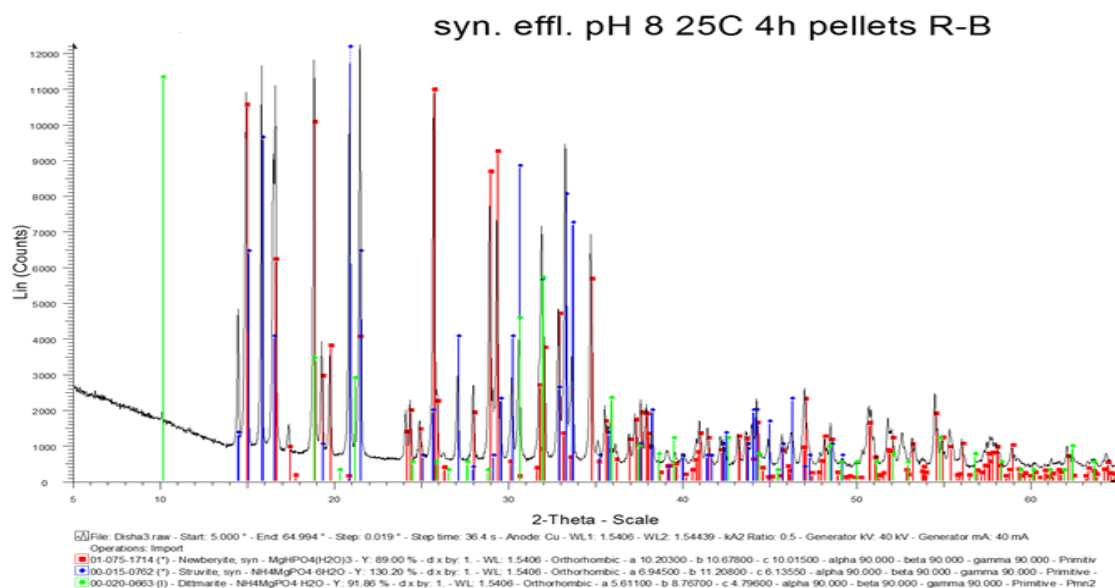


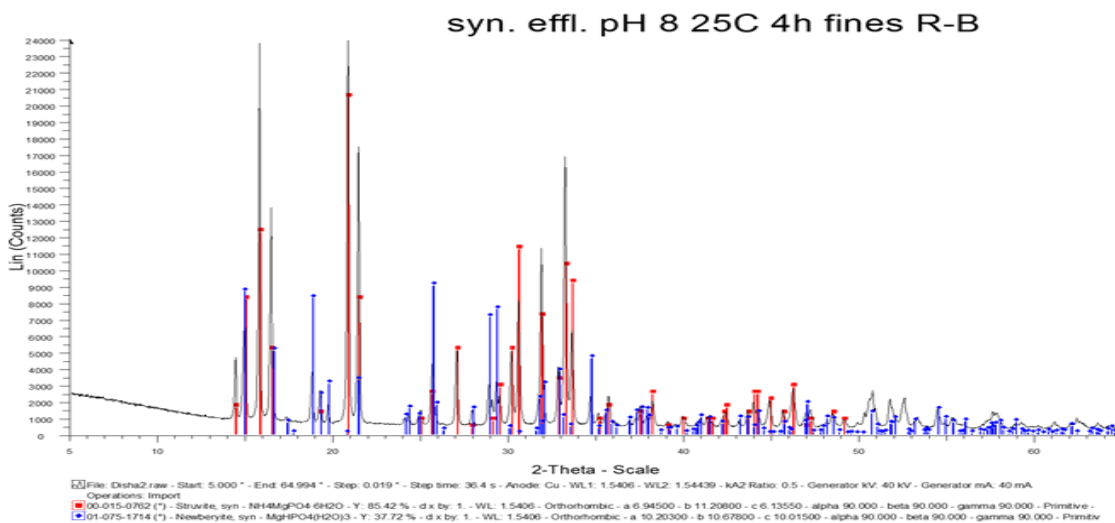
Figure 4.4 Ortho Phosphate concentration with time for Annacis Centrate

4.1.3 Analysis of Solid Phase Mixture

The solid samples collected after each experiment were assumed to contain a mixture of undissolved newberyite pellets and newly-formed struvite. The samples consisted of both powder (fine) and pellets and were analyzed separately.



(a)



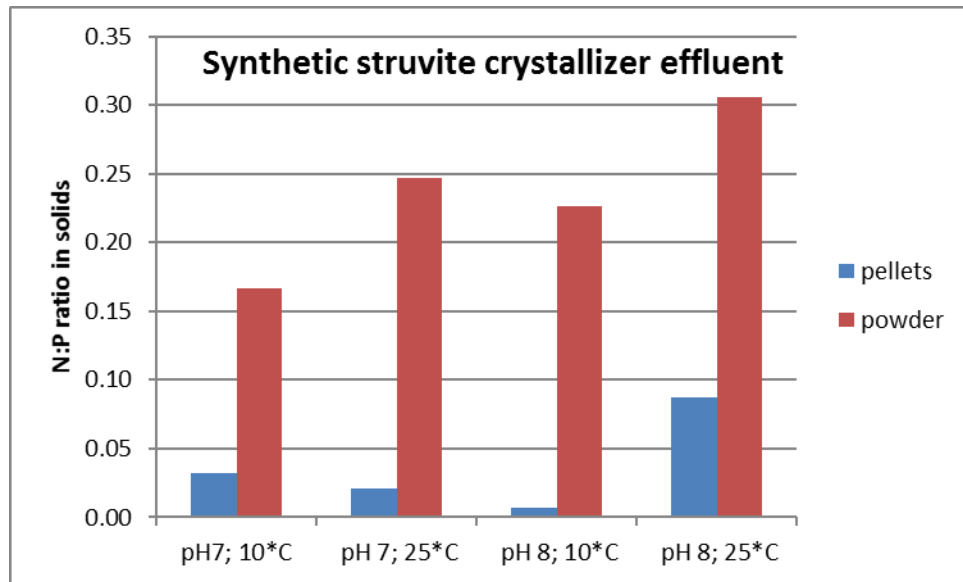
(b)

Figure 4.5 XRD analysis for the solid sample collected at 4 hours for batch test containing synthetic effluent at pH 8 at 25°C 9 (a) Pellet sample (b) Fine sample

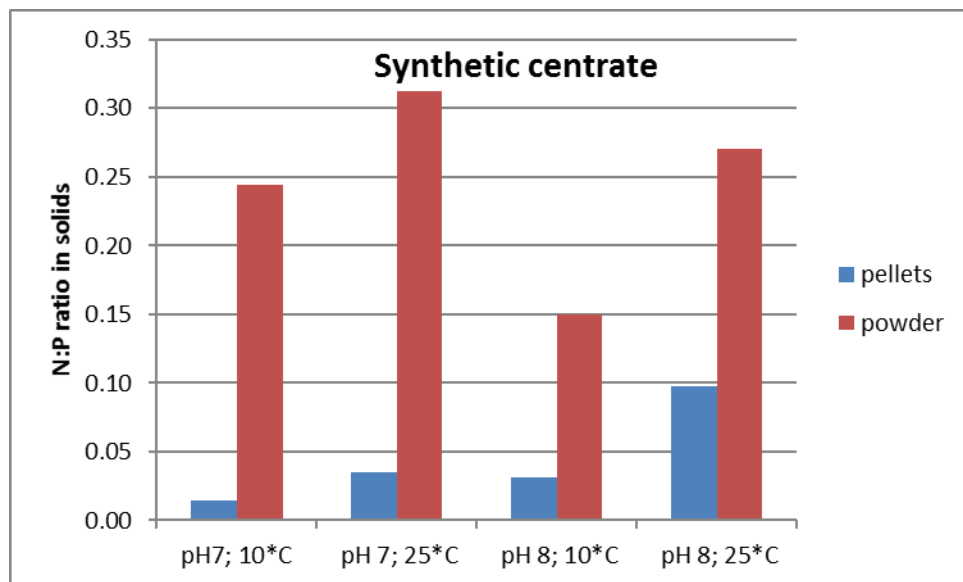
XRD analysis was performed for selected samples to identify the solid phase. A sample XRD result is shown in Figure 4.5. The presence of struvite and newberyite was confirmed in all the fine samples and no other compounds were detected in the fines. Whereas, some of the pelleted samples contained dittmarite, in addition to struvite and newberyite. The newberyite that was used at the beginning of the experiment, as an alternate source of magnesium and phosphate were in pelleted form. Some of these pellets may have remained undissolved and transformed into ditmarite. The transformation of newberyite into other solid phases is undesirable, as it will reduce the amount of magnesium and orthophosphate available for ammonia removal.

Struvite peaks were more dominant in fines, which corresponded to increased struvite formation. The presence of struvite in pellet samples indicated the formation of struvite in pellets form, in the bench-scale reactor. Another possible scenario would be layers of struvite forming on the surface of the newberyite pellets.

The XRD analysis can only identify the crystalline compounds in the solid phase. To quantify the extent of phase transformation from newberyite to struvite, chemical analyses were performed for all the solid samples. Figure 4.6 compares the N: P ratio of the fines and pellet sample collected at the end of each batch test, on synthetic wastewater. Since newberyite contains no ammonium, the N:P molar ratio basically represents the molar fraction of struvite (Wilson, 2013). It is clearly seen that the fines (powder) contained higher nitrogen content, compared to the pellets, indicating high struvite yield and consistent with XRD analysis result.



(a)



(b)

**Figure 4.6 N:P molar ratio of solid phase mixtures sample at 4 hours (a) Synthetic effluent
(b) Synthetic wastewater**

4.1.4 Effect of Temperature and pH on Ammonia Removal Efficiency from Different Influent

Newberyite dissolution and struvite crystallization – the two, separate mechanisms that occurred simultaneously in these sets of experiments, are significantly affected by operational pH and temperature.

Struvite crystallization is enhanced at a lower temperature, while newberyite dissolution significantly increases (Wilson, 2013). Thus, it is expected that higher ammonia recovery efficiency is possible at lower temperatures. Figure 4.7 and Figure 4.8 illustrate the ammonia recovering efficiency for different wastewaters, at different pH and temperature.

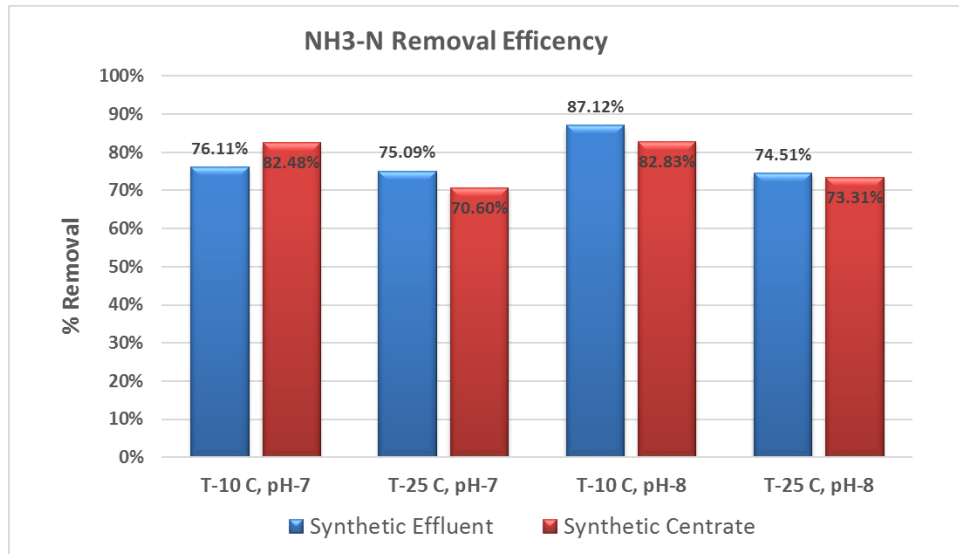


Figure 4.7 Ammonia recovering efficiency for newberyite to struvite transformation batch tests in synthetic wastewater

It can be seen from Figure 4.7 that the percentage of ammonia removal efficiency was somewhat higher for 10⁰C, compared to that of 25⁰C, for both pH 7 and 8, and for both sets of synthetic feed. However, the difference was not very significant for most cases. Hence, 25⁰C temperature was selected for the remainder of the experiments, for operational convenience. For synthetic effluent, the highest ammonia recovery potential was observed to be 87.1% at 10⁰C, while the lowest was 74.5% at 25⁰C. For synthetic centrate, the highest and lowest ammonia recovery efficiency was 82.8% (at T~10⁰C) and 70.6% (at T~25⁰C), respectively.

