

**DEVELOPMENT OF CONTROL STRATEGIES FOR THE
OPERATION OF A STRUVITE CRYSTALLIZATION
PROCESS**

by

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ABSTRACT

In this study, a dynamic control model for struvite crystallization process was developed that incorporated both chemistry and control software, which could be used to increase the efficiency and ease process operation. This process model was the basis of an automatic controller that had the capability to manipulate flows and chemical additions, and thereby control the system at a desired set point. The control model was then used as a prediction tool to determine conditions that influence the supersaturation ratio of the process.

A pilot scale crystallizer was operated at a local treatment plant to test the model. The struvite produced from the operation of the process was then examined to determine the influence of various operating parameters on its quality. Supersaturation ratio (SSR) and upflow velocity in the crystallizer were found to influence the size and shape of the pellets developed. Mid-sized pellets (2.0-2.5 mm), had the highest crushing strengths; SSR did not appear to influence the crushing strength of pellets formed. High concentration of magnesium in the crystallizer was related to the formation of pellets having greater crushing strengths.

To determine a single solubility constant for struvite, a study was conducted under varying experimental conditions. Results showed that, for a particular temperature, and in the working pH range of 7.0-9.0, the solubility constant was independent of the pH and water matrix. These experimental values, along with values found in literature, were used to derive a universal constant and a linear equation relating solubility product (pK_{sp}) with temperature.

In this study, the effectiveness of two carbon dioxide strippers, in reducing caustic usage, were evaluated. Results showed that carbon dioxide stripping was efficient in reducing caustic costs, by as much as 46%. The potential saving in caustic cost due to CO₂ stripping was calculated to be as high as 38 cents per thousand liters treated.

The determination of the concentration of Mg in a struvite crystallization process is important because of its influence on SSR, the associated operational cost and its struvite forming potential when unused chemical is passed back to the treatment plant. In this study, methods were tested, with acceptable degree of accuracy, which can provide information, on-site, on the concentration and rate of application of the element.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
AIWWTP	Annacis Island Wastewater Treatment Plant
ANN	Artificial Neural Network
ASR	Air Supply Rate
ATM	Atmosphere, Unit of pressure
AWWTP	Advanced Wastewater Treatment Plant
BC	British Columbia
BN	Baffle Number
BOD	Biochemical Oxygen Demand
CAD	Canadian Dollar
Cond.	Conductivity
(E)BNR	(Enhanced) Biological Nutrient Removal
EC	Electric Conductivity (mS/cm)
EDTA	Ethylene diamine tetraacetic acid
ERR	Effluent Recycle Ratio
GUI	Graphical User Interface
HP	Horse power
HRT	Hydraulic Retention Time (min)
IAP	Ionic Activity Product
IBC	Influent Buffering Capacity
ICP	Inductively Coupled Plasma
IFR	Influent Flow Rate
ISE	Ion Selective Electrode
IT	Influent Temperature
K	Kelvin, Unit of Temperature
K _{sp}	Solubility Product
K _{sp} eq	Equilibrium K _{sp}
LIWWTP	Lulu Island Wastewater Treatment Plant

MAP	Magnesium Ammonium Phosphate Hexahydrate; Struvite
MGD	Millions Gallons per Day
MLD	Million Liters per Day
Mol	Moles
MS	Mass Spectrometer
mS/cm	Milli Siemens per centimeter
P	Phosphorus
PAC	Polyaluminum chloride
PM	Peroxide Microwave
Ps	Conditional Solubility Product
Pseq	Equilibrium Ps
PVC	Polyvinyl chloride
Qf	Feed flow
Qr	Recycle flow
Qt	Total flow
R	Gas constant
R #1	Reactor (system) 1
R #2	Reactor (system) 2
RCF	Relative Centrifugal Force
RMS	Root Mean Square
RR	Recycle Ratio
SD	Standard Deviation
SEM	Scanning Electron Microscope
SSE	Sum of Squared Error
SSR	Supersaturation Ratio
SSR ^c	Conditional Supersaturation Ratio
T	Temperature in degrees Kelvin
TSS	Total Suspended Solids
UBC	University of British Columbia
WWTP	Wastewater Treatment Plant
XRD	X-ray diffraction

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DEDICATION

To my wife

Farah Laj Chowdhury

For all her love, support and patience

CHAPTER ONE: INTRODUCTION

1.1 Background

The recovery of phosphorus, as struvite, from wastewater provides an environmentally sound and renewable nutrient source to the agricultural, landscaping and recreational industry, as well as solving wastewater treatment plant problems. Although there are different phosphorus recovery processes in use, struvite is usually grown in fluidized bed reactors by a crystallization process.

The pilot-scale crystallizer used at the University of British Columbia (UBC) is different from others reported in the literature in that the reactor has different sections of varying diameters, as opposed to the more common conical shape. Previous studies at the UBC have successfully demonstrated the applicability of struvite precipitation as a means of reducing, and recovering, phosphates from wastewater. Although different control parameters can be used for struvite (magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation, the primary control parameter used in most of the studies was the supersaturation ratio (SSR), which is the degree of struvite saturation in the crystallizer. This value is dependent on the struvite solubility product, or K_{sp} , more commonly referred to as the $\text{p}K_{sp}$ ($-\log K_{sp}$) value. Numerous solubility constants are found in the literature with respect to struvite formation. Due to these wide range of reported values, experiments are needed to determine if there exists a correlation between values obtained with different water matrices (distilled water, tap water, digester supernatant and centrate), at different temperatures and pH. By using several combinations of experimental conditions involving the aforementioned variables, the struvite solubility product was determined in the present study.

The acceptance of struvite precipitation as a means of wastewater treatment and a commercial source of phosphorus will, to a large extent, depend on the economics of the process. One of the primary expenses arises from the need to increase the pH of the system by the addition of a caustic substance, usually sodium hydroxide. Carbon dioxide stripping

can help increase the pH of the system, thereby providing a viable and cheaper option than the traditional method of only chemical addition. Although carbon dioxide stripping is not a new phenomenon, its use, efficiency and cost benefits, when applied to a struvite crystallization process, have not been studied in great detail. The present study examined the efficiency of two types of carbon dioxide strippers in reducing chemical cost, as well as, determined operating conditions and issues arising from their use.

Struvite precipitation in a fluidized bed crystallizer is a continuous process. Therefore, variations in the constituent ions (magnesium, ammonium and phosphate) can result in the formation, or dissociation, of the compound. Consequently, it is important to monitor the concentration of these ions. Since most wastewater used for phosphorus recovery as struvite lacks magnesium (Mg), an external source is usually applied to increase the concentration in the system. The determination of the concentration of Mg during this addition is important, because not only does it determine the value of the supersaturation ratio, unused Mg in the effluent can increase struvite formation potential elsewhere in the treatment plant. Although ammonium and phosphate ions can be measured in real time using online analyzers, there are no suitable analyzers for measuring real-time magnesium concentrations in wastewater and in the external source. The usual method of measuring magnesium [by atomic absorption (AA) spectroscopy] is a time consuming and expensive process. Therefore, a suitable on-site method that is quick and cheap would go a long way in optimizing the magnesium addition. In the present study, two methods to determine magnesium addition requirements on-site were proposed and tested for their efficiency.

Despite numerous studies being conducted worldwide on phosphorus precipitation as struvite, most of the research is based on the chemistry of the process, and few have dealt with actual operation and optimization of the process at the pilot- or full-scale installations. Studies carried out have demonstrated the need for tighter control of process variables, such as temperature, conductivity, pH and constituent ions, for improved product quality and ease of process control of a struvite crystallization process. In order to maintain this “narrow working window” in process conditions, it is important that the effects of the variations in these process variables be as limited as possible. The variations in variables are natural

during wastewater treatment processes, and as struvite crystallization uses the effluent from these processes, it is natural to expect these variations during struvite processes as well. The changes in the variables are responsible for changing the primary control parameter – the supersaturation ratio in a struvite crystallizer. The problem with the present method of manual control of a struvite crystallization process is that any sudden and unexpected change in any of the variables during its operation (when no operator is present on-site) is not noticed until the next day. Consequently, struvite growth and quality can be compromised.

As mentioned above, the production of struvite, from wastewater, in a crystallizer depends on a number of variables, which bring about complex and non-linear changes in the process chemistry. This complex situation can be handled diligently by gaining an insight into the process using models. Models can help in determining the effects of individual, or the combined effects, of process variables. Models also allow operators to determine the best possible method of operating a phosphorus recovery process. In order to keep a process in a desired state, it is necessary to counteract influences that disturb the process. Although various chemical-based models are present that predict formation of struvite, there are no known automatic controller programs that are capable of maintaining a struvite crystallization system at the desired set point, such as a particular supersaturation ratio. It is widely believed that the efficiency and economy of process operations can be increased by providing continuous, suitable, and stable conditions by automatic control. During the last decade, interest in the recovery of phosphate from wastewater has grown tremendously, and methods are being developed in laboratory, pilot- and full-scale operations at treatment plants are beginning to show up worldwide. This rapid growth shows the significance of the process in recovering the phosphorus from wastewater. Consequently, development of on-line instrumentation, modeling of the process, and the integration of the two, promises to enhance the efficiency of a struvite crystallization system and improve product quality. The present study attempted to develop a control system that can be used to efficiently operate a phosphorus recovery/struvite crystallizer at a pilot-scale installation. Through computer modeling of the chemical process, the effects of different variables were also determined.

1.2 Organization of the Dissertation

This dissertation has been written in the classical style, and contains all pertinent experimental methodology, data and results. The following provides an outline of the organization of the various chapters in this dissertation.

Chapter One provides an introduction to the topic of phosphorus recovery from wastewater as struvite, and the reasons for pursuing the different topics dealt with in this research. A summary of the different chapters presented in this dissertation is also provided.

Chapter Two provides a background and literature review of phosphorus removal-recovery and struvite chemistry, as well as, presenting an overview of the various factors affecting struvite formation. This chapter provides information on struvite modeling, struvite solubility product, carbon dioxide stripping and magnesium determination. It points out some of the areas where knowledge gaps exist in struvite crystallization process operation. It provides the basis and motivation for carrying out the present study.

Based on information gathered, and with the intention of addressing the knowledge gap identified in Chapter Two, Chapter Three lists the hypothesis and objectives of the present study, and the rationale for the various supplementary studies carried out.

Chapter Four provides a description of the different experiments conducted, the water matrix and instruments used in each experiment, and the samples collected and analyzed. Because of the variation in the nature of the experiments and studies carried out, each set of experiments have been separated under a new heading for the sake of clarity. The purpose of each experiment has also been provided in brief.

The first part of the chapter introduces the struvite process system as used in the present study, followed by the development of the methodology and formulation of the codes and programs used to develop a process controller for struvite precipitation. Methods and materials used for the supplementary experiments, namely, struvite solubility product, carbon

dioxide stripping, indirect measurements of concentration and application rates of external magnesium during struvite crystallization process are then introduced and elaborated.

Chapter Five provides a summary of the experimental results that support the hypothesis of the research and the need and effectiveness of the supplementary studies. The chapter also discusses the impact(s) of the research and results on struvite crystallization process.

Chapter Six summarizes the main findings from the present study. Similar to the organization in Chapter Four, conclusions for each set of experiments have been placed separately. This chapter provides an identification of the significance and contribution of the thesis research to the field of phosphorus removal-recovery as struvite.

Chapter Seven provides a list of recommendations and directions for future study on phosphorus recovery from wastewater as struvite.

CHAPTER TWO: BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Although phosphorus (P) is one of the key elements that sustain all life forms, it is a non-renewable resource and has the least reserves/resources globally. Phosphorus is primarily used by the agricultural fertilizer industry, followed by household products. Phosphorus originating from detergents, metabolic processes, diffuse runoff from agricultural land and inputs from the air find their way into the domestic wastewater system. Even at low concentrations of approximately 10 µg/L of phosphorus, secondary reactions, also known as eutrophication, may occur in the receiving water. Discharge of partially treated wastewater into water bodies has been linked to increased numbers of algal blooms around the world (Barnard, 2009). Algal blooms reduce the amenity value and compromise ecological health of water bodies such as lakes, slow moving rivers and drinking water reservoirs.

2.2 Motivation for Phosphorus Removal

The current source for commercial phosphorus is still primarily phosphate rock. However, given that around 161 million tonnes of phosphate (expressed as P_2O_5) were extracted in 2008 (Gilbert, 2009), and the highest-grade (with respect to percentage of phosphorus) deposits are rapidly being depleted, it is expected that economically viable mining could last or be depleted within the next few decades. With global oil reserves dwindling and increased cost for petroleum products, new technologies involving the use of corn as a biofuel have brought about an increased demand for fertilizers. A recent study suggested that by 2033, the demand for phosphate-based fertilizers would exceed supply, forcing an increase in the price of fertilizers, which in turn would increase the cost of food to the rapidly growing population (Cordell *et al.* 2009). Another factor that influences the price of fertilizers is the transportation cost, and that is related to the increasing global price of oil. Although phosphorus in the ground is limited, other potential sources, such as human sewage and animal manure and slurries, could be used in the future to supplement the demand for the

element. For phosphorus to be useful, it must be in a form which is both technically and economically recoverable. Although current recovery methods are not always economical, the processes offer a sustainable source of phosphorus. Numerous studies have already been completed and more are being conducted every day, to identify new sources of phosphorus.

In most cases, phosphorus is one of the limiting nutrients that may cause eutrophication in freshwaters. The growth of algae leads to a decrease in the aesthetic values and usefulness of the water bodies. Phosphorus concentrations as low as 0.01 mg/L have been known to initiate eutrophication (Lee, 1970); on the other hand, 4-15 mg/L of phosphorus in untreated domestic wastewater is common (Tchobanoglous *et al.* 2003). It was estimated that as a result of human activity, more than 12,000 tonnes of P entered fresh, ground and coastal waters of Canada in 1996. The largest point source was municipal sewage, which added an estimated 5600 tonnes of P (Chambers *et al.* 2001). In general, the current discharge limit on total phosphorus in North America ranges from 2 to 0.1 mg/L (Tchobanoglous *et al.* 2003).

To combat the increase in eutrophication occurrences and other related effects from discharge of municipal sewage into water bodies, governments all over the world are placing stringent regulations on nutrient discharge criteria; this has brought about the growth of several biological nutrient removal (BNR) plants. Despite being removed from wastewater and into sludge during treatment, phosphorus is re-released into the liquid phase during anaerobic digestion of the sludge. Various studies show that 26% to 90% of the phosphorus at the head of the treatment plant is due to phosphorus feedback, that is, phosphorus in the return liquors (Jaffer *et al.* 2002; Mavinic *et al.* 1998). Some plants have even reported recirculated phosphorus loads of up to 100% (Pitman *et al.* 1991). This liquid phase, called supernatant or centrate, depending on dewatering process at the plant, is usually re-routed back to the front of the treatment process. The net result is that phosphorus is never fully removed by the treatment process, and it accumulates in the treatment plant. This leads to an increase in the phosphorus inventory in the plant, and is one of the primary causes of scaling or encrustation of piping and equipment. Although the excess phosphorus can be chemically precipitated, it produces extra sludge volumes that are costly to dispose of. In addition,

increased phosphate loads can harm the optimal operation of a BNR process, which depends heavily on the BOD:P ratio of the wastewater (Mavinic *et al.* 1998).

A major problem in many wastewater treatment plants is the accumulation of different forms of phosphate precipitates, such as struvite, vivianite, hydroxyapatite to name a few, in various sections of the treatment system. Among the precipitates, struvite tends to be most prevalent. Struvite can form in locations having high turbulence, such as pump impellers and pipe bends and in piping and other equipment (e.g. digestion tanks pumps, valves, etc). Struvite precipitation occurs when the combined concentrations of Mg^{2+} , NH_4^+ and PO_4^{3-} exceeds the struvite solubility product. The removal of struvite from these locations is difficult, expensive and time consuming, and often requires the parts to be taken out of service, repaired or replaced. Cleaning of parts often requires the use of corrosive and concentrated acids and the use of a hammer and chisel. It was reported that the annual costs for a mid-size treatment plant (3785 cubic meter or 25 MGD) related to struvite accumulation exceeded 100,000 US dollars (Doyle *et al.* 2000). **Error! Reference source not found.** illustrates the presence of struvite in clogging post-digestion piping treatment plants.



Figure 2.1. (a) Struvite in pipe leading to centrate pump at Lulu Island WWTP, (b) Struvite in adjacent piping to the digester pump at Annacis Island WWTP (courtesy of Brian Hystad, Metro Vancouver, 2007).

Although the most common practice for removing phosphorus in wastewater treatment plants is the use of chemicals to precipitate out the element, the process increases sludge production, and consequently increases sludge disposal costs. Another method is the use of enhanced BNR (EBNR) process. In recent times, focus has shifted from removal to recovery of phosphorus through different technologies (CEEP, 2001; Jeanmaire, 2001; Seckler *et al.* 1996). In a feasibility study, Woods *et al.* (1999) estimated that, when phosphorus recovery is carried out, sludge volumes could be reduced by up to 30% (compared to EBNR) and up to 49% (compared to chemical phosphorus precipitation). Another study conducted by Jeanmaire and Evans (2001) concluded that a decrease in sludge mass of 2-8% could be expected, if phosphorous recovery was undertaken at an operating BNR facility, with anaerobic sludge digestion.

The above mentioned problems, related to the increase of phosphorus inventory in wastewater treatment plants, have made recovery of the element an alternative option to the traditional chemical phosphorus precipitation. Although the value in recovering phosphorus from wastewater is straight forward, two basic considerations have to be considered before the method(s) is implemented. The first is the potential for cost savings - in terms of reduced chemical additions in treatment plants (where used), reduced struvite occurrences leading to downtime, and clean up and sludge handling costs – versus the cost of production that includes capital and operating costs. The second is the demand for this phosphorus (from wastewater), which in turn will depend on the availability, demand and cost of mining phosphorus from ores, and the potential revenue from the sale of phosphorus as struvite. There is a general consensus among wastewater experts that the cost of sludge disposal will increase significantly in the coming years, because of limitations to agricultural spreading of sludge, costly land filling and the increase in transportation costs. The recovered product may be used either as a source of phosphorus (instead of phosphate rock) or as a fertilizer (in case of struvite precipitation). Most of the recovered product is of higher purity than the phosphate rock and contains lower quantities of heavy metals (Fattah *et al.* 2008b), a factor that may increase the value of the product. Struvite has also been found to be a good fertilizer because it can release nutrients slowly. Extensive studies focusing on comprehensive evaluation of the economics related to phosphorus removal and recovery have shown that the

value of phosphorus-based fertilizers continues to increase, and recovery of the element is crucial for a sustainable future (Dockhorn, 2009; von Horn and Sartorius, 2009).

2.3 Methods of Phosphorus Recovery

Within the last decade, the interest in phosphorus recovery has grown tremendously, with research topics ranging from use of chemicals in wastewater, to recovery studies involving both domestic and animal wastewater. Despite the widespread interest, there are only a handful of full scale plants in the world recovering phosphorus. Potential technologies for phosphorus recovery from wastewater include: calcium phosphate precipitation, struvite precipitation, aluminum and iron precipitation and membrane or ion exchange technologies, followed by precipitation.

Among the methods available for phosphorus recovery, precipitating phosphorus as calcium phosphate may be the most promising (Driver *et al.* 1999), because the forms produced are close to the forms found in mined phosphate, and can thus be recycled by the existing thermal or wet route processes of the P-industry. Numerous studies involving the use of calcium as a medium to remove and recover phosphate have been conducted using both domestic and animal wastewater. Rendl (2007) provides a summary of the various studies regarding the use of calcium to precipitate phosphate, as hydroxyapatite. A full-scale fluidized bed reactor, the DHV CrystalactorTM, was in operation in the Netherlands, where the solid was precipitated on a seeding grain, usually sand, with up to 11% P content (Seckler *et al.* 1996). The Kurita fixed bed crystallization column process uses phosphate rock as seed material and is based on the same chemistry as that of the CrystalactorTM process. The difference between the two processes is that the Kurita process uses magnesium hydroxide as the source of magnesium, whereas the DHV process uses magnesium chloride (Greaves *et al.* 1999). Vanotti and Szogi (2009) applied lime to recover phosphorus from livestock wastewater both at pilot-scale and full-scale, in North Carolina, USA.

Although struvite cannot replace mined phosphorus used by the P-industry, it can reduce the demand for the element, as it can be used directly as a fertilizer. In recent times, several

studies have been conducted involving the removal-recovery of phosphate as struvite. A number of full-scale plants, utilizing fluidized bed reactors, are already in operation to recover phosphorus as struvite. The available processes include the Unitika Phosnix Process (Stratful *et al.* 1999) and the Ostara Nutrient Recovery Process. The latter process was developed at The University of British Columbia (UBC), Canada. Details of recovering phosphate in the form of struvite are described in subsequent sections.

Ferric chloride is more widely used in Europe for P-removal, but the process is not sustainable because it cannot be used in existing P-industry processes and probably has low or zero fertilizer value (Jeanmaire, 2001). The AlPO_4 form is more promising as it can be recycled in the P-industry, using the thermal route.

Technologies involving the use of membrane or ion exchange followed by precipitation have also been tested successfully and commercialized. An example of this technology is the REM-NUT process (Liberti *et al.* 2001) that uses ion exchange, followed by struvite precipitation. This process removes phosphate and ammonium ions from tertiary wastewater.

2.4 Advantages of Phosphorus Recovery as Struvite

The application of phosphorus recovery from municipal wastewater, through struvite (magnesium ammonium phosphate, MAP) precipitation, provides a viable and sustainable alternative to mined rocks as a source of phosphorus (Jaffer *et al.* 2002; Berg, 1982), and offers both environmental and economical benefits. Controlled and intentional struvite precipitation in wastewater treatment plants, especially those employing biological nutrient removal (BNR) technologies, also provides necessary phosphorus removal from the system. The reduction of phosphorus inventories can also reduce the probability of unintentional struvite formation, a costly nuisance that is common in wastewater treatment plants. Studies have shown that more than 90% of dissolved phosphorus can be removed from anaerobic digester supernatant and centrate in the form of struvite precipitation (Fattah *et al.* 2008b; Britton *et al.* 2005). Although effective, this method is costly, due to the need for large amounts of caustic to keep the pH of the system steady. The pH is especially important in

preserving the reactor supersaturation ratio (SSR) (Fattah *et al.*, 2008b). However, struvite crystallization at wastewater treatment plants employing biological phosphorus processes contains high amounts of phosphate in the digester effluent, and therefore, may require little or no caustic addition. Thus, the success of introducing struvite crystallization processes in wastewater treatment plants will mostly depend on its economical sustainability. The operational costs of struvite crystallization mainly depend on two factors - costs of chemicals and energy requirements for pumping. In their study, (Jaffer *et al.* 2002) showed that, compared to the cost of chemicals, the energy costs are quite insignificant, and 97% of the total chemical cost was due to the addition of caustic, which was used to achieve the desired operating pH. However, when determining the economics of struvite recovery, attention must be given to the potential savings, such as lower operational downtime, lower sludge production, and improved process operation, to name a few.

Struvite is an effective slow release fertilizer that can be used for agriculture (Owen *et al.* 2009; Ponce and De Sa, 2007; Gaterell *et al.* 2000). The beneficial effect of the slow release is that it allows the possibility of lower rates of application. With lower phosphate reserves and increasing fertilizer costs, the application of crystallization to recover phosphate as struvite from wastewater provides a long term solution and a sustainable approach. A major advantage of struvite recovered from wastewater for use as fertilizer is the presence of low heavy metal concentrations, such as for cadmium or uranium (Fattah *et al.* 2008b). With the quality degradation of phosphate rock, the heavy metal content is likely to increase; current fertilizer production from phosphate rocks does not eliminate heavy metals, and upgrading the processing plants is not very economical (von Horn and Sartorius, 2009).

Human activities during the past century, particularly intensive forest practices, fishing, urbanization, industrialization and impoundment construction, have had a negative impact on the health of British Columbia's numerous wild salmonid stocks (Slaney *et al.* 1996). Overharvesting and alteration of salmonid habitat reduces the return of spawning adults which naturally fertilize streams for their progeny (Larking and Slaney, 1996). Consequently, there is a lack of marine-derived nutrients to freshwater habitats, resulting in nutrient deficient streams. Oligotrophic stream conditions, both human-induced and naturally-

occurring in granitic coastal systems, can be made adequately fertile with low level addition of nutrients. Struvite has been found to be an effective, slow release fertilizer, to increase the nutrient levels in streams, and more tests are underway to fertilize inland water bodies in British Columbia (Sterling and Ashley, 2003).

2.5 Chemistry of Struvite

Struvite, magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a sparingly soluble crystal that contains equimolar amounts of magnesium, ammonium and phosphate, bound together by six waters of hydration, and forms according to Equation 2.1. During the formation of struvite in wastewater systems, many side reactions also occur concurrent to struvite formation. These include the interactions of each of the various species present in the wastewater; some common ones are summarized in Table 2.1. In wastewater systems, many other different species are present which may indirectly influence struvite equilibrium. Other researchers have suggested interaction of various other ionic species, such as H_2CO_3 , CH_3COO^- , CH_3COOH , $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Loewenthal *et al.* 1994), K^+ , Cl^- , Ca^{2+} , Na^+ , K^+ (Gadekar *et al.* 2009).



Table 2.1. Competing reactions in struvite formation in a distilled water system

Equilibrium	pKsp (25 °C)	ΔH° (kJ/mole)	Reference
$\text{MgOH}^+ \leftrightarrow \text{Mg}^{+2} + \text{OH}^-$	2.56	-10.89	Morel <i>et al.</i> 1983
$\text{NH}_4^+ \leftrightarrow \text{H}^+ + \text{NH}_3$	9.3	52.21	Snoeyink <i>et al.</i> 1980
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	2.15	-10.14	Martell <i>et al.</i> 1989
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{-2} + \text{H}^+$	7.2	4.90	Martell <i>et al.</i> 1989
$\text{HPO}_4^{-2} \leftrightarrow \text{PO}_4^{-3} + \text{H}^+$	12.35	13.87	Martell <i>et al.</i> 1989
$\text{MgH}_2\text{PO}_4^+ \leftrightarrow \text{H}_2\text{PO}_4^- + \text{Mg}^{+2}$	0.45	-14.25	Morel <i>et al.</i> 1983
$\text{MgHPO}_4 \leftrightarrow \text{HPO}_4^{-2} + \text{Mg}^{+2}$	2.91	-13.83	Taylor <i>et al.</i> 1963
$\text{MgPO}_4^- \leftrightarrow \text{PO}_4^{-3} + \text{Mg}^{+2}$	4.8	-12.99	Childs, 1970
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	14	55.94	Martell <i>et al.</i> 1989

2.6 Solubility of Struvite

Struvite production for recovering phosphorus from domestic wastewater has gained substantial interest and progress in recent times. However, discrepancies continue to exist between reported values of some of the most important operating parameters for struvite crystallization. One such parameter is the solubility product or K_{sp} , more commonly referred to as the pK_{sp} ($-\log K_{sp}$) value. This parameter is important in the determination of supersaturation ratio (SSR), the parameter that determines if struvite formation is possible or not. SSR is defined as the ratio of the ion activity product (IAP) to the equilibrium solubility product of struvite (K_{sp}^{eq}) (Equation 2.2a). Sometimes, for simplicity, a supersaturation ratio, called conditional SSR, SSR^c , (Equation 2.2b) is also calculated as the ratio of conditional solubility (P_S) to the *equilibrium* conditional solubility product (P_S^{eq}). In the conditional product, the ionic activity of the species is not considered.

$$SSR = IAP/K_{sp}^{eq} \quad (2.2a)$$

$$SSR^c = P_S / P_S^{eq} \quad (2.2b)$$

where,

$$IAP = \{Mg^{+2}\}\{NH_4^+\}\{PO_4^{-3}\} \quad (2.3a)$$

$$P_S = [Mg^{+2}][NH_4^+][PO_4^{-3}] = \frac{K_{sp}}{\alpha_{Mg^{+2}}\gamma_{Mg^{+2}}\alpha_{NH_4^+}\gamma_{NH_4^+}\alpha_{PO_4^{-3}}\gamma_{PO_4^{-3}}} \quad (2.3b)$$

α is the ionization fraction and γ is the activity coefficient.

The [] brackets indicate concentration, while the { } brackets indicate ionic concentration in moles per liter, corrected for activity. The determination of ion activity product involves the speciation of analytically determined concentrations using published acid and base dissociation constants, as well as an adjustment for activity. The activity is a function of the concentration of the ion and its activity coefficient, γ . The activity is given by the Güntelberg approximation of the Debye-Hückel equation shown in Equation 2.4 (Sawyer *et al.* 1994). The ionic strength of the solution can be determined based on electrical conductivity (EC)

measurements. Additional coefficients have been suggested relating ionic strength and EC. By processing data from various studies carried out at the University of British Columbia using centrate, supernatant and synthetic waters, Rahaman *et al.* (2006) suggested a value of 5×10^{-6} for the activity coefficient. Considering the temperature dependence of EC, an activity coefficient of 7.22×10^{-6} was suggested by Bhuiyan *et al.* (2009).

$$\log \gamma = \frac{0.5z^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (2.4)$$

where,

γ = the activity coefficient for the species of interest

z = the ionic charge of the species of interest

μ = ionic strength = $1.6 \times 10^{-6} \text{EC}$

Although K_{sp} is theoretically constant, K_{sp}^{eq} is highly correlated with pH, due to the changing component concentrations, each time a new equilibrium is reached. If SSR is to be used as a control variable for struvite recovery, it is essential to know the true value of K_{sp} for the pH range that the systems are expected to operate in. The SSR of the bulk fluid is the primary control variable used by the P-recovery team at the University of British Columbia (Fattah *et al.* 2008b; Forrest *et al.* 2008a; Forrest *et al.* 2007). Although extensive studies on the value of K_{sp} of struvite have been conducted, there still exists significant variation between reported values: 5.50×10^{-14} - 3.89×10^{-10} corresponding to pK_{sp} values of 9.41 to 13.27 (Rahaman *et al.* 2006). This variation may be related to the large range of experimental methodologies. The standard method for the experimental determination of a K_{sp} value of a particular reaction involves either the formation of precipitate or the dissolution of a previously formed salt in distilled water. In either approach, experiments are conducted under carefully controlled conditions in which constant mixing energy, constant pH, constant temperature or a set conductivity is maintained. Widely varying procedures in experimental methodologies account for much of the discrepancy that exists between the reported values for the struvite solubility product. In addition, some of the studies neglected the influence of ionic strength in the determination of the solubility product. Some additional factors that may also influence the value of K_{sp} are discussed by Rahaman *et al.* (2006).

2.7 Factors Affecting Struvite Solubility

2.7.1 pH

Struvite solubility depends on the concentrations of the constituent ions. Formation or dissolution of struvite in a water matrix depends on its solubility, at a particular pH, to the equilibrium solubility product. The availability of the species in IAP depends on the pH of the system; at high pH, the concentration of ammonium ion (NH_4^+) decreases rapidly, converting to ammonia (NH_3). The proportion of orthophosphate (PO_4^{3-}) ions also varies with the pH, and at a pH value of 9.5 and above, magnesium ion converts to MgOH^+ . In addition, depending on the pH, and in the presence of phosphate, magnesium forms a number of complexes such as $\text{MgH}_2\text{PO}_4^+$, MgPO_4^- and MgHPO_4 .

In general, the solubility of struvite decreases with increasing pH of the solution. However, above pH 9.0, an increase in solubility was suggested because of the decrease in ammonium concentration (Booker *et al.* 1999; Buchanan *et al.* 1994; Snoeyink and Jenkins, 1980). Other studies found a minimum solubility at a pH of 10.3 (Ohlinger *et al.* 1998). One of the main reasons for this discrepancy in solubility is the selection of different K_{sp} values.

2.7.2 Temperature

Similar to the pH effect, there are different opinions on the effect of temperature on solubility of struvite. Maximum solubilities occurring at 20°C (Durrant *et al.* 1999), 30°C (Bhuiyan *et al.* 2007) and 50°C (Aage *et al.* 1997) have been suggested. Doyle and Parsons (2002) found that at high temperature, the structure of struvite pellets changed, which affected its solubility. Burns and Finlayson (1982) determined the K_{sp} at different temperatures and showed that K_{sp} increased with increasing temperature in the range from 25°C to 45°C.

The effect of temperature on the solubility of a substance can be related to the enthalpy of reaction. The enthalpy change of a chemical reaction (ΔH°) is the amount of heat that is released or taken up during the course of the reaction (Snoeyink and Jenkins, 1980). Burns

and Finlayson (1982) reported an enthalpy value of 24.23 kJ.mol⁻¹ for struvite formation, showing that the formation of struvite is endothermic. Standard enthalpy change values, ΔH° , for reactions are most commonly used in water chemistry to determine the effect of temperature on the position of equilibrium. A useful expression relating ΔH° to K_{sp} is given by the van't Hoff equation (Equation 2.5 to 2.7) (Snoeyink *et al.* 1980).

$$\frac{d \ln K_{sp}}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (2.5)$$

$$\text{or, } \ln \frac{K_{sp}(T_2)}{K_{sp}(T_1)} = -\frac{\Delta H^\circ}{R} \times \frac{T_1 - T_2}{T_1 \times T_2} \quad (2.6)$$

$$\text{or, } \Delta H^\circ = R \left(\frac{\ln(10^{pk_2 - pk_1})}{\frac{1}{T_2} - \frac{1}{T_1}} \right) \quad (2.7)$$

where,

T = temperature (in K)

pk_1 and pk_2 = solubility constants at temperature T_1 and T_2 , respectively

ΔH° = enthalpy of reaction (J/mol)

R = ideal gas constant (8.314 J/mol.K).

2.8 Chemical Requirements for Struvite Crystallization Process

2.8.1 Caustic

The formation of struvite is accompanied by a lowering of pH in the system, and for efficient operation of a struvite crystallization process, control of the pH is paramount. pH plays an important role in maintaining the supersaturation ratio, one of the key operating parameters, and controlling it by manipulating the pH has been preferable preferred approach. Unintentional struvite growth in wastewater treatment plants is sometimes removed by changing the pH of the location - providing acidic conditions, as struvite is soluble under acidic conditions and highly insoluble under alkaline solutions; minimum solubility of

struvite occurs at pH 10.3 (Ohlinger *et al.* 1998). Several methods have been used to increase the pH of a struvite crystallization system – from using caustic (NaOH) to carbon dioxide stripping (Fattah *et al.* 2008a; Jaffer *et al.* 2002; Battistoni *et al.* 2001; Munch and Barr 2001; Ohlinger *et al.* 1999), although the former is more prevalent in use. For optimized struvite crystallization from wastewater, a pH in the range of 7.5-9.0 is usually suggested. Some recommended pH values found in the literature are given in Table 2.2.

2.8.2 Magnesium addition

For phosphorus precipitation as struvite, equimolar concentrations of phosphorus and magnesium are necessary. In most wastewaters, struvite precipitation is limited due to insufficient magnesium, and, as a result, an external source of magnesium is added during intentional struvite precipitation. Primarily, there are two sources commonly used to supplement Mg requirements – magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and magnesium chloride (MgCl_2). The chloride form is sometimes preferable because it is easier to transport as it can be obtained as pellets, and it dissociates faster than the hydroxide, therefore requiring a shorter reaction time (Jaffer *et al.* 2002). $\text{Mg}(\text{OH})_2$ has the advantage of being cheaper and can also help raise the pH, thereby requiring less caustic. However, using magnesium hydroxide to serve both the functions of magnesium dose and pH increase means that one cannot be optimized independent of each other (Jaffer *et al.* 2002; Munch and Barr, 2001). Sea water has also been used successfully as a magnesium source, without affecting the overall performance of the process (Kumashiro *et al.* 2001). Some sources of magnesium with their corresponding pH values are given in Table 2.2. For optimal P-removal, there should be an excess of soluble magnesium, that is, greater than stoichiometric requirements. Although, theoretically, a Mg:P molar ratio of 1:1 is required for struvite precipitation, in most cases for efficient growth of struvite, the required ratio is in the range of 1.3-2.0 (Jaffer *et al.* 2002; Munch and Barr, 2001). The influence of magnesium on struvite formation is discussed in detail in Chapter Five.

Table 2.2. Sources of magnesium studied with their corresponding pH values

Base added	Magnesium source	Suggested pH value	Reference
NaOH	MgCl ₂	7.7-8.2	Fattah <i>et al.</i> 2008b; Britton <i>et al.</i> 2005; Forrest <i>et al.</i> 2008a
NaOH and CO ₂ stripping	MgCl ₂	7.8-8.3	Fattah <i>et al.</i> 2008a
NaOH, Mg(OH) ₂	MgCl ₂ , Mg(OH) ₂	pH value $\geq$ 8.5	Jaffer <i>et al.</i> 2002
NaOH	MgCl ₂ , MgO	8.5 < pH value < 9	Celen and Turker, 2001
NaOH	Seawater	pH value $\sim$ 7.7	Kumashiro <i>et al.</i> , 2001
Only CO ₂ stripping (if alkalinity is low)	Not required	8.2 < pH value < 8.8	Battistoni <i>et al.</i> 2001

2.9 Reduction of Gases by Stripping

In wastewater treatment plants, struvite precipitation usually occurs at locations where carbon dioxide is stripped from the solution, with a corresponding increase in pH. This reaction (Equation 2.8) also takes place naturally in aquatic environments through the uptake of CO₂ by algae. Detailed chemistry, relating the increase of pH through carbon dioxide stripping, can be found in Cohen and Kirchmann (2004). Areas of high turbulence, such as pipe elbows, mixer blades, valves, and pumps are main locations of struvite deposits (Neethling and Benisch, 2004). In these locations, a reduction of partial pressure of CO₂ takes place. The relationship between partial pressure of a gas and its concentration in liquid is given by Equation 2.9. Hence, Loewenthal *et al.* (1994) concluded that the partial pressure of CO₂ is one of the driving forces for struvite precipitation. In their study, Pitman *et al.* (1991) demonstrated the possibility of increasing pH with aeration. This phenomenon was attributed to CO₂ stripping. In a different study, Loewenthal *et al.* (1994) showed that the partial pressure of CO₂ controls struvite precipitation inside an anaerobic digester. Using anaerobic supernatant as feed, Battistoni *et al.* (1997) investigated the application of air

stripping to raise the pH in a struvite crystallizer using two modes of stripping - external gradual aeration (EGA) and external continuous aeration (ECA). The study found that the pH of the system could be increased from 7.9 to 8.6 with increase in upflow rate, (which was increased from 1.8 L/min to 5 L/min), while keeping the airflow rate constant at 15 L/min. They were able to obtain up to 80% phosphorus removal by the ECA method only. The EGA method was not as efficient and was unable to remove phosphorus rapidly.



$$P_i = X_i \cdot P \quad (2.9)$$

where, P_i is the partial pressure of the individual gas in the gas mixture

X_i is the mole fraction of the individual gas component in the gas mixture

P is the total pressure of the gas mixture

Carbon dioxide stripping to increase pH in a pilot scale struvite crystallization system using centrate as process feed has been shown to be an efficient method in reducing overall process cost, by as much as 46-65% (Fattah *et al.* 2008a). Hiroyuki and Toru (2003) used 1 L bench scale reactors to demonstrate the affect of aeration on phosphorus precipitation. Along with aeration, NaOH solution was also fed continuously to increase the pH. They found that, by increasing the aeration intensity from 2.1 to 10.5 mg/L, the rate of phosphorus removal also increased. The authors concluded that aeration influenced the quantities of CO_2 in solution, which helped to raise pH, and resulted in an increased rate in phosphorus removal.

Ammonium ions in wastewater exist in equilibrium with gaseous ammonia. As the pH of the wastewater is increased above 7, ammonium ion is converted to ammonia, which may then be removed by air/gas stripping. However, the Henry's law constant of ammonia is only 0.75 atm (mol H_2O /mol air), which makes it hard to strip this gas (Tchobanoglous, 2003; Musvoto *et al.* 2000). During stripping of gases from wastewater, ammonia and CO_2 , the stripping rate for CO_2 is higher by two orders of magnitude than for ammonia. This happens since the Henry's law constant for ammonia is much lower than for CO_2 (the dimensionless Henry's law constants for ammonia and CO_2 are 0.011 and 0.95, respectively).

Various factors determine the rate of ammonia stripping from wastewater, such as pH, temperature, relative ammonia concentrations, and agitation of the air-water interface. Theoretically, the rate of stripping is proportional to the increase in these factors. At room temperature, a high efficiency ammonia removal usually takes place at pH up to 10.5-11.0 (Liao *et al.* 1995). With a decrease in temperature, the amount of air required increases significantly for the same degree of removal (Tchobanoglous, 2003). However, it is important to limit the amount of air flow for stripping because it can lead to a cooling effect, which in turn reduces stripping (Liao *et al.* 1995). One of the benefits of removing ammonia by stripping is that it can be recovered by absorption in sulfuric acid, and then used by the fertilizer industry. Therefore, control of the pH is important when choosing air stripping of gas for the purpose of increasing the pH, as a high operating pH tends to reduce higher amounts of ammonia, which in turn suppresses the tendency for pH to increase, due to carbon dioxide stripping.

2.10 Determination of Magnesium Usage for Struvite Precipitation

As mentioned earlier, in wastewater treatment systems, magnesium is normally the limiting ion for struvite precipitation, and it is commonly supplied by adding an external magnesium source. In the present study, magnesium deficiency was overcome by adding magnesium chloride. However, it is important to determine the magnesium requirements as insufficient addition limits phosphate removal, while excess addition results in higher concentration in the effluent; this, in turn, increases struvite formation potential downstream of the system and reduce struvite purity (Demeestere *et al.* 2001).

The common method for the determination of Mg involves costly atomic absorption (AA) or inductively coupled plasma (ICP) tests; the downside of these methods in a continuous struvite crystallization process is the lag time between sampling and analysis. For efficient process control and optimal product quality, it is imperative that the Mg concentration in the reactor and process feed be known in real time, or at least be measured by a process that requires little time to provide results. Although the determination of magnesium is important because of its widespread use, little work has been reported on the

development of ion-selective electrodes (ISEs) for magnesium (Gupta *et al.* 2002). Some applications of the sensors are in molten metal processing and for biological liquids, such as blood. Of the few electrodes that have been reported, the reliability in measuring in-line magnesium is reduced due to interference from other metals, especially calcium and potassium (Gunzel and Schlue, 2002). An added disadvantage of the use of magnesium ISE in the wastewater industry is the fact that these few probes are easily fouled.

Magnesium can also be determined indirectly by calculating the water hardness, assuming that the hardness is a function of only calcium and magnesium ions. By determining the total hardness and calcium hardness, magnesium hardness can be estimated, which can then be used to estimate the magnesium concentration. However, this technique has not been used in the operation of a struvite crystallization process till now.

In the absence of a suitable and reliable online analyzer for the determination of magnesium, the quantity of magnesium required for suitable struvite growth can be determined indirectly. This can be accomplished by introducing the phenomenon of pH and electric conductivity changes in accordance with the struvite reaction. Conductivity is a direct measurement of the ions in solution, and is proportional to the type and number of ions (Shepherd *et al.* 2009). Since formation of struvite reduces the number of ions, this in turn is expected to reduce the conductivity of the solution. The relationship between ionic concentrations and specific conductivity, κ , can be calculated from Equation 2.10 (Shepherd *et al.* 2009).

$$\kappa = \nu * N/1000 \tag{2.10}$$

where, N = normality of the solution (eq/L)

κ = specific conductivity (S/cm)

ν = equivalent conductance of the solution (S m²/ mol)

For simplicity, the theoretical conductivity of the present system was assumed to derive from only magnesium, chloride, ammonium and phosphate ions (Equation 2.11). The initial

theoretical conductivity was corrected to correspond to the actual conductivity of centrate, so that both theoretical and practical conductivity values had the same starting point.

$$\kappa = [\text{Mg}^{+2}] v_0^{\text{Mg}^{+2}} + [\text{Cl}^-] v_0^{\text{Cl}^-} + [\text{PO}_4^{-3}] v_0^{\text{PO}_4^{-3}} + [\text{NH}_4^+] v_0^{\text{NH}_4^+} \quad (2.11)$$

where, κ = specific conductivity (S/cm)

v_0 = Molar (equivalent) conductance of the solution at infinite dilution ($\text{S m}^2/\text{mol}$).

Values are taken from Lide (1991).

The MAP reaction with magnesium chloride (MgCl_2) is obtained from Equation 2.12. The theory behind this indirect determination is as follows. When MgCl_2 is added to centrate (or crystallizer constituents), electric conductivity increases as the chloride ion concentration increases. However, it has been shown (Sasai *et al.* 1995) that the increase in conductivity up to the completion of the MAP reaction, when theoretically all phosphate has been removed, is slower than after the equivalence point – the point where theoretically all the phosphate has been precipitated. As a result, there exists a bending point (details in Section 5.11.2) at the equivalence point. On the other hand, since hydroxide ion is consumed during the reaction, the pH decreases as MAP reaction proceeds. That is, there exists another bending point for pH. Thus, by determining the bending points for completion of the MAP reaction, the amount of magnesium needed can be determined. In order to apply this approach, it will be necessary to calculate the location of the bending point, and then calculate the magnesium concentration required. One advantage of this method is that there is no need to measure the individual magnesium concentration in the wastewater (digester supernatant or centrate) and the matrix present in the reactor.



Despite the need for a quick and on-site determination of magnesium addition, there are no known methods available to accomplish this requirement. Therefore, the approaches mentioned above could possibly be used in determining the concentration and amount of external magnesium addition to a struvite crystallization process.

2.11 Morphology of Struvite Pellets

Among the methods used to detect the presence of struvite in precipitates from phosphorus recovery processes, characterization by X-ray diffraction (XRD) and by scanning electron microscopy (SEM) is common. Struvite is a white crystalline substance that has a distinctive orthorhombic structure (Doyle and Parsons, 2002). The structure can be identified via X-ray diffraction (XRD) by matching the intensity and positions of the peaks produced to a database for the crystal structure. Depending on the conditions during growth, struvite pellets can be variable from equant, wedge shaped, short prismatic, to thick tubular (Durrant *et al.* 1999). One of the drawbacks of this determination is that it does not provide information on the composition of the struvite particles. To determine actual ionic concentrations, the common practice of dissolving the struvite, and then measuring the concentrations, still has to be carried out. Reports on the spontaneous formation of struvite in supersaturated solutions suggest that the pellet structure of struvite depends on the solution pH, the solution supersaturation, the Mg:P molar ratio, impurities in solution and the kinetic factors (Bouropoulos and Koutsoukos, 2000; Wierzbicki *et al.* 1997; Abbona and Boistelle 1979).

Struvite solubility is dependent on the solution pH and temperature, and these factors highly influence struvite formation and morphology (Al-Jibbouri *et al.* 2002; Booker *et al.* 1999). Abbona and Boistelle (1979) found that, at very high levels of supersaturation, bi-dimensional and tri-dimensional twinned pellets were formed, and on changing the supersaturation from high to low, the pellet structure changed from tubular to increasing elongation. However, studies made by Bouropoulos and Koutsoukos, (2000) found that the degree of supersaturation did not have any impact on the morphology of the pellets.

Studies on struvite pellets have found that the sizes of the pellets were influenced by the Mg:P molar ratio and the magnesium concentration in the effluent (Fattah *et al.* 2008b; Bouropoulos and Koutsoukos 2000). A study by Hirasawa *et al.* (1997) found that at Mg:P molar ratio of 2, the crystals agglomerated, resulting in large crystals. On the other hand, when the molar ratio was increased to 4, together with fine crystals, needle-like crystals were

formed. The presence of calcium in the wastewater was found to influence the growth of struvite pellets by acting as a binding agent (Le Corre *et al.* 2005). Another important parameter that influences crystal growth is the mixing energy in the crystallizer, which, depending on the value, can enhance or reduce pellet size. Adequate mixing energy is required to enhance mass transfer of the constituent ions to form struvite. On the other hand, a high mixing energy, brought about by higher upflow velocities in the crystallizer, can increase pellet-pellet collisions, which in turn can lead to attrition of the larger pellets.

2.12 Quality of Struvite Pellets and its Applications

Although the recovery of the phosphate is relatively simple, conditions required for the production of “good quality” struvite have not been studied in great deal. The quality of struvite has to be of certain grade to be used as a fertilizer or for nutrient enrichment of water bodies. Quality can refer to the composition, size, shape and crushing strength of the pellets formed. It is important to determine and understand how and why crystals bind to form pellets. Pellet formation in animal feed preparation has been documented (Thomas and vander Poel, 1996) where a three-phase condition was suggested. It was concluded that the binding strength of the pellets was higher with decreasing radius of the particles, and that the finer the grind, the better the production of pellets. In struvite formation in a crystallizer, a liquid-solid two-phase condition is normally assumed, but the assumption of better pelletization with smaller crystals probably holds true. In addition, solid-solid interactions between particles, through collisions, also factor into pelletization when the distance between the two is small, such as when the struvite crystallizer’s pellet inventory is high.

The dissolution of struvite, a sparingly soluble material, is generally controlled by surface reaction and therefore, the size (0.5-2.0 mm) of the struvite pellets influences the dissolution kinetics (Bhuiyan *et al.* 2008). Smaller pellets, having a greater surface area to volume ratio, are more easily dissolved than larger pellets, under the same conditions. These dissolution rates are important for struvite applications. The use of struvite as an agricultural fertilizer may demand lower dissolution rates for slow release, where a single high-dose may be applied without burning of the crop. On the other hand, small pellets are desirable for stream

nutrient enhancement that will provide “relatively faster”, slow-release of nutrients. In addition to the size requirements, the formation of pellets with stronger crushing strengths is desirable for transport and application of the struvite in the field. The pellets also have to be durable, since fine or crushed struvite may lead to loss of material during manufacture, harvesting and application.

The quality of struvite can be described in terms of both composition/purity and crushing strength, and the requirements are different for varying applications. Struvite needs to have a considerably greater crushing strength when applied with a fertilizer spreader, than when used for stream nutrient enhancement. Thomas and Poel (1996) described different devices used to determine hardness of pellets for animal feed manufacturing. There are also instruments in the pharmaceutical industry that measure crushing strength of pharmaceutical pills, but this equipment cannot be applied for struvite due to the struvite size range and the relatively lower crushing strengths of struvite pellets (Key International Inc.). In order to quantify crushing strength of struvite, it is necessary to develop a device that can be used on-site as a quick means of checking the strength for product quality assurance.

Various studies have developed struvite pellets from wastewater with sizes varying from less than 0.5 mm to as big as 6.5 mm (Le Corre *et al.*, 2007; Fattah, 2004; Ueno and Fujii, 2001). However, few studies have been able to handle the production of fines and growing large pellets. There are different techniques to control and handle of the fines. A two-stage tank, where fines are grown to 300 μm in a sub-reaction tank before being fed to the main reaction tank, has been proposed by Shimamura *et al.* (2003). Others have used these fines as a seeding material in the crystallization process (Ueno and Fujii, 2001). A coagulant was also used by Le Corre *et al.* (2007) to increase the sizes of the fines so that they could be used in fluidized beds. Studies at UBC have successfully and consistently produced pellets as large as 4-5 mm (Fattah *et al.* 2008b; Forrest *et al.* 2008a). In most applications, larger pellets are desirable because they are easier to handle, transport and apply, whereas managing fine precipitates may result in loss of the material during the recovery to application processes. However, there are still needs for smaller and softer struvite pellets as well, such as when applied to increase the nitrogen and phosphorus content of a nutrient deficient water body.

Therefore, there is a need to determine conditions that can produce, consistently and without interruption, struvite of a particular quality and size. In addition to the determination of conditions, another important factor is the operation of the struvite crystallization process. The importance of this topic is discussed in the next section.

2.13 Operation of Crystallizer for Struvite Formation

Various studies involved the use of struvite precipitation as a means of removing and recovering phosphorus from both domestic and dairy wastewater. Struvite formation can be easily accomplished once the supersaturation (SSR) of the system, with respect to struvite, is greater than unity. For efficient precipitation and pelletization, the SSR value is normally kept between 3-5 (Fattah *et al.* 2008b; Forrest *et al.* 2008a). In pilot-scale or full-scale application at wastewater treatment plants, variation in process feed characteristics is normal. Therefore, the development of a control system is important and necessary to: (i) counteract the variations in the process water, especially concentrations of those species that influence struvite precipitation and SSR directly, such as Mg^{+2} , NH_4^+ and PO_4^{-3} , the pH, temperature and conductivity of the water matrix; and to (ii) optimize the precipitation process. Optimization is to provide conditions for smooth operation of the process, and to develop products that are of good quality.

As mentioned earlier, although a number process variables determine the supersaturation ratio of the system, SSR in a struvite crystallization process is usually controlled by either, or a combination of, three methods – controlling the pH, adjusting the external magnesium loading and controlling the recycle flow (the effluent flow from the crystallizer that is put back into the system, as illustrated in Figure 4.1). Controlling the pH seems to be preferable for running the process for phosphorus recovery as struvite, as the other methods for control are more complex and difficult. Varying the magnesium loading influences the SSR in two ways – by changing magnesium concentration in the system, and by changing the pH. Therefore, it is difficult to optimize one without influencing the other. Control via recycle flow is also complex because it changes the mass loading of all the component ions, as well as influences the conductivity and temperature in the crystallizer. The optimum operational

pH for different wastewaters varies greatly, depending on the particular waste stream. Although some of the literature cite pH between 8.2 and 9.0, to ensure higher (above 80%) phosphorus removals (Munch and Barr, 2001; Stratful *et al.* 2001), others were able to achieve over 90% phosphorus removal using different feeds, such as synthetic water, digester supernatant and centrate, at pH of 7.3 to 7.8 (Fattah *et al.* 2008b; Forrest *et al.* 2008a). Since the use of caustic for pH adjustment is expensive, a large fraction of the struvite crystallization operational costs can be reduced by controlling and efficiently using the chemical, as well as using other methods to increase the pH. One such method is air stripping of CO₂ to aid in raising the pH. Results from a study by Fattah *et al.* (2008a) found that, depending on the operating conditions, the stripper was able to reduce 46% to 65% of caustic chemical addition. In a study at the Treviso wastewater treatment plant, Italy, Cecchi *et al.* (2003) used air stripping to raise the pH to 8.5. The results demonstrated that, depending on the type of air stripping process applied, costs associated with caustic addition could be reduced significantly.

2.14 Modeling and Control of Struvite Precipitation

Struvite crystallization is a complex process that involves a number of process variables, as well as complex process chemistry. In most cases, control of all the factors involved with the process is not possible. However, there exist some control variables, such as pH and flows, which can effectively keep the process running smoothly and efficiently. As mentioned earlier, control of the process is usually accomplished by keeping a constant SSR in the system. Predicting formation potentials and controlling struvite precipitation in crystallizers are important for both designers and operators at a treatment plant. Although various physico-chemical, equilibrium-based mathematical models related to struvite formation and its kinetics have been developed previously (Gadekar *et al.* 2009; Ali and Schneider 2008; Harada *et al.* 2006; Ohlinger *et al.* 1998; Loewenthal *et al.* 1994), none of the models actually involves process optimization or control.

Loewenthal *et al.* (1994) tested their struvite model on a synthetically-prepared solution that was designed to mimic anaerobic digester effluent. The model developed by Ohlinger *et*

al. (1998) included more chemical reactions than the model of Loewenthal *et al.* (1994), and also included the influence of ionic strengths on species concentrations. Harada *et al.* (2006) used his model to predict formation of struvite in urine, and included more solid formations. Ali and Schneider (2008) developed a model to predict struvite formation and incorporated growth kinetics. They tested their model in batch experiments using synthetic solutions in a pilot scale reactor. At UBC, different chemical-based models have been developed that have been used successfully in process control, both in bench-scale and pilot-scale studies (Fattah *et al.* 2008b; Forrest *et al.* 2008a; Adnan *et al.* 2003). However, since the models were not used in developing any control system, the studies lacked real-time control and the possibility of automation.

Many different software packages, such as, Matlab (Hanhoun *et al.* 2009, PHREEQC (Bhuiyan *et al.* 2008), MINTEQA2 (Ali, 2005), MINELQL+ (Ohlinger *et al.* 1999), ChemEQL (Bouropoulos *et al.* 2000) have been used to solve the equilibrium problem. Each model performs an iterative analysis, using an internal thermodynamic database and user-defined input concentrations, to calculate the equilibria of all considered complexes. Kinetic-based modeling approaches have also been used to develop a kinetic model of struvite formation. A three-phase (aqueous/solid/gas) model was proposed by Musvoto *et al.* (2000) for application in anaerobic digester liquors. Black box models using artificial neural networks (ANN) have also been suggested for applications when it is difficult to determine, with accuracy, the constituent ionic characteristics (Forrest *et al.* 2007). However, the downside of this method is that operators are unaware of the relationship(s) between various variables and the process condition, and therefore it is difficult to control the process. Despite their ability to predict struvite formation, none of the programs mentioned above are able to handle changes in process variables on a continuous basis. One group of researchers attempted to provide a solution to the change in variable problem mentioned by using Matlab's *fsolve* function to solve 16 chemical reactions, but they did not have much success (Hanhoun *et al.* 2009). Later, although they reduced the problem size by substituting some variables, they found solutions ranging in an unfeasible physical domain. They finally found a solution, based on a rearranged set of equations so that a linear relationship was developed,

and using multiobjective genetic algorithm to determine a good initial solution point, but concluded that the method was very inefficient.

CHAPTER THREE: OBJECTIVES OF THE STUDY

Based on literature review on phosphorus recovery from wastewater through struvite precipitation, it was found that major knowledge gaps still exist in terms of actual crystallizer operation. Although major components in the chemistry related to recovery of phosphate as struvite are well documented, few studies have actually been carried out with respect to the control of the crystallization process. The present study gave emphasis on the efficient operation of a struvite crystallization system as a whole.

This dissertation is based on the hypothesis that “*development of a process controller is essential for efficient operation of a phosphorus removal-recovery process by struvite crystallization*”.

The reason for building such a controller was to provide a means of automatic control of the crystallization process. This would be accomplished by controlling the supersaturation ratio of the system through manipulating the required pH setpoint.

The efficiency of the struvite crystallization process, as defined in the present study, was based on the following.

- The ability to detect and take action against changes in process variables, such as temperature, pH, conductivity and ionic concentrations;
- Possible increase in struvite quality through greater process stability brought about by the use of a process controller;
- Increase in ease of operation, due to lower operator time required to maintain the struvite formation process and the crystallizer system; and
- Use of the models developed as a means of predicting the influence of various variables and operating conditions that favor struvite formation.

In order to develop a universal supervisory control system and efficient operation of a struvite crystallization process, some related studies had to be carried out. These, supplementary studies, and their objectives, are the following.

1. Solubility Test

Objective: To determine struvite solubility constant using four different water matrices, under varying pH and temperature, and to determine the influence of temperature on the value.

Reasoning: Depending on the nature of the experiment carried out, there still exist different values in the literature for struvite solubility product. However, the need for a single and universally applicable/acceptable constant is felt in the struvite recovery community.

2. Carbon Dioxide Stripping Tests

Objective: (i) To evaluate the effectiveness of two carbon dioxide strippers in reducing caustic usage, and consequently reducing chemical cost, during the operation of a struvite crystallization process. (ii) To develop a chemistry-based model for the operation of one of the strippers.

Reasoning: (i) Chemical cost related to pH increase (by adding caustic) in the operation of a struvite crystallization process is high, and methods to reduce it are needed. (ii) The development of the stripping model is needed to incorporate carbon dioxide stripping in the main supervisory control system developed in the present study, and to determine the extent of carbon dioxide stripping possible and its related pH increase.

3. Magnesium Prediction Techniques

Objective: To develop methods that can provide information quickly, and on-site, on the concentration and rate of application of external magnesium addition in a struvite crystallization process.

Reasoning: One of the primary operational costs of a struvite crystallization process arises from the need to add external magnesium to the system. In addition to

chemical cost, maximum utilization of the external magnesium added is necessary so that the process effluent does not contain high amounts of the chemical.

4. Influence of Variables on Structure of Struvite Pellets

Objective: To identify engineering factors that affect struvite pellet growth and its characteristics.

Reasoning: The quality of struvite formed in a crystallizer depends on engineering factors, such as upflow velocity, in-reactor magnesium concentration and supersaturation ratio.

5. Determination of Crushing Strength

Objective: To develop a device that can be used as a quick method to determine the crushing strength of struvite pellets.

Reasoning: Due to lack of a suitable instrument, a device is needed for quick, on-site measurement of pellet strength. The device is needed to determine the relationship(s) between process variables and crushing strength of struvite.

CHAPTER FOUR: METHODS AND METHODOLOGY

4.1 Struvite Recovery Process

The process used in this study for the removal and recovery of phosphorus (as struvite) was developed in the Civil Engineering Department of the University of British Columbia, Vancouver, BC, Canada. Pilot scale testing of the crystallization process was conducted at the Lulu Island Wastewater Treatment Plant (LIWWTP) in Richmond, BC. The setup contains two parallel processes, each of which contains a crystallizer, an external clarifier, tanks for magnesium feed and caustic, pumps for the centrate, recycle flow, magnesium flow and a pH controller. Centrate from the plant was used as a process feed that was stored in tanks to reduce suspended solids contents. The basic flow diagram of the individual process is shown in Figure 4.1.

Centrate is fed at the bottom of the reactor along with the recycle stream. Magnesium chloride and sodium hydroxide is added to the reactor through the injection ports, just above the feed and recycle flows. The pH of the system is monitored by a pH meter at the top of the first section and controlled using a pH controller.

The reactor has four distinct zones of different pipe diameters. The bottom part of the fluidized reactor is called the ‘harvest zone’, because this is the section from which struvite is harvested. The second, ‘active zone’, is the location where flows are turbulent enough to allow for agglomeration and formation of larger pellets. The last fluidized section, called the ‘fines zone’, is the location where individual crystals and small pellets reside until they grow large enough to fall to the lower sections. To avoid the loss of fines from the crystallizer, a settling zone, called the ‘seed hopper’, is located at the top. The dimensions of the various sections are given in Table 4.1. The crystallizer, when first developed, was unique in the sense that the diameter of each section was varied, increasing with increasing height. This setup was considered to develop varying degrees of turbulence in each section, and to help in classifying the fluidized particles according to size. As the pellets increase in size (and mass),

they are able to overcome higher upflow velocities and, thereby, move down to the lower sections of the reactor. As mentioned, harvesting of struvite pellets is accomplished by emptying the harvest zone (the lowest section), ensuring that only the largest pellets are harvested.

The crystallizer was constructed of clear PVC piping connected with standard Schedule 40 or Schedule 80 PVC fittings. In the construction of the reactor, the inside joints between piping and fittings were kept as smooth as possible, to minimize dead zones where the fluidized particles could settle and struvite encrustation problems could occur. Clear piping was used, in order to monitor, visually, the behavior of the struvite crystals in the fluidized bed and to watch for signs of plugging or encrustation.

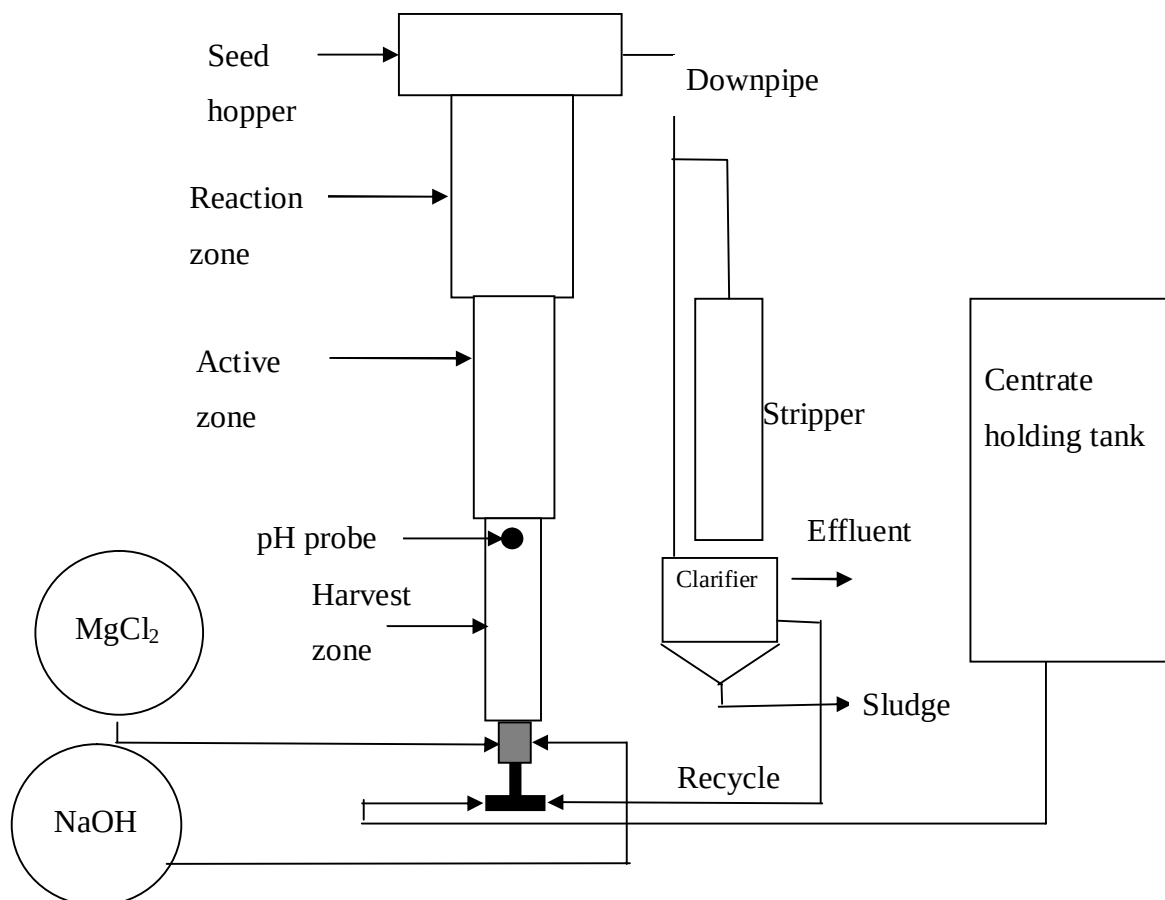


Figure 4.1. Pilot-scale struvite crystallizer reactor process design.

Table 4.1. Dimensions of the reactor

Section	Length (mm)	Diameter (mm)	Volume (dm ³)
Harvest zone	749	76	3.42
Active zone	1549	102	12.6
Fines zone	1270	152	23.2
Seed hopper	457	381	52.1
Below harvest zone	521	--	--

4.2 Chemicals, Storage Tanks and Pumps

4.2.1 *Centrate*

Centrate used for the study was stored in three 5600 liter capacity holding tanks, which were filled every day from LIWWTP centrate holding tank. These holding tanks served two purposes – (i) help in reducing the total suspended solids by settling them and (ii) control feed composition variations. The centrate was pumped to the reactor through 1.9 cm ($\frac{3}{4}$ inch) tubing, using a $\frac{1}{2}$ HP motor Monyo (Model 500 332) progressive cavity pump that was connected to a digital speed controller.

4.2.2 *Magnesium feed*

The magnesium feed for the study was made from commercial grade magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) pellets. The pellets were dissolved in water and stored in a 1600 L tank and pumped into the reactor using a MasterFlex L/S variable speed peristaltic pump with a standard pump head.

4.2.3 *pH control*

Caustic solutions made from sodium hydroxide pellets was stored in two 120 L tanks and used to control the pH of the system. A carbon dioxide trap (concentrated caustic in a bottle)

was used to absorb carbon dioxide from the air, before the air entered the caustic tank. This setup was made to ensure minimal loss of caustic strength in the holding tank and which, in turn, could reduce the amount of caustic needed. The pH in the crystallizers and external clarifiers were monitored continuously with Oakton pH monitors, each equipped with an Oakton gel filled, epoxy body pH probe. The pH meters were regularly calibrated by the two point method, using standard buffer solutions of pH 7 and pH 10. Figure 4.2 shows the crystallizer setup of the study area at the Lulu Island Wastewater Treatment Plant.

4.3 Sample Collection, Storage and Analysis

Samples were collected daily from each of the clarifiers, one of the centrate holding tanks (because centrate was pumped into the crystallizer from one tank only) and from the magnesium holding tank. Samples were first centrifuged and filtered onsite with 0.45 micron membrane filter papers, before being preserved according to Standard Methods (APHA *et al.*, 1995). For NH_4^+ and PO_4^{3-} , 5 mL samples were taken in small test tubes to which was added one drop of 5% v/v sulfuric acid, to lower the pH to below 2. Two drops of concentrated nitric acid were added to each 10 mL of sample to preserve the metal samples. Analytical measurements of phosphorus and ammonium were carried out in the laboratory using colorimetric flow injection analysis (model LaChat QuikChem[®] 8000). Magnesium and sodium ions were analyzed using flame atomic absorption spectroscopy (AA) (model Varian Inc. SpectrAA220[®]). Caustic samples were collected for analysis from the individual (one each for Reactors 1 and 2) tanks, and the caustic usage (in terms of volume) by the crystallization processes was recorded daily. By measuring the sodium concentration in the caustic tanks, the amount of caustic (NaOH) used was calculated. Dissolved CO_2 samples were collected from the seed hopper and clarifier effluent. The concentration of dissolved gaseous carbon dioxide, in liquid solution, was measured by an Accumet Gas-Sensing Combination ISE. The hardness test methods were followed according to Standard Methods. The pH, temperature and conductivity of the samples were recorded, using a Horiba D54 portable meter onsite.