Struvite precipitation takes place in alkaline conditions (Dastur, 2001; Britton, 2002). For synthetic centrate and synthetic effluent, highest ammonia recover efficiencies were observed at pH-8, whereas for ANNACIS centrate, a maximum of ~ 95% ammonia was recovered at pH-8.5. (See Figure 4.8)

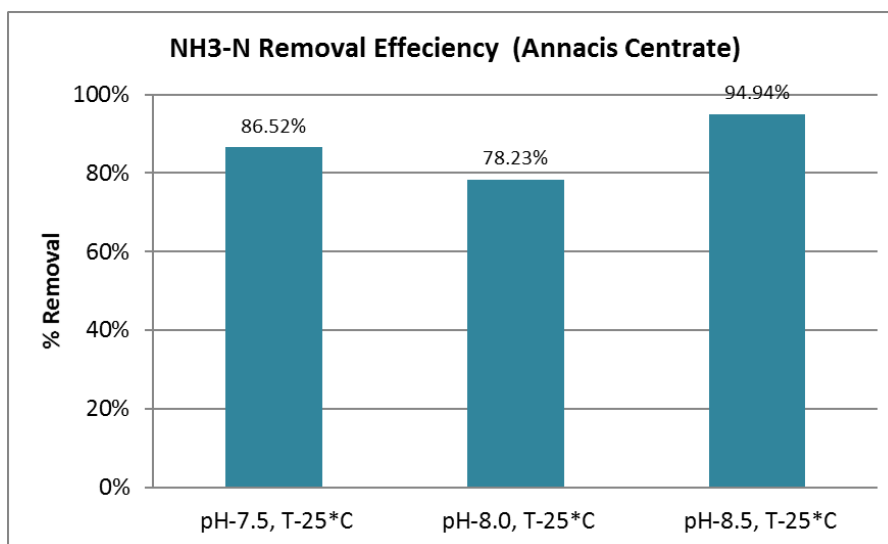


Figure 4.8 Ammonia recovering efficiency for newberyite to struvite transformation batch tests in actual wastewater-ANNACIS centrate

4.2 Newberyite Solubilization Batch Test

Although the results of the newberyite to struvite transformation batch test were promising, the major challenge was to recover nitrogen in the form of pure struvite. As discussed in Section 4.1, it was possible to remove ammonium -nitrogen up to 94%, but the final solid obtained through this process was found to be a mixture of newberyite and struvite. In order to resolve this problem, newberyite was solubilized in acid in a separated chamber, prior to providing favorable conditions for struvite crystallization.

Several newberyite solubilization batch tests were performed to develop a continuous process, where an expected percentage of orthophosphate and magnesium would be released into the feed. Due to the limited availability of newberyite pellets, synthetic newberyite was used for Phase I of the solubilization experiments (detailed description in Section 3.2.1). However, the test data did not exhibit satisfactory results. It was a challenge to set the optimum speed without losing fines through the outlet tube. The mixing speed in the reactor was insufficient to properly mix the high volume of newberyite fines (approx 1.5 kg). A higher speed would have enhanced the mixing. But, it was not a feasible option, as there were already a large amount of fines accumulated in the clarifier, indicating newberyite fines escaped the reactor before dissolving. Hence, the entire system required significant modification.

For Phase II, the experimental set up was modified to a small-scale reactor and actual newberyite pellets were solubilized. A chemical equilibrium model was constructed using PHREEQC to determine the operational pH for 100%, 60 % orthophosphate release and maximum possible pH, without forming any struvite at 20°C. PHREEQC is a powerful tool that allows the user to input

initial suspension characteristics and predict the equilibrium liquid/solid phase composition for certain pH and temperature. The model predicted that the maximum (100%) orthophosphate would be released at pH 4.5 for the test condition (discussed in Section 3.2.2) and the highest pH we can solubilize newberyite, without forming any struvite, would be 6.0. In addition to pH 4.5 and 6.0, the experiment was also performed at pH 5, where partial newberyite dissolution was expected to occur.

XRD analysis as illustrated in Figure 4.9 of the solid residue, confirmed that no struvite was formed during the solubilization process.

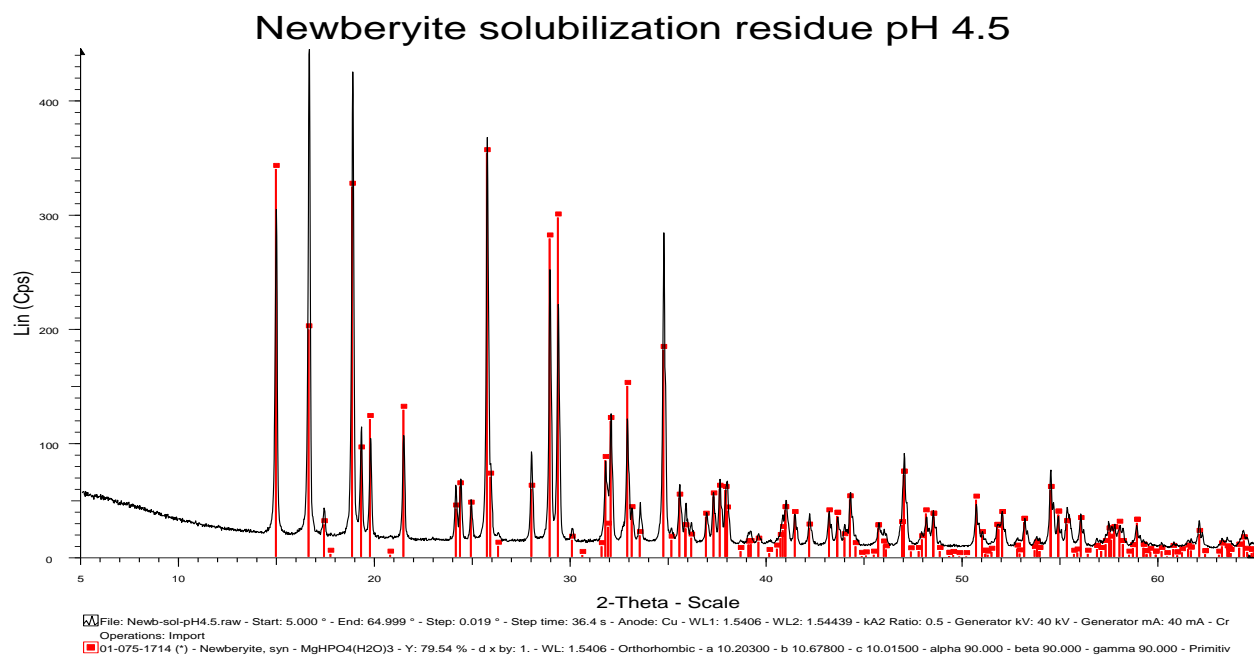


Figure 4.9 Sample XRD analysis of newberyite solubilization residue

The retention time for all the experiments were 20 minutes. The orthophosphate and magnesium residual plots are shown in Figure 4.10 and Figure 4.11, respectively.

The highest orthophosphate and magnesium residual were observed at pH-4.5, while the lowest occurred at pH-6.0. However, only 30 % orthophosphate was released into the solution at pH-4.5, whereas the model prediction was 100%. The 20-min retention time was evidently, not sufficient to solubilize all of the newberyite. A longer retention time may result in an increased percentage of newberyite solubilization, perhaps as long as one hour.

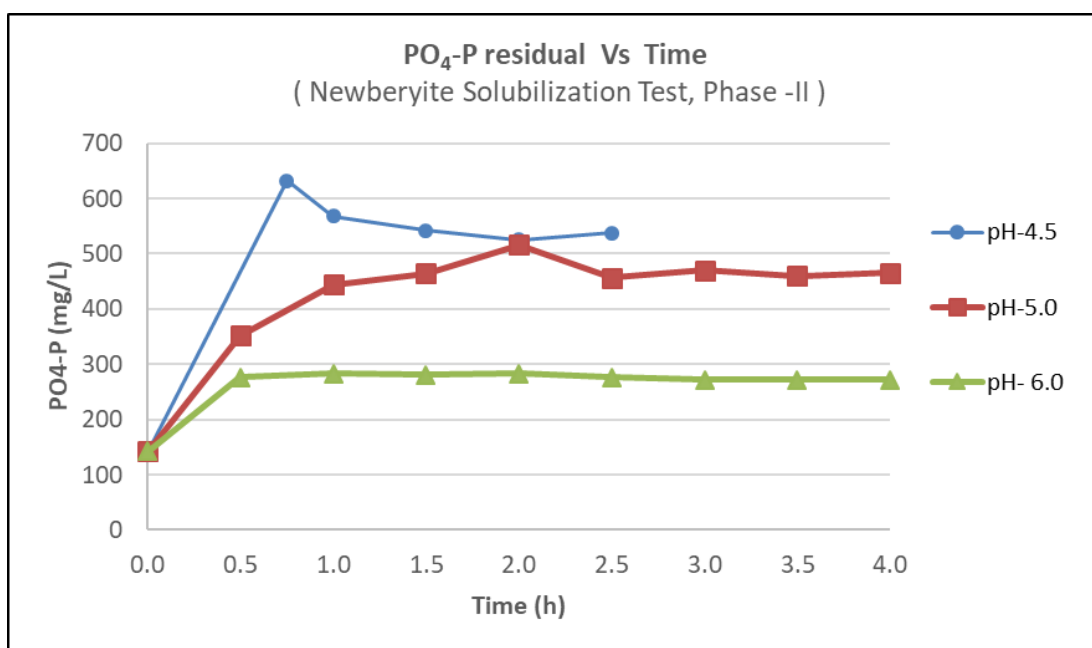


Figure 4.10 Residual PO₄-P for the newberyite solubilization batch test, phase-II