(a)



(b)



(c)

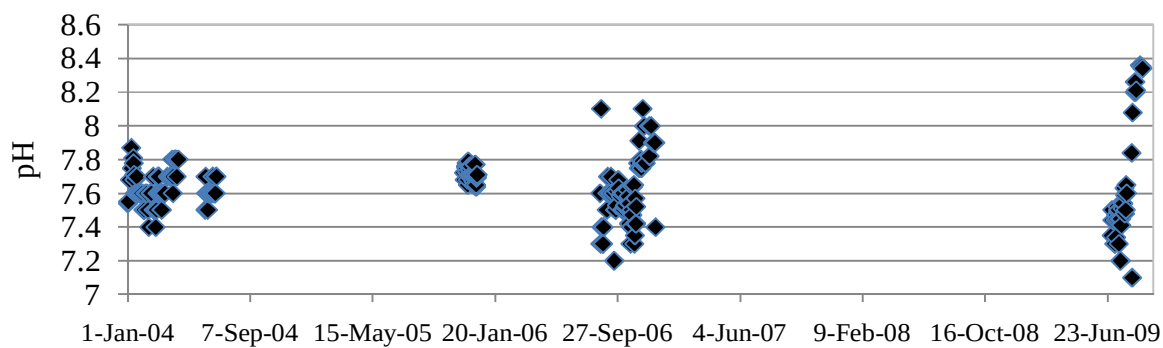


(d)

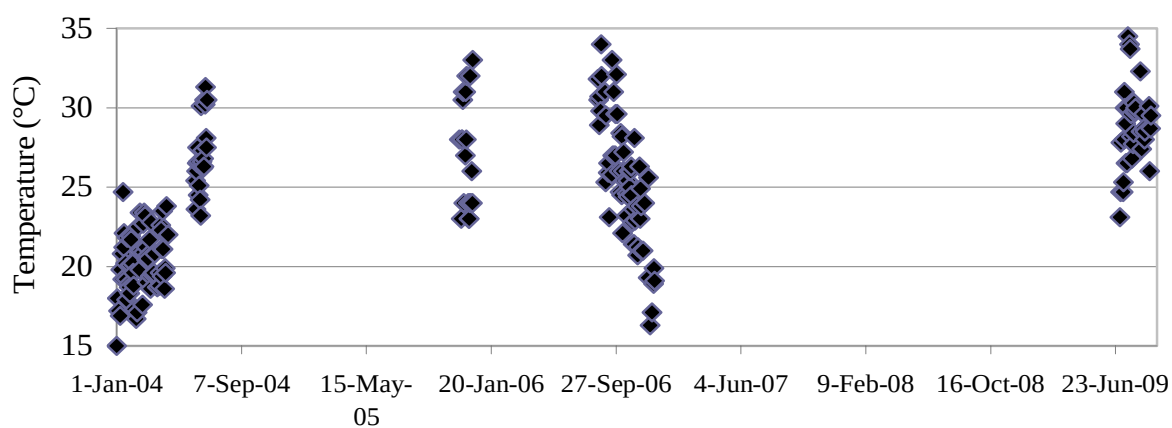
Figure 4.2. Setup of crystallizers, clarifiers and stripping columns at the LIWWTP (a) crystallizer (R#1) with compact media stripper attached and without instrumentation and control – the manually controlled system (b) crystallizer (R#2) with cascade stripper attached and with instrumentation and control – the automated system (c) transmitters, pH meter and pH pump for R # 2 system (d) location of conductivity and pH probe in harvest zone of R#2.

4.4 Lulu Island Wastewater Treatment Plant

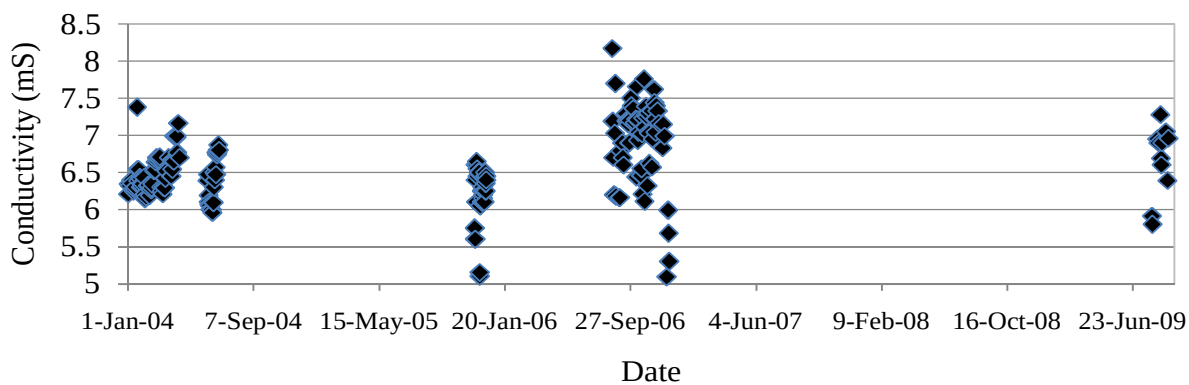
The Lulu Island Wastewater Treatment Plant (LIWWTP) is a secondary wastewater treatment plant that has an average flow of 75 million liters per day. It is operated by Metro Vancouver of the Province of British Columbia, Canada, and primarily serves residents of Richmond, B.C. Biosolids at the treatment plant are digested using mesophilic anaerobic digestion, at 35°C, and thickened with two centrifuges. The centrate is then recycled back to the headworks of the treatment plant. The biosolids dewatering processes result in soluble phosphate being released from the sludge, which then accumulates in the centrate. Due to the buildup of phosphorus, and the presence of ammonia and some magnesium in the liquid centrate, the plant has, in recent times, encountered rapid growth of struvite in the piping system. The current method used to reduce the struvite formation potential at the plant is to dilute the centrate with treated water. However, this only delays the inevitable formation of struvite, as the phosphate and magnesium in the centrate are never fully removed from the system. Figure 4.3 illustrates the trends in some of the important parameters during studies carried out at LIWWTP by the research group. Each point represents a day's data. The gaps in the graphs represent periods when no study was conducted, and hence no samples were taken. The characteristics of the trends are important to note, because they help determine the struvite formation potential at any time and the change over the years. It also provides background information for future studies. As illustrated in Figure 4.3, depending on the time of the year, the temperature of the centrate can vary from 15°C to 35°C. Similarly, high variability in the concentrations of magnesium (zero to 22 mg/L), ammonium (400 mg/L to above 900 mg/L) and phosphate (30 mg/L to 100 mg/L) can be found. Since struvite crystallization efficiency depends on having a stable process in the crystallizer, and these parameters control the process, the variations show the need for developing a control system which will address these variations.



(a)

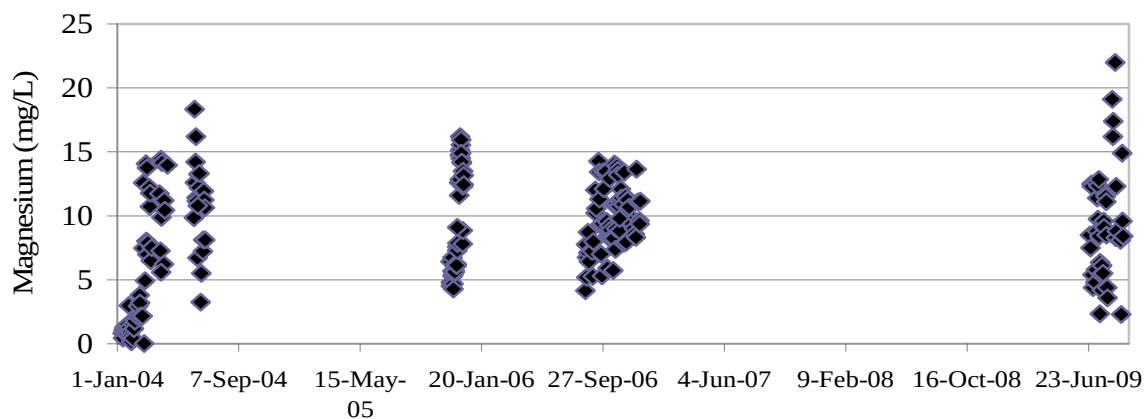


(b)

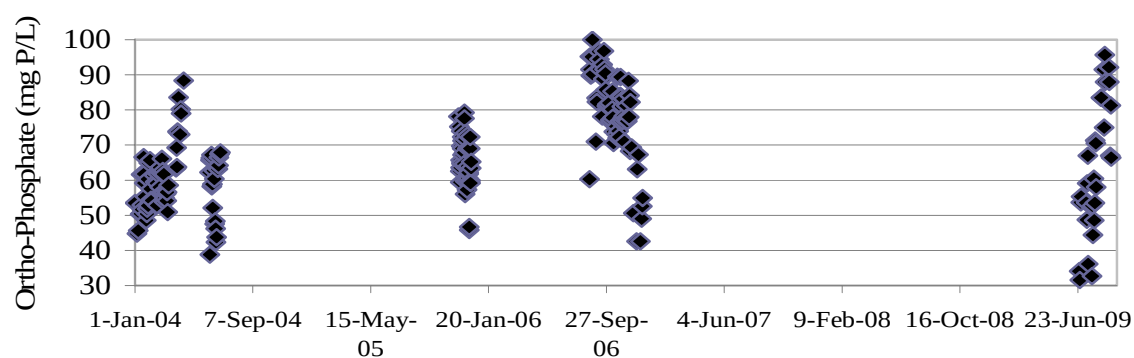


(c)

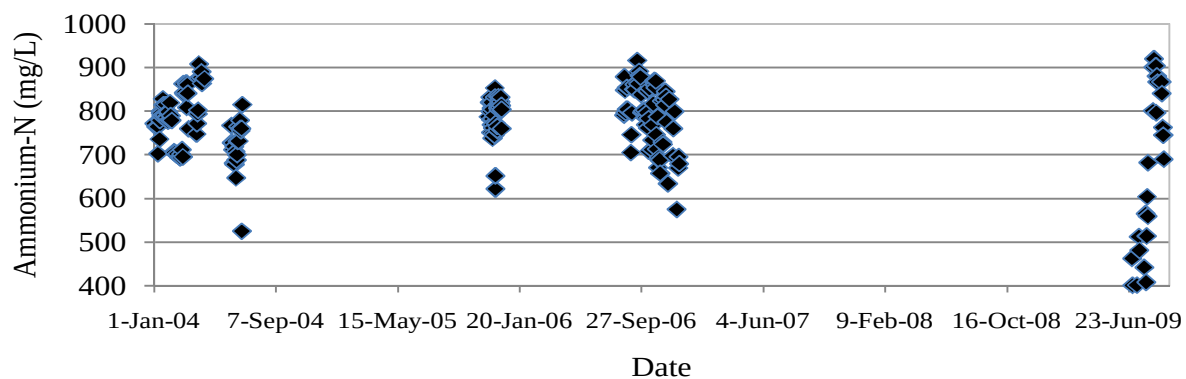
Figure 4.3. Trends in important parameters in centrate at LIWWTP over the last few years. (a) pH, (b) temperature and (c) conductivity.



(d)



(e)



(f)

Figure 4.3 cont'd. Trends in important parameters in centrate at LIWWTP over the last few years. (d) magnesium concentration, (e) ortho-phosphate concentration and (f) ammonium concentration.

4.5 Instrumentation and Process Monitoring

In order to efficiently apply a control model to a process, a fully functional and complete process monitoring system should be in place. In this study, the important variables that determined the condition of the process were monitored in the pilot-scale setup. These included the pH, conductivity, temperature, flows, and the ionic concentrations of magnesium, ammonium and phosphate.

Figure 4.4 illustrates the basic process components and the locations of sensors and other control variables for monitoring the process. Conductivity, pH and temperature were monitored in-situ continuously, while grab samples were tested for phosphate, magnesium and ammonium concentrations. Conductivity, pH and temperature were measured using sensors that were connected to individual analog transmitters, respectively. Magnesium, ammonium and phosphate concentrations were measured in the laboratory.

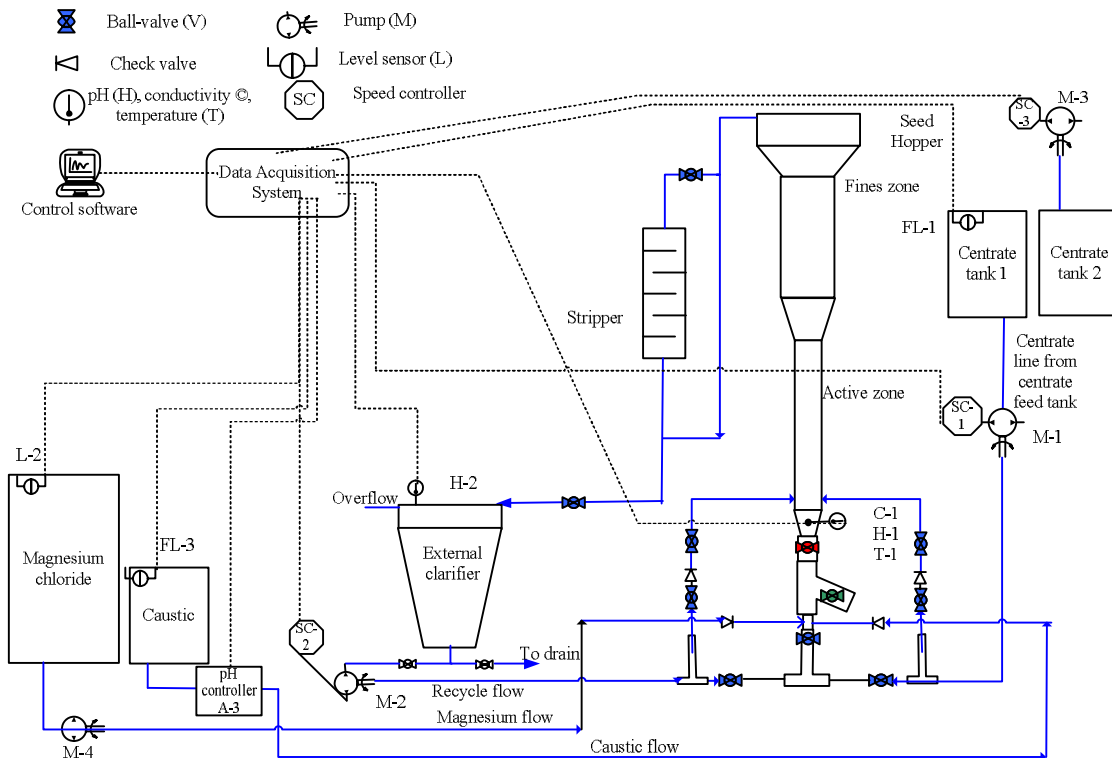


Figure 4.4. Schematic of phosphorus recovery process with instrumentation locations at the Lulu Island Wastewater Treatment Plant.

4.6 Struvite Control Process

The struvite process control model was designed to control the reactor supersaturation ratio by manipulating the pH in the crystallizer. This was achieved by calculating the effects of different chemical reactions that can take place in the reactor. These well-established chemical reactions, along with their equilibrium constants, are given in Table 2.1. The effect of temperature on the equilibrium constants is given in Table 4.2. The equations in Table 4.2 have been derived from Equation 2.6 and the enthalpy values have been taken from Parkhurst and Appelo (1998). Although numerous other chemical reactions have been suggested, the present study included the ones that were most likely to affect the process at the given pH of operation and to simplify the code. The efficiency of the process using the reactions specified has been proven in earlier studies (Fattah *et al.* 2008b). The effect of temperature on these reactions was also considered in deriving the equilibrium constants. The influences of these reactions, as well as pH, conductivity and temperature, on the system, were taken into account. The model was based on two programs (mentioned in Table 4.3) to control the crystallization process at the desired, optimum condition. The control model was developed using Matlab and Simulink software from MathWorks™. The software was chosen because of its wide use in development of industrial process designs and the ability to control complicated chemical reactions, as well as to provide tools for the process. The program also had the ability to smoothly integrate with current industrial software and hardware. A schematic of the control methodology is illustrated in Figure 4.5.

The total concentrations of the reacting species were calculated according to Equations 4.1-4.3. The concentrations were based on a mass balance that included both influent and the recycled effluent, that is, species present in the crystallizer.

$$T\text{-PO}_4 = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] + [\text{MgH}_2\text{PO}_4^+] + [\text{MgPO}_4^-] + [\text{MgHPO}_4] \quad (4.1)$$

$$T\text{-NH}_4\text{-N} = [\text{NH}_3] + [\text{NH}_4^+] \quad (4.2)$$

$$T\text{-Mg} = [\text{Mg}^{+2}] + [\text{MgOH}^+] + [\text{MgH}_2\text{PO}_4^+] + [\text{MgPO}_4^-] + [\text{MgHPO}_4] \quad (4.3)$$

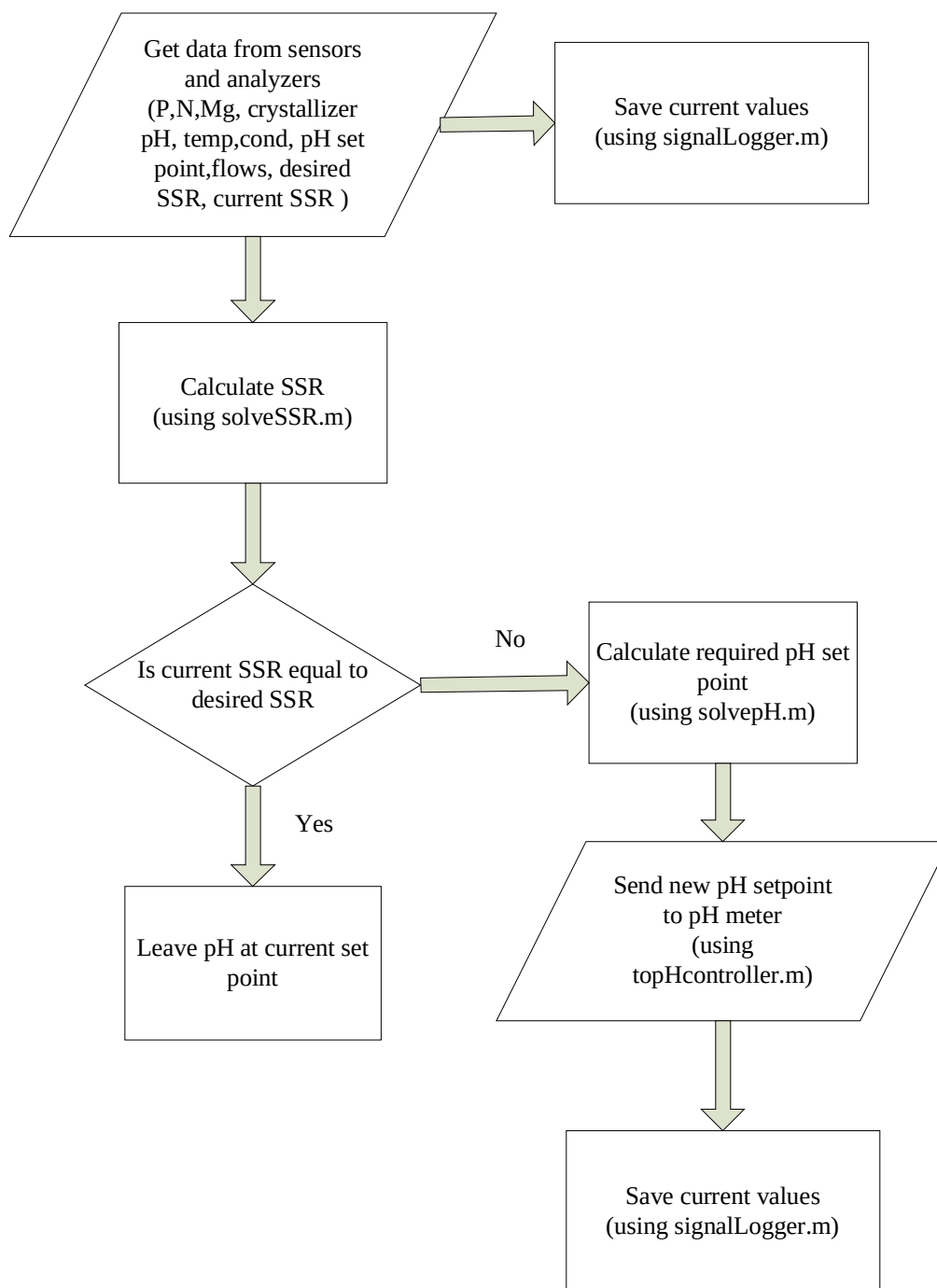


Figure 4.5. Schematic of the control strategy for struvite crystallization process.

Table 4.2. Sets of equations used to account for the impact of temperature on the equilibrium constants. The equations are based on Equation 2.6 and values in Table 2.1

$$pK_{MAP} = 13.2835 + \frac{7.55}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_{MAP} = 10^{-pK_{MAP}}$$

$$pK_{MgOH} = 2.56 - \frac{2.6}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_{MgOH} = 10^{-pK_{MgOH}}$$

$$pK_N = 9.3 + \frac{12.46}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_n = 10^{-pK_N}$$

$$pK_{P1} = 2.15 - \frac{2.42}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_1 = 10^{-pK_{P1}}$$

$$pK_{P2} = 7.2 + \frac{1.17}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_2 = 10^{-pK_{P2}}$$

$$pK_{P3} = 12.35 + \frac{3.31}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_3 = 10^{-pK_{P3}}$$

$$pK_{Mg1} = 0.45 - \frac{3.4}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_{Mg1} = 10^{-pK_{Mg1}}$$

$$pK_{Mg2} = 2.91 - \frac{3.3}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_{Mg2} = 10^{-pK_{Mg2}}$$

$$pK_{Mg3} = 4.8 - \frac{3.1}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

$$K_{Mg3} = 10^{-pK_{Mg3}}$$

$$pK_w = 14 + \frac{13.35}{ThermoR} * \left(\frac{1}{IT + 273.15} - \frac{1}{T_{25}} \right) * \log_{10} 2.718282$$

4.7 Coding Controller Program in Matlab

In the present study, Matlab was used as the program to write the codes for the SSR controller (which determined the pH required for set SSR) and the SSR calculator (which calculates the SSR based on the reactor pH). As mentioned in Section 2.14, although different programs have been developed and tried, none have had much success in using their models to operate a struvite crystallizer. The beauty of the codes written in the present study is the simplification of the nonlinear feature of the chemical reactions. In order to reduce the number of variables (from the different nonlinear equations), the codes written for the present study related all phosphate and magnesium-phosphate complexed species to phosphate; this new phosphate equation, together with the nitrogen and magnesium species, was then related to pH only (Section 4.7.1). By setting an initial H^+ value, pH was calculated by using the built-in function *fzero* in Matlab. The activities of the reacting species were used in the determination of SSR, with temperature corrections applied in calculating the equilibrium constants. By substituting and rearranging the various equations, an equation was then developed where SSR was a function of hydrogen ion only. Data collection and processing was performed in Simulink, which used codes written in Matlab to calculate the SSR and required pH. Three graphical user interfaces (GUIs) were also developed for ease of operation and control of the process and to calculate some process parameters. The various codes written are listed in Table 4.3, along with their application(s).

4.7.1 Coding to relate hydrogen ion concentration to SSR (in *solvepH.m*)

The simplified coding used to determine the hydrogen ion activity for a struvite crystallization process is given below. The different symbols and abbreviations used are defined in Appendix A.

Hfunction = @(H)... (function of H)

...% C1:

$a/(b + c/H + (d + e*H + f*H^2) * ...$

$(-((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i) + ...$

$\text{sqrt}(((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i)^2 - ...$

$4*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))*(-i * (b + c/H))) ...$

$/ (2* ((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))) ...$

...% C2:

$* g / (1 + h/H) ...$

...% C3:

$* (-((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i) + ...$

$\text{sqrt}(((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i)^2 - ...$

$4*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))*(-i * (b + c/H))) ...$

$/ (2* ((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))) ...$

...% SSR * KMAP:

- SSR * KMAP;

Table 4.3. List of files written and developed in Matlab with their uses

Code Number	Program code name and extension	Application	Link to other codes
1	fromHEX.m	Converts HEX code (from pH meter) to regular decimal number	Used by code 3
2	toHEX.m	Converts regular decimal number to HEX code (for pH meter)	Used by code 4
3	frompHcontroller.m	Used to acquire data from the pH meter	
4	topHcontroller.m	Used to set required pH in pH meter	
5	solvepH_block.m	Set block in Simulink environment for using Matlab code	Used by code 6
6	solvepH.m	Used to calculate the desired pH set point for particular SSR	
7	solveSSR_block.m	Set block in Simulink environment for using Matlab code	Used by code 8
8	solveSSR.m	Calculates the SSR for reactor conditions	Used by code 10,11 13
9	strippermodel.m	Calculates efficiency of carbon dioxide stripping and potential pH increase	12
10	SSRcalculator.m	Calculates the SSR on a system	
11	SSRcalculator.fig	Code for developing SSR calculator GUI	
12	strippermodelgui.fig	Code for Carbon dioxide stripping GUI.	
13	reactoroperation.fig	Code for developing reactor operation GUI	
14	signalLogger_block.m	For logging the signals of the process	15
15	signalLogger.m	Logs process data from listed signals into Excel file	
16	System.mdl	Simulink window for operation of a struvite crystallization process	

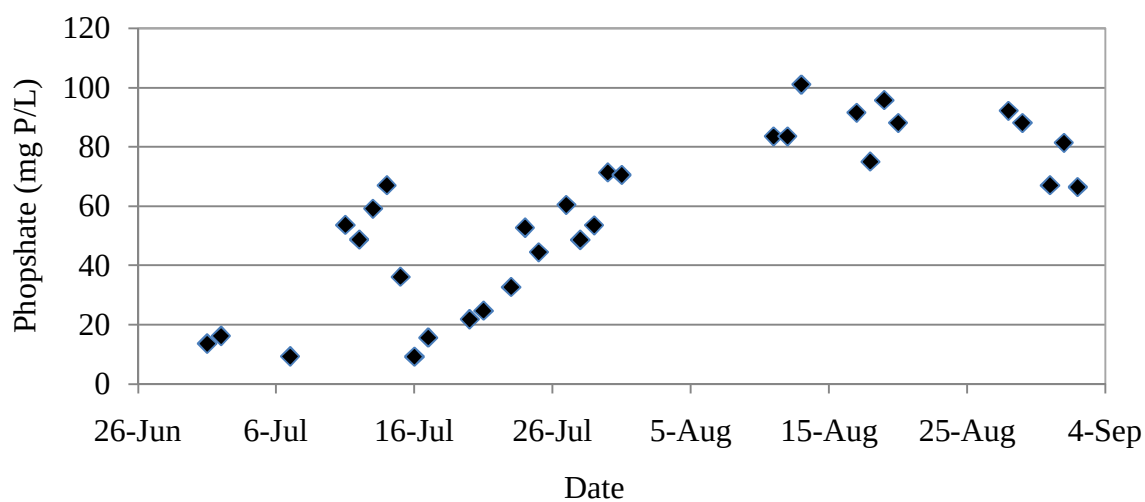
4.8 Characteristics of Process Feed during Pilot Scale Studies with Instrumentation

During the course of the study, some major changes occurred in the characteristics of the centrate that was used as process feed. It should be noted that the process feeds for the two crystallizers were obtained from the same centrate tank. Some of the characteristics of the centrate are shown in Table 4.4 and illustrated in Figure 4.6.

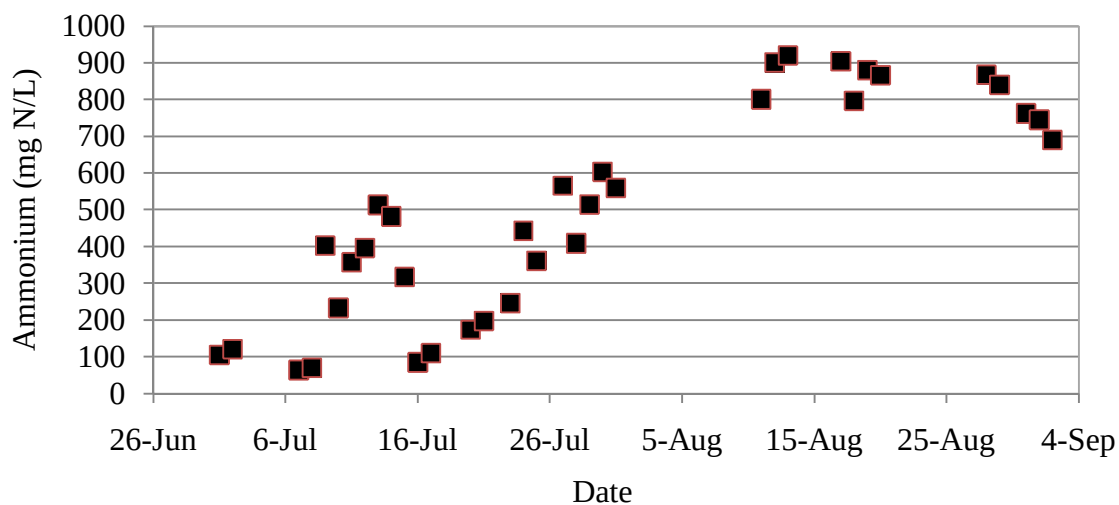
In general, the high variability in phosphate and ammonium concentrations illustrated in Figure 4.6 is not common. At the initial part of the study, from the start to the end of July, 2009, it was found that centrate from the plant was being diluted by processed water to reduce the potential for struvite formation; this in turn, reduced the concentrations of the ions. In general, phosphate and ammonium concentrations at the plant varied from 60-120 mg/L and 700-100 mg/L, respectively (Fattah *et al.* 2008b). Table 4.5 provides the values of the operating parameters used for the study. Since the objective of this study was to develop and validate a control system, operating conditions were based on a previous study undertaken at the same location (Fattah *et al.* 2008b).

Table 4.4. Characteristics of the process feed used during pilot-scale operation (2009)

	pH	Conductivity mS/cm	Temperature C	PO ₄ -P mgP/L	NH ₄ -N mg/L	Mg mg/L	N:P
Minimum	7.1	2.2	23.1	9.2	63.5	2.3	14.7
Maximum	8.4	7.3	38.9	101.0	920.0	22.0	25.2
Average	7.4	4.7	28.5	57.7	507.5	9.5	19.8

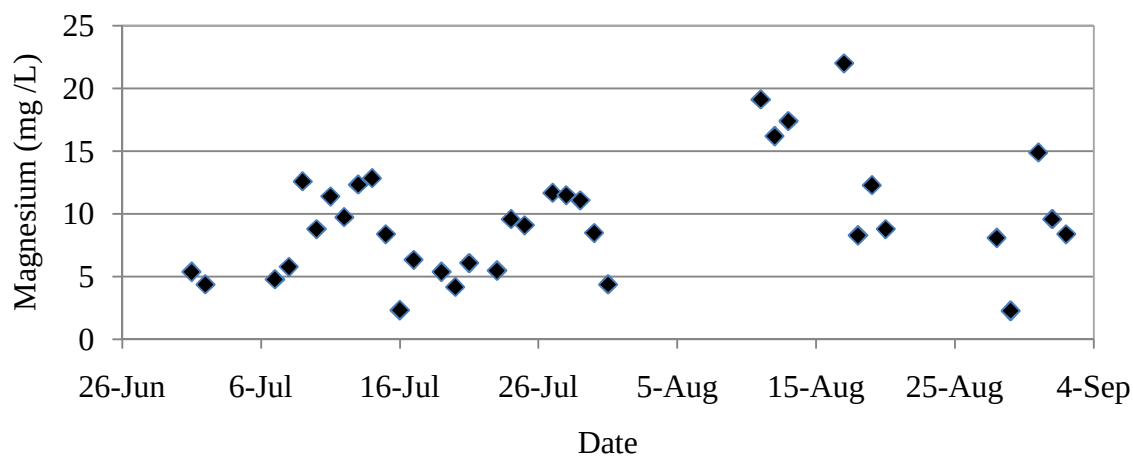


(a)

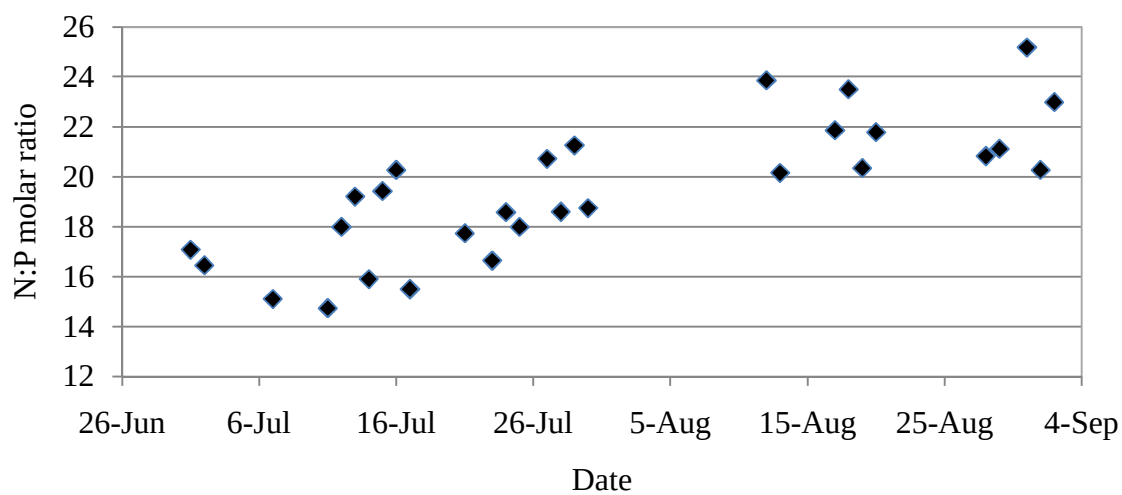


(b)

Figure 4.6. Centrate characteristics at the Lulu Island Wastewater Treatment Plant during pilot-scale validation of process control in 2009 (a) phosphate, (b) ammonium.



(c)



(d)

Figure 4.6 cont'd. Centrate characteristics at the Lulu Island Wastewater Treatment Plant during pilot-scale validation of process control in 2009 (c) magnesium and (d) N:P molar ratio.

Table 4.5. Operating conditions in each struvite crystallizer

Parameter	Unit	Value
Centrate flow	L/min	2.51
Recycle ratio (RR)	-	6
Recycle flow	L/min	15.63
Mg:P ratio	-	1.3
Total flow in crystallizer	L/min	18.24
Magnesium feed concentration	mg/L	2000
pH	-	Depends on feed concentration (7.8-8.2)
Caustic feed concentration	N	0.3
Upflow velocity (in harvest zone)	mm/sec	67
Number of baffles in stripper	-	10
SSR in crystallizer	-	3

4.9 Experimental Setup

The present study encompassed experiments carried out in both laboratory- and pilot-scale setups over several months. It was found that centrate characteristics were different during different experimental runs, and therefore, the characteristics have been placed in different sections. In addition, several different water matrices were used during the course of the study in the laboratory. The following section has been sub-divided according to the type of experiment performed.

4.9.1 Purpose of the study – solubility tests

The water matrix for typical struvite recovery installations range from advanced wastewater treatment plant (AWWTP) supernatant to centrate, making it necessary to eliminate as much of the chemical variability from the operating control loop as possible. Experiments conducted in the present study aimed at determining a working value for K_{sp} , which reflects the operating conditions (in terms of pH and temperature) of the various field installations. These experiments were designed to establish equilibrium between struvite crystals in the solid phase and their dissolved component ions in an aqueous system. Ideally, this would be done under a closed system to prevent the absorption and escape of gases, such as carbon dioxide and ammonia; however, due to experimental constraints, tests were conducted under open conditions, as the top of the beakers were not covered. Digester supernatant and centrate from local treatment plants, and artificial solutions formed from distilled and tap water, were used as water matrix. Multiple matrices were used in order to quantify appreciable differences, if any, in K_{sp} (due to inherent chemical composition).

4.9.2 Experimental setup and methodology for solubility tests

For all the solubility tests, a six-station paddle stirrer (Phipps and Bird) was used with square jars in a temperature-controlled room (Figure 4.7). About 10 g of struvite (previously grown in the water matrix used) was added to 1.5 L of the water matrix (either distilled water, tap water, centrate or digester supernatant) in each jar. The idea was to insert enough struvite in the jars to attain saturation. The paddle stirrers were set to operate at 70 ± 2 RPM. Samples of 20 L of each water matrix were brought to the testing temperature by storing them in the controlled temperature room before the experiment. Since high levels of ammonia and phosphate were already present in the wastewater, only magnesium chloride was added, in order to supersaturate the solutions with respect to each of the component ions. In the distilled and tap water systems, additional diammonium hydrogen phosphate $\{(NH_4)_2HPO_4\}$ and magnesium chloride ($MgCl_2$) were added to achieve the same concentration levels as in the centrate and digester supernatant water matrices. The rationale for using struvite previously grown in a given matrix was to maintain the chemical uniqueness of a water matrix, as much as possible. The final concentration ranges that were

being targeted for Mg^{+2} , $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ were 180-200 mg/L, 150-180 mg/L and >300mg/L respectively. The prepared solutions were kept at a pH of 4.0, to discourage struvite formation.

Since K_{sp} is highly temperature dependant, trials were conducted at 10, 15 and 20°C (chosen to reflect seasonal operational temperatures in Vancouver, BC). As K_{sp} is also pH dependant, tests for each of the trial temperatures were conducted for multiple pH values, starting from 6.0 to 9.0 in 0.2 - 0.3 pH increments. In order to keep the pH at the desired value, dilute hydrochloric acid or sodium hydroxide solutions were added to each of the jars. Previous studies (Fattah, 2004) showed that equilibrium could be achieved after 24 hours; however, in order to provide a further degree of safety, sampling was undertaken when the pH had remained constant for 3 hours after assumption of equilibrium (after 24 hours). Once equilibrium was considered to be established, the pH and conductivity in each jar were measured. Samples were taken from each jar to determine magnesium, ammonium and ortho-phosphate concentrations.



Figure 4.7. Setup of solubility determination.

4.9.2.1 Speciation Model

The model used to calculate the supersaturation ratio was an in-house program coded in Microsoft Excel, entitled SimpleMAP v1.0, to perform the chemical speciation of the tested solutions. The chemical equilibrium reactions (Table 2.1) and values (corrected for temperature) were used in the program. The ionic activity coefficient was determined using the empirical formula presented in Chapter Two, which relates the coefficient with conductivity measurements. The pK_{sp} was determined using the speciation model, by entering the measured values for each of the three species of interest (ortho phosphate, magnesium and ammonium), as well as the measured pH, conductivity and temperature. An iterative analysis was then conducted in order to calculate the value of pK_{sp} that would set the SSR value to 1.0. The assumption made here is that each batch test reached equilibrium. Details on the model can be found in Fattah (2004).

4.9.3 *Purpose of the study - carbon dioxide stripping*

As mentioned earlier, carbon dioxide stripping may reduce the amount of caustic needed to increase the pH in a struvite crystallization process. Experiments were carried out at Metro Vancouver's Lulu Island Wastewater Treatment Plant in Richmond, B.C. Canada, using centrate generated at the plant. In order to determine the effects of stripper configurations, two types of strippers were used in the present study – a compact media stripper and a cascade stripper. The strippers were located between the overflow pipe of the crystallizer and the clarifier. Some of the parameters used in this section were sampled, measured and evaluated by Sabrina (2007).

4.9.4 *Experimental setup for carbon dioxide stripping*

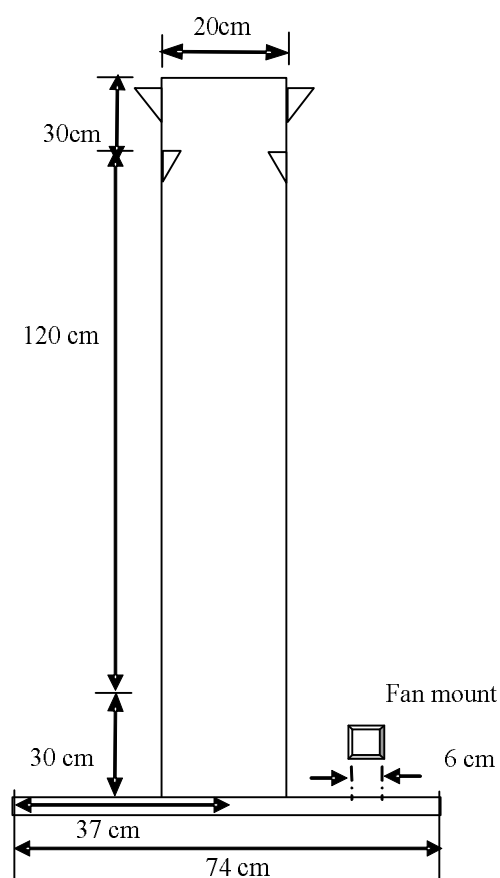
4.9.4.1 Compact media stripper

One of the two strippers used in this study was a compacted media type developed by Ostara Nutrient Recovery Technologies Inc., Canada, and connected to R#1 (Figure 4.2a). It consisted of a circular stripping tower, a supporting plate for the packing material near the bottom, a liquid distributor system located above the packing material, and a fan at the bottom of the stripping tower (Figure 4.8a and b). The total height of the stripping tower was

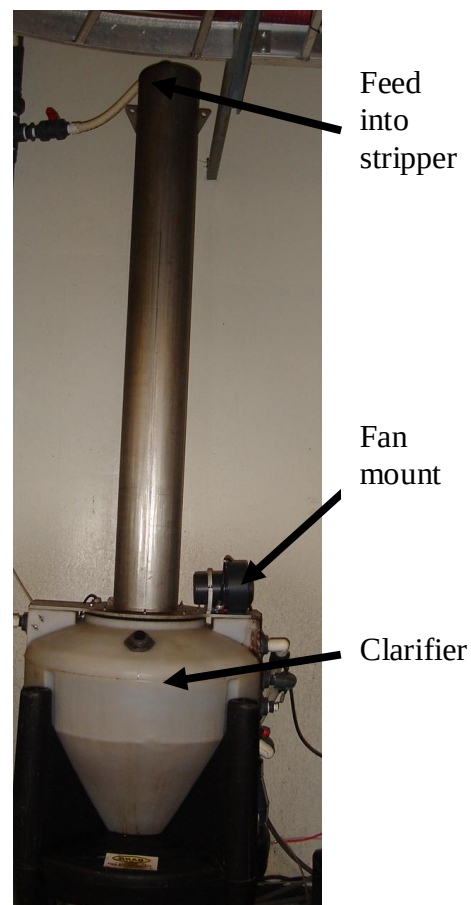
1.8 m, 1.2 m of which were packed with 25.4 mm diameter hollow plastic balls, as packing material. The balls were placed to provide a larger specific surface area and allow the flowing liquid stream adequate water/air contact time to increase the rate of carbon dioxide stripping. Initially the balls (Figure 4.8c) were suspended between plates, but due to clogging of the surface (detailed in Chapter Five), the setup was changed, whereby the balls were attached to strings (Figure 4.8d). The stripper was placed directly on top of the external clarifier.

4.9.4.2 Cascade Stripper

The second type of stripper used in this project was a cascade stripper (Figure 4.9) that was designed at UBC. Details of the design can be found in Zhang (2006). Essentially, this was a rectangular vessel with baffles placed at an inclination of 10° . This stripper was connected to R#2 (Figure 4.2b). The cascade stripper was designed for a maximum hydraulic loading rate of 20 L/min, and was incorporated into the crystallizer system just before the external clarifier, substituting almost 1/3 of the reactor downpipe. The top of the stripper was sealed by placing a plate that had a connection for external air pump tubing. The bottom of the stripper was placed 30 cm above the external clarifier.



(a)



(b)

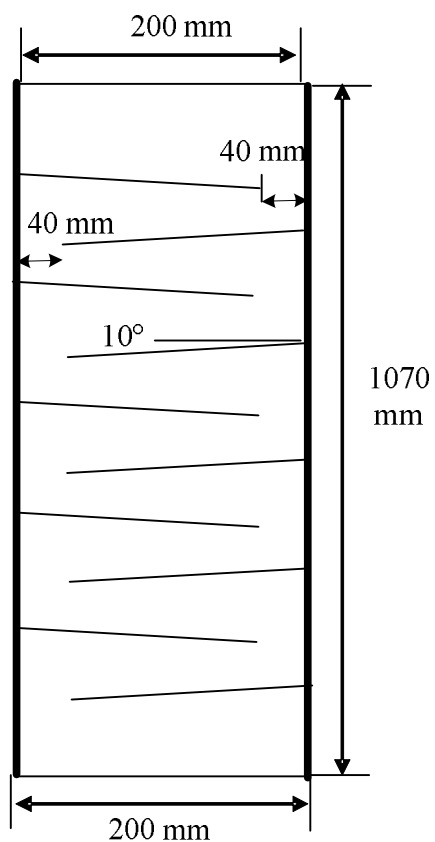


(c)



(d)

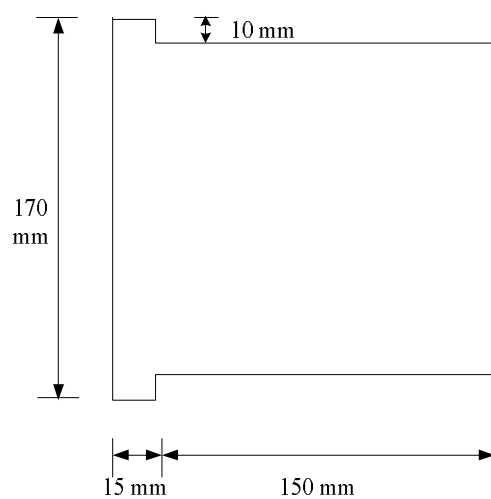
Figure 4.8. (a) Compact media stripper schematic, (b) stripper at setup at LIWWTP, (c) hollow plastic balls used and (d) final arrangement of balls in the stripper.



(a)



(b)



(c)

Figure 4.9. (a) Dimensions of the cascade stripper, (b) stripper at setup at LIWWTP and (c) dimensions of individual baffles.

4.9.5 Methodology to determine efficiency of the carbon dioxide strippers

During the course of the present study, four experiments (Table 4.6) were conducted – one without strippers, and the rest with strippers under different operating conditions. The first experiment was carried out to determine if the two reactors used in this study were similar, regarding overall performance, so that a direct comparison could be made between the two. The results showed that they were very similar and hence, all performances of the two strippers were compared directly. In the first run (Run1) the struvite crystallizers were operated without strippers. In subsequent runs, the strippers operated with air (Run 2) and without air (Run 3), to determine the influence of air on CO₂ stripping. In the last test run (Run 4), the recycle ratio (defined in Section 4.11.1) and upflow velocity (defined in Section 4.11.2) were set to 9 and 75 mm/sec, respectively and the external air supply was resumed.

Air was pumped into the cascade stripper through an airflow meter from the top of the stripper; the maximum airflow rate was 107.5 L/min. The air into the compact media stripper could not be controlled, since it was provided by a fan having fixed speed. While running without external air supply, the top surface of the cascade stripper was kept open. With the introduction of the airflow, the top surface of the stripper was covered with a plexiglass lid. The total flow of water matrix, which is the recycle flow from the crystallizer, through the strippers was 18.24 L/min. The characteristics of the centrate that was used for the process is given in Table 4.7 and the variation illustrated in Figure 4.10. Each point in the figure represents concentration based on daily grab samples. Table 4.8 summarizes the operating conditions for the crystallizers; these values were based on previous studies carried out at the site. As expected, the magnesium concentration in the centrate was the limiting factor for struvite crystallization. The molar ratio of Mg:P was always below 1, the minimum ratio required for struvite precipitation. Hence, magnesium feed (in the form of MgCl₂) was injected into the reactors, to raise the Mg:P ratio. The average supersaturation ratio (SSR) of centrate during the study period was 0.96.

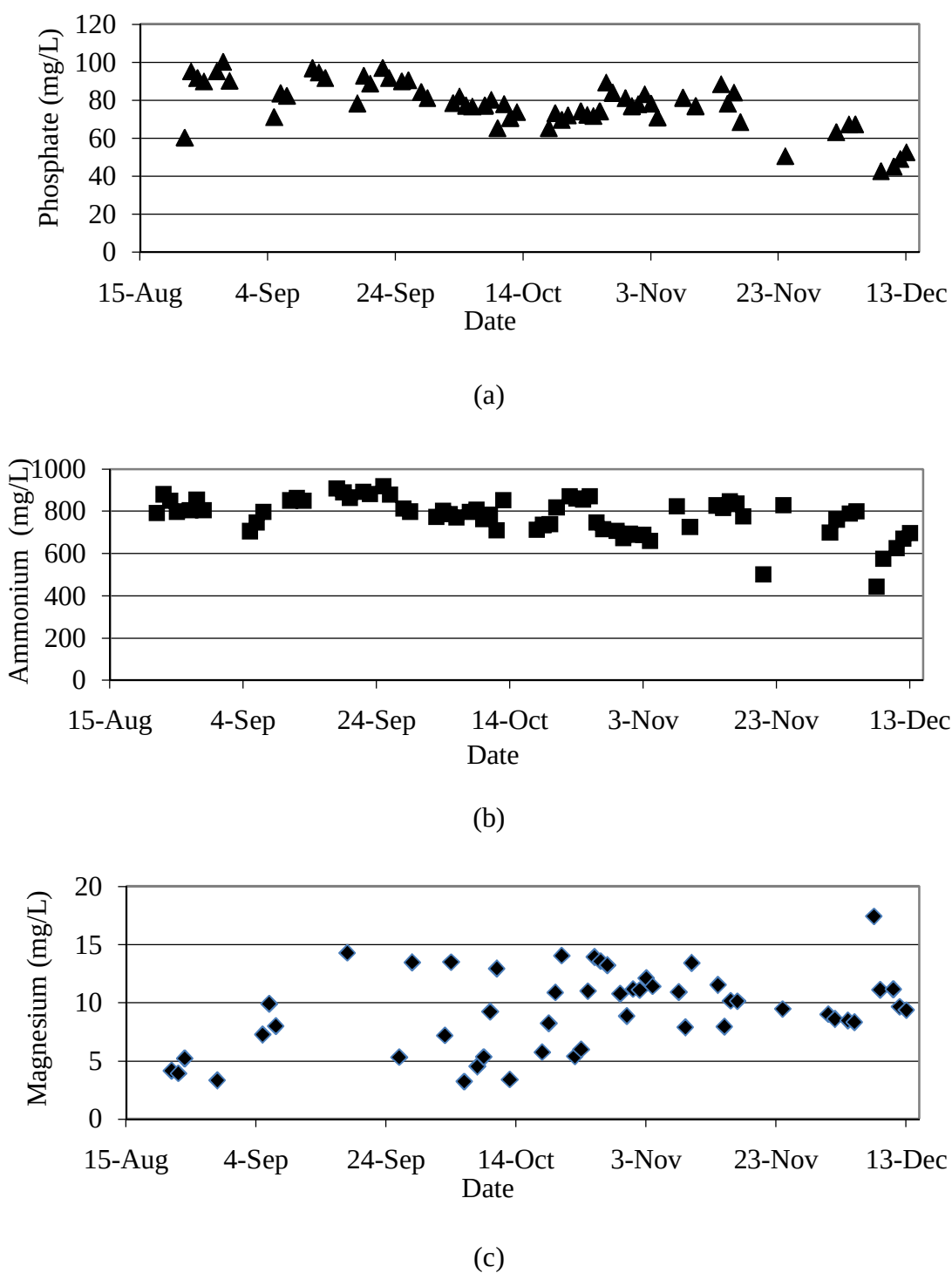


Figure 4.10. Centrate characteristics during experiments testing the efficiency of the carbon dioxide stripper (a) phosphate, (b) ammonium and (c) magnesium.

Table 4.6. Test conditions in the crystallizers and strippers for the comparison of strippers

	Stripper	Air	Recycle Ratio ^a	Upflow velocity ^b (mm/sec)
Run #1	×	×	6	67
Run #2	√	√	6	67
Run #3	√	×	6	67
Run #4	√	√	9	75

^a Recycle Ratio = recycle flow/feed flow^b Upflow velocity = flow velocity in the harvest zone of the crystallizer

Table 4.7. Characteristics of centrate used during carbon dioxide stripping tests

	pH	Temp (°C)	Cond (mS/cm)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)	Molar Ratio Mg:P	N:P
Minimum	7.2	15.3	4.11	4.1	42.6	500	0.01	18
Maximum	8.1	34	12.48	17.4	100.0	916	0.39	36
Average	7.6	25	7.01	9.8	77.7	782	0.17	23

Table 4.8. Summary of operating conditions in the crystallizers

	Total feed (L/min)	Centrate flow (L/min)	Mg feed flow (mL/min)	Recycle ratio	Recycle flow (L/min)	Total flow (L/min)	pH	Upflow velocity (mm/sec)
Unit	(L/min)	(L/min)	(mL/min)		(L/min)	(L/min)		(mm/sec)
Value	2.61	2.51	100	6	15.63	18.24	8.1	67

For cascade stripper the air flow rate was 107.5 L/min; the air in the compact media stripper could not be controlled

4.9.6 Purpose of the study - Determination of magnesium usage for struvite precipitation

Common methods of determining the concentration of magnesium in a water matrix involves the use of expensive and time consuming methods, such as use of atomic absorption or inductively coupled plasma. In a continuous process, such as in a struvite crystallizer,

methods that provide results quickly are needed. In the present study, two methods that could potentially be used to provide information on magnesium concentration and addition requirements were tested. The first method involved the use of pH and conductivity, while the second one involved the use of hardness test methods.

4.9.7 Experimental setup and methodology for the determination of magnesium usage for struvite precipitation

4.9.7.1 Use of pH and conductivity

Several experiments, using synthetic water and centrate from Lulu Island wastewater treatment plant (LIWWTP), were carried out to determine the applicability of using conductivity and pH for magnesium requirements during struvite precipitation. The synthetic water was prepared by adding ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), ammonium chloride (NH_4Cl) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), for a final solution having phosphate, ammonium and magnesium concentrations of 300 ppm, 180 ppm and 180 ppm, respectively. The phosphate concentration was deliberately set high so that it would not be a limiting ion during the precipitation process. A magnesium standard of 3000 ppm was prepared in water using MgCl_2 .

All experiments were carried out in well-mixed 1L Nalgene beakers using 500 mL of water sample. The prepared magnesium chloride standard was added to the solution in 0.5 mL increments every minute; conductivity and pH were logged one minute after chloride addition. Conductivity was measured using a Hanna Instruments HI9033 multi range conductivity meter, while pH was measured with an Oakton[®] pH meter.

Chemical coagulants, such as ferric chloride, ferric sulfate and alum, and polymers (such as poly aluminum chloride), are commonly used to reduce phosphate concentrations in wastewater. The same principle was used for the present study to reduce phosphate concentrations, so that its presence did not interfere with hardness tests. Phosphate concentrations of around 20 mg/L and higher can interfere with hardness tests (APHA *et al.*, 1995). Therefore, exploratory tests were carried out with two chemicals – polyaluminum

chloride (PAC) and alum – to determine the dosages required to reduce phosphate concentrations to values that would not interfere with the hardness tests.

For the second set of experiments, phosphate interference was removed by the following method: a 200 mL centrate sample was taken in a beaker and mixed with PAC or alum in a jar tester for 1.5 hours. After settling the mixture for an hour, the sample was centrifuged at 8000 relative centrifugal force (RCF) for 15 minutes. The supernatant was then used for the hardness tests. The standard alum was prepared by dissolving 5 g of aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{ H}_2\text{O}$) in 500 mL of distilled water, producing a concentration of approximately 855 mg/L of Al. The standard PAC concentration was $2 \times 10^{-5} \%$ (v/v) of 30% PAC as Al_2O_3 .

4.9.7.2 Use of hardness tests

Hardness tests were carried out according to Standard Methods (APHA *et al.*, 1995) for both calcium (Method 3500-Ca D) and total hardness (Method 2340 C). The magnesium concentration was calculated based on the difference between total and calcium hardness, assuming that the hardness was derived from only Ca^{+2} and Mg^{+2} ions. Due to low concentrations usually found in centrate (Fattah *et al.*, 2008b), the presence of interfering cations, such as cadmium, zinc, iron, nickel and cobalt, were ignored. The interference due to aluminum was reduced by adding a magnesium salt of 1, 2-cyclohexanediaminetetraacetic acid (MgCDTA).

4.10 Product Quality Determination

Struvite produced from the pilot-scale operation was tested for different characteristics. With the intention of harvesting only relatively large size (3-5 mm and above) pellets, harvesting was carried out when there was sufficient quantity in the reactor, or when necessary (e.g. to clean the injection port). The harvested crystals were collected and dried in air on trays.

The quality of the harvested pellets was determined by analyzing their composition, morphology and crushing strength. In order to determine the composition and purity of the pellets, approximately 0.2 g of struvite pellets was dissolved in 50 mL of distilled water and 10 drops of concentrated nitric acid. In order to accelerate dissolution, the samples were mixed in a mechanical shaker for 24 hours, after which samples were analyzed for magnesium, ammonium, ortho-phosphate, calcium, aluminum and iron. Inductively coupled plasma (ICP)/mass spectrophotometer (MS) analysis of harvested struvite was also carried out on some samples. The morphology of the harvested crystals was examined, using a scanning electron microscope (SEM) (model Hitachi S-3000N). As described in the next section, the crushing strength was determined using a newly developed device.

4.10.1 Development of strength tester

The absence of a strength tester device in the laboratory made it necessary to construct a new “gadget” that could be used to quantify crushing strength of struvite, which, until now, was described only qualitatively – ability/unability to crush a pellet between fingers (Fattah *et al.* 2008b). The device made for this struvite study consisted of a load cell at the tip of a handle (Figure 4.11) that was connected to a computer via a data acquisition box (PMD-1208 LS, Measurement ComputingTM). A program was developed in DASyLab[®]9.0 (Measurement ComputingTM) to collect continuous force data during each particle test (Figure 4.12). The peak load required to crush a particle was recorded first in the program and then saved as an ASC file which was accessible from Microsoft Excel for data processing and developing graphics. This device allowed for quick and easy measurement of crushing strength of pellets. On average, over 100 pellets were randomly picked and crushed for each data set/struvite harvest.

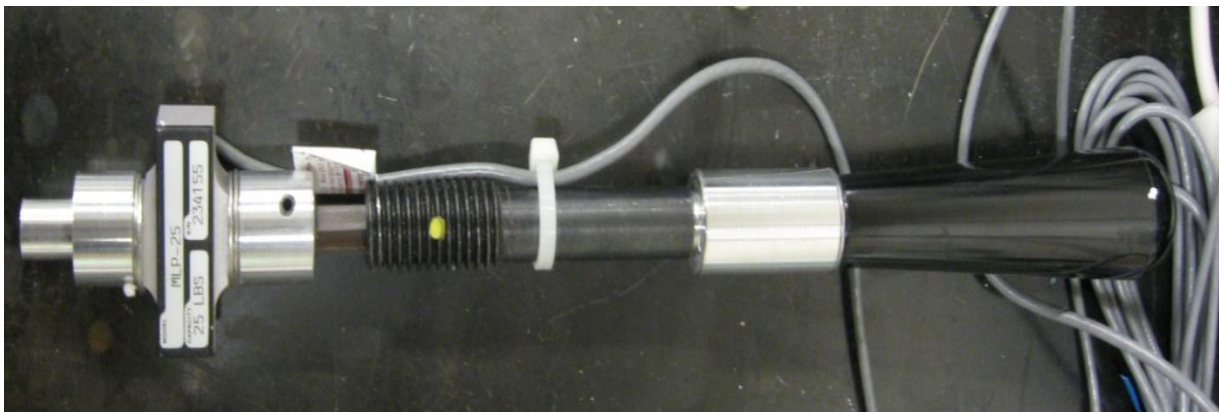
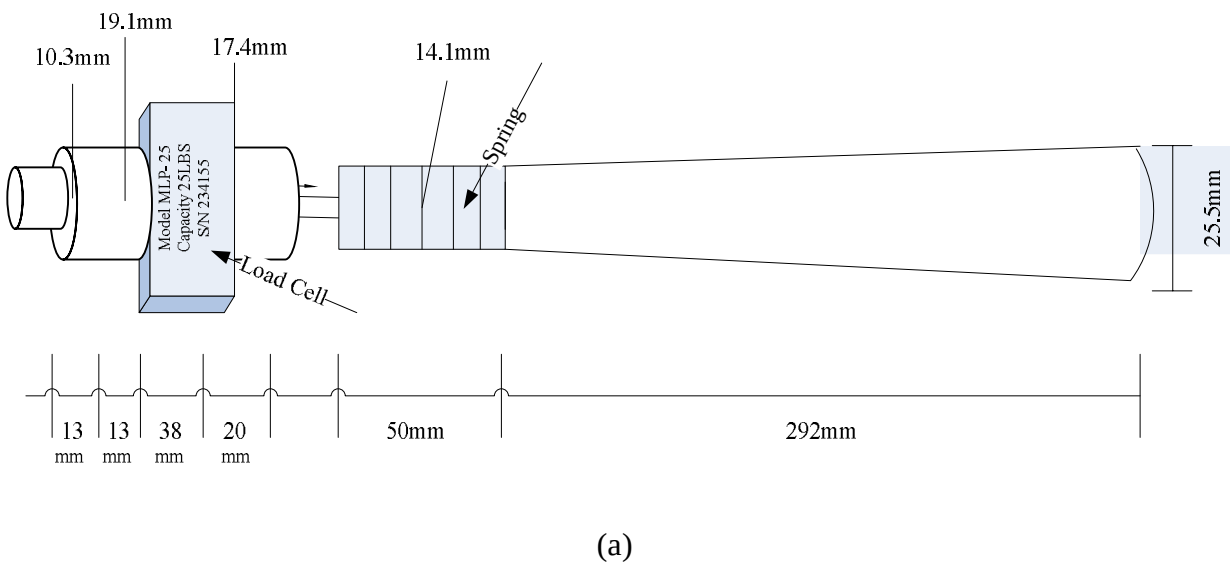


Figure 4.11. Device used to determine crushing strength of struvite (a) sketch (not to scale) and (b) actual device.

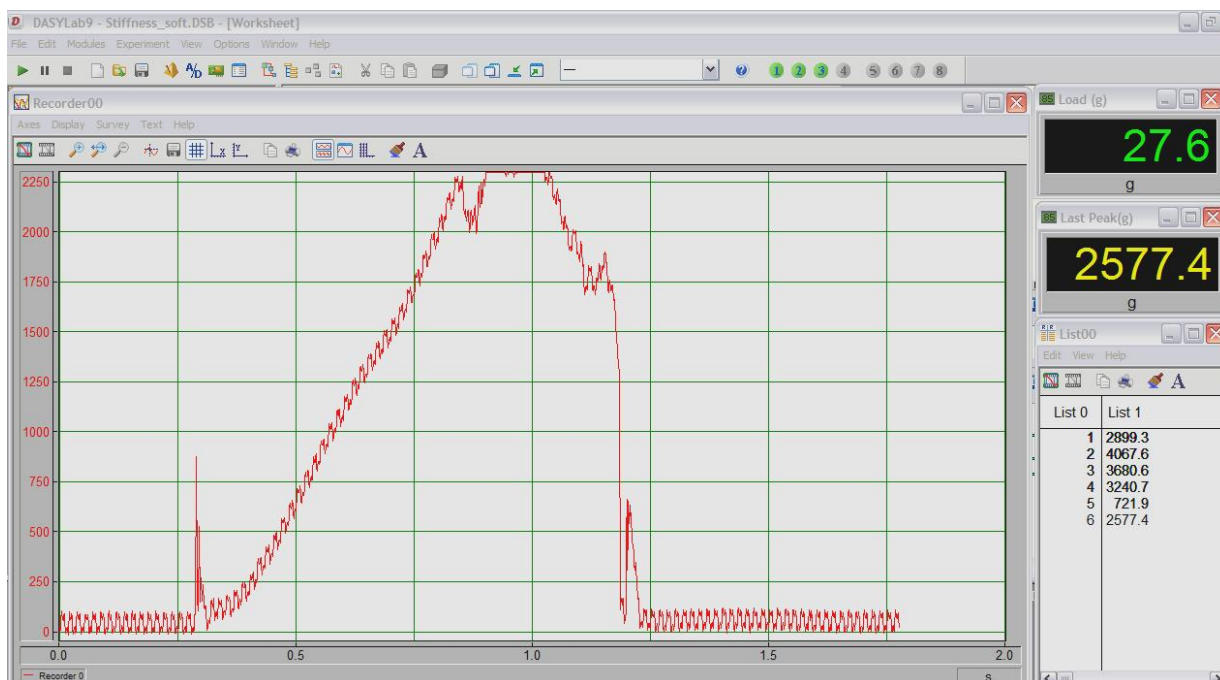


Figure 4.12. Program window used to graphically illustrate force as a function of time and to determine peak load.

4.11 Terminology

Some uncommon terms used in this study are described in this section.

4.11.1 Recycle ratio

Effluent from the crystallizer was collected in the clarifier and then recycled back into the process. The recycle ratio represents the ratio of the flow from the clarifier (by using the recycle pump) to the combined flow from the centrate and chemical pumps. This recycling had two purposes - to dilute the centrate so that the operating pH was around 7.5-8.0, and to provide adequate total water matrix flow into the crystallizer. The recycle ratio was calculated according to Equation 4.4.

$$\text{Recycle Ratio} = Q_r/Q_f = (Q_r - Q_f)/Q_f \quad (4.4)$$

where, Q_r is the recycle flow

Q_t is the total combined flow into the crystallizer (feed + recycle), (mm^3/sec or L/min).

Q_f is the feed flow (magnesium and centrate flow) (mm^3/sec or L/min)

4.11.2 Upflow velocity

The upflow velocity (Equation 4.5), as used in the present study, is the velocity of the liquid in the harvest (lowest section of the crystallizer) zone. This parameter was used to calculate the feed and recycle flows into the system.

$$\text{Upflow velocity (mm/sec)} = Q_f/A_H \quad (4.5)$$

where, A_H is the area of the harvest zone (mm^2)

4.11.3 Removal efficiency

Two of the primary parameters that defined the efficiency of the system were the removal efficiencies of phosphate and ammonium from the system. They are given by Equations 4.6 and 4.7.

$$\%P \text{ removal} = \{[P_{\text{influent}}] - [P_{\text{effluent}}]\} / [P_{\text{influent}}] \times 100 \quad (4.6)$$

$$\%N \text{ removal} = \{[N_{\text{influent}}] - [N_{\text{effluent}}]\} / [N_{\text{influent}}] \times 100 \quad (4.7)$$

$[P_{\text{influent}}]$, $[N_{\text{influent}}]$ = concentrations of centrate ortho-phosphate and ammonium, respectively, at the inlet (mg/L) (i.e. multiplying the respective concentrations with the centrate flow rate and dividing by the total feed flow)

$[P_{\text{effluent}}]$, $[N_{\text{effluent}}]$ = concentration of ortho-phosphate and ammonium, respectively, in the reactor effluent collected from the external clarifier (mg/L)

4.11.4 Confidence limit/Error

The 95% confidence limit has been calculated for some data. The relationship between standard deviation and the error, or confidence limit, is given by Equation 4.8.

$$95 \% \text{ Confidence Limit} = 1.96 * SD/\sqrt{n} \quad (4.8)$$

where,

SD = standard deviation

n = number of samples

4.11.5 Root mean square

The root mean square (RMS) value was used to determine the efficiency of the automated controller developed in the present study in keeping the actual process pH similar to the desired process pH.