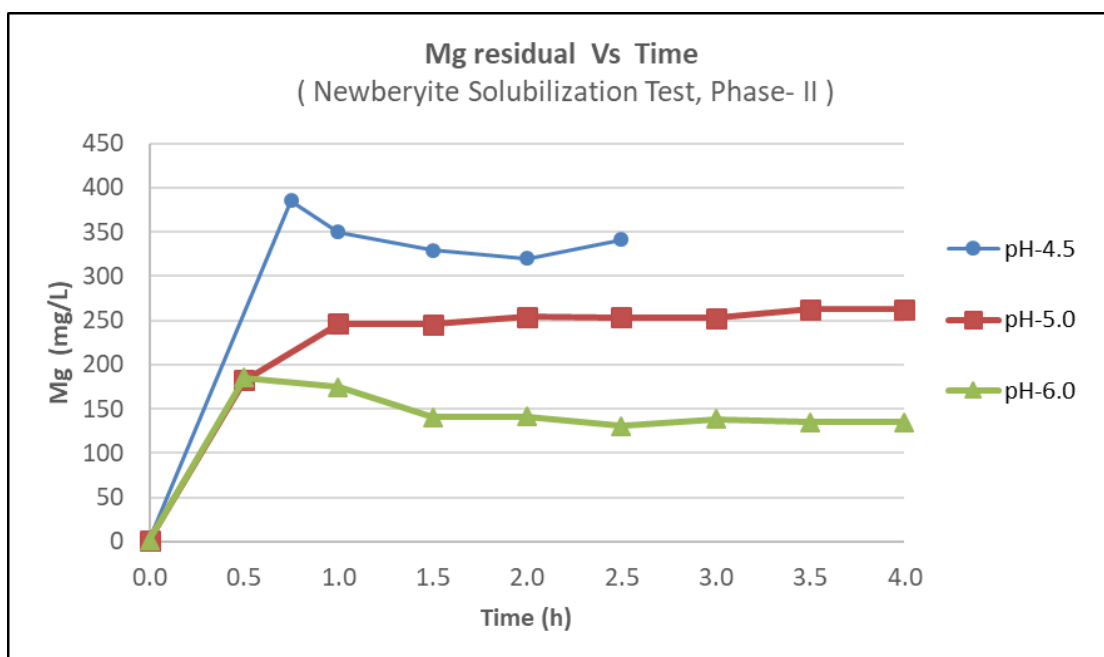


Figure 4.11 Residual Mg for the newberyite solubilization batch test, phase-II

4.3 Pilot Scale Experimental Results

Due to time and resource constraint, the pilot-scale experiments were conducted in a UBC struvite crystallizer, using a synthetic feed whose Mg, N, and P concentration would be similar, if hypothetically all the newberyite were dissolved in it.

The main objective was to produce struvite pellets from a very highly-concentrated feed, by going from a batch process to a continuous process. Influent feed characteristics are listed in Section 3.3.2.1. Experimental parameters were set through continuous stimulation with the Dann Potts model and PHREEQC. SSR 4 was reported as a desired supersaturation ratio, for the UBC

fluidized bed reactor to achieve the most favorable condition for struvite crystal growth (Kalam, 2015).

For test run 1, the pH set point was calculated as 8.7 to maintain the required SSR of 4. However, it was a big challenge to maintain a constant SSR throughout the experiment. The SSR varied from 4 to as high as 26 (illustrated in Figure 4.12), due to a sharp spike of pH in the system.

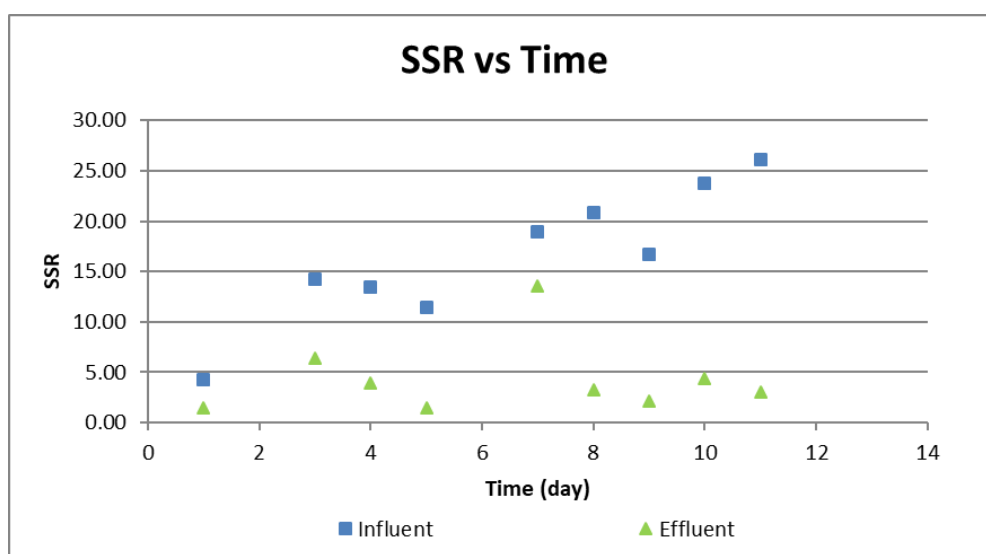


Figure 4.12 Variation of SSR during the pilot-scale experiment, test run 1

The average pH value was around 8.6, but, there were issues with the pH probe losing its calibration, the time delay between the caustic entering the reactor and pH probe registering the reading etc., thus causing a sharp increase/ decrease.

Despite the setbacks, the nitrogen recovery was high, ranging from 80%~92%, while simultaneously recovering 97%~98% orthophosphate. Figure 4.13 and Figure 4.14 shows orthophosphate and ammonia-nitrogen residuals, respectively. However, the recovered struvite was mostly fines, as proper hydrodynamic conditions were not achieved in the reactor, due to erratic SSR variation. The major objective of this study was to recover nitrogen in a usable form; hence, it is important to recover struvite in pellet form, so that it can be easily separated from the mixture and be reused for further nutrient recovery techniques. As such, another test run was performed in the UBC reactor.

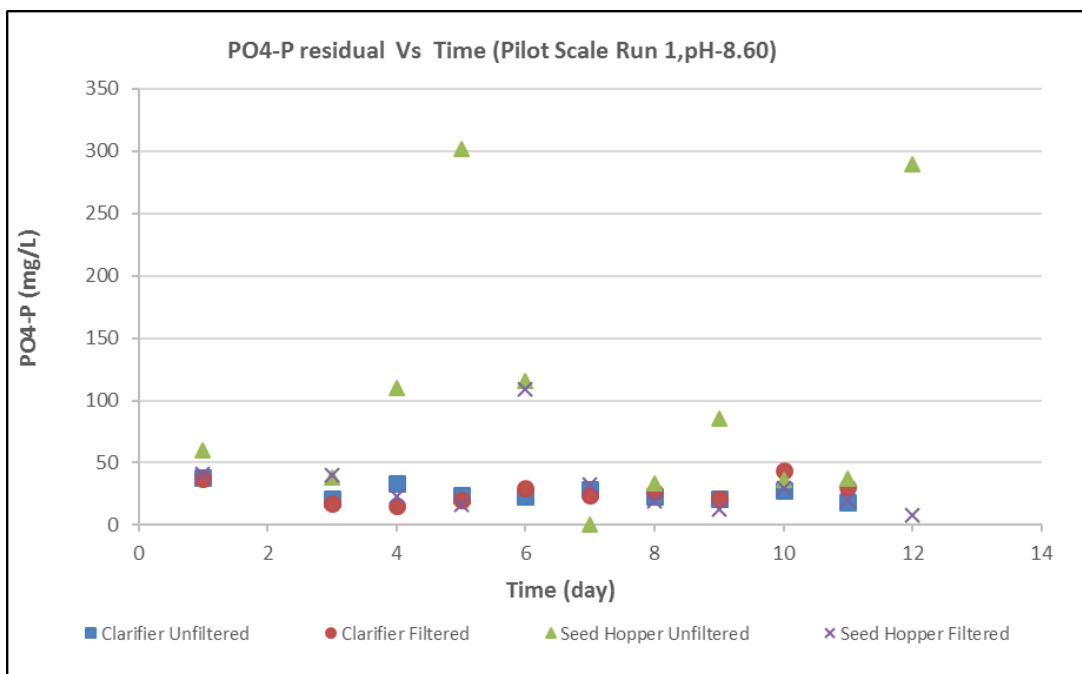


Figure 4.13 Orthophosphate removal in the pilot-scale experiment, test run 1

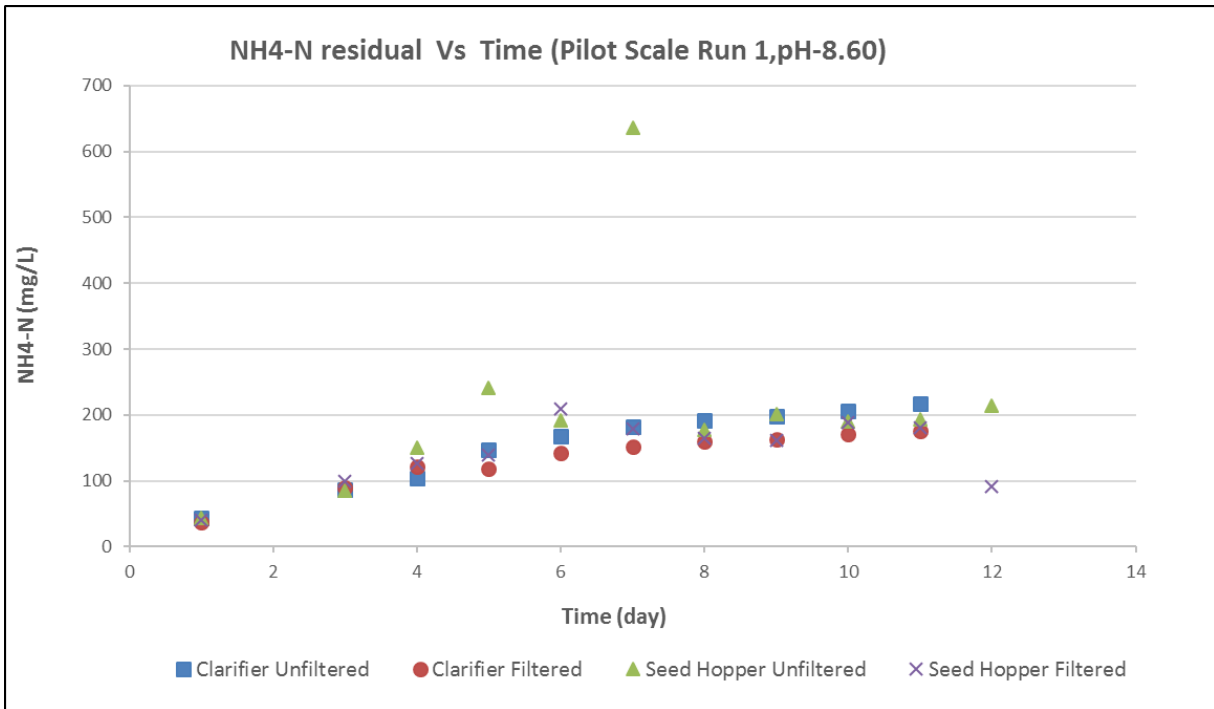


Figure 4.14 Nitrogen removal in the pilot-scale experiment, test run 1

The second experiment started with maintaining the SSR 4 (pH – 8.02 based on influent characteristics) and continued for 2 days. Struvite fines continued to form but no particle growth was observed. On the 3rd day, the SSR was set to 3, by adjusting the pH set point at 7.76. No significant changes were observed. Finally, on day 6, the pH was again adjusted to achieve an SSR 2 and continued for rest of the experiments. There was some particle growth on day 6; however, they were not large enough to settle out in the harvesting zone, in the time frame allocated. The final effluent nitrogen was found to be 326 mg/l, compared to the initial concentration of 950 mg/l. The residual orthophosphate and ammonia-nitrogen for test run 2 are plotted in Figure 4.15 and Figure 4.16, respectively.