For a set of n values $\{x_1^2 + x_2^2 + \dots + x_n^2\}$, the RMS value is given by Equation 4.9.

$$RMS = \sqrt{\frac{x_1^2 + x_2^2 + \dots + x_n^2}{n}} \quad (4.9)$$

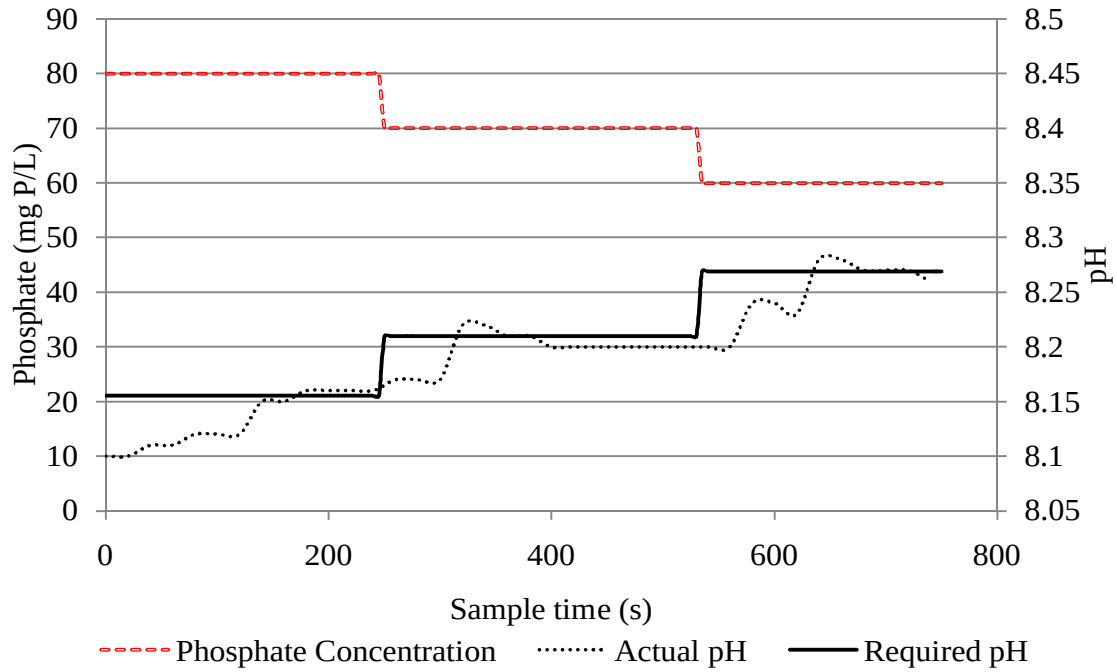
CHAPTER FIVE: RESULTS AND DISCUSSIONS

5.1 Testing of Control Program

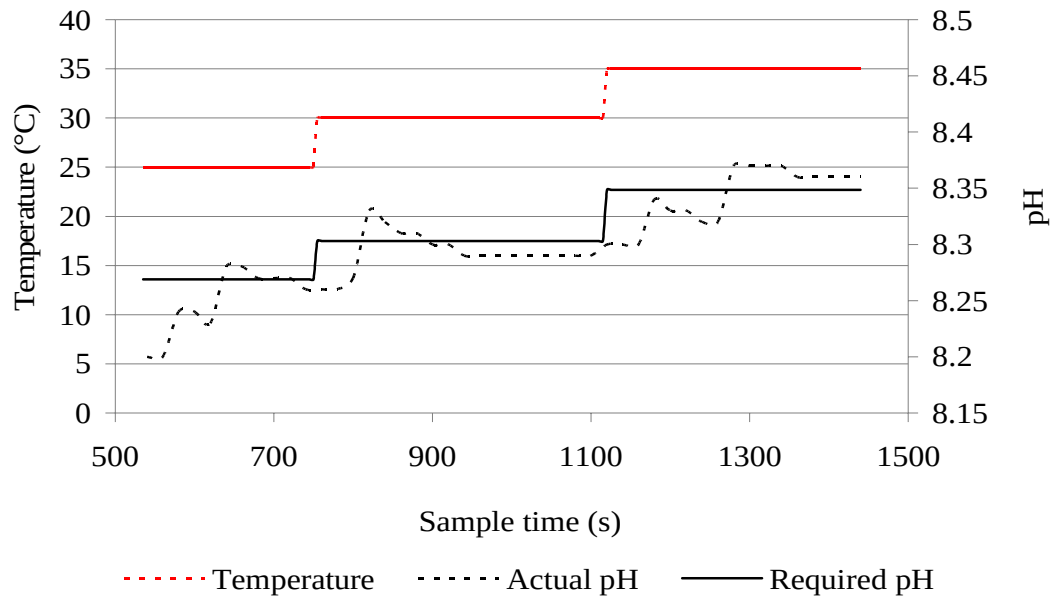
Once the control program was developed, it was tested in the laboratory before being used at the pilot-scale process at LIWWTP.

5.1.1 *Laboratory simulations*

The SSR controller program was initially evaluated in the laboratory by simulating changes in the variables, or process parameters, and determining their influences on the controlled variable SSR. The SSR was calculated based on actual measurements of pH, conductivity and temperature. The program was then tested at pilot-scale, at the treatment plant. The laboratory simulation was carried out by changing one variable at a time and then allowing the control program to adjust the required pH for a set SSR. The pH of tap water in a 500 ml beaker was reduced by adding dilute hydrochloric acid to mimic struvite formation, and then adjusted by adding caustic from a pump, simulating the crystallization process. Although all factors involved with the struvite crystallization can bring about a change in the SSR (and consequently the pH required to keep the SSR steady) only two variables were tested, since it can be concluded that the program would work the same with other variable changes. Figure 5.1 shows the effects of phosphate and temperature changes on the required pH, and the pH of the system as controlled by the pump. Phosphate was chosen because it is the parameter that needs to be optimized with respect to removal-recovery, and temperature was found to have the greatest influence on SSR. As illustrated in the figure, the controller was able to detect the change in the variable (phosphate or temperature) and calculate the required pH. Once the pH was calculated, the appropriate signal was sent to the pH pump, which added caustic to the water matrix to reach the desired pH.



(a)



(b)

Figure 5.1. Effectiveness of the SSR controller in calculating and maintaining required pH due to (a) changing phosphate concentration, (b) changing temperature.

5.1.2 *Experimental runs*

Once the SSR controller was successfully tested at the laboratory-scale through simulations-batch tests, the system was applied to the operation of a crystallizer (R#2) at LIWWTP – the automated crystallizer system. This system (R#2) differed from the R#1 system, which was manually controlled. Due to economic constraints, not all the required real-time data could be obtained, and hence, the full applicability of the model could not be realized. It is expected that in the future, when this model is applied in a full-scale installation, with adequate instrumentation, the process can be operated at a higher efficiency. Despite the need for more real-time data, the model was still able to operate the crystallizer with a high degree of efficiency, by keeping the SSR, and the pH, at the desired levels. Figure 5.2a illustrates the variation in the measured conductivity and temperature in the crystallizer, while Figure 5.2b illustrates the set point and the actual measured pH in the crystallizer. Other than the conductivity, temperature and pH of the crystallizer system, all process variables were kept constant during this period. Figure 5.2b also shows the absolute error in pH. The sudden jump in the set point pH was attributed to the sudden increase in conductivity, as illustrated in Figure 5.2a. The regular variations in the desired set point pH could be linked to the combined influences of temperature and conductivity on the crystallizer SSR. It must be remembered that the pH values measured in the process were sometimes limited by the accuracy of the pH meter and its transmitter, so an absolute error less than 0.03 (RMS value of 0.098) seemed satisfactory. The crystallizer was operated continuously for few months using the control program, with great success. Struvite harvested from the system was of better quality (as mentioned in later sections) compared with that formed in previous studies, at the same location.

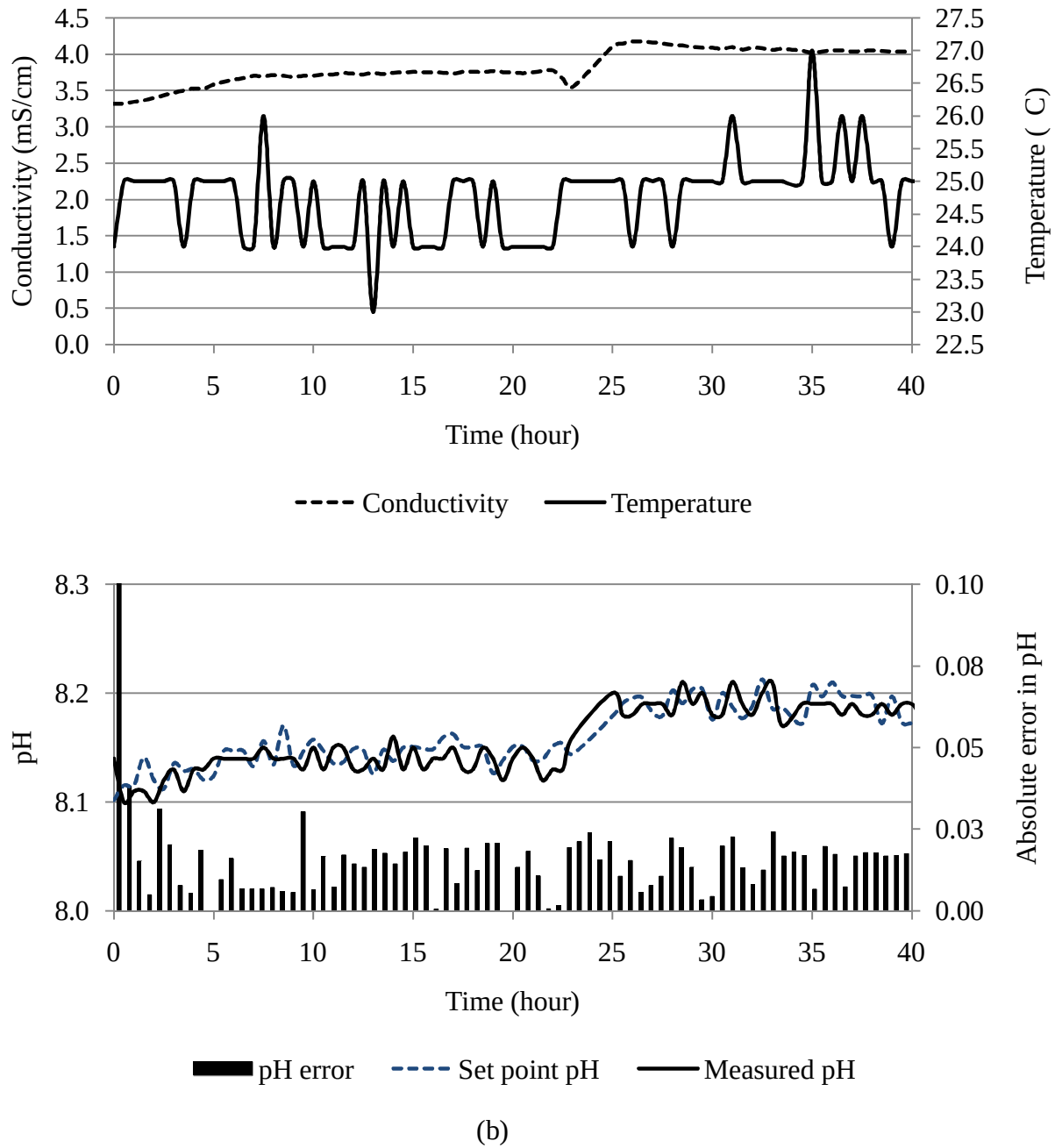


Figure 5.2. (a) Variation of conductivity and temperature in the crystallizer, (b) variation between set point pH (for particular SSR) and measured pH in a pilot-scale struvite crystallizer controlled by the SSR controller.

5.2 Application of Model to Predict Different Scenarios for Control of Struvite Formation Potential

Although the primary use of the developed model was in operating a struvite crystallization process, it could also be used as a predictive tool. Many studies (Fattah *et al.* 2008b; Forrest *et al.* 2008a; Bhuiyan *et al.* 2007; Ohlinger *et al.* 1999) have reported the influence of chemical species' concentration on the solubility of struvite, system supersaturation and struvite crystallization feasibility. However, few have reported the effect of temperature and conductivity on supersaturation ratio. Among the controlling conditions for struvite product quality, the influence of the Mg:P molar ratio has been suggested (Hanhoun *et al.*, 2009; Wang *et al.* 2006). Therefore, by using the SSRcalculator.m model (Table 4.3), the sensitivity of SSR to temperature was tested with varying Mg:P molar ratios. The results are illustrated in

Figure 5.3. What the figure illustrates is the strong inter-dependence of the variables, and that changing one parameter alone (while others are low) does not necessarily increase the SSR, or the struvite formation potential. This figure can be used by practitioners to determine their system's struvite formation potential and to assess what particular change(s) could lead to lowering the SSR value.

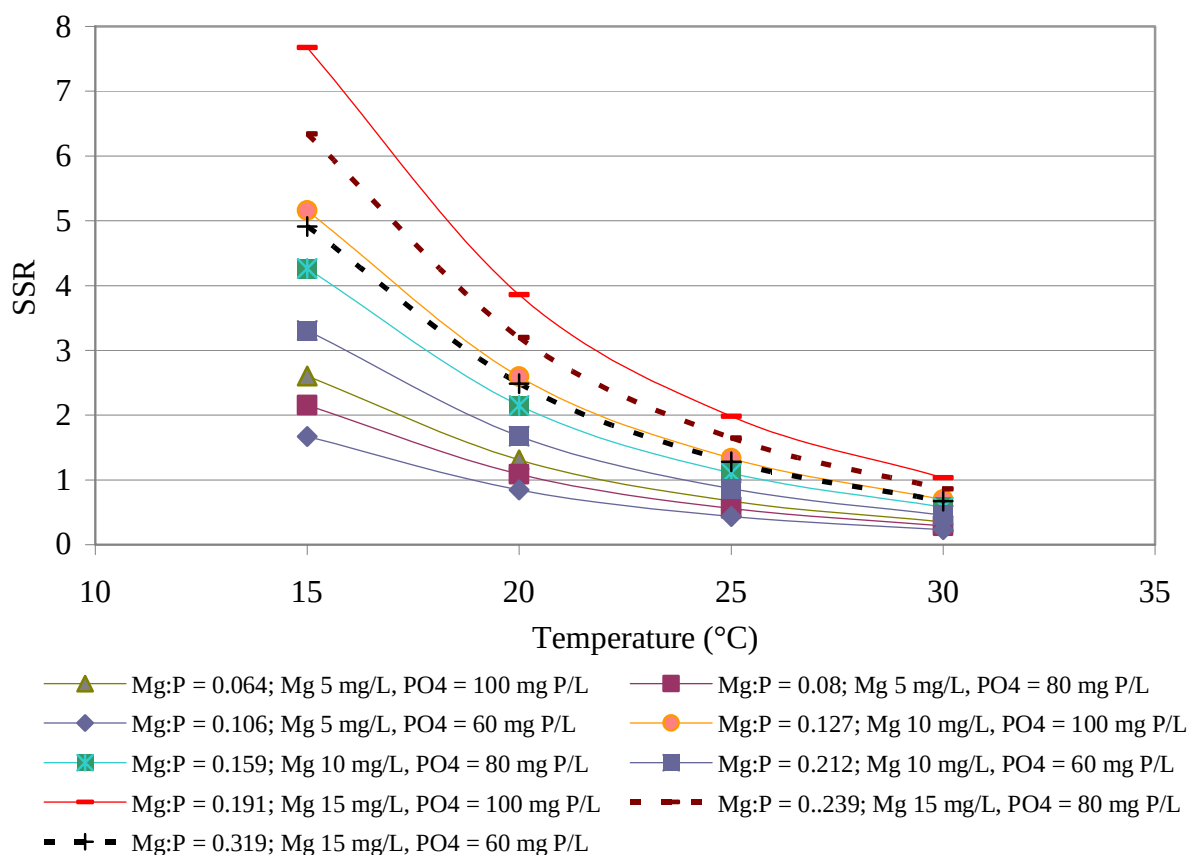


Figure 5.3. Influence of temperature and Mg:P molar ratios on calculated system SSR.

Both Figure 5.4 and Figure 5.5 illustrate the strong influence of temperature on SSR. The SSR values shown in Figure 5.4 and Figure 5.5 were calculated based on the variables values shown in the figures. It is seen that there was more than a 90% increase in SSR due to a 5°C drop in temperature. The variation was more pronounced at lower temperatures, where the SSR nearly doubled (between 15 and 20°C). The variable values used for this simulation are representative of those found at the LIWWTP. Since phosphate was not the limiting ionic species for struvite growth at the treatment plant, its influence (Figure 5.4) on SSR was less than that of the more limiting Mg ion (Figure 5.5). As illustrated in Figure 5.5, irrespective of the temperature, at the lower concentrations (between 5-10 mg/L Mg), the SSR nearly doubled (a 200% increase), whereas the increase in SSR at higher concentrations was only 100%. Thus, treatment plants that have low magnesium concentrations may not have

encountered struvite in there system as yet, but if other conditions are present, a small increase in magnesium concentration will increase struvite formation many folds.

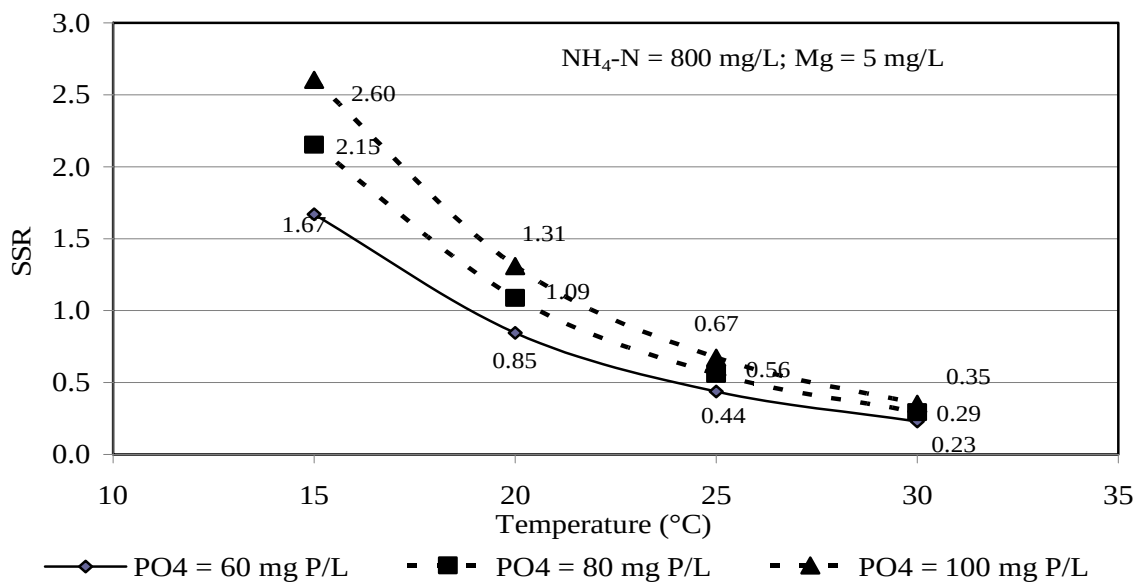


Figure 5.4. Influence of temperature on supersaturation ratio at different phosphate concentrations.

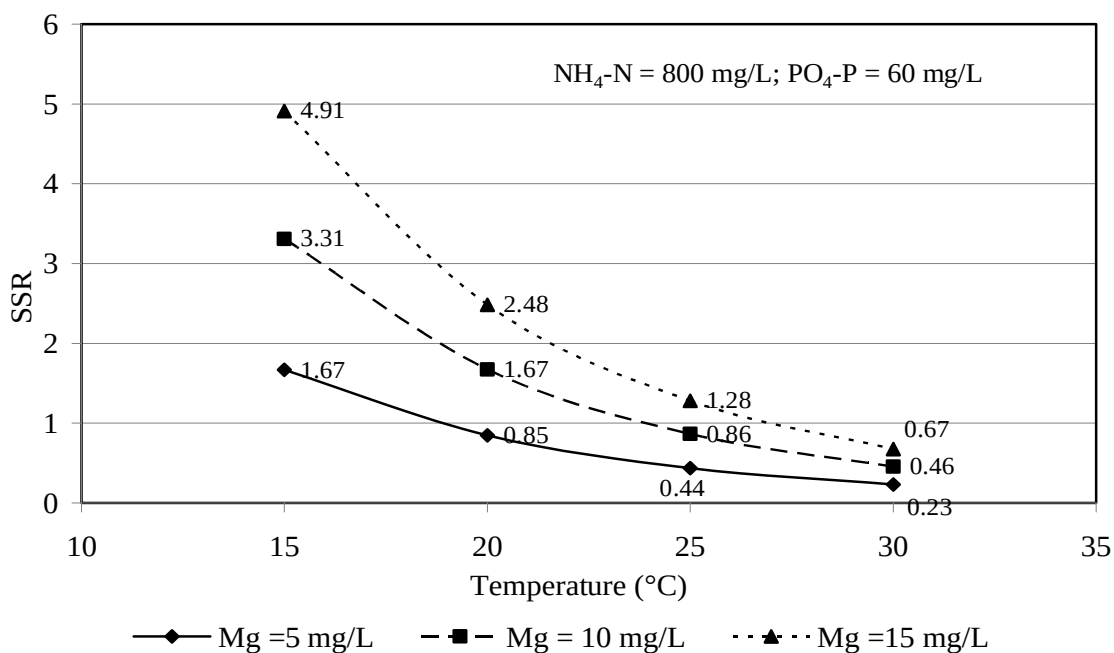
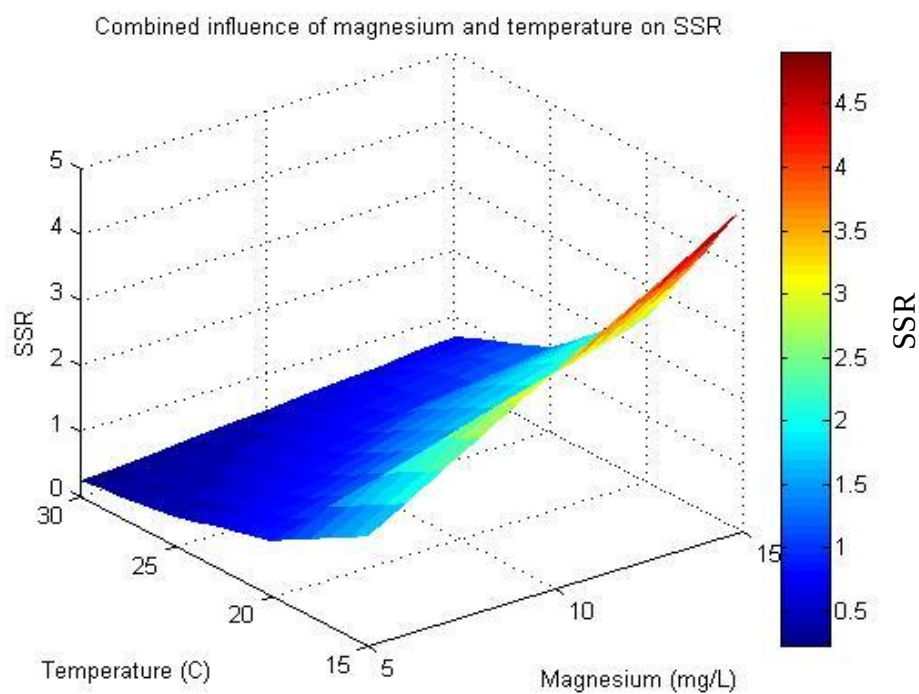


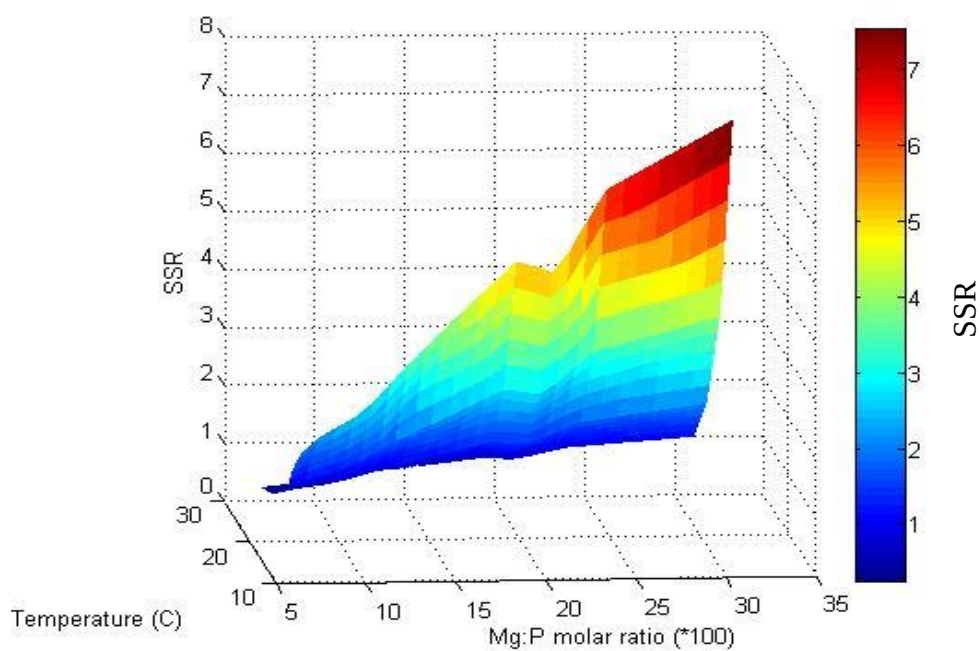
Figure 5.5. Influence of temperature on supersaturation ratio at different magnesium concentrations.

5.3 Application of Model for Decision Making

The decrease in SSR, due to an increase in temperature, was shown above (Figure 5.4 and Figure 5.5). This is probably why treatment plants having high temperature anaerobic digestion are less likely to see struvite forming in the digester, during early years of operation. However, as mentioned earlier, in later years, the concentrations of phosphate and magnesium can increase due to recirculation within the treatment plant, and these may increase struvite formation potential. Since the temperature is not the only driving force, substantial increases in the other controlling parameters can easily drive the SSR above unity, and provide conditions for rapid struvite formation, even at high temperatures. This fact is illustrated in Figure 5.6 where SSR was above 1 at 30°C. This 3-D graphical representation provides a more visual summary of the relationship between the different parameters, and can help practitioners make decisions regarding their operating schemes.



(a)



(b)

Figure 5.6. (a) Influence of magnesium concentration and temperature on SSR and (b) influence of Mg:P molar ratio and temperature; all other parameters constant.

Another application of the model could be to perform various simulations, as well as to see the combined effects of all the parameters. The simulated parameter values are provided in Appendix B and the effects of the parameter change on SSR is illustrated in Figure 5.7. The parameter values used for the simulation are based on ranges found at LIWWTP. As struvite formation is heavily dependent on concentrations of the constituent ions, temperature and conductivity, it is reasonable to use these parameters simultaneously, under different scenarios, to determine their combined effects on the supersaturation ratio in the system (shown by the last graph in Figure 5.7). As previously shown with the LIWWTP simulation, the system temperature and limiting magnesium ion concentration had the most influence on the SSR. The pH of the simulation in Figure 5.7 was kept constant at 7.7 throughout the simulation. The sample number represents the number of data collected by the data acquisition toolbox in Simulink software; 180 data points were collected each second.

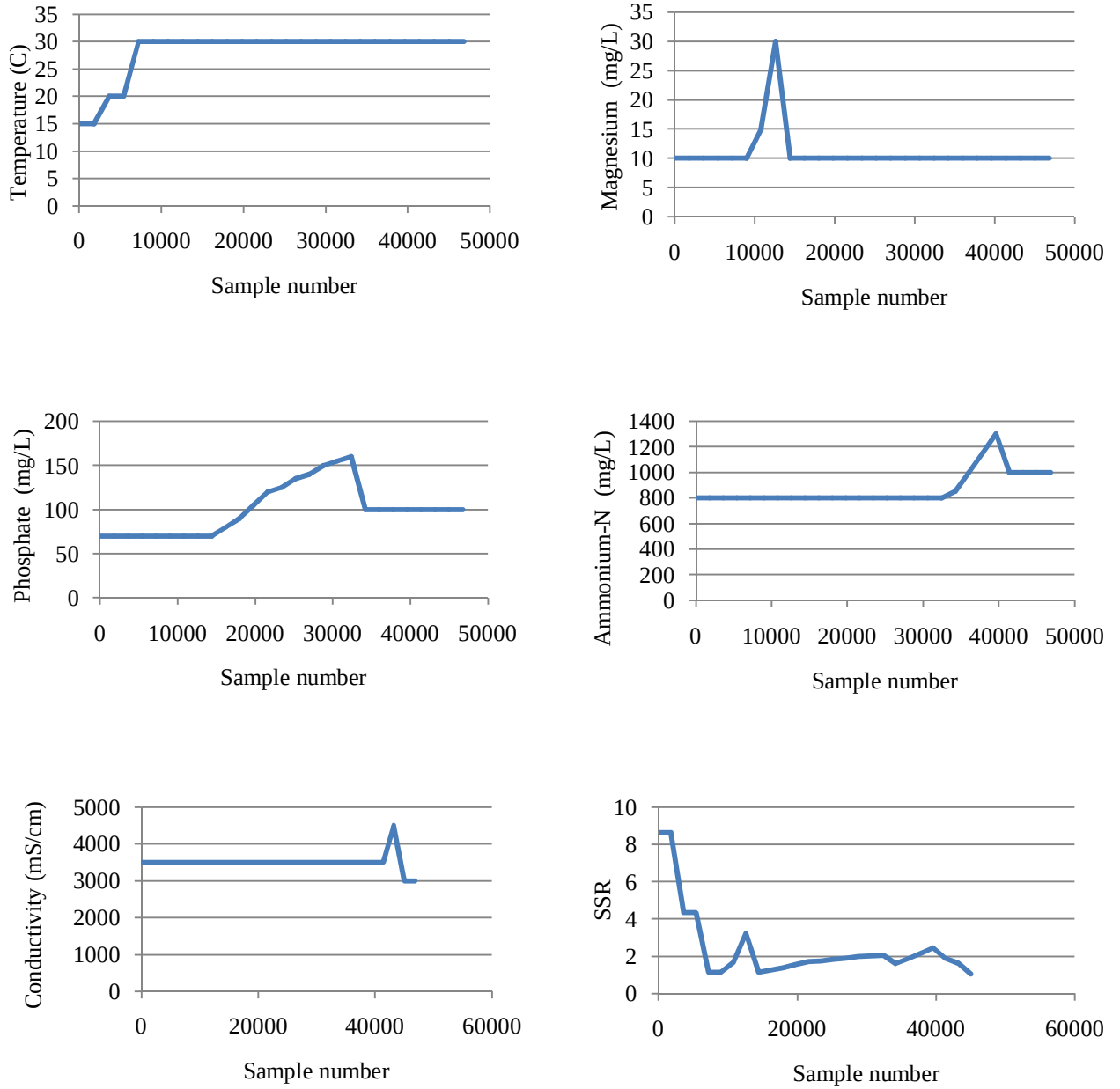


Figure 5.7. Graphical representation showing the level of influence each parameter has (while keeping others constant) on supersaturation ratio (shown in the last graph).

5.4 Carbon Dioxide Stripping Model

Previous studies (Fattah *et al.* 2008a) at this same treatment plant found that the cascade stripper was very effective in saving caustic usage, ranging from 35% to 86%, depending on the operating conditions. A carbon dioxide stripper model was proposed. In the present study, the proposed model was coded in Matlab, so that it could be easily integrated into the process control model. This model takes into account various factors that influence the stripping of carbon dioxide, namely, the baffle number, the effluent recycle ratio, the influent flow rate, the air supply rate, the influent temperature, the influent dissolved CO₂ concentration and the influent buffering capacity. This model facilitates prediction of the change in pH within the stripper. The basic equation of the stripping model is given by Equation 5.1. Detailed expressions for A~G, based on a statistical evaluation of the results by Zhang (2006), are provided in Appendix C.

$$SE = SE^{\ominus} * A * B * C * D * E * F * G \quad (5.1)$$

where,

SE = predicted CO₂ stripping efficiency, %

SE[⊖] = CO₂ stripping efficiency under reference conditions, 74 %

A = coefficient for baffle number (BN)

B = coefficient for effluent recycle ratio (ERR)

C = coefficient for influent flow rate (IFR)

D = coefficient for air supply rate (ASR)

E = coefficient for influent temperature (IT)

F = coefficient for influent's dissolved CO₂ concentration ([CO₂]_{inf})

G = coefficient for influent's buffering capacity (IBC)

5.5 Struvite Crystallization Operation Control Windows

As mentioned in Chapter Four, various program codes were written in Matlab to be used in the Simulink environment, to control and monitor the pilot scale struvite crystallization process at the LIWWTP. This section provides the various graphical user interface tools, or

screens, developed for the purpose. The first level control window (Figure 5.8) is used to calculate the in-reactor species concentrations (in terms of mass) and also to calculate the external magnesium flow rate required. The in-reactor concentrations are determined by calculating the centrate and recycle ionic concentrations and using the flow rates. Since the system did not have any flow meters or online analyzers, these values were manually inserted, based on determinations at the pilot plant and in the laboratory. This window provides the necessary information required for the second level window (Figure 5.9), which is the actual heart of the control system.

The second level control block, named reactor pH regulator in the first level block, contains the SSR and pH calculator codes written in Matlab. In essence, this window calculates the present SSR value in the reactor and compares it to the desired SSR. A difference of $SSR = 0.1$ between the two SSR values is used as the criterion to trigger a change in the pH set point; this is then passed on to the pH meter attached to the crystallizer.

5.6 Graphical User Interfaces (GUI) used for Operation of Crystallization Process

The use of a graphical user interfaces provides a simple and efficient method of operating any system, and therefore, three GUIs were coded in this study – the reactor operation model, the SSR calculator model and the stripper efficiency model. These three GUIs are illustrated in Figure 5.10 to Figure 5.12. The purposes of the reactor operation GUIs were to provide information regarding the conditions required for operating the crystallizer, as well as to provide some useful information, such as struvite production and expected effluent concentrations. As inputs, it requires the concentrations of the various ionic concentrations, the pH, temperature and conductivity, as well as the desired upflow velocity and recycle ratio. The GUI uses the solvepH.m code to determine required pH and calculates the required feed rates, based on flow characteristics. The SSR calculator GUI is a more simplistic window that calculates SSR value, given the required information. Recalling that struvite growth is SSR dependent, this GUI can be used to determine the struvite formation potential at any treatment plant. The carbon dioxide stripper GUI is based on the carbon dioxide stripping model presented earlier, and can be used to predict potential stripping efficiency

and the expected pH increase. This model can be used to predict if the installation of a stripper will actually be economical, before installing one and spending time, money and resources in carrying out studies.

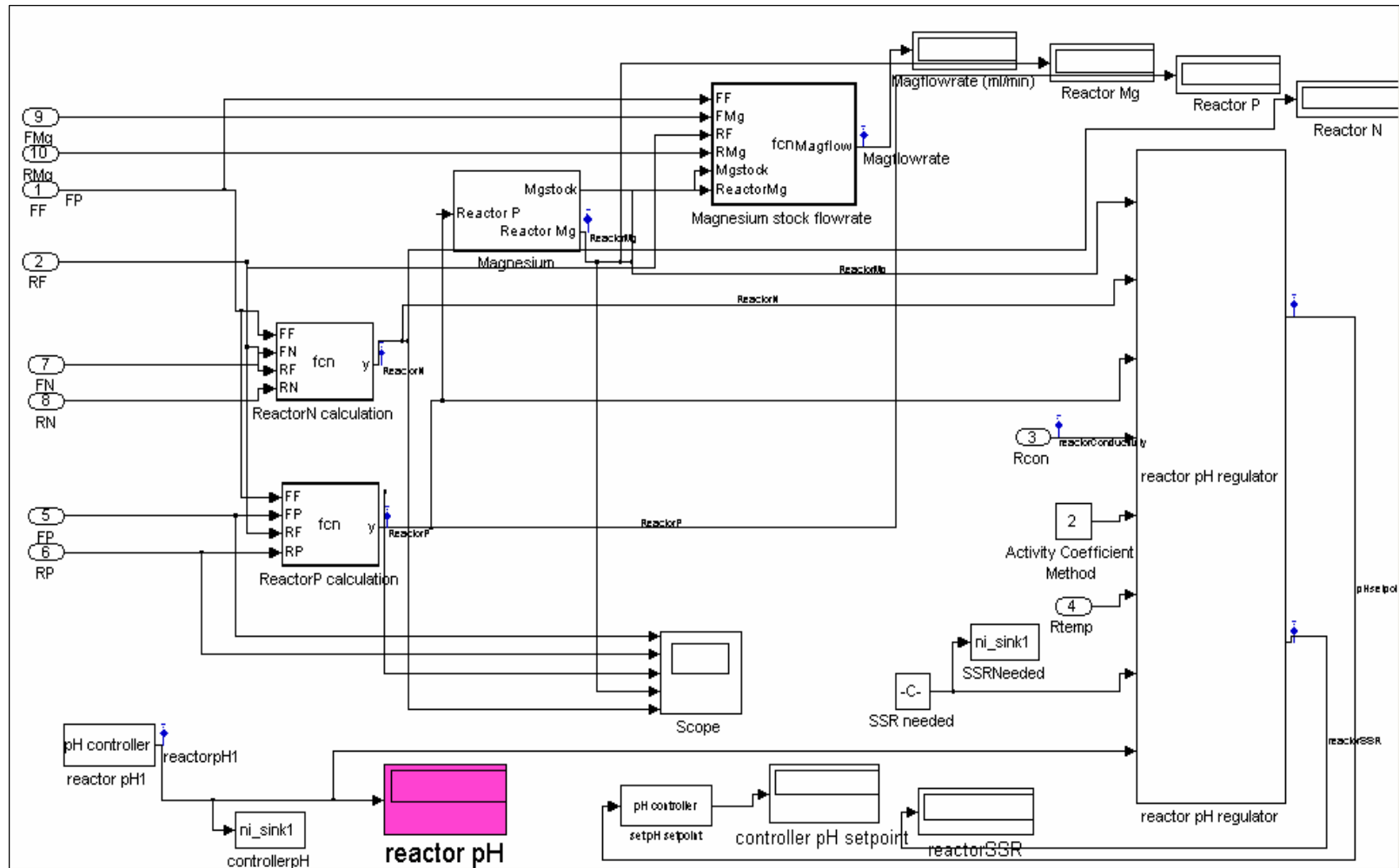


Figure 5.8. First level of control window for struvite crystallization process.

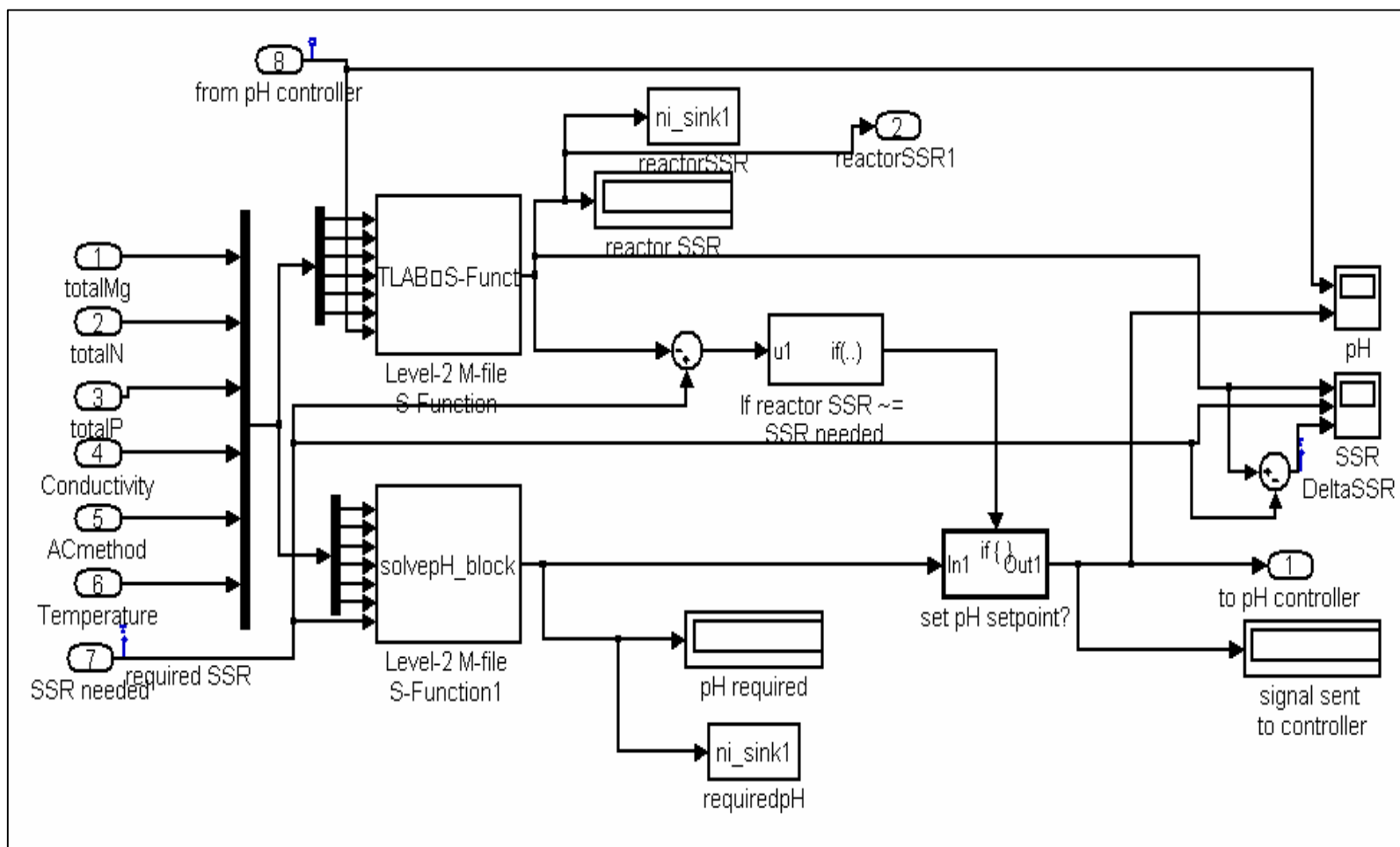


Figure 5.9. Second level control block containing the SSR and pH control codes.



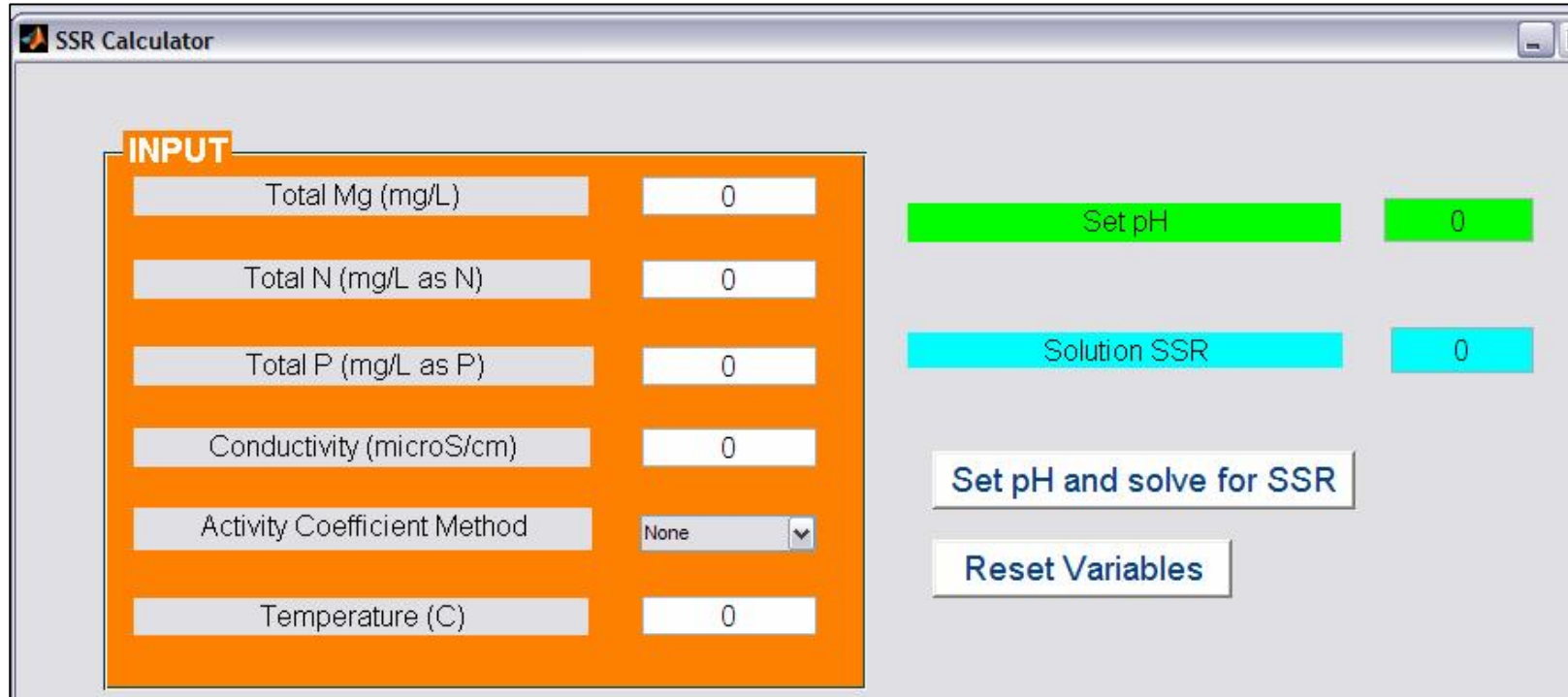
The graphical user interface (GUI) for reactor operation is divided into two main sections: INPUT and OUTPUT. The INPUT section is highlighted in orange and contains 14 parameters, each with a text input field and a numeric input field (all set to 0). The OUTPUT section is highlighted in green and contains 11 parameters, each with a text input field and a numeric input field (all set to 0). At the bottom of the GUI are two buttons: 'Solve for pH' and 'Reset Values'. A small inset image in the top right corner shows a photograph of a laboratory reactor setup with various pipes, tanks, and a control panel.

INPUT	
Feed Mg (mg/L)	0
Feed N (mg/L)	0
Feed P (mg/L)	0
Conductivity (S/cm)	0
Temperature (C)	0
Effluent SSR (assumed)	0
Mixed influents SSR (desired)	0
Drop in pH in reactor	0
Harvest Zone Area (sq. cm)	0
Desired Upflow Velocity (cm/min)	0
Required Recycle Ratio	0
Required Mg Flow (ml/min)	0

OUTPUT	
Required pH	0
Effluent Mg (mg/L)	0
Effluent N (mg/L)	0
Effluent P (mg/L)	0
Required Feed Rate (L/min)	0
Centrate flow (L/min)	0
Required Recycle Flow (L/min)	0
Struvite Production (g/day)	0
P-Removal as Struvite (%)	0
Current pH set point	0

Solve for pH Reset Values

Figure 5.10. Graphical user interface for reactor operation.



The image shows a graphical user interface for an "SSR Calculator". The window has a title bar with the text "SSR Calculator" and a small icon. The main area is divided into two sections. On the left, there is an orange-bordered box labeled "INPUT" in orange text. Inside this box, there are six input fields: "Total Mg (mg/L)" with a value of 0, "Total N (mg/L as N)" with a value of 0, "Total P (mg/L as P)" with a value of 0, "Conductivity (microS/cm)" with a value of 0, "Activity Coefficient Method" with a dropdown menu showing "None", and "Temperature (C)" with a value of 0. On the right side of the window, there are two rows of output fields. The first row has a green button labeled "Set pH" and a green field with the value 0. The second row has a cyan button labeled "Solution SSR" and a cyan field with the value 0. Below these, there are two more buttons: "Set pH and solve for SSR" and "Reset Variables".

INPUT	
Total Mg (mg/L)	0
Total N (mg/L as N)	0
Total P (mg/L as P)	0
Conductivity (microS/cm)	0
Activity Coefficient Method	None
Temperature (C)	0

Set pH	0
Solution SSR	0

Set pH and solve for SSR

Reset Variables

Figure 5.11. Graphical user interface for calculating the supersaturation ratio.

INPUT	
Baffle number	0
Effluent recycle ratio	0
Influent flow rate (L/min)	0
Air supply rate (L/min)	0
Temperature (C)	0
Influent dissolved carbon dioxide (mg/L)	0
Influent pH	0
Total ammonia (mg/L as N)	0
Total alkalinity (mg/L as CaCO ₃)	0
Total phosphate (mg/L as P)	0

Carbon dioxide stripping (%)	0
Expected pH increase	0
Solve	
Reset Variables	

Figure 5.12. Graphical user interface for determining the efficiency of a cascade carbon dioxide stripper.

5.7 Performance Comparison of the Two Systems

The two crystallizer systems, identified as Manual Control (System 1) for Reactor 1 and Automated Control for Reactor 2 (R#2), were operated in parallel, with the intention of determining if continuous control of SSR was beneficial for phosphate removal-recovery and struvite growth. Conductivity, pH and temperature were continuously monitored in Reactor 2, and the required pH, for a particular SSR, was controlled in real-time by using the SSR controller program previously described (Chapter Four). No operating parameters were measured or logged in real-time in Reactor 1. Based on the temperature and conductivity at the pilot-scale setting, the required pH in Reactor 1 was calculated manually each day using the SSR controller program. Due to lack of automation, and in the absence of an operator, variations during the day in the required pH were ignored in Reactor 1. Detailed comparison data are provided in Appendix D.

Figure 5.13 illustrates the difference between the effluents from the two crystallizer systems. Each sample number in the figure represents days on which a sample was taken and tested; due to operational problems, samples could not be taken every day the crystallizers were operated. It should be recalled that the operating centrate was the same for both systems. As shown in Table 5.1, System 2 exhibited better performance in most instances in reducing the phosphate concentration. The difference was significant. Since the concentration of ammonium in the centrate was high and the removal efficiency low, there was little difference in ammonium concentrations between the effluents from the two systems. As mentioned above, the centrate phosphate and ammonium concentrations were much lower than expected at the beginning of the study; consequently, a higher-than-required amount of magnesium was added to each of the crystallizers, resulting in high magnesium concentrations in the effluent. This showed that continuous and real-time data collection are vital for process operation efficiency. The latter part (after sample 12) of the magnesium graph is more representative of the effluent magnesium concentrations that would be expected from operating the process.

In terms of purity (% struvite in pellets), System 2 pellets were slightly higher in struvite content.. This was expected, since the two reactors were operated at very similar operating conditions, and the pH of the manually controlled crystallizer was physically changed each day to produce good quality struvite. Although the struvite quality was not very different, operation of Reactor 2 was easier than Reactor 1, since the pH did not need be monitored and controlled. In addition, the effects of temperature and conductivity could not be accounted for in Reactor 1, and therefore, data from Reactor 2 were used. As shown previously, both conductivity and temperature have large impacts on the supersaturation ratio, and therefore, it is important to monitor these parameters. Table 5.1 provides a summary of different parameters observed the two systems.

Table 5.1. Summary of results from the operation of the two crystallizers

Parameter	System 1 – Reactor 1 (without instrumentation and control)	System 2 – Reactor 2 (with instrumentation and real-time control)
Average (and maximum) ^a removal efficiency		
Phosphate (%)	52 ± 11 (80)	73 ± 8 (88)
Ammonium-N (%)	13 ± 4 (30)	15 ± 4 (34)
Magnesium (%)	54 ± 10 (100)	63 ± 8 (100)
Amount of struvite in pellet % (based on magnesium concentration)	88 ± 2	90 ± 2
Average crushing strength of struvite pellet harvested (g)	2180 ± 670	2460 ± 240

^aValues in brackets are the maximum obtained

Error at 95% confidence interval

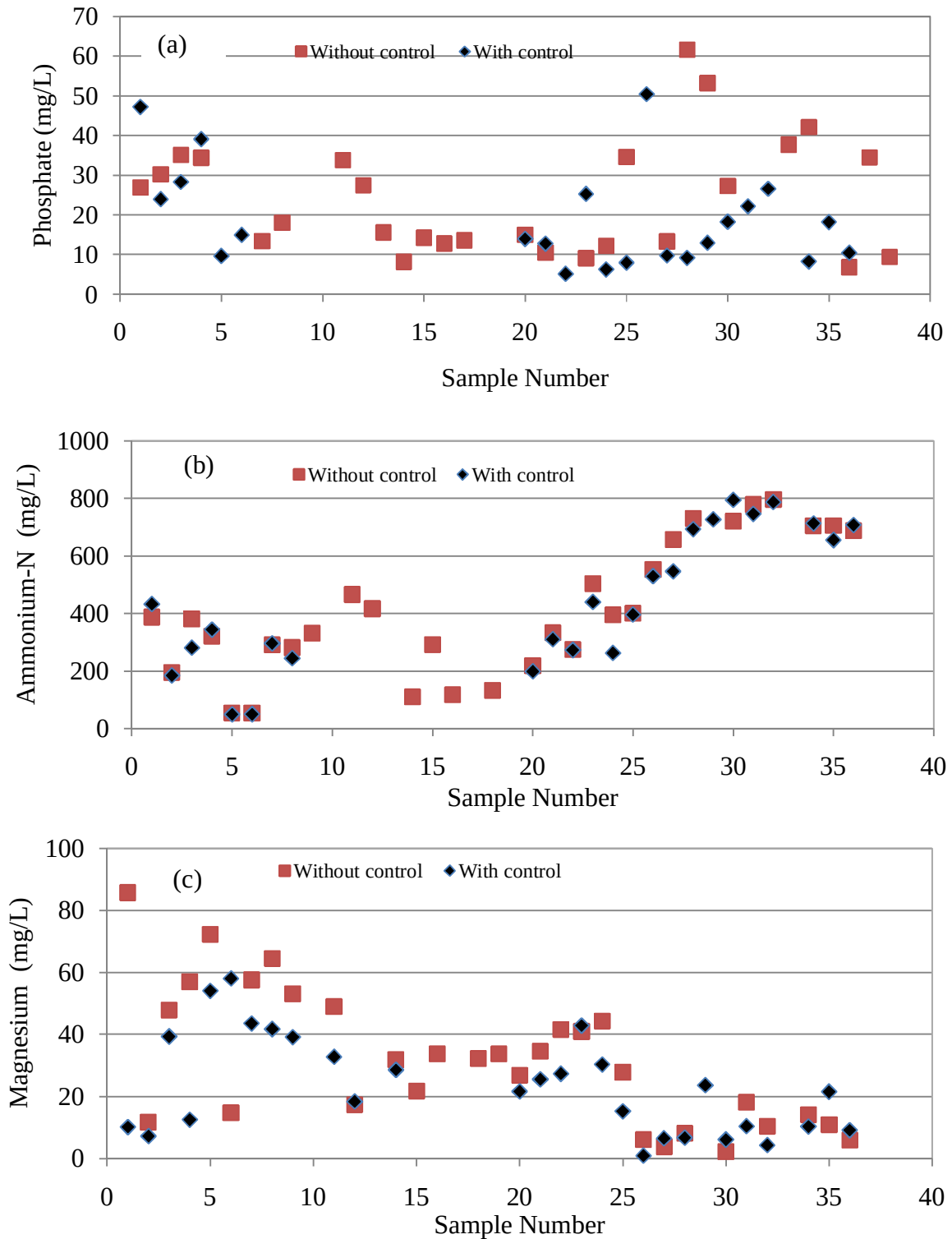


Figure 5.13. Effluent characteristics from the two systems (a) phosphate, (b) ammonium and (c) magnesium concentrations. Sample numbers represents a day's sample.

5.8 Solubility Tests

Although extensive studies on the value of solubility constants for struvite have been conducted, there still exist significant variations between reported values. The objective of this part of the study was to determine the struvite solubility constant in four water matrices, and to examine the influence of both temperature and water matrix on the results. It was expected that a single value of solubility constant could be derived that could be used in the control model. Solubility experiments were carried out with struvite pellets in a six-station paddle stirrer with square jars in a temperature-controlled room. Based on the results, the Speciation Model was then used to examine the influence of both temperature and water matrix on the results. Experimental data are provided in Appendix E.

Test data showed very similar trends for each of the study temperatures (Figure 5.14). As demonstrated, there are two distinct regions in the data, with the change in slope at a pH of approximately 7.0. As the typical pH operating range of the crystallizer is 7.0 and 8.5 (Fattah *et al.*, 2008b; Forrest *et al.*, 2008a), pK_{sp} determination was restricted to this region.

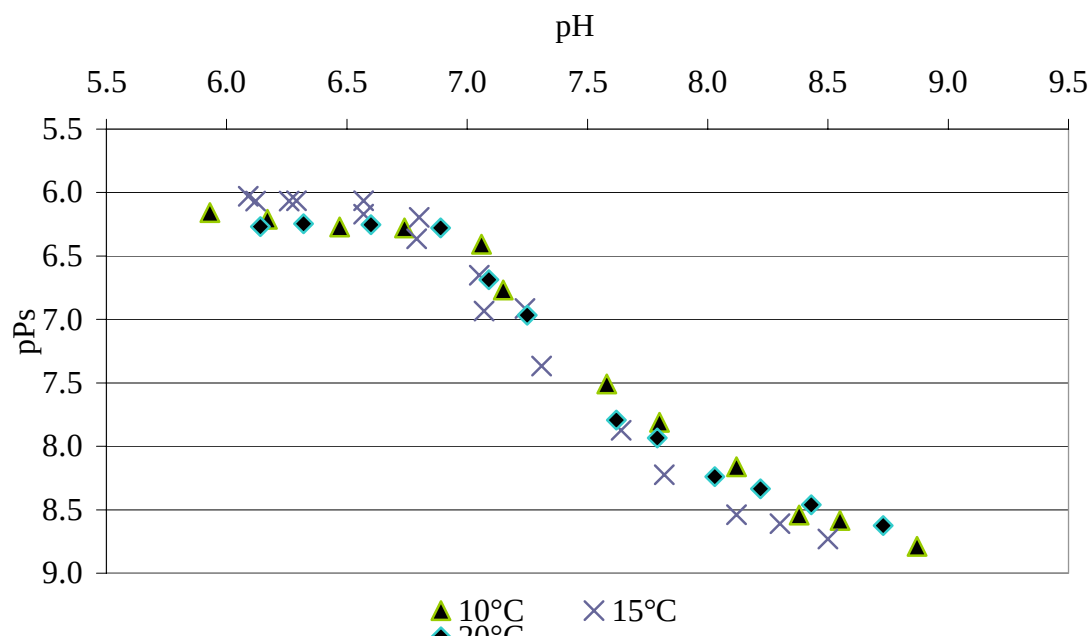
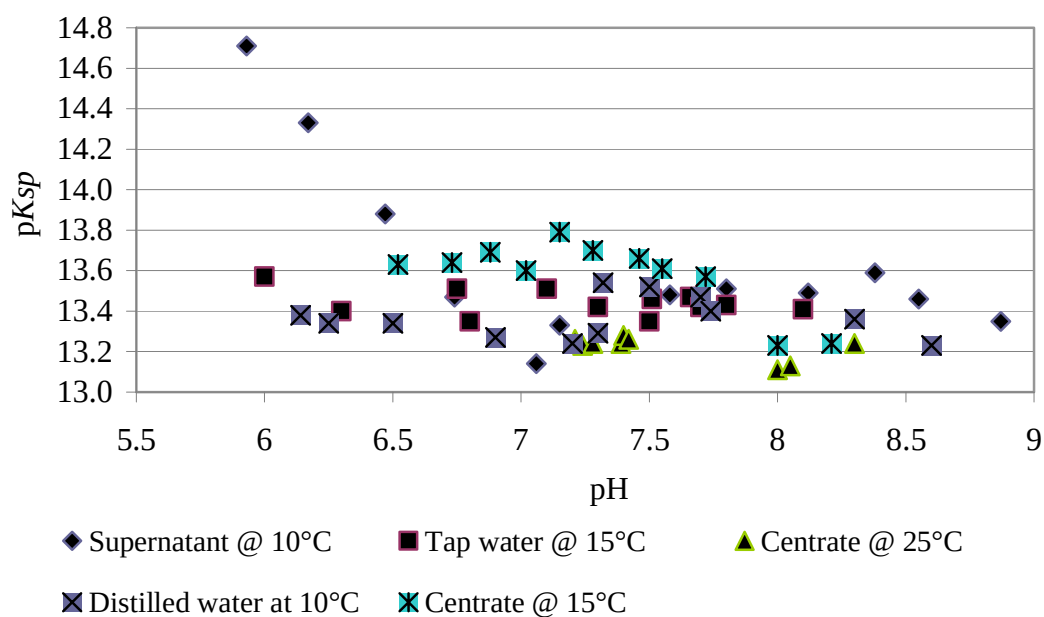


Figure 5.14. pP_s^{eq} curve of a batch experiment trial of supernatant at different temperatures (Adapted from Forrest, 2004).

5.8.1 pK_{sp} prediction using speciation model

At each of the testing temperatures and water matrix, the dependence of pK_{sp} on pH produced very similar results. Typical results are shown in Figure 5.15. Table 5.2 provides a breakdown of each of the pK_{sp} values determined using the Speciation Model.

The predicted values compared well with values in the literature, and demonstrated that the value was independent (within the standard deviation) of the water matrix used. The results for the four water matrices tested in the present study were 13.58 ± 0.11 , 13.50 ± 0.11 and 13.35 ± 0.09 for 10, 15 and 20°C, respectively. This temperature dependence can then be used to calculate the enthalpy change (ΔH°) for struvite, which is defined as the amount of heat absorbed or released during the course of the reaction; reported values for struvite ΔH° display as much discrepancy as do reported pK_{sp} values.

Figure 5.15. Typical pK_{sp} predictions using Speciation Model.Table 5.2. pK_{sp} values for each water matrix as calculated using the Speciation Model

Model	10°C (n = 6)		15°C (n = 6)		20°C (n = 6)	
	Average	S.D.	Average	S.D.	Average	S.D.
Distilled Water	13.63	0.19	n/a	n/a	13.39	0.20
Tap Water	13.65	0.20	13.44	0.16	13.26	0.06
Supernatant	13.42	0.14	13.63	0.24	13.30	0.03
Centrate	13.63	0.19	13.44	0.16	13.45	0.17
Average of the matrices	13.58	0.11	13.50	0.11	13.35	0.09
Prediction using Equation 5.2	13.60		13.49		13.38	

The experimentally determined pK_{sp} values for struvite were combined with values from the literature (Table 5.3) (Bhuiyan *et al.* 2007; Babić-Ivančić *et al.* 2002; Ohlinger *et al.* 1999; Burns *et al.* 1982) in Figure 5.16 and a linear regression of the data was carried out to

derive an equation (Equation 5.2) relating the influence of temperature on solubility constant. A strong correlation ($R^2 = 0.88$) was found between the results from the different tests. This relationship probably provides the most updated value amongst published data, since it was derived using six different studies with eight different water matrices. From the above conclusions, it can be hypothesized that the pK_{sp} value is independent of the water matrix. This conclusion is important, because it allows a single parameter to be used in developing a control model for the struvite crystallization processes. The average enthalpy value (ΔH°) from all the tests was calculated to be 31.62 kJ/mol, which is similar to values published in the literature (23.62 kJ/mol by Bhuiyan *et al.* 2007; 34.48 kJ/mol by Aage *et al.* 1997; 24.23 kJ/mol by Burns *et al.* 1982).

$$pK_{sp} = -0.022 \times \text{Temp } (^\circ\text{C}) + 13.82 \quad (5.2)$$

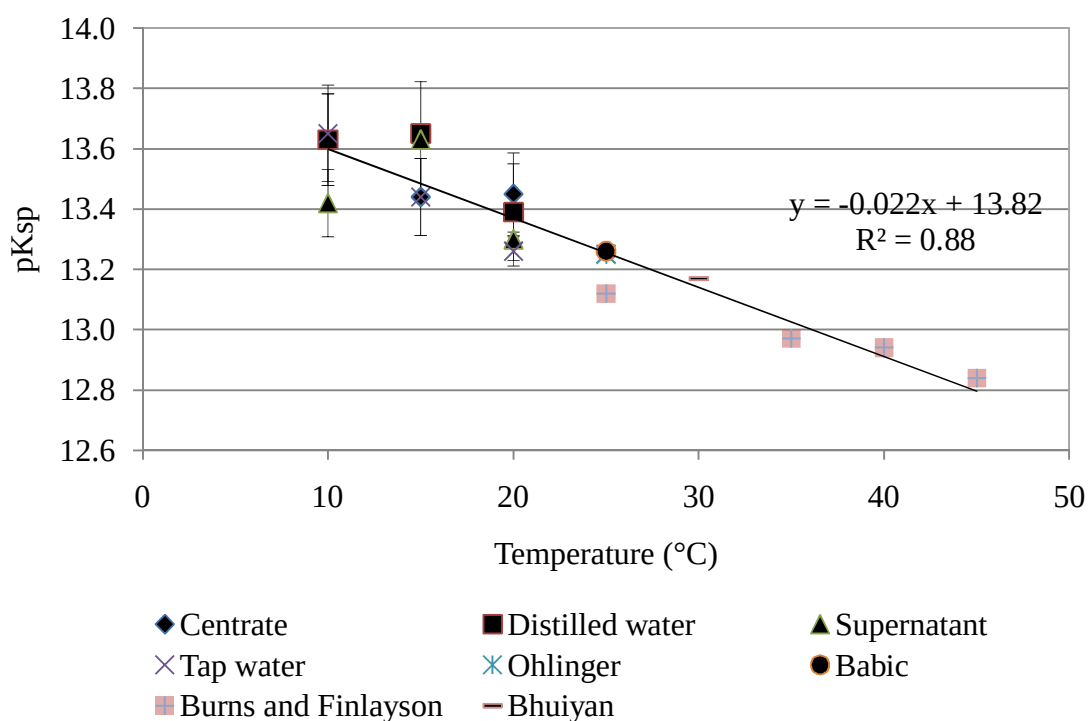


Figure 5.16. Variation of pK_{sp} values with temperature. Error bars at 95% confidence interval.

Table 5.3. pK_{sp} values used to derive Equation 5.2

Reference*	Water matrix	Temperature (°C)	pK_{sp}	Standard deviation	Error
Fattah (2004)	Centrate	10	13.63	0.19	0.15
	Centrate	15	13.44	0.16	0.13
	Centrate	20	13.45	0.17	0.14
Fattah (2004)	Distilled water	10	13.63	0.19	0.15
	Distilled water	15	13.65		
	Distilled water	20	13.39	0.20	0.16
Forrest (2004)	Supernatant	10	13.42	0.14	0.11
Forrest (2004)	Supernatant	15	13.63	0.24	0.19
Forrest (2004)	Supernatant	20	13.3	0.03	0.02
Forrest (2004)	Tap water	10	13.65	0.20	0.16
	Tap water	15	13.44	0.16	0.13
	Tap water	20	13.26	0.06	0.05
Ohlinger <i>et al.</i> 1998	Synthetic Water	25	13.25		
Babić-Ivančić <i>et al.</i> 2002	Synthetic Water	25	13.26		
Burns and Finlayson, 1982		25	13.12		
		35	12.97		
		40	12.94		
		45	12.84		
Bhuiyan <i>et al.</i> 2007	Distilled water	30	13.17	0.05	

* Unless mentioned, experiments were carried out in the present study. Error at 95 % confidence limit

5.8.2 *Summary from solubility tests*

This investigation used an in-house Speciation Model, named SimpleMAP v1.0, to predict values of pK_{sp} . The predicted values compared well with values taken from the literature and demonstrated that the value was independent of the working fluid. This work also revealed that the pK_{sp} is independent of pH in the typical working range of the crystallization process. The data from this study were combined with those found in literature, and a linear relationship between pK_{sp} and temperature was determined. The enthalpy value determined was also similar to those from other studies. The relationship between pK_{sp} and temperature has a significant impact on potential control systems that can be developed for the struvite crystallization process.

5.9 Carbon Dioxide Stripping

The purpose of these experiments was to determine the applicability of strippers to reduce caustic usage in a struvite crystallization process, by stripping of carbon dioxide gas from the system. Two types of strippers were operated in parallel to compare the efficiency in their application.

The efficiency of the strippers was determined by comparing the amount and percentage of caustic saved. At the start of the study, the reactors were operated without the strippers, to confirm that they performed identically, so that a direct comparison could be made between the performances of the strippers. The study was operated under four different conditions (Table 4.6), the conditions being the same for both reactors that were operated in parallel in this study. Table 4.7 lists the characteristics of the centrate used. Detailed operational data are provided in Appendix F. Some of the data are part of a study carried out by Sabrina (2007).

5.9.1 *Run No 1.*

In this run, the crystallizers were operated without any stripper. The recycle ratio was set to 6 and the upflow velocity in the crystallizer was 400 cm/min.

In this run, the removal rates achieved for magnesium, phosphorus and ammonium were 69%, 88% and 7%, respectively in R#1, and 66%, 90% and 10%, respectively, in R#2. On an average, more caustic was used by R#1 than R#2. The average difference of caustic used by the two crystallizers was 91%. Although both systems saw an average pH increase of 0.65, R#1 needed an average 2.35 kg/d of caustic, compared to an average 1.23 kg/d of caustic used by R#2.

Figure 5.17 illustrates the relationship between molar P-removal and the molar caustic use. Although both reactors were identical and were expected to operate similarly, it was found that there were differences with respect to caustic usage. One possible explanation for this is that both strippers were already connected to the respective reactors (compact media stripper with R#1 and cascade stripper with R#2) during the test period. Although the process flow was going directly from the seed hopper to the clarifier, by bypassing the strippers, the compact media stripper was installed directly over clarifier #1, thereby totally blocking the top of the clarifier. On the other hand, the top of clarifier #2 was open, as the cascade stripper was installed about 30 cm above the top surface. The consequence of this setup is that stripped CO_2 (while falling along the downpipe) could escape through this opening. As the compact media stripper sealed R#1 system, stripped CO_2 eventually dissolved back into the liquid stream. As a result of this, recycle flow from the clarifier #1 carried a solution higher in CO_2 to R#1, which reduced the pH of the return stream, and therefore, R#1 required more caustic. Since there was a background difference in the quantity of caustic used by the two systems, the efficiency of the crystallizers was based on the individual systems' Run #1 data.