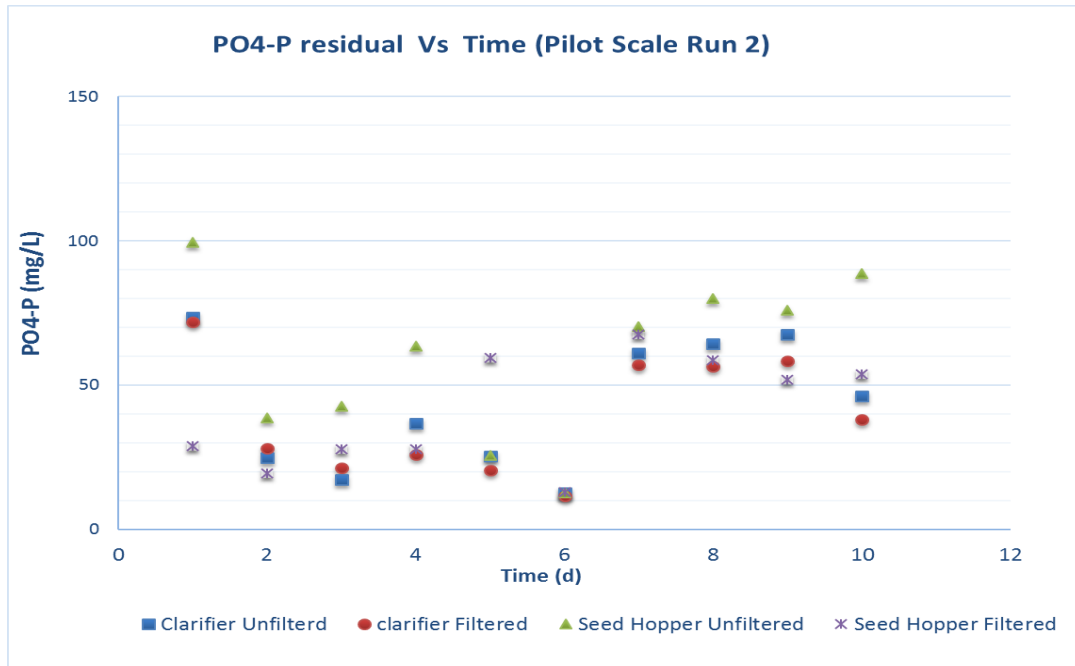


Figure 4.15 Orthophosphate removal in pilot-scale experiment, test run 2

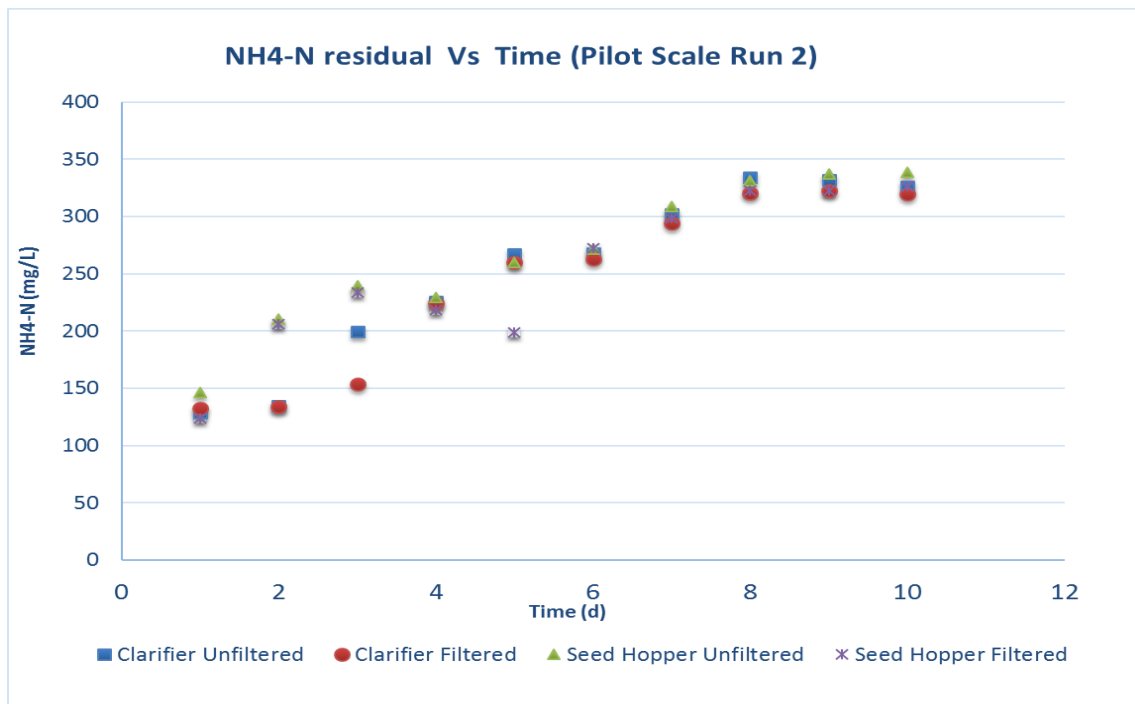


Figure 4.16 Nitrogen removal in pilot-scale experiment, test run 2

One important factor to be noted was the recycle ratio in this experiment. It is required to obtain a certain up-flow velocity in the reactor, to induce necessary turbulence for struvite pelletization. A recycle line was used to maintain the desired up-flow velocity and induce turbulence for pelletization to occur. For both sets of experiments, the recycle ratio was set at 40, to maintain about 288cm/min up-flow velocity in the harvesting zone. In the practical world, such a high recycle ratio would be very inefficient as only a small amount of raw influent would be treated each time. Thus, a balance would be required, between recycle, upflow velocity and nitrogen removal, with the goal of achieving pure pelletization.

Although nitrogen can be removed in this process, the efficiency of this experiment, for struvite pelletization potential, from high influent concentrations of nitrogen and phosphorus remained unanswered.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The main conclusions from this research, based on the experimental findings, are summarized below:

- It was possible to recover up to 94% ammonia from Annacis WWTP dewatering centrate, using newberyite pellets as an alternate source of orthophosphate and magnesium to enhance struvite formation.
- 74%~ 87% ammonia removal efficiency was achieved for primary struvite crystallizer effluent.
- The orthophosphate residual, resulting from newberyite dissolution, could be kept as low 23.8mg/l, at pH 8.
- pH was found to be the dominant factor, compared to temperature, with respect to final orthophosphate residual for the systems operated in this research program.
- No other compound was formed during newberyite to struvite conversion. The final residual solid was a mixture of fines and pellets, where struvite constituted the major portion of the fines. The presence of nitrogen in some particles suggested that newberyite pellets were entrapped by struvite forming on their surface.

- Using thermally decomposed struvite i.e newberyite, the pellets had little or no effect on ammonia recovery efficiency, compared to using synthetic newberyite powder.
- Model-predicted orthophosphate and magnesium concentration were significantly different than that produced in the newberyite solubilization batch test. Although no struvite was formed during this stage (which was one of the objectives), a good portion of the newberyite remained undissolved. An increase in the reactor retention time may result in higher orthophosphate release.
- The main objective of the pilot-scale experiment in the UBC struvite crystallizer was to assess the potential to produce pelletized struvite, from solubilized newberyite and an ammonia-laden solution, while maintaining low orthophosphate residual. Although the orthophosphate residual results were positive, the recrystallized struvite obtained was mostly in the form of fines. With the high recycle ratio of 40, optimization and maximum efficiency of this process remained unanswered.

5.2 Recommendations for Future Work

A strong recommendation for future work would be to develop a stable, continuous or semi-continuous newberyite solubilization system, with a higher retention time (>20min) to achieve 100% dissolution. Tests up to 60 minutes would be ideal, to realize an HRT “sweet spot”.

Another recommendation for future work includes the investigation of the efficacy of the newly developed UBC reactor (which overcomes the design limitation of existing UBC FBR) for struvite pelletization potential, from a highly concentrated feed with varying SSR. This type of follow up research would facilitate scale up and potential technology transfer.

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Appendices

Appendix A Operational settings for instruments

Table A.1 Settings for magnesium analysis using flame atomic absorption spectrophotometer

Parameter	Setting
Mode	Absorbance
Measurement	Mode Integration
Flame Type	Air/C ₂ H ₂
Lamp Current	4.0 mA
Wavelength	202.6 nm
Calibration Range	0-250 mg/L

Table A.2 Settings for ammonia and orthophosphate analysis using flow injection analysis

Parameter	NH ₄ -N	PO ₄ -P
Method	4500-NH ₃ H ¹	4500-P G ¹
Temperature	63° C	63° C
Calibration Range	0-50 mg/L	0-25 g/L

Table A.3 Settings for x-ray diffraction (XRD), using a Bruker D8 Advance X-ray diffractometer

Parameter	Setting
Type of radiation	CuK α
Starting scanning angle, 2 θ min ⁻¹ (Low angle XRD)	0.8°
Scanning angle, 2 θ min ⁻¹ (Normal angle XRD)	5°
Average scanning rate	0.019°

Appendix B Liquid Sample Analysis Result

The following table reports the mean of triplicate analysis of liquid samples.

Table B.1 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer

Effluent, pH 8 Temperature 25°C

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	878.89	878.89	8.70	8.70	13.81	13.81	8.01	8.00	25.0	25.0
0.17	899.30	924.80	48.80	41.50	38.85	36.65	8.02	8.04	25.0	25.1
1	572.90	623.90	31.50	25.93	25.44	24.25	8.02	8.00	25.0	25.1
3	334.56	423.30	36.33	25.60	28.64	24.38	8.02	8.03	25.0	25.1
4	224.06	446.59	36.20	25.90	30.00	23.22	8.01	8.01	25.0	25.1
4(old)	282.37	366.35	38.67	27.80	30.53	28.37	8.01	8.01	25.0	25.1

Table B.2 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer

Effluent, pH 7 Temperature 25°C

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	878.89	878.89	8.70	8.70	13.81	13.81	7.01	7.03	25.30	25.00
0.17	1037.00	1045.50	205.67	197.33	126.10	118.09	7.00	7.01	25.30	24.90
1	695.30	821.10	142.00	145.67	80.45	81.40	7.02	6.98	25.30	24.90
3	344.25	437.92	175.00	139.00	98.74	77.76	7.03	7.02	25.20	24.80
4	218.96	272.17	140.50	125.00	109.12	97.19	7.04	7.04	25.20	24.80
4(old)	277.95	342.89	191.50	166.67	109.97	96.79	7.04	7.04	25.20	24.80

Table B.3 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer**Effluent, pH 7 Temperature 10°C**

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	878.89	878.89	8.70	8.70	13.81	13.81	7.01	7.02	9.8	10.1
0.17	827.90	858.50	175.63	195.07	104.87	123.21	7.04	7.03	9.9	10.1
1	464.27	608.60	117.33	114.77	68.71	67.90	6.98	7.04	9.9	10.1
3	280.50	363.12	244.57	206.43	189.20	130.37	6.96	7.12	9.9	10.1
4	209.95	296.31	108.00	129.07	86.88	95.18	7.03	7.02	9.9	10.1
4(old)	228.31	311.78	145.57	160.23	83.64	97.42	7.03	7.02	9.9	10.1

Table B.4 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer**Effluent, pH 8, Temperature 10°C**

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	878.89	878.89	8.70	8.70	13.81	13.81	8.01	7.98	9.9	10.0
0.17	822.80	885.7	72.30	55.07	55.68	42.93	7.99	8.02	9.9	10.0
1	442.34	753.1	54.47	30.27	41.20	24.56	7.98	8.22	9.9	10.1
3	183.6	562.7	69.55	54.43	39.51	41.94	7.96	8.04	9.9	10.0
4	113.22	476.34	40.80	30.87	31.89	25.93	7.95	7.96	9.9	10.0
4(old)	137.19	501.33	41.93	31.30	29.49	24.37	7.95	7.96	9.9	10.0

Table B.5 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH**7, Temperature 10°C**

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	947.78	947.78	150.78	150.78	0	0	7.00	7.05	10.0	10.2
0.17	884	872.1	134.67	103.00	100.38	162.22	6.99	7.03	9.9	9.9
1	490.28	608.6	74.93	42.37	56.20	114.62	7.04	7.00	10.0	9.9
3	218.79	408.85	98.17	57.43	72.47	124.30	7.10	7.03	10.0	9.9
4	166.09	327.08	117.67	64.63	93.24	132.91	7.02	6.99	10.0	9.9
4(old)	178.5	352.58	122.33	66.47	88.98	129.53	7.02	6.99	10.0	9.9

**Table B.6 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH
8 Temperature 10⁰C**

Sampling	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	947.78	947.78	150.78	150.78	0	0	7.99	8.00	10.0	10.1
0.17	712.30	770.1	47.57	46.03	52.54	43.14	8.04	8.01	10.0	10.1
1	490.45	516.12	24.67	26.90	21.51	19.62	8.04	8.02	10.0	10.0
3	295.12	311.78	27.73	28.03	22.57	27.49	8.01	7.97	10.0	10.0
4	162.69	186.83	38.90	22.10	21.55	18.85	8.02	7.99	10.0	9.9
4(old)	251.43	268.77	33.17	23.80	20.04	17.45	8.02	7.99	10.0	9.9

**Table B.7 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH
7, Temperature 25⁰C**

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	947.78	947.78	150.78	150.78	0	0	7.01	7.00	25.0	25.0
0.17	751.4	782	149.67	166.00	119.04	114.06	6.99	6.97	25.0	25.0
1	512.55	627.3	106.67	105.33	78.79	73.03	7.05	7.03	25.0	25.1
3	268.26	484.67	138.00	104.67	98.25	71.43	6.99	7.01	25.0	25.1
4	278.63	361.76	138.00	106.33	108.02	85.43	7.00	7.04	25.0	25.1
4(old)	226.44	452.71	145.00	111.33	99.19	76.71	7.00	7.04	25.0	25.1

**Table B.8 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH
8 ,Temperature 25⁰C**

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	947.78	947.78	150.78	150.78	0	0	7.99	7.98	25.0	25.1
0.17	795.60	834.70	36.43	30.37	30.18	24.32	8.04	8.02	25.0	25.2
1	466.82	561.00	22.97	25.37	18.69	20.33	8.07	8.01	25.0	25.1
3	278.29	235.96	29.53	29.83	23.61	20.78	8.01	8.03	25.0	25.0
4	252.96	274.55	30.07	29.30	26.49	21.98	8.00	8.03	25.0	25.0
4(old)	145.18	189.38	32.13	31.93	24.69	21.12	8.00	8.03	25.0	25.0

Table B.9 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 8 ,Temperature 25°C

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0.00	1056.67	1056.67	148.80	148.80	4.77	4.77	8.000	8.02	25.10	25.10
0.17	714.00	827.90	34.47	72.87	34.52	62.72	7.970	7.87	25.10	25.10
1.00	506.43	508.98	25.23	26.70	25.79	25.48	8.000	8.01	25.00	25.10
2.00	464.10	405.28	158.00	40.63	126.86	35.57	8.005	8.00	25.00	25.10
3.00	341.70	295.80	26.13	29.20	25.18	27.04	8.017	8.01	25.10	25.10
4.00	296.65	230.86	34.93	30.50	30.95	27.07	8.042	8.01	25.10	25.10
5.00	301.92	247.69	30.47	34.00	27.56	29.82	8.031	8.01	25.00	25.00
6.00	295.97	230.01	28.63	36.77	25.73	31.34	8.089	8.03	25.10	25.20

Table B.10 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 8.5 ,Temperature 25°C

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	1056.67	1056.67	148.80	148.80	4.77	4.77	8.513	8.51	24.8	24.7
0.17	550.80	474.13	25.53	28.50	16.99	19.61	8.493	8.53	24.9	25.0
1	309.06	334.05	115.67	28.93	87.05	18.21	8.541	8.48	25.1	25.1
2	172.21	242.08	116.67	49.90	87.62	37.78	8.553	8.51	25.0	25.1
3	70.04	168.98	117.33	32.07	86.28	18.28	8.492	8.51	25.0	25.1
4	18.31	111.01	124.67	35.87	94.70	16.42	8.504	8.49	25.1	25.1
5	6.07	82.11	155.67	43.63	116.66	17.92	8.511	8.52	25.0	25.1
6	6.51	53.52	163.00	51.83	128.88	23.21	8.524	8.51	25.1	25.1

Table B.11 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 7.5 ,Temperature 25°C

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH		Temperature (°C)	
	A	B	A	B	A	B	A	B	A	B
0	1056.67	1056.67	148.80	148.80	4.77	4.77	7.500	7.50	25.2	25.2
0.17	741.20	748.00	132.00	132.67	58.33	47.25	7.520	7.46	25.3	25.3
1	629.00	634.10	146.00	115.33	65.24	34.28	7.498	7.48	25.1	25.1
2	436.73	484.84	100.53	102.83	27.75	24.33	7.461	7.47	25.1	25.1
3	304.13	243.95	111.00	93.23	33.97	19.03	7.502	7.55	25.3	25.4
4	237.32	279.31	382.00	326.00	278.92	199.27	7.509	7.52	25.1	25.2
5	171.36	211.48	122.00	111.33	39.55	26.89	7.512	7.53	25.1	25.2
6	174.08	142.46	129.67	109.67	42.82	28.60	7.531	7.53	25.4	25.4

Table B.12 Liquid Sample Analysis of Newberyite Solubilization – Phase I at pH-4.1

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH	Temperature (°C)
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered		
0	1030.77	1030.77	10.87	10.87	20.83	20.83	4.1	20.0
1	909.50	936.70	81.13	74.43	79.30	72.87	4.1	20.0
2	916.30	950.30	70.47	65.67	66.83	65.97	4.1	20.0
3	943.50	938.40	61.40	58.70	59.09	59.09	4.1	20.0
4	931.60	946.90	55.50	53.17	55.41	54.29	4.1	20.0
5	933.30	929.90	59.33	55.47	58.03	53.87	4.1	20.0
6	926.50	935.00	61.70	60.43	60.21	63.49	4.1	20.0
7	955.40	902.70	64.40	57.17	58.85	57.63	4.1	20.0

Table B.13 Liquid Sample Analysis of Newberyite Solubilization – Phase I at pH-4.6

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH	Temperature (°C)
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered		
0	842.35	842.35	8.92	8.92	15.19	15.19	4.60	20.0
0.17	652.80	685.10	426.67	410.67	312.54	297.68	4.60	20.0
1	705.50	724.20	188.33	184.33	144.13	139.16	4.60	20.0
2	725.90	739.50	114.67	112.67	92.95	106.93	4.60	20.0
3	746.30	753.10	56.67	54.23	51.57	63.61	4.60	20.0
4	748.00	753.10	34.07	33.63	33.86	38.54	4.60	20.0
5	742.90	768.40	28.20	27.77	28.92	29.74	4.60	20.0
6	754.80	773.50	24.83	24.87	26.47	26.90	4.60	20.0

Table B.14 Liquid Sample Analysis of Newberyite Solubilization – Phase I at pH-5.0

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH	Temperature (°C)
	Unfilterd	Filtered	Unfilterd	Filtered	Unfilterd	Filtered		
0	860.20	860.20	10.77	10.77	13.01	13.01	5.0	20.0
1	878.90	979.20	42.73	38.63	36.11	31.86	5.0	20.0
2	897.60	977.50	43.43	40.00	35.45	32.79	5.0	20.0
3	929.90	989.40	50.37	46.67	41.95	36.97	5.0	20.0
4	962.20	982.60	51.67	45.87	42.79	38.67	5.0	20.0
5	974.10	1014.90	50.80	50.17	42.56	41.08	5.0	20.0
6	963.90	1023.40	57.80	54.90	48.80	45.85	5.0	20.0
7	967.30	1035.30	57.77	56.73	49.00	47.17	5.0	20.0

Table B.15 Liquid Sample Analysis of Newberyite Solubilization – Phase I at pH-5.6

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH	Temperature (°C)
	Unfilterd	Filtered	Unfilterd	Filtered	Unfilterd	Filtered		
0	817.70	817.70	8.89	8.89	7.16	7.16	5.6	20.0
1	940.10	882.30	61.17	61.97	62.13	57.28	5.6	20.0
2	933.30	943.50	60.10	52.67	56.26	54.99	5.6	20.0
3	931.60	941.80	50.73	54.17	51.15	50.66	5.6	20.0
4	926.50	1004.70	47.73	47.70	49.15	49.15	5.6	20.0
5	935.00	977.50	46.17	43.77	47.40	46.82	5.6	20.0
6	962.20	974.10	46.97	44.67	47.99	47.05	5.6	20.0
7	955.40	958.80	46.60	44.90	47.71	46.96	5.6	20.0

Table B.16 Liquid Sample Analysis of Newberyite Solubilization – Phase I at pH-5.9

Sampling Time (hour)	NH ₄ -N (mg/L)		PO ₄ -P (mg/L)		Mg (mg/L)		pH	Temperature (°C)
	Unfilterd	Filtered	Unfilterd	Filtered	Unfilterd	Filtered		
0	836.40	836.40	10.88	10.88	16.58	16.58	5.9	20.0
1	829.60	821.10	488.33	262.67	401.87	191.39	5.9	20.0
2	826.20	824.50	233.33	143.67	175.66	139.22	5.9	20.0
3	821.10	822.80	101.93	82.80	83.91	86.20	5.9	20.0
4	841.50	867.00	76.03	69.83	65.14	66.02	5.9	20.0
5	821.10	919.70	51.60	47.97	47.48	52.18	5.9	20.0
6	826.20	846.60	20.13	84.23	24.48	63.70	5.9	20.0

Table B.17 Liquid Sample Analysis of Newberyite Solubilization – Phase II at pH-4.5

Sampling Time (hour)	NH ₄ -N (mg/L)	PO ₄ -P (mg/L)	Mg (mg/L)	pH	Temperature (°C)
	Unfilterd	Unfilterd	Unfilterd		
0	873.8	142.8	1.73	4.50	21.0
0.75	763.3	632.4	385.09	4.50	21.0
1	790.5	567.8	349.52	4.50	21.0
1.5	816	542.3	329.09	4.50	21.0
2	814.3	525.3	320.16	4.50	21.0
2.5	816	537.2	341.54	4.50	21.0

Table B.18 Liquid Sample Analysis of Newberyite Solubilization – Phase II at pH-5.0