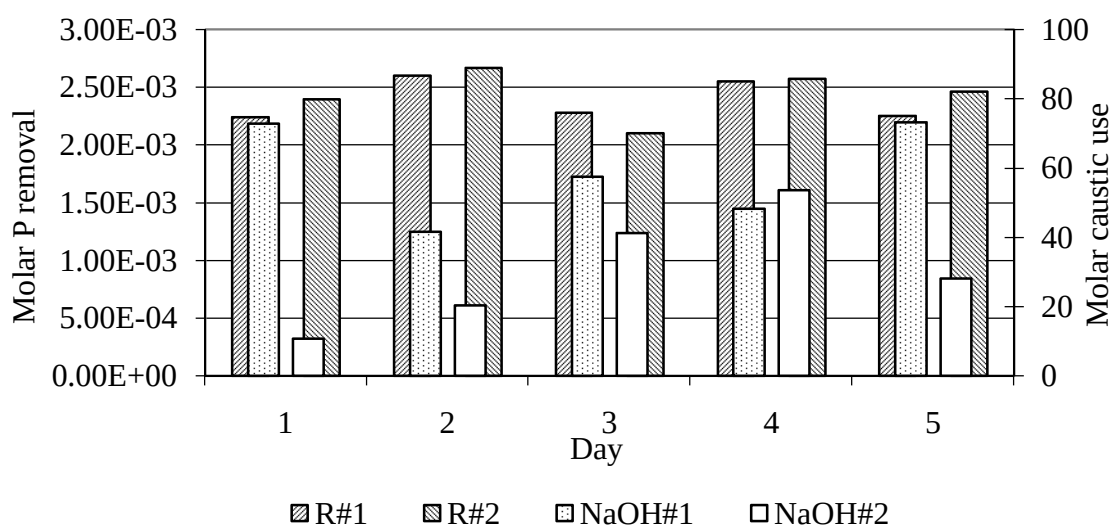


Figure 5.17. Molar phosphorus removal and caustic use in R#1 and R#2 – Run No. 1.

5.9.2 Run No. 2

In this Run, the strippers were connected to the crystallizers and operated with air. The recycle ratio and upflow velocity were 6 and 400 cm/min, respectively.

During this test period, 90% phosphorus removal was achieved by both systems. The average removal efficiency of ammonium was 6% and 5% in R#1 and R#2, respectively. Average magnesium removal efficiency was 74% in R#1 and 75% in R#2. Throughout the test period, the amount of caustic used by R#2 was consistently lower than by R#1. On average, R#2 used 0.84 kg/d of caustic, whereas in case of R#1, this amount was 1.41 kg/d. It should be noted that almost the same amount of phosphorus was removed by both the crystallization processes during this period. Figure 5.18 illustrates the relationship between molar caustic consumption and molar P-removal during the test run.

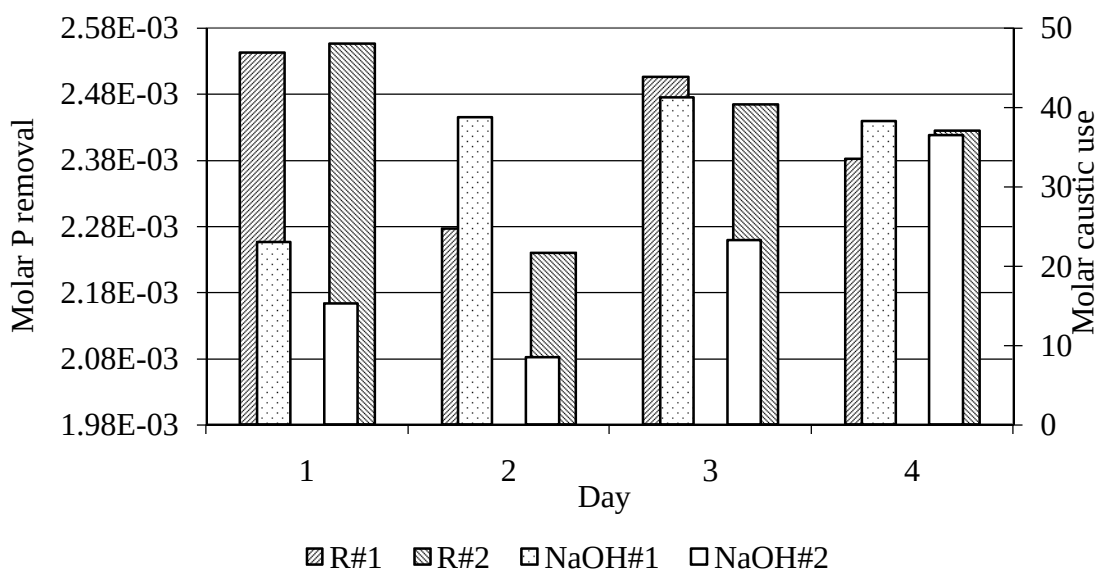


Figure 5.18. Molar phosphorus removal and caustic use in R#1 and R#2 – Run No. 2.

Comparing these results with the results obtained by running the crystallizers without strippers, it can be seen that, by introducing the cascade stripper into the system, an average of 32% savings in caustic use was achieved, while the compact media stripper saved 40%. However, the absolute amount of caustic used by R#1 was higher than for R#2. In addition to the problem mentioned earlier regarding placement of the stripper, it was found that the compact media stripper was also prone to clogging, which may explain the reason for limited carbon dioxide stripping. These two factors may explain why consistently higher caustic was used in R#1. Thus, the cascade stripper proved to be more effective in stripping CO₂ than the compact media stripper, and lowered the daily requirement of caustic. The overall CO₂ removal rate for R#1 was 11%, and 20% for R#2.

5.9.3 Run No. 3

In this experiment, the strippers were operated without an external air supply. The recycle ratio and upflow velocity was kept unchanged from the previous two runs.

The other operating parameters remained the same as in the second run. Both systems were able to remove around 90% of phosphorus during this period, as well. The ammonium removal efficiency increased in both reactors, with a value of approximately 18% in R#1 and 15% in R#2, compared to 6% and 5%, respectively, during the second run. As expected, without an external air supply, the caustic use rate increased in both systems. Again, the cascade media stripper used smaller amounts of caustic than the compact media stripper. The molar caustic use per mole of phosphorus removed showed the same trend as in previous runs, as illustrated in Figure 5.19. During this period, the cascade media stripper saved an average 26% of caustic chemical, compared to 32% in the previous run. On a daily basis, the compact media stripper used an extra 4% of caustic, compared to the previous run.

Without an external air supply, the CO₂ removal efficiency was expected to decrease. Surprisingly, a slightly higher amount of CO₂ removal was achieved by the compact media stripper. One explanation for this could be that the stripper media was cleaned before the start of the run, resulting in higher CO₂ stripping efficiency. The average CO₂ removal efficiency for R#1 was around 14% during this test, whereas this amount was only about 11% in the previous run, with the air supply. On the other hand, the CO₂ removal efficiency for R#2 decreased, as expected, from 20% to 17%.

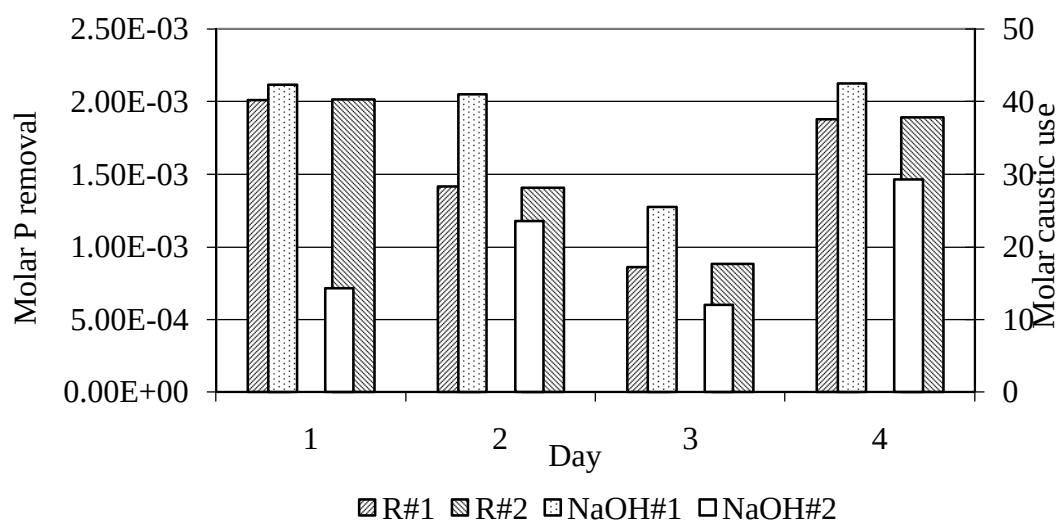


Figure 5.19. Molar phosphorus removal and caustic use in R#1 and R#2 – Run No. 3.

5.9.4 Run No. 4

In this test run, the recycle ratio and the upflow velocity were 9 and 75 mm/sec, respectively, and the external air supply resumed.

In this run, R#1 was able to remove an average 89% of phosphorus. The R#2 system was slightly better in removing phosphorus, achieving an average 92% during this test period. Both systems showed improvement in magnesium removal, compared to the previous runs. The magnesium removal efficiency for R#1 and R#2 averaged 55% and 42%, respectively. In this run, the ammonium removal efficiency averaged 9% in R#1 and 8% in R#2. Regarding daily caustic use, higher recycle ratio and upflow velocity proved to have positive impacts on the performance of the strippers. R#1 used an average 1.35 kg/d of caustic during this time. The improvement was more pronounced in case of R#2, where the average caustic used during this run was only 0.66 kg/d. Both systems were removing almost same amount of molar phosphorus from the system (Figure 5.20).

Comparing results from this run with the results from Run No. 1 showed that the amount of caustic saved by the cascade stripper was 46%, and by the compact media stripper 42%. In

Run 4, the cascade stripper showed an improvement under higher recycle ratio and upflow velocity. Under a higher recycle ratio and upflow velocity, both strippers performed better in stripping CO_2 than in the previous runs, and, as a result, less caustic was used by the systems.

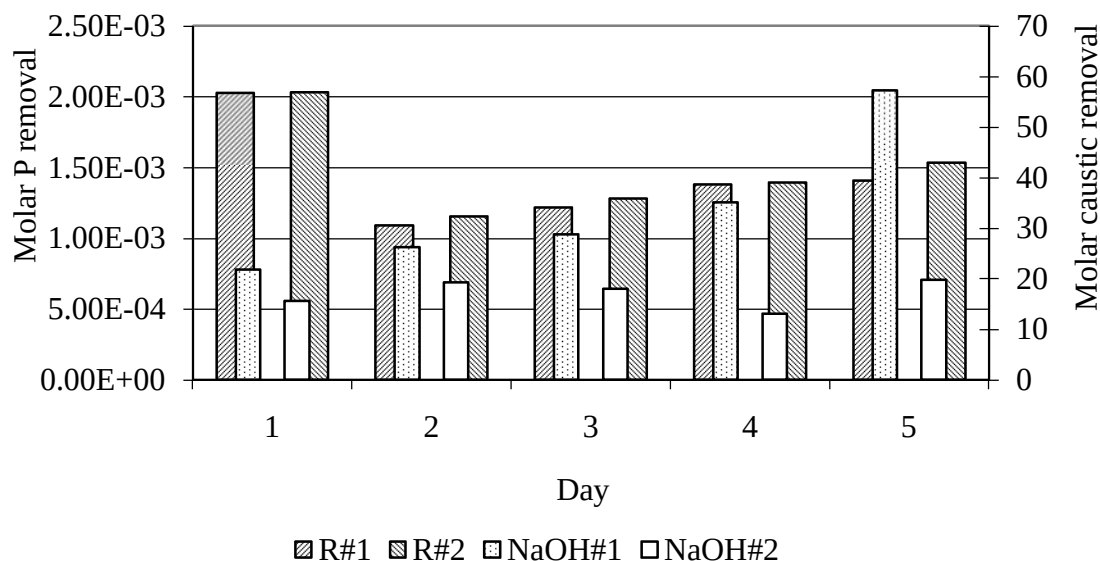


Figure 5.20. Molar phosphorus removal and caustic use in R#1 and R#2 – Run No. 4.

Both strippers proved effective in reducing caustic usage. The amount of caustic saved by the cascade stripper ranged from 26% (without an external air supply) to 46% (with air, higher recycle ratio and upflow velocity). In the previous study at the LIWWTP, the reduction in caustic addition ranged from 46% to 65% (Fattah *et al.* 2009). Even though the previous study did not use an external air supply, the operators were able to obtain a higher amount of caustic savings than in the present study, where only 26% caustic was saved when the stripper was run without an external air supply (the amount was 32% with an external air supply at the recycle ratio of 6.0). However, it should be noted that the operating pH during the previous study was lower (7.9 and 8.0) than in the current study, where the operative pH was maintained at 8.1; hence there was a higher caustic saving. Therefore, it can be concluded that, with a lower operating pH (if conditions satisfy all criteria of struvite formation and recovery), the cascade stripper will be more effective in saving caustic; thus, a

lower cost of struvite production can be expected. A summary of all the test results is provided in Table 5.4.

Table 5.4. Summary of findings from four stripping tests

	Without Stripper		With Stripper					
	R #1	R #2	Run No 2 ^a		Run No 3 ^b		Run No 4 ^c	
			Compact media stripper	Cascade stripper	Compact media stripper	Cascade stripper	Compact media stripper	Cascade stripper
P removal (%)	88	90	90	90	90	90	89	92
Caustic use (kg/d)	2.35	1.23	1.41	0.84	1.51	0.91	1.35	0.66
Caustic savings ^d (%)		-	40	32	36	26	42	46
CO ₂ stripping (%)		-	11	20	14	17	14	21
NH ₃ stripping (%)		-	2	1	9	7	6	5
a	: With air, Recycle ratio (RR) = 6, Upflow velocity = 400 cm/min							
b	: Without air, RR = 6, Upflow velocity = 400 cm/min							
c	: With air, RR = 9, Upflow velocity = 450 cm/min							
d	: Caustic savings were calculated comparing the results of the Runs (2 nd , 3 rd and 4 th) to Run 1							

5.10 Potential for Stripper Fouling

5.10.1 Clogging of the compact media stripper

Comparing the two strippers, operational problems in the compact media stripper were more frequent. From the beginning of the study, the major problem that was faced in operating the compact media stripper was its susceptibility to clogging. When the experiments began, the plastic balls were suspended between the liquid distributor and the

supporting plate. However, it was soon noticed that flow restrictions occurred and, upon investigation, it was found that the balls were totally coated with fine struvite particles and suspended solids. Little success was achieved in removing the solids, despite applying a hot water jet to the balls inside the stripping column. In order to reduce the coating effects, the balls were then rearranged by attaching them to vertical strings, as illustrated in Figure 4.8d. Although this setup permitted easier cleanup, the stripper required constant monitoring and had to be cleaned more regularly (on alternate weeks) than the cascade stripper.

The cascade stripper, which was made of plexiglass, was subject to lower solid buildup due to its relatively smooth surface along which the water flowed. As expected, with the stripping of carbon dioxide, some struvite and suspended solids build-up was visible on the sides, after prolonged operation. This can be explained in terms of the increase in pH of the water matrix. As the pH increased, the SSR of the water matrix increased, which provided suitable conditions for struvite growth. However, since the water matrix passing through each baffle is low in magnesium and phosphate – most of it had been removed in the crystallizer – there was a lower potential for struvite growth. The amount of struvite present did not hamper the operation or clog the stripper. The path of the water flow was always clean, as struvite did not accumulate in place. Moreover, cleanup of the stripper was straightforward as the accumulation was easily removed by hosing it with hot water. Figure 5.21 shows a cross-section of the stripper, showing the struvite accumulation.

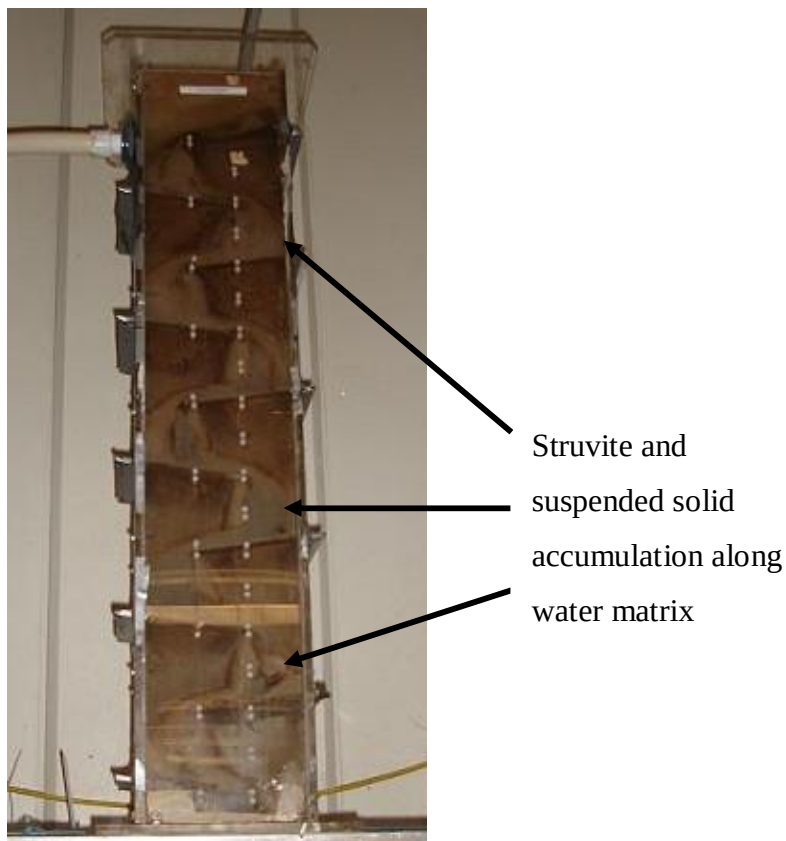


Figure 5.21. Struvite accumulation in stripper during operation.

5.10.2 Cost analysis

Due to the higher efficiency and ease of operation of the cascade stripper, it was decided that future studies would be made with this stripper. Hence, the following sections contain details on this stripper only.

The construction cost of the stripper was reasonable (about \$ 2000), relative to the cost of the pilot-scale struvite reactor, which was around \$ 20,000 (including materials and labor). Once installed, there was little or no cost associated with its maintenance. As mentioned previously, the incorporation of the stripper resulted in lower caustic use to keep the crystallizer at the desired pH level. Lower caustic use can be directly correlated to operational costs. Lulu Island WWTP is a relatively small secondary treatment plant treating, on average, seventy five million liters per day (75 MLD). The crystallizer in the present study operated with a centrate flow of only 2.61 L/min, which is equivalent to approximately

3800 L/day. This is only 3% of the total centrate production at the treatment plant. Based on the current caustic price of \$ 2.57/kg, the potential yearly plant savings in caustic is substantial. Based on this calculation, the potential caustic saving at the larger (average 469 MLD) treatment plant in Metro Vancouver's Annacis Island could be as high as \$ 79,200. A summary of the cost study is given in Table 5.5.

Table 5.5. Cost analysis for caustic usage in a pilot scale struvite crystallizer fitted with a cascade stripper

	Without Strippers	With Strippers		
	Run 1	Run 2 ^a	Run 3 ^b	Run 4 ^c
Caustic use (kg/d)	1.23	0.84	0.91	0.66
Caustic savings (kg/d)	-	0.39	0.32	0.57
Caustic savings (%)		32	26	46
Current caustic savings ^d \$/day)		1.00	0.82	1.46
Potential annual savings at Lulu Island WWTP ^e (\$)		12,200	10,000	17,800
Potential annual savings at Annacis Island WWTP ^e (\$)		54,500	44,500	79,200

^a Stripper run with external air

^b Stripper run without external air

^c Stripper run with higher upflow velocity and RR

^d Caustic cost \$ 2.57/kg

^e For full scale installations

5.10.3 Conclusions

Based on the results from the pilot-scale study of phosphorus recovery with carbon dioxide stripping, the following conclusions can be drawn.

Through the process, over 90% of phosphorus was easily removed from the centrate at a pH of 8.1, with or without air stripping. With and without air stripping, an average of 32% and 26% caustic savings was achieved using the cascade stripper, compared to the no-stripper condition, respectively. For the same conditions, the compact media stripper saved, on average, 40% and 36%. It is expected that, with a lower operating pH (if conditions satisfy all criteria for struvite formation), the cost of the crystallizer could be recovered within 3-4 years; consequently, the cost of producing struvite pellets would be reduced. Although struvite did accumulate on the sides and baffles of the stripper, there were no plugging problems related to the presence of struvite. The accumulation was easily removed by washing with hot water. On the other hand, although the compact media stripper was more efficient in reducing caustic usage, its operation and maintenance was more difficult and time consuming. The study confirms that stripping of carbon dioxide, to raise pH in the production of struvite, is a viable means of reducing caustic usage, and thereby reducing operating and production costs.

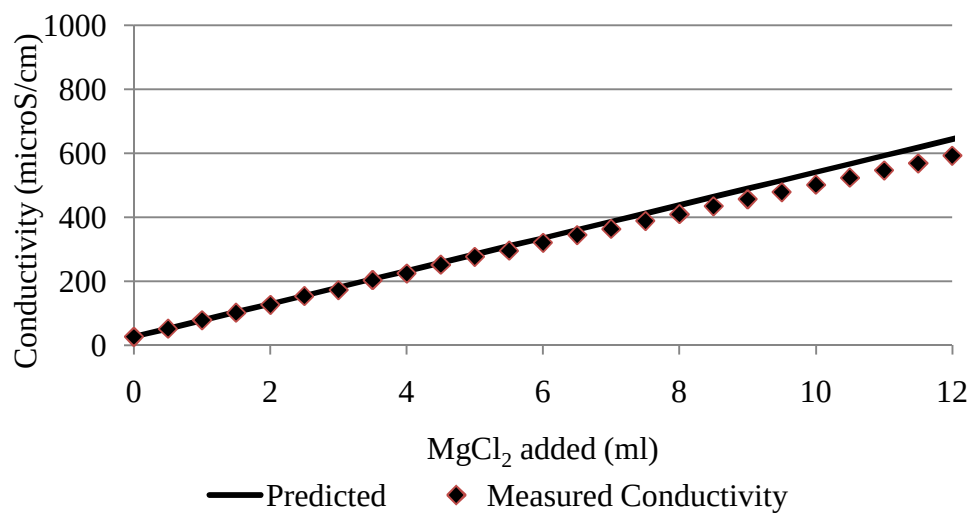
5.11 Prediction of Magnesium Requirements from Conductivity-pH Measurements

Since the quantification of magnesium in the process feed and crystallizer is time consuming, a new detection method was needed, that would be able to provide information regarding magnesium concentrations and application rates in real-time, or at least require little time to provide results. One of the two methods examined in the present study is the use of conductivity and pH to determine magnesium application rates.

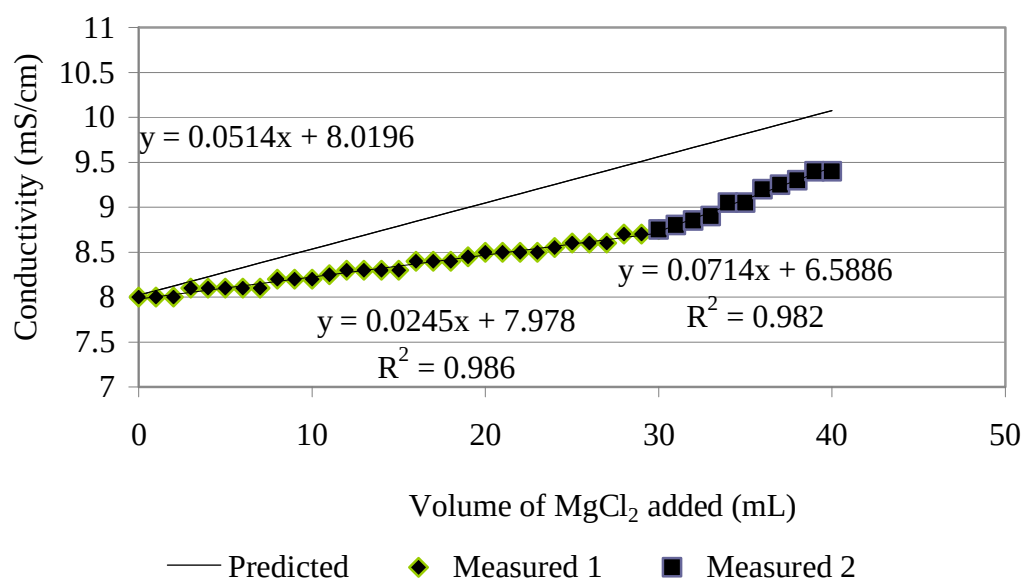
5.11.1 Theoretical versus practical change in conductivity

In the present study, experiments were carried out in the laboratory to predict (using Equation 2.10) the conductivity increase with the addition of external magnesium chloride, and then to compare this value to the actual change in conductivity. As illustrated in Figure 5.22a, the actual conductivity in distilled water could be predicted according to this equation, with a high degree of accuracy. However, when the same principle was used to predict the conductivity increase in real centrate solution, the values did not increase as predicted (Figure 5.22b). This was assumed to be due to the formation of struvite, and removal of other

ions through subsidiary reactions. The initial (Measured 1 in Figure 5.22b) rate of change in conductivity was lower compared to the latter part, indicating that the rate of increase in ionic concentrations was lower. After 30 mL (Measured 2 in Figure 5.22b) of magnesium chloride addition, the rate of conductivity increase changed and became higher than that at the beginning. The location of the increased rate of change was then assumed as the bending/transition point where all phosphate is expected to have precipitated out. The process of locating the bending point is further explained in the following section.



(a)



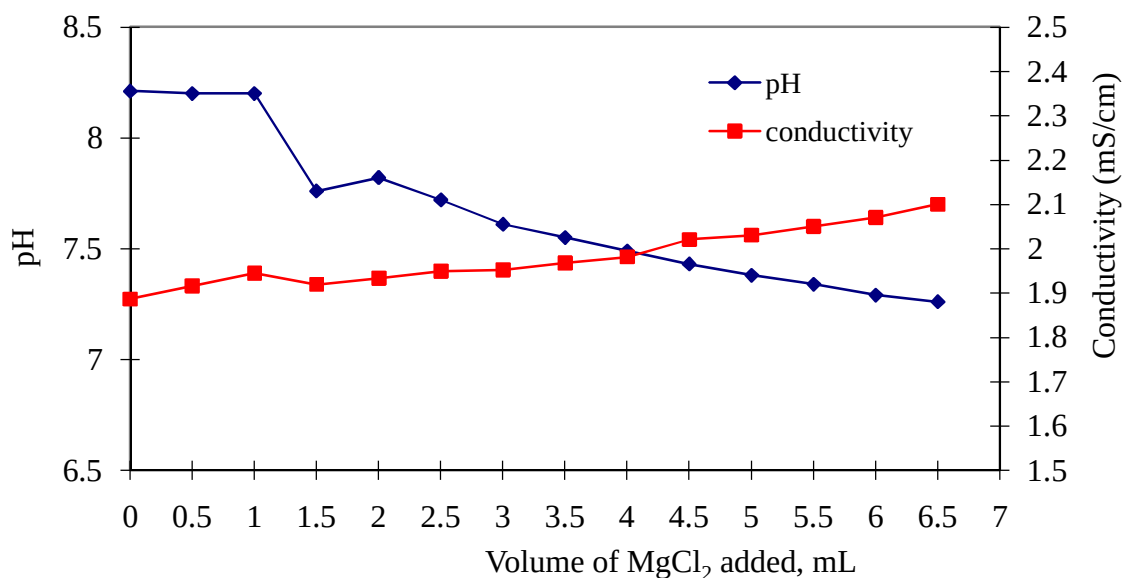
(b)

Figure 5.22. Influence of magnesium chloride addition on the conductivity – (a) predicted vs. measured in distilled water (with no P and N), and (b) predicted vs. measured in centrate sample.

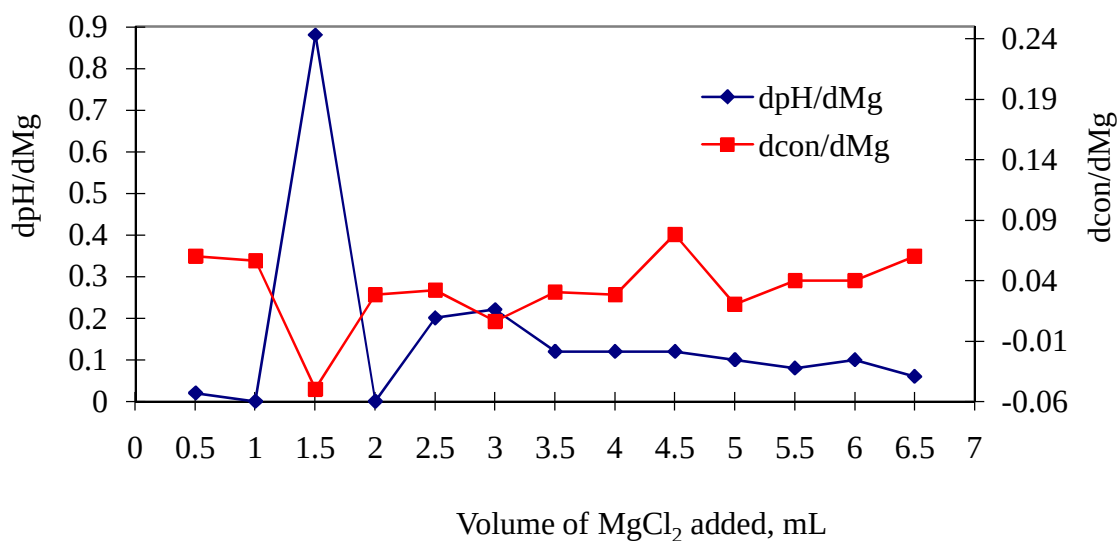
5.11.2 *Experimental runs to determine bending point for magnesium addition*

The objective of this section was to determine the presence-absence of a bending or transition point in the conductivity and pH trends, when magnesium chloride is added to the water matrix.

Figure 5.23 and Figure 5.24 illustrate the influence of magnesium chloride additions on the conductivity and pH in experimental runs with synthetic and LIWWTP centrate. Detailed analytical data are provided in Appendix G. By using the first derivatives of pH and conductivity, a more graphic and ‘easy-to-comprehend’ location of the bending point can be determined. The bending point is the location where the dpH/dMg ratio is highest, while the dcon/dMg ratio is lowest. This corresponds to 1.5 mL of MgCl_2 in Figure 5.23. Figure 5.25 is expanded to provide an explanation of the phenomena occurring, and the method to detect the bending point (which is enhanced in Figure 5.26). In this experiment, three conductivity zones were distinguishable – the initial rapid increase in conductivity, the middle low conductivity rise and a final increased rate of conductivity change. By theory, the slope of the conductivity curve in the final section should be higher than that at the beginning, but as was found from the test, this was not the case. Three zones in the pH-magnesium chloride addition was also noticeable – the initial slow pH change, the rapid pH decrease and the final slow pH decrease. The addition of magnesium chloride to water would normally increase the pH of the system into which it is added. However, since struvite formation is accompanied by lowering of the pH, the end of the middle section was hypothesized as the end of struvite formation. Since the final pH section did not show an increase in pH, as expected, due to continued addition of magnesium chloride, it could be hypothesized that certain reactions, which reduces the pH of the system, were still occurring. The equations shown in the figure are based on linear trend lines of the three distinguishable zones.

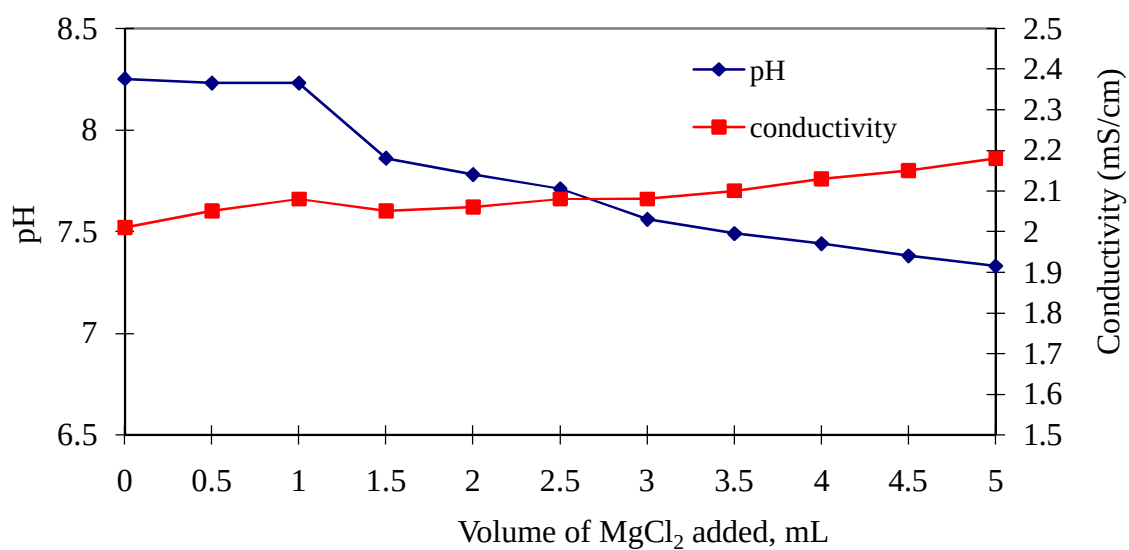


(a)

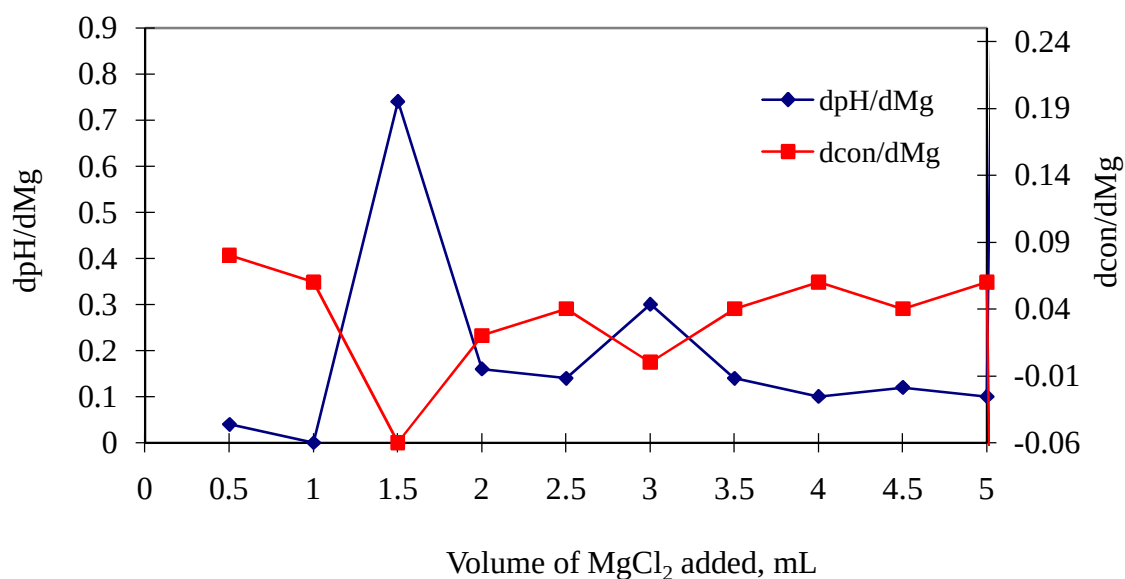


(b)

Figure 5.23. (a) Influence of magnesium chloride addition on pH and conductivity of a synthetic wastewater and (b) change in pH and conductivity as a function of magnesium chloride addition - Run 1.