Sampling Time (hour)	NH ₄ -N (mg/L)	PO ₄ -P (mg/L)	Mg (mg/L)	pH	Temperature (°C)
	Unfilterd	Unfilterd	Unfilterd		
0.0	873.80	142.80	1.73	5.0	22.0
0.5	1045.50	351.73	182.55	5.0	22.0
1.0	1035.30	444.21	246.16	5.0	22.0
1.5	1059.10	464.44	245.68	5.0	22.0
2.0	1193.40	515.78	254.33	5.0	22.0
2.5	1055.70	456.45	253.41	5.0	22.0
3.0	1076.10	470.05	252.67	5.0	22.0
3.5	1045.50	459.68	262.84	5.0	22.0
4.0	1069.30	465.29	262.33	5.0	22.0

Table B.19 Liquid Sample Analysis of Newberyite Solubilization – Phase II at pH-6.0

Sampling Time (hour)	NH ₄ -N (mg/L)	PO ₄ -P (mg/L)	Mg (mg/L)	pH	Temperature (°C)
	Unfilterd	Unfilterd	Unfilterd		
0.0	873.80	142.80	1.73	5.0	22.0
0.5	892.50	276.42	185.18	5.0	22.0
1.0	921.40	283.56	174.96	5.0	22.0
1.5	921.40	281.18	140.28	5.0	22.0
2.0	926.50	283.05	141.26	5.0	22.0
2.5	936.70	276.08	130.86	5.0	22.0
3.0	938.40	271.49	138.69	5.0	22.0
3.5	948.60	271.49	135.03	5.0	22.0
4.0	952.00	271.66	134.75	5.0	22.0

Table B.20 Liquid Sample Analysis of Pilot Scale Experiment - Run 1

Sampling Time (day)	NH4-N (mg/L)				PO4-P (mg/L)				Mg (mg/L)				pH		Temperature(C)	Flow (ml/min)	
	Clarifier		Seed Hopper		Clarifier		Seed Hopper		Clarifier		Seed Hopper		Controller	Clarifier	Clarifier	Actual	Adjusted
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered					
0	1131.00	1131.00			1735.00	1735.00			1411.00	1411.00							
1	43.41	37.33	44.33	39.91	38.43	37.07	59.64	40.57	30.18	31.43	49.53	32.84	8.54	8.45	17.1	1600	780
3	87.23	89.26	84.59	99.02	21.47	17.14	38.37	39.67	20.87	18.52	39.51	36.16	8.85	8.78	21.8	900	850
4	104.11	121.80	149.65	125.66	33.08	15.39	109.80	22.79	17.08	17.41	96.39	25.76	8.71	8.85	24.4	830	
5	146.40	119.15	241.56	138.88	24.01	19.97	302.15	16.59	26.45	23.01	237.94	20.32	8.6	8.59	25.7	840	
6	167.55	141.93	191.34	209.84	22.63	29.22	115.70	108.99	26.62	26.86	45.37	48.85	8.67	8.62	22.3	<400	850
7	182.19	151.48	636.43	178.93	28.51	23.65	--	32.61	39.75	26.18	--	34.07	8.66	8.97	21.5	900	810
8	191.95	160.02	177.51	165.31	23.42	26.41	33.27	19.30	24.93	29.96	39.20	26.35	8.65	8.69	23		
9	198.45	162.67	201.50	161.65	21.00	20.76	85.20	13.01	31.50	23.71	76.62	22.87	8.63	8.72	23.4	880	
10	206.38	171.21	189.51	187.88	27.78	43.92	36.25	29.69	28.87	28.49	39.28	32.43	8.6	8.48	23.2	840	
11	216.96	175.48	193.57	180.97	18.69	30.15	36.72	19.91	23.90	22.73	37.95	24.48	8.59	8.62	23.3	800	
12			213.91	91.70			289.14	7.93			479.73	20.76					

Table B.21 Liquid Sample Analysis of Pilot Scale Experiment – Run 2

Sampling Time (day)	NH4-N (mg/L)				PO4-P (mg/L)				Mg (mg/L)				pH		Temperature(C)
	Clarifier		Seed Hopper		Clarifier		Seed Hopper		Clarifier		Seed Hopper		Controlle r	Clarifier	Clarifier
	Unfiltre d	Filtered	Unfiltre d	Filtered	Unfiltre d	Filtered	Unfiltre d	Filtered	Unfiltre d	Filtered	Unfiltre d	Filtered			
0	949.80	949.80			1754.67	1754.67			1306.00	1306.00					
1	128.91	132.78	146.20	124.03	73.40	71.78	99.63	28.91	85.00	84.94	105.95	59.60	8.12	7.28	21.8
2	134.81	133.79	210.25	205.98	24.73	28.02	38.59	19.44	62.58	62.55	112.11	101.66	7.98	7.73	22.9
3	199.47	153.72	239.73	233.43	17.18	21.37	42.72	27.88	97.50	71.09	135.33	125.01	7.62	8.01	23.4
4	225.70	224.48	229.36	218.38	36.72	25.84	63.54	27.86	120.11	121.54	140.98	117.69	7.66	7.64	23.2
5	267.18	260.06	260.27	199.06	25.25	20.48	25.56	59.33	141.64	143.83	141.97	146.28	7.74	7.7	23.9
6	267.99	263.11	271.65	272.26	12.61	11.59	12.57	12.99	140.24	143.43	140.29	144.26	7.82	7.84	24.8
7	302.15	293.82	309.07	298.49	61.12	57.04	70.35	67.71	193.84	193.48	189.83	202.02	7.08	7.19	24.3
8	333.87	320.25	331.23	322.89	64.46	56.61	80.11	58.56	213.83	209.95	214.72	208.95	7.16	7.08	23.7
9	331.84	322.69	336.92	322.49	67.51	58.46	76.05	51.89	217.61	214.49	221.84	187.40	7.09	7.04	24.1
10	326.55	319.64	338.35	325.94	46.24	38.06	88.65	53.76	203.23	198.88	230.25	171.99	7.22	7.3	21.7

Appendix C Solid Sample Analysis Result

Table C.1 Liquid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer Effluent, pH 8 Temperature 25°C

Feed- Synthetic Effluent, pH- 8 , T-25o			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run1, Powder 1_Reactor A	0.0998	108.49	21.03	123.33	10.85	2.70	0.25	37.80	48.20	0.45	0.15	0.25	0.40	2.68	1.12	0.38	0.62	1.00	6.73
	Run1, Powder 2_Reactor A	0.1007	105.61	15.53	126.67	10.56	2.00	0.30	38.82	49.03	0.43	0.11	0.30	0.41	2.72	1.06	0.27	0.73	1.00	6.67
	Run1, Powder 3_Reactor A	0.0999	102.34	13.27	123.67	10.23	1.71	0.30	37.90	49.76	0.42	0.09	0.30	0.40	2.76	1.06	0.24	0.76	1.00	6.93
	Run1_Pellet 1_Reactor A	0.1010	119.61	5.86	148.67	11.96	0.75	0.44	45.56	42.29	0.49	0.04	0.44	0.48	2.35	1.03	0.09	0.91	1.00	4.90
	Run1_Pellet 2_Reactor A	0.1012	119.34	6.84	140.67	11.93	0.88	0.40	43.11	44.87	0.49	0.05	0.40	0.45	2.49	1.08	0.11	0.89	1.00	5.49
	Run1_Pellet 3_Reactor A	x																		
	Run1, Powder 1_Reactor B	0.1005	108.51	19.97	130.67	10.85	2.57	0.28	40.04	46.76	0.45	0.14	0.28	0.42	2.60	1.06	0.34	0.66	1.00	6.16
	Run1, Powder 2_Reactor B	0.1000	104.00	19.47	127.00	10.40	2.50	0.27	38.92	47.91	0.43	0.14	0.27	0.41	2.66	1.04	0.34	0.66	1.00	6.50
	Run1, Powder 3_Reactor B	0.1006	102.57	15.67	128.00	10.26	2.01	0.30	39.23	48.80	0.42	0.11	0.30	0.41	2.71	1.02	0.27	0.73	1.00	6.57
	Run1_Pellet 1_Reactor B	0.1004	121.47	4.91	148.00	12.15	0.63	0.44	45.35	41.82	0.50	0.04	0.44	0.48	2.32	1.05	0.07	0.93	1.00	4.87
	Run1_Pellet 2_Reactor B	0.1000	121.30	6.21	148.67	12.13	0.80	0.44	45.56	41.08	0.50	0.04	0.44	0.48	2.28	1.04	0.09	0.91	1.00	4.76
	Run1_Pellet 3_Reactor B	0.1004	122.36	4.93	147.33	12.24	0.63	0.44	45.15	41.94	0.50	0.04	0.44	0.48	2.33	1.06	0.07	0.93	1.00	4.90

Table C.2 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer Effluent, pH 7 Temperature 25°C

Feed- Synthetic Effluent, pH- 7 , T-25o			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run2, Powder 1_Reactor A	0.1005	108.38	13.50	127.67	10.84	1.74	0.32	39.12	48.49	0.45	0.10	0.32	0.41	2.69	1.08	0.23	0.77	1.00	6.54
	Run2, Powder 2_Reactor A	0.1007	104.07	13.90	126.00	10.41	1.79	0.31	38.61	49.59	0.43	0.10	0.31	0.41	2.75	1.05	0.24	0.76	1.00	6.78
	Run2, Powder 3_Reactor A	0.1003	104.44	17.07	126.00	10.44	2.19	0.28	38.61	48.76	0.43	0.12	0.28	0.41	2.71	1.06	0.30	0.70	1.00	6.67
	Run2_Pellet 1_Reactor A	0.0949	125.66	1.48	153.33	12.57	0.19	0.48	46.99	34.67	0.52	0.01	0.48	0.49	1.93	1.05	0.02	0.98	1.00	3.89
	Run2_Pellet 2_Reactor A	x																		
	Run2_Pellet 3_Reactor A	x																		
	Run2, Powder 1_Reactor B	0.1006	109.39	12.37	134.00	10.94	1.59	0.34	41.06	46.66	0.45	0.09	0.34	0.43	2.59	1.04	0.20	0.80	1.00	6.00
	Run2, Powder 2_Reactor B	0.1002	109.31	15.43	131.33	10.93	1.98	0.31	40.25	46.72	0.45	0.11	0.31	0.42	2.60	1.06	0.26	0.74	1.00	6.13
	Run2, Powder 3_Reactor B	0.1001	107.91	14.37	134.33	10.79	1.85	0.33	41.17	45.96	0.44	0.10	0.33	0.43	2.55	1.02	0.24	0.76	1.00	5.89
	Run2_Pellet 1_Reactor B	0.1005	133.33	1.48	164.67	13.33	0.19	0.52	50.46	35.99	0.55	0.01	0.52	0.53	2.00	1.03	0.02	0.98	1.00	3.76
	Run2_Pellet 2_Reactor B	x																		
	Run2_Pellet 3_Reactor B	x																		

Table C.3 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer Effluent, pH 7 Temperature 10°C

Feed- Synthetic Effluent, pH- 7 , T-10°	Solid Sample)	Mass (g)	actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
			Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run3, Powder 1_Reactor A	0.1003	107.23	9.98	135.00	10.72	1.28	0.36	41.37	46.56	0.44	0.07	0.36	0.44	2.59	1.01	0.16	0.84	1.00	5.94
	Run3, Powder 2_Reactor A	0.1004	105.44	10.17	133.67	10.54	1.31	0.36	40.96	47.23	0.43	0.07	0.36	0.43	2.62	1.01	0.17	0.83	1.00	6.08
	Run3, Powder 3_Reactor A	0.1008	113.26	10.53	134.00	11.33	1.35	0.36	41.06	46.70	0.47	0.08	0.36	0.43	2.59	1.08	0.17	0.83	1.00	6.00
	Run3_Pellet 1_Reactor A	0.0997	124.04	1.96	160.00	12.40	0.25	0.50	49.03	37.51	0.51	0.01	0.50	0.52	2.08	0.99	0.03	0.97	1.00	4.04
	Run3_Pellet 2_Reactor A	0.0998	128.44	2.79	166.33	12.84	0.36	0.52	50.97	35.11	0.53	0.02	0.52	0.54	1.95	0.99	0.04	0.96	1.00	3.64
	Run3_Pellet 3_Reactor A	x																		
	Run3, Powder 1_Reactor B	0.1008	105.44	8.00	135.00	10.54	1.03	0.38	41.37	47.48	0.43	0.06	0.38	0.44	2.64	1.00	0.13	0.87	1.00	6.06
	Run3, Powder 2_Reactor B	0.1001	105.43	10.40	137.00	10.54	1.34	0.37	41.98	45.87	0.43	0.07	0.37	0.44	2.55	0.98	0.17	0.83	1.00	5.77
	Run3, Powder 3_Reactor B	0.1000	102.45	11.40	132.00	10.25	1.47	0.34	40.45	47.49	0.42	0.08	0.34	0.43	2.64	0.99	0.19	0.81	1.00	6.20
	Run3_Pellet 1_Reactor B	x																		
	Run3_Pellet 2_Reactor B	x																		
	Run3_Pellet 3_Reactor B	x																		

Table C.4 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Crystallizer Effluent, pH 8, Temperature 10°C

Feed- Synthetic Effluent, pH- 8 , T-10°	Solid Sample)	Mass (g)	actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
			Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run4, Powder 1_Reactor A	0.1009	109.04	18.23	140.00	10.90	2.34	0.32	42.90	44.43	0.45	0.13	0.32	0.45	2.47	0.99	0.29	0.71	1.00	5.47
	Run4, Powder 2_Reactor A	0.0992	107.02	11.63	137.33	10.70	1.50	0.36	42.09	44.56	0.44	0.08	0.36	0.44	2.48	0.99	0.19	0.81	1.00	5.59
	Run4, Powder 3_Reactor A	0.1006	108.46	9.30	140.33	10.85	1.20	0.39	43.01	45.17	0.45	0.07	0.39	0.45	2.51	0.99	0.15	0.85	1.00	5.54
	Run4_Pellet 1_Reactor A	0.1009	136.72	0.27	178.00	13.67	0.03	0.57	54.55	32.07	0.56	0.00	0.57	0.57	1.78	0.98	0.00	1.00	1.00	3.10
	Run4_Pellet 2_Reactor A	0.1000	143.38	0.11	176.00	14.34	0.01	0.57	53.94	31.14	0.59	0.00	0.57	0.57	1.73	1.04	0.00	1.00	1.00	3.05
	Run4_Pellet 3_Reactor A	0.0995	133.43	0.12	173.67	13.34	0.02	0.56	53.22	32.36	0.55	0.00	0.56	0.56	1.80	0.98	0.00	1.00	1.00	3.21
	Run4, Powder 1_Reactor B	0.1005	103.49	20.80	132.33	10.35	2.67	0.28	40.55	46.64	0.43	0.15	0.28	0.43	2.59	1.00	0.35	0.65	1.00	6.07
	Run4, Powder 2_Reactor B	0.0999	105.30	12.20	133.00	10.53	1.57	0.34	40.76	46.70	0.43	0.09	0.34	0.43	2.59	1.01	0.20	0.80	1.00	6.05
	Run4, Powder 3_Reactor B	0.0993	105.99	10.90	131.00	10.60	1.40	0.34	40.15	46.81	0.44	0.08	0.34	0.42	2.60	1.03	0.18	0.82	1.00	6.15
	Run4_Pellet 1_Reactor B	0.1014	133.91	1.68	168.33	13.39	0.22	0.53	51.59	35.68	0.55	0.01	0.53	0.54	1.98	1.01	0.02	0.98	1.00	3.65
	Run4_Pellet 2_Reactor B	x																		
	Run4_Pellet 3_Reactor B	x																		

Table C.5 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH 7, Temperature 10°C

Feed- Synthetic Centrate, pH- 7 , T-10°			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run5, Powder 1_Reactor A	0.0994	101.45	17.40	130.67	10.14	2.24	0.30	40.04	46.68	0.42	0.12	0.30	0.42	2.59	0.99	0.29	0.71	1.00	6.15
	Run5, Powder 2_Reactor A	0.0990	103.27	10.77	131.00	10.33	1.38	0.35	40.15	46.80	0.42	0.08	0.35	0.42	2.60	1.01	0.18	0.82	1.00	6.15
	Run5, Powder 3_Reactor A	0.1001	104.63	17.90	130.33	10.46	2.30	0.29	39.94	47.10	0.43	0.13	0.29	0.42	2.62	1.02	0.30	0.70	1.00	6.22
	Run5_Pellet 1_Reactor A	x																		
	Run5_Pellet 2_Reactor A	x																		
	Run5_Pellet 3_Reactor A	x																		
	Run5, Powder 1_Reactor B	0.0999	103.96	13.83	126.00	10.40	1.78	0.31	38.61	48.81	0.43	0.10	0.31	0.41	2.71	1.05	0.24	0.76	1.00	6.67
	Run5, Powder 2_Reactor B	0.1008	101.02	7.77	124.33	10.10	1.00	0.35	38.10	51.25	0.42	0.06	0.35	0.40	2.85	1.04	0.14	0.86	1.00	7.10
	Run5, Powder 3_Reactor B	0.0994	98.10	16.57	121.67	9.81	2.13	0.27	37.28	49.90	0.40	0.12	0.27	0.39	2.77	1.03	0.30	0.70	1.00	7.06
	Run5_Pellet 1_Reactor B	0.1008	130.66	1.17	166.67	13.07	0.15	0.53	51.08	35.98	0.54	0.01	0.53	0.54	2.00	1.00	0.02	0.98	1.00	3.72
	Run5_Pellet 2_Reactor B	0.1004	130.09	1.42	162.33	13.01	0.18	0.51	49.75	36.95	0.54	0.01	0.51	0.52	2.05	1.02	0.02	0.98	1.00	3.92
	Run5_Pellet 3_Reactor B	0.0998	130.83	0.63	164.67	13.08	0.08	0.53	50.46	35.65	0.54	0.00	0.53	0.53	1.98	1.01	0.01	0.99	1.00	3.73

Table C.6 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH 8 Temperature 10°C

Feed- Synthetic Centrate, pH- 8 , T-10°			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run6, Powder 1_Reactor A	0.1001	105.63	5.10	129.67	10.56	0.66	0.38	39.74	48.76	0.43	0.04	0.38	0.42	2.71	1.04	0.09	0.91	1.00	6.48
	Run6, Powder 2_Reactor A	0.0999	104.86	6.66	128.33	10.49	0.86	0.37	39.33	48.86	0.43	0.05	0.37	0.41	2.71	1.04	0.11	0.89	1.00	6.56
	Run6, Powder 3_Reactor A	0.1006	107.07	9.77	131.33	10.71	1.26	0.35	40.25	48.04	0.44	0.07	0.35	0.42	2.67	1.04	0.16	0.84	1.00	6.30
	Run6_Pellet 1_Reactor A	0.1004	123.12	2.30	165.33	12.31	0.30	0.52	50.67	36.61	0.51	0.02	0.52	0.53	2.03	0.95	0.03	0.97	1.00	3.81
	Run6_Pellet 2_Reactor A	0.1000	120.09	2.55	149.67	12.01	0.33	0.46	45.87	41.33	0.49	0.02	0.46	0.48	2.30	1.02	0.04	0.96	1.00	4.76
	Run6_Pellet 3_Reactor A	0.0990	122.23	2.30	151.67	12.22	0.30	0.47	46.48	39.53	0.50	0.02	0.47	0.49	2.20	1.03	0.03	0.97	1.00	4.49
	Run6, Powder 1_Reactor B	0.1006	106.24	11.77	130.00	10.62	1.51	0.34	39.84	48.29	0.44	0.08	0.34	0.42	2.68	1.04	0.20	0.80	1.00	6.40
	Run6, Powder 2_Reactor B	0.1008	104.91	8.77	127.67	10.49	1.13	0.35	39.12	49.71	0.43	0.06	0.35	0.41	2.76	1.05	0.15	0.85	1.00	6.71
	Run6, Powder 3_Reactor B	0.0998	103.58	10.43	127.33	10.36	1.34	0.34	39.02	48.74	0.43	0.07	0.34	0.41	2.71	1.04	0.18	0.82	1.00	6.59
	Run6_Pellet 1_Reactor B	0.0995	124.80	1.73	155.67	12.48	0.22	0.49	47.70	38.60	0.51	0.01	0.49	0.50	2.14	1.02	0.02	0.98	1.00	4.27
	Run6_Pellet 2_Reactor B	0.1000	125.68	2.39	158.00	12.57	0.31	0.49	48.42	38.21	0.52	0.02	0.49	0.51	2.12	1.01	0.03	0.97	1.00	4.17
	Run6_Pellet 3_Reactor B	0.1003	126.09	1.99	158.00	12.61	0.26	0.50	48.42	38.52	0.52	0.01	0.50	0.51	2.14	1.02	0.03	0.97	1.00	4.20

Table C.7 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH 7, Temperature 25°C

Feed- Synthetic Centrate, pH- 7 , T-25°			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run7, Powder 1_Reactor A	0.0996	100.32	16.60	128.00	10.03	2.13	0.29	39.23	47.91	0.41	0.12	0.29	0.41	2.66	1.00	0.29	0.71	1.00	6.45
	Run7, Powder 2_Reactor A	0.0996	100.29	17.30	128.67	10.03	2.22	0.29	39.43	47.62	0.41	0.12	0.29	0.42	2.65	0.99	0.30	0.70	1.00	6.37
	Run7, Powder 3_Reactor A	0.1007	102.43	16.27	132.00	10.24	2.09	0.31	40.45	47.60	0.42	0.12	0.31	0.43	2.64	0.99	0.27	0.73	1.00	6.21
	Run7_Pellet 1_Reactor A	0.1000	124.30	1.93	161.67	12.43	0.25	0.51	49.54	37.27	0.51	0.01	0.51	0.52	2.07	0.98	0.03	0.97	1.00	3.97
	Run7_Pellet 2_Reactor A	x																		
	Run7_Pellet 3_Reactor A	x																		
	Run7, Powder 1_Reactor B	0.0995	99.81	21.70	128.33	9.98	2.79	0.26	39.33	47.14	0.41	0.16	0.26	0.41	2.62	0.99	0.37	0.63	1.00	6.33
	Run7, Powder 2_Reactor B	0.1004	99.20	18.63	135.00	9.92	2.40	0.30	41.37	46.41	0.41	0.13	0.30	0.44	2.58	0.94	0.31	0.69	1.00	5.92
	Run7, Powder 3_Reactor B	0.0996	100.84	19.30	128.00	10.08	2.48	0.28	39.23	47.53	0.41	0.14	0.28	0.41	2.64	1.00	0.33	0.67	1.00	6.40
	Run7_Pellet 1_Reactor B	0.1000	129.89	3.90	168.67	12.99	0.50	0.52	51.69	34.31	0.53	0.03	0.52	0.54	1.91	0.98	0.05	0.95	1.00	3.50
	Run7_Pellet 2_Reactor B	0.0999	129.27	2.79	167.00	12.93	0.36	0.52	51.18	34.92	0.53	0.02	0.52	0.54	1.94	0.99	0.04	0.96	1.00	3.60
	Run7_Pellet 3_Reactor B	0.1000	128.85	1.91	167.67	12.89	0.25	0.53	51.38	34.96	0.53	0.01	0.53	0.54	1.94	0.98	0.03	0.97	1.00	3.59

Table C.8 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Synthetic Centrate, pH 8 ,Temperature 25°C

Feed- Synthetic Centrate, pH- 8 , T-25°			actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
	Solid Sample)	Mass (g)	Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run8, Powder 1_Reactor A	0.0995	102.73	16.43	129.33	10.27	2.11	0.30	39.63	47.18	0.42	0.12	0.30	0.42	2.62	1.01	0.28	0.72	1.00	6.28
	Run8, Powder 2_Reactor A	0.1001	104.48	13.57	131.33	10.45	1.74	0.33	40.25	47.33	0.43	0.10	0.33	0.42	2.63	1.01	0.23	0.77	1.00	6.21
	Run8, Powder 3_Reactor A	0.1004	103.90	13.20	130.33	10.39	1.70	0.33	39.94	48.05	0.43	0.09	0.33	0.42	2.67	1.02	0.22	0.78	1.00	6.35
	Run8_Pellet 1_Reactor A	0.1000	123.20	4.89	155.67	12.32	0.63	0.47	47.70	38.88	0.51	0.03	0.47	0.50	2.16	1.01	0.07	0.93	1.00	4.30
	Run8_Pellet 2_Reactor A	0.1006	122.83	6.00	154.33	12.28	0.77	0.45	47.30	39.79	0.51	0.04	0.45	0.50	2.21	1.02	0.09	0.91	1.00	4.44
	Run8_Pellet 3_Reactor A	0.0816	99.36	4.95	126.33	9.94	0.64	0.37	38.72	31.94	0.41	0.04	0.37	0.41	1.77	1.00	0.09	0.91	1.00	4.35
	Run8, Powder 1_Reactor B	0.1000	102.01	16.87	127.00	10.20	2.17	0.29	38.92	48.42	0.42	0.12	0.29	0.41	2.69	1.02	0.29	0.71	1.00	6.57
	Run8, Powder 2_Reactor B	0.0999	106.84	14.33	134.67	10.68	1.84	0.33	41.27	45.77	0.44	0.10	0.33	0.43	2.54	1.01	0.24	0.76	1.00	5.85
	Run8, Powder 3_Reactor B	0.0999	103.01	21.23	130.67	10.30	2.73	0.27	40.04	46.56	0.42	0.15	0.27	0.42	2.59	1.01	0.36	0.64	1.00	6.14
	Run8_Pellet 1_Reactor B	0.1001	115.91	10.30	151.33	11.59	1.32	0.41	46.38	40.39	0.48	0.07	0.41	0.49	2.24	0.98	0.15	0.85	1.00	4.60
	Run8_Pellet 2_Reactor B	0.1003	119.04	6.90	149.00	11.90	0.89	0.43	45.66	41.42	0.49	0.05	0.43	0.48	2.30	1.02	0.10	0.90	1.00	4.79
	Run8_Pellet 3_Reactor B	0.1005	120.06	5.96	152.00	12.01	0.77	0.45	46.58	40.70	0.49	0.04	0.45	0.49	2.26	1.01	0.09	0.91	1.00	4.61

Table C.9 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 8 ,Temperature 25°C

	Solid Sample)	Mass (g)	actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
			Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
Feed- Annacis Centrate, pH-8, T-25°	Annacis Centrate(6hr solid)																			
	Run9, Powder 1_Reactor A	0.1008	99.78	14.13	122.00	9.98	1.82	0.29	37.39	51.33	0.41	0.10	0.29	0.39	2.85	1.04	0.26	0.74	1.00	7.25
	Run9, Powder 2_Reactor A	0.1006	99.64	16.40	98.97	9.96	2.11	0.20	30.33	58.00	0.41	0.12	0.20	0.32	3.22	1.28	0.37	0.63	1.00	10.09
	Run9, Powder 3_Reactor A	0.1002	97.18	24.63	124.67	9.72	3.17	0.23	38.20	48.88	0.40	0.18	0.23	0.40	2.72	0.99	0.44	0.56	1.00	6.75
	Run9_Pellet 1_Reactor A	0.0993	105.92	12.53	133.67	10.59	1.61	0.34	40.96	45.79	0.44	0.09	0.34	0.43	2.54	1.01	0.21	0.79	1.00	5.90
	Run9_Pellet 2_Reactor A	0.1003	106.69	10.67	133.33	10.67	1.37	0.35	40.86	47.05	0.44	0.08	0.35	0.43	2.61	1.02	0.18	0.82	1.00	6.08
	Run9_Pellet 3_Reactor A	x																		
	Run9, Powder 1_Reactor B	0.0996	97.83	19.33	110.00	9.78	2.49	0.22	33.71	53.40	0.40	0.14	0.22	0.35	2.97	1.13	0.39	0.61	1.00	8.36
	Run9, Powder 2_Reactor B	0.0998	99.73	20.00	125.00	9.97	2.57	0.26	38.31	48.69	0.41	0.14	0.26	0.40	2.70	1.02	0.35	0.65	1.00	6.71
	Run9, Powder 3_Reactor B	0.0994	99.17	10.37	123.33	9.92	1.33	0.32	37.80	50.03	0.41	0.07	0.32	0.40	2.78	1.03	0.19	0.81	1.00	6.99
	Run9_Pellet 1_Reactor B	0.1004	106.40	9.73	134.00	10.64	1.25	0.36	41.06	47.08	0.44	0.07	0.36	0.43	2.62	1.01	0.16	0.84	1.00	6.05
	Run9_Pellet 2_Reactor B	0.1000	110.89	5.86	138.00	11.09	0.75	0.40	42.29	45.46	0.46	0.04	0.40	0.45	2.53	1.03	0.09	0.91	1.00	5.67
	Run9_Pellet 3_Reactor B	0.1008	109.88	7.16	137.67	10.99	0.92	0.39	42.19	46.31	0.45	0.05	0.39	0.44	2.57	1.02	0.12	0.88	1.00	5.79

Table C.10 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 8.5 ,Temperature 25°C

	Solid Sample)	Mass (g)	actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
			Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
Feed- Annacis Centrate, pH-8.5, T-25°	Run10, Powder 1_Reactor A	0.1005	103.03	19.03	129.00	10.30	2.45	0.28	39.53	47.94	0.42	0.14	0.28	0.42	2.66	1.02	0.33	0.67	1.00	6.40
	Run10, Powder 2_Reactor A	0.0999	103.61	17.73	123.00	10.36	2.28	0.27	37.69	49.30	0.43	0.13	0.27	0.40	2.74	1.07	0.32	0.68	1.00	6.90
	Run10, Powder 3_Reactor A	0.1008	110.99	23.93	130.33	11.10	3.08	0.25	39.94	46.43	0.46	0.17	0.25	0.42	2.58	1.09	0.41	0.59	1.00	6.14
	Run10_Pellet 1_Reactor A	0.0997	125.16	9.06	133.67	12.52	1.16	0.37	40.96	44.69	0.52	0.06	0.37	0.43	2.48	1.19	0.15	0.85	1.00	5.76
	Run10_Pellet 2_Reactor A	x																		
	Run10_Pellet 3_Reactor A	x																		
	Run10, Powder 1_Reactor B	0.0999	109.36	11.87	133.33	10.94	1.53	0.35	40.86	46.23	0.45	0.08	0.35	0.43	2.57	1.05	0.20	0.80	1.00	5.97
	Run10, Powder 2_Reactor B	0.0997	111.48	16.60	137.33	11.15	2.13	0.32	42.09	44.01	0.46	0.12	0.32	0.44	2.44	1.04	0.27	0.73	1.00	5.52
	Run10, Powder 3_Reactor B	0.1006	109.13	11.40	136.67	10.91	1.47	0.36	41.88	45.98	0.45	0.08	0.36	0.44	2.55	1.02	0.18	0.82	1.00	5.79
	Run10_Pellet 1_Reactor B	0.0999	119.17	5.90	149.67	11.92	0.76	0.44	45.87	40.92	0.49	0.04	0.44	0.48	2.27	1.02	0.09	0.91	1.00	4.71
	Run10_Pellet 2_Reactor B	0.1005	120.03	4.21	148.00	12.00	0.54	0.45	45.35	42.15	0.49	0.03	0.45	0.48	2.34	1.03	0.06	0.94	1.00	4.91
	Run10_Pellet 3_Reactor B	0.0999	117.97	4.40	149.00	11.80	0.57	0.45	45.66	41.43	0.49	0.03	0.45	0.48	2.30	1.01	0.07	0.93	1.00	4.79

Table C.11 Solid Sample Analysis for Mg:N:P molar ratio 1:1:1 in Annacis Centrate, pH 7.5 ,Temperature 25⁰C

Feed- Annacis Centrate, pH-7.5, T-25°	Solid Sample)	Mass (g)	actual, in 100 ml solution, mg/L			mass in solid sample, mg					mmoles in solid sample					molar ratios				
			Mg	N	P	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O	Mg	NH4	H	PO4	H2O
	Run11, Powder 1_Reactor A	0.1003	97.61	25.03	122.00	9.76	3.22	0.21	37.39	49.72	0.40	0.18	0.21	0.39	2.76	1.02	0.45	0.55	1.00	7.02
	Run11, Powder 2_Reactor A	0.1002	96.57	14.07	121.67	9.66	1.81	0.29	37.28	51.16	0.40	0.10	0.29	0.39	2.84	1.01	0.26	0.74	1.00	7.24
	Run11, Powder 3_Reactor A	0.1004	100.07	13.17	122.33	10.01	1.69	0.30	37.49	50.91	0.41	0.09	0.30	0.39	2.83	1.04	0.24	0.76	1.00	7.17
	Run11_Pellet 1_Reactor A	x																		
	Run11_Pellet 2_Reactor A	x																		
	Run11_Pellet 3_Reactor A	x																		
	Run11, Powder 1_Reactor B	0.0999	101.26	15.90	125.67	10.13	2.04	0.29	38.51	48.93	0.42	0.11	0.29	0.41	2.72	1.03	0.28	0.72	1.00	6.71
	Run11, Powder 2_Reactor B	0.1007	100.14	14.43	125.67	10.01	1.86	0.30	38.51	50.02	0.41	0.10	0.30	0.41	2.78	1.02	0.25	0.75	1.00	6.85
	Run11, Powder 3_Reactor B	0.1001	100.92	14.50	125.67	10.09	1.86	0.30	38.51	49.33	0.42	0.10	0.30	0.41	2.74	1.02	0.26	0.74	1.00	6.76
	Run11_Pellet 1_Reactor B	0.1003	111.55	6.07	138.67	11.15	0.78	0.40	42.49	45.47	0.46	0.04	0.40	0.45	2.53	1.03	0.10	0.90	1.00	5.65
	Run11_Pellet 2_Reactor B	0.1006	111.21	11.20	140.00	11.12	1.44	0.37	42.90	44.76	0.46	0.08	0.37	0.45	2.49	1.01	0.18	0.82	1.00	5.51
	Run11_Pellet 3_Reactor B	0.1008	109.22	10.49	139.00	10.92	1.35	0.37	42.60	45.56	0.45	0.07	0.37	0.45	2.53	1.00	0.17	0.83	1.00	5.64