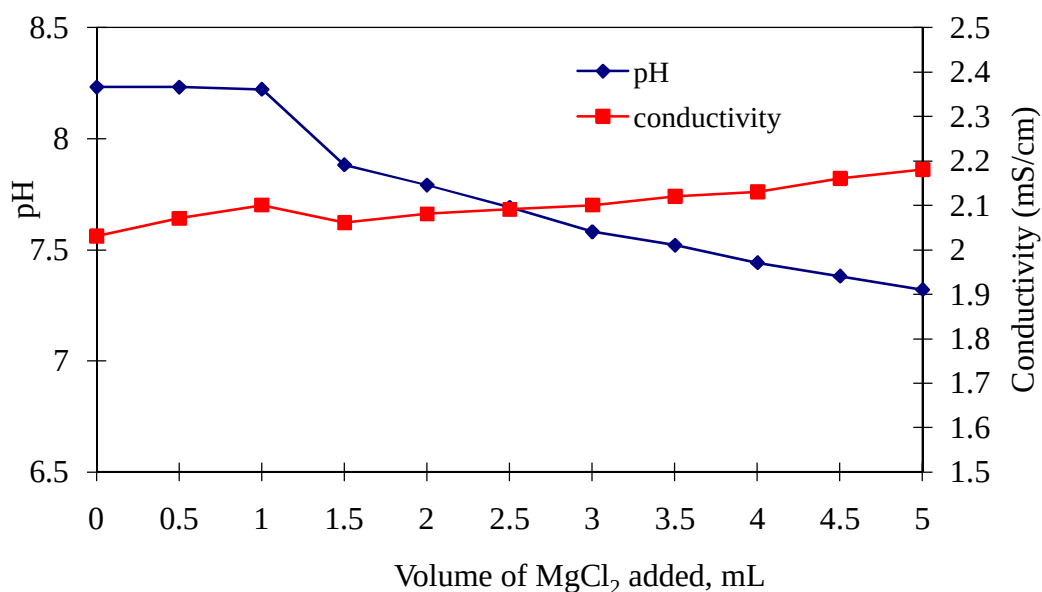


(a)

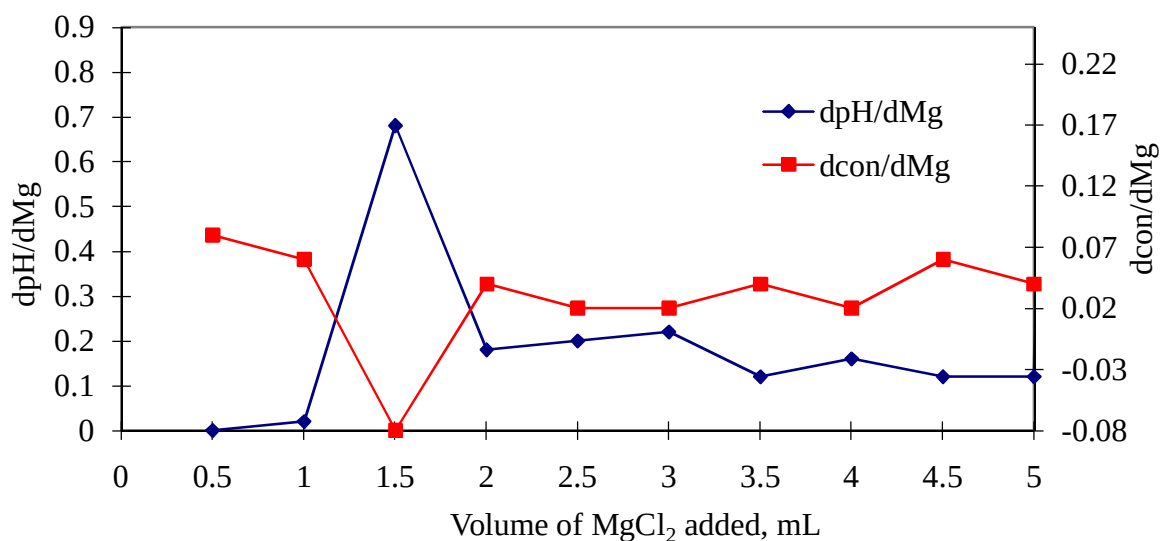


(b)

Figure 5.23. cont'd. (a) Influence of magnesium chloride addition on pH and conductivity of a synthetic wastewater and (b) change in pH and conductivity as a function of magnesium chloride addition - Run 2.



(a)



(b)

Figure 5.23.cont'd. (a) Influence of magnesium chloride addition on pH and conductivity of a synthetic wastewater and (b) change in pH and conductivity as a function of magnesium chloride addition - Run 3.

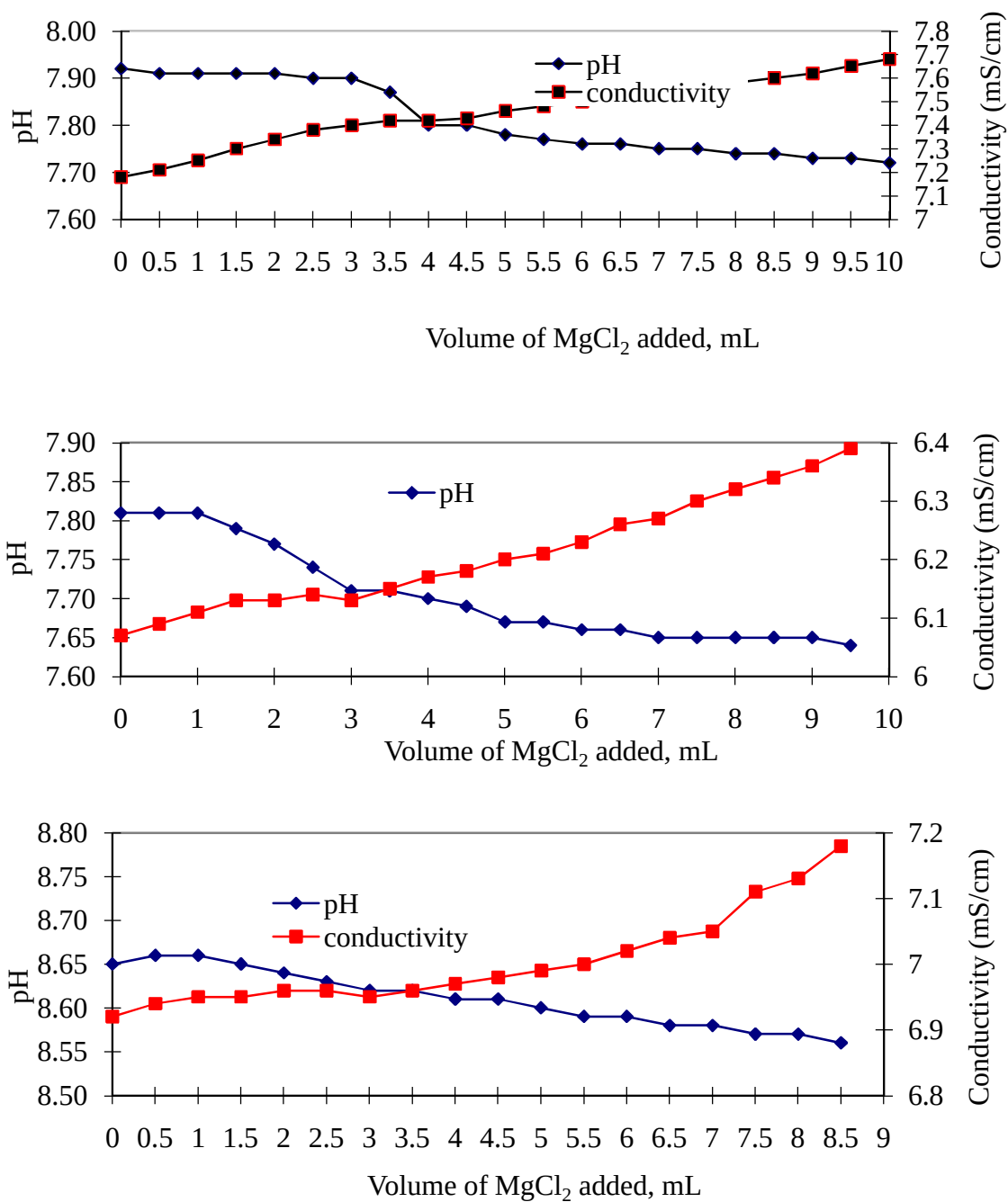


Figure 5.24. Influence of magnesium chloride addition on pH and conductivity in centrate sample for three different runs.

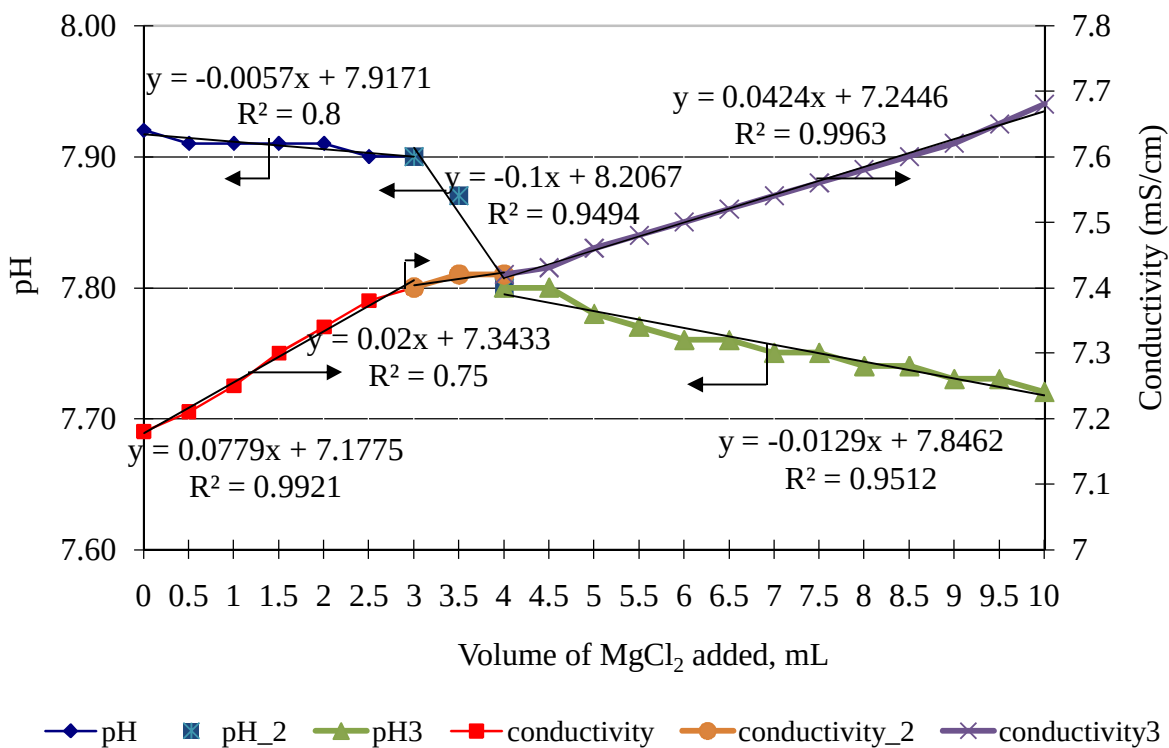


Figure 5.25. Influence of magnesium chloride addition on conductivity and pH of centrate – determination of transition point.

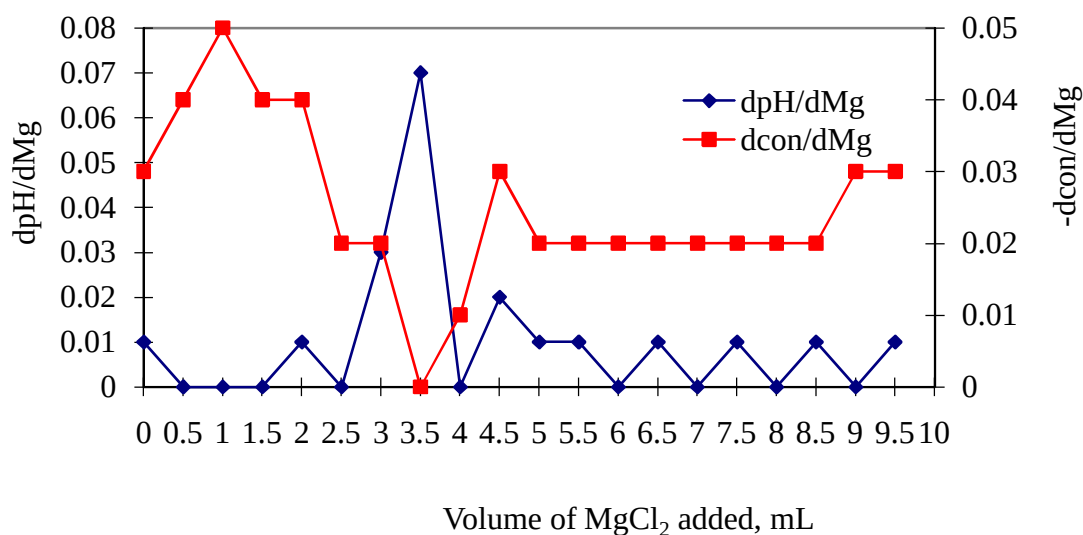


Figure 5.26. Change of pH and conductivity with magnesium chloride addition in centrate matrix. The primary data used is the same as for Figure 5.25.

Several tests were carried out to determine if the process of finding the transition point could be replicated, and each time the same transition location was found. Upon determining the molar concentrations at the bending points, it was found that, for each mole of phosphate removed, the Mg:P molar ratio was between 1.3 and 2.0 (Figure 5.27). This ratio is important, because, although it does not signal the end of the reaction, it determines the quantity of magnesium chloride required to remove one mole of phosphate. By knowing the phosphate concentration through use of online analyzers, the amount of Mg required to completely precipitate phosphate can then be calculated more easily; that is, the phosphate molar concentration would be multiplied by a factor of 1.3-2.0 to get the required magnesium dosages.

Although pure struvite crystallization occurs at a Mg:P molar ratio of 1:1, the Mg:P molar ratio determined here can be explained in terms of the activity and concentration of MgCl_2 in the standard. Normal detection of Mg, by AA, provides values for the total magnesium concentration. However, the portion of the measured Mg that actually takes part in the reaction is represented by the activity of soluble magnesium ion, which, with most ions

concerned with struvite precipitation, is lower than the actual concentration. Therefore, this technique provides a better estimate of the dosages required. Conductivity changes, due to magnesium chloride addition on swine manure slurries by Shepherd *et al.* (2009) found that an inflection point occurred around 50% of the stoichiometric magnesium demand. However, they were unable to use their data to provide any ratio or estimate the rate of magnesium addition that would provide for optimized application.

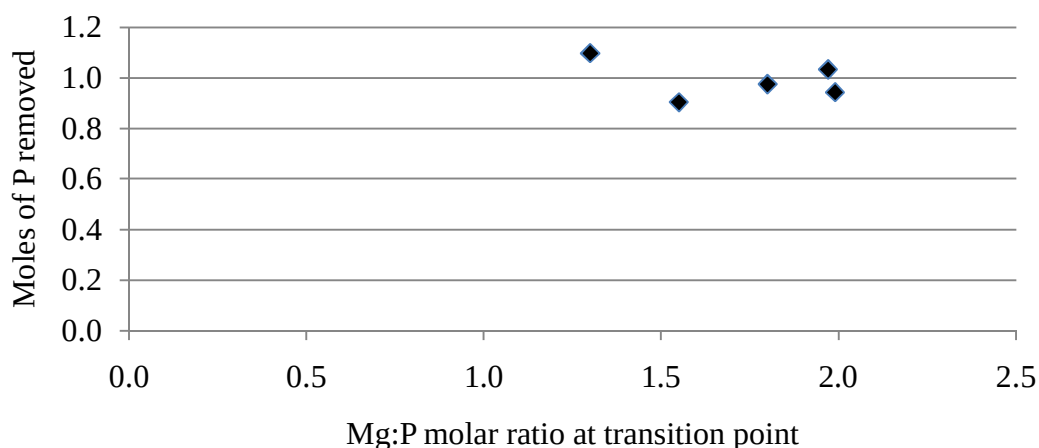


Figure 5.27. Relationship between moles of phosphate removed and Mg:P molar ratio at the transition point.

5.12 Use of Chemicals to Reduce Phosphate Interference

As previously mentioned, for hardness tests, it is important that phosphate concentrations are low enough to reduce interference during the test. Two chemicals – polyaluminum chloride (PAC) and alum - were tested to determine their efficiency in reducing the phosphate concentration to levels that would be acceptable for hardness testing.

5.12.1 Use of polyaluminum chloride (PAC)

Results from multiple tests (data presented in Appendix H) using centrate as working fluid were used to derive an equation that could be used to predict the quantity of PAC

required, given the initial phosphate concentration. Data from these tests were then compared to tests by Forrest (2004) to determine if the method was feasible.

During the present study, the concentration of PAC was lower than that used by Forrest (2004), so that more data points could be obtained within the range below the point of phosphate re-release.

Figure 5.28 illustrates the results of multiple tests, and it was found that the initial removal of phosphate was high and reached an asymptotic curve with 1 ml of PAC addition. In all experiments, PAC additions of more than 1 ml increased the phosphate concentration. However, since phosphate concentrations below 20 mg/L are not known to cause major interference during hardness tests, this method of phosphate reduction can be efficiently conducted. The first two runs produced a linear relationship (Figure 5.28) in the range tested; however, the third run reduced phosphate concentrations more rapidly than the first two. Therefore, the relationship between PAC addition and phosphate removal should be determined for each the water matrix used for struvite crystallization. This linear relationship, once developed, could be applied in subsequent experiments, to determine the amount of PAC required. However, it must be pointed out that the amount of PAC required may be dependent on the total solids present in the water matrix, as some amount will be consumed in reducing the solids.

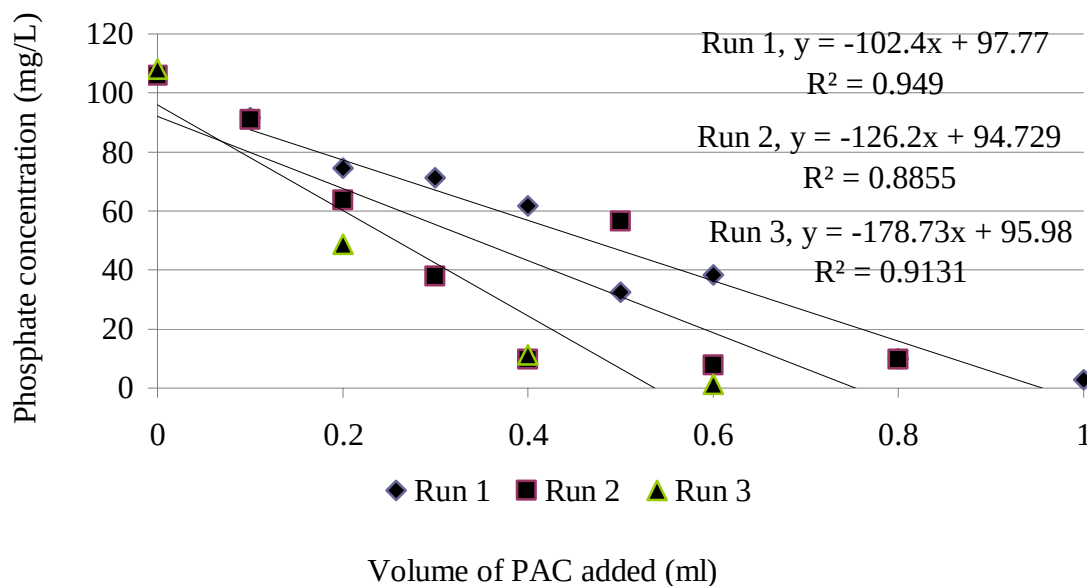


Figure 5.28. Removal of phosphate from centrate with addition of PAC.

5.12.2 Use of alum

Multiple tests were carried out to determine the quantity of standard alum (855 mg/L as Al) to be added to the LIWWTP centrate and to reduce phosphate concentration. The data are presented in Appendix H. The influence of alum addition on phosphate concentration is illustrated in Figure 5.29. The trendline depicts data from several tests carried out in the laboratory. As illustrated, a high linear correlation ($R^2 = 0.9$) was found between phosphate concentration and the volume of standard alum (0.0159 M) added. Given the initial phosphate concentration, this equation (Figure 5.29 for centrate) can now be used in subsequent tests to decide on the amount of alum to be added. In order to predict the applicability of the method with different water matrices, centrate from the Annacis Island wastewater treatment plant (AIWWTP) was also used. Although the two water matrices did not produce the same slope, the rate of phosphate removal was linear in both instances. Therefore, this method can be used for initial testing of new wastewater samples to determine the equation, which can then be used to determine the amount of alum needed to reduce phosphate concentrations.

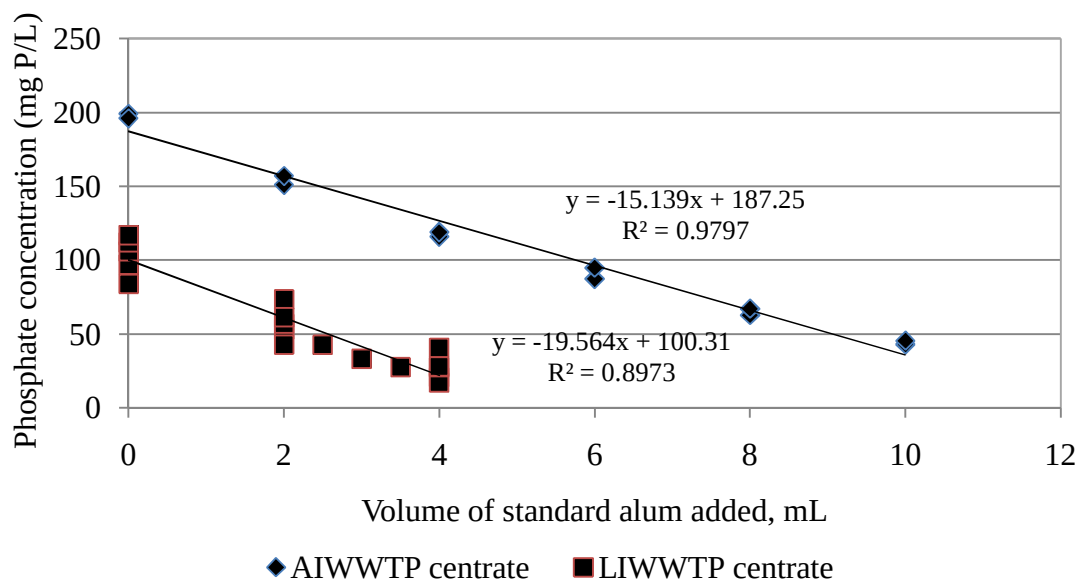


Figure 5.29. Influence of alum on phosphate concentration.

The influence of alum addition on magnesium concentration in the sample was also studied (Figure 5.30) by measuring the concentrations over the range of alum addition. Results showed that there was little influence of adding alum, and so using the chemical as a phosphate precipitator did not lower the magnesium concentration. Although the results indicate that both PAC and alum can efficiently remove phosphate from the water matrix, the final choice of chemical will depend on the availability and choice of the experimenter. In the present study, the use of alum was deemed to be more suitable.

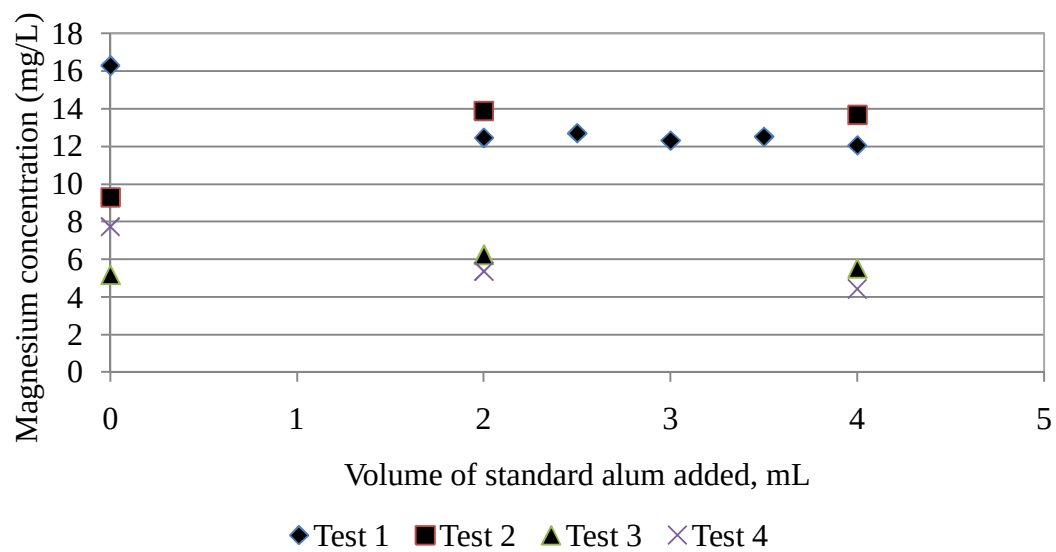


Figure 5.30. Influence of alum addition on magnesium concentration.

5.13 Hardness Test Results

The hardness method for determining the magnesium concentration required the determination of both total hardness and Ca-hardness. The result for calcium detection has been included in this section to illustrate the use and efficiency of the method in determining the concentration of the metal.

From Ca-hardness test, the calcium concentration was calculated and compared with values determined by the AA. Figure 5.31 illustrates that, in most instances, the hardness method gave higher than actual values; the average absolute error in the values was only 3.8 mg/L (15%). Given that hardness test results, by themselves, have limitations (such as in detecting the end point), the predictability of this method was deemed acceptable.

Similar to the calcium values, it was found that, on most occasions, magnesium concentrations determined by the hardness test method were higher than those measured by the AA (Figure 5.32); the absolute average error between the two tests was only 2.0 mg/L (20%). The relatively higher experimental values can probably be attributed to, in addition to titration limitations/errors, the addition of MgCDTA inhibitor during the hardness test. Tests carried out to determine magnesium concentration in a parallel study found an absolute error of 3.9 mg/L (Dirk, B. pers. comm., 2009). Therefore, although not 100% accurate, this method provides a good estimate of the Mg^{+2} concentration in the sample; also the method can be performed on site, and is much quicker and cheaper than AA or ICP. Detailed data for the hardness tests are provided in Appendix I.

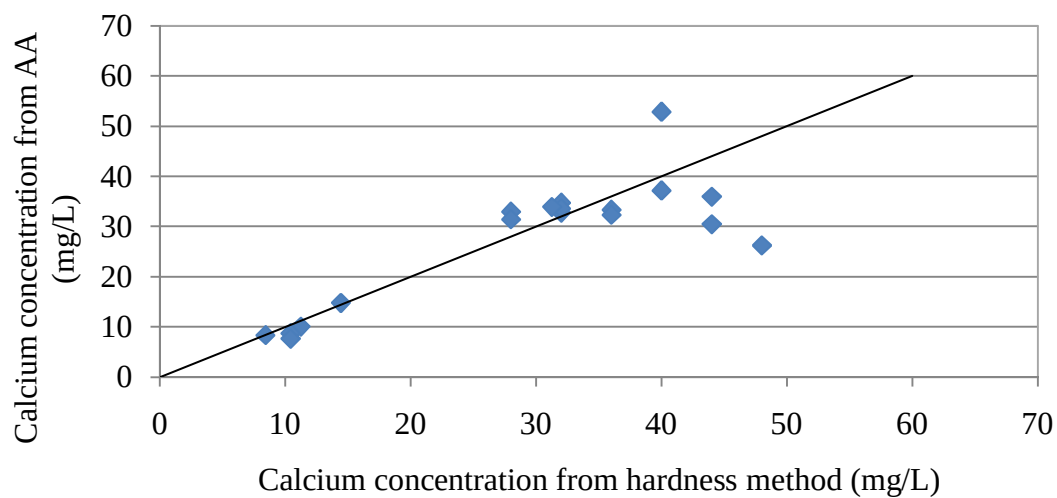


Figure 5.31. Comparison of calcium concentrations via hardness method and AA. The line depicts the equivalence line.

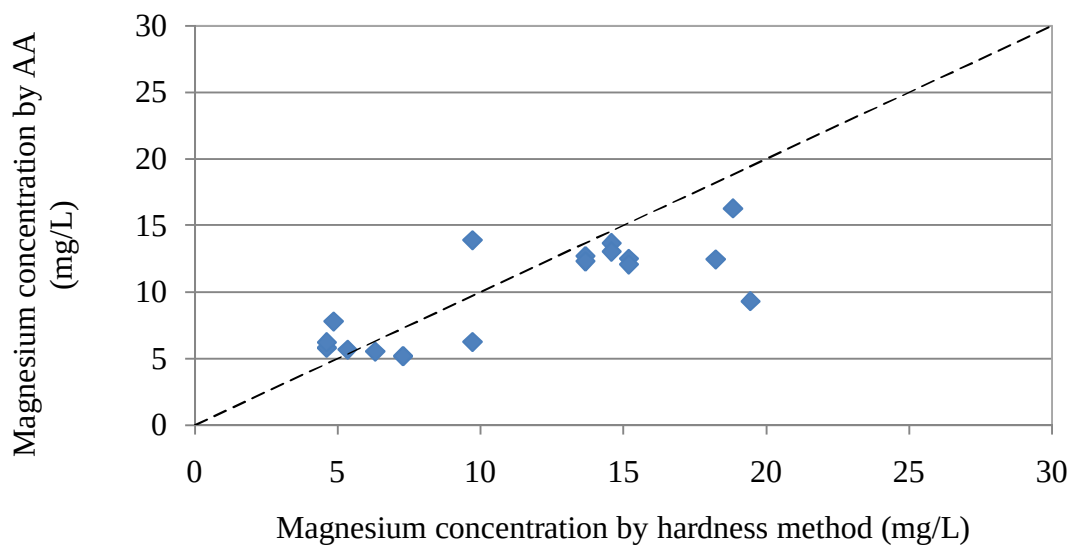


Figure 5.32. Comparison of magnesium concentrations via hardness method and AA. The line depicts the equivalence line.

5.14 Composition of Struvite Formed During Pilot Scale Operation

Struvite formed during the study was tested for various metals, ammonium-nitrogen and phosphate to determine the composition and purity of the product. ICP tests were also performed on certain samples to determine the concentration of heavy metals. It is important to note the heavy metal concentrations, because they may determine whether the struvite product can be used as a fertilizer, either on land or in a nutrient-deficient water body. Previous analysis of struvite from the same location found that the concentrations of heavy metals in the struvite grown were much lower than those present in commercial fertilizers and phosphate ore (Fattah *et al.* 2008b). Struvite harvested from the crystallizer with automated process control was consistently of larger size, and with higher breaking strength than that harvested at the same location in a previous (Fattah *et al.* 2008b) study. Operational data collected during the pilot-scale study at LIWWTP are detailed in Appendix J.

5.14.1 Magnesium to phosphate (Mg:P) molar ratio

Various studies (Fattah *et al.* 2008b; Stratful *et al.* 2001) have determined that the quantity of magnesium in a pellet influences the morphology and purity of the struvite. For pure struvite pellets, the Mg:P molar ratio should be unity; however, as illustrated in Figure 5.33, for all the samples tested, this ratio was lower than unity, inferring that the pellets/solids tested were not 100% struvite; this indicated that other phosphate compounds may be present. It was not possible to test what other compounds may have been present, but studies carried out previously (Bhuiyan *et al.*, 2008) have suggested the presence of calcium phosphate, hydroxyapatite (HAP) and dolomite.

Although the potential for formation of these non-struvite compounds is low at the operating pH of 8.1, the mode of operating the crystallizer, with respect to pH stabilization, may help to explain their presence. At the injection zone, where concentrated caustic is added to the system, the localized pH may be much greater than the set point. This high pH can lead to the utilization of calcium in forming a phosphate compound. By simulating potential for solid formation at different conditions, Bhuiyan *et al.* (2007) found that, at very low Ca:P

ratios, the solution could be supersaturated with dolomite and HAP. It has been suggested that excess magnesium in the reactor can lead to greater phosphate percentage removal (Stratful *et al.* 2001), but via formation of struvite of lower purity (Demeestere *et al.* 2001). Although purity of recovered struvite is important, there are other side benefits (as explained below) of having excess magnesium in the effluent.

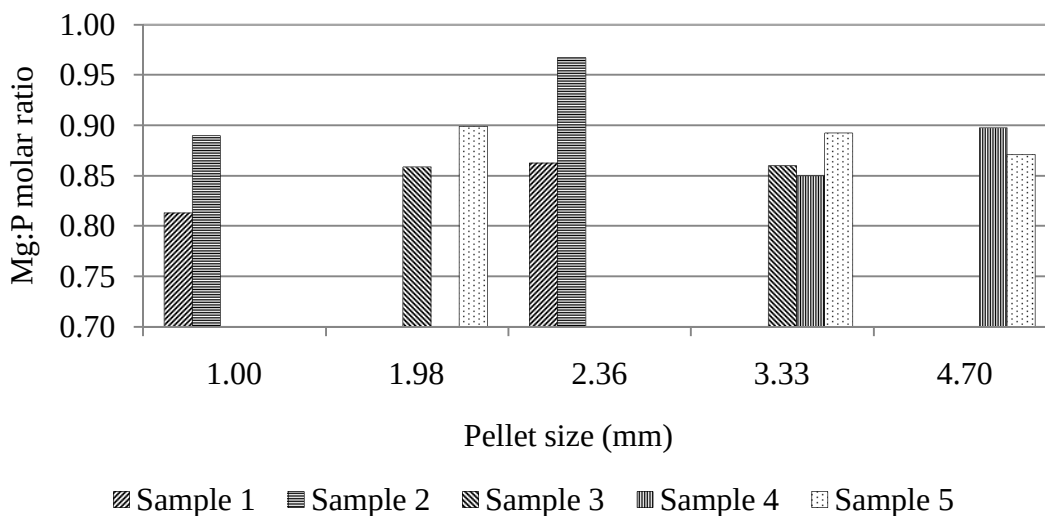


Figure 5.33. Measured magnesium to phosphate molar ratio of struvite samples.

5.14.2 Ammonium-nitrogen (N:P) to phosphate molar ratio

Figure 5.34 illustrates the measured molar ratios of ammonium-N to phosphate in harvested struvite. As was the case with Mg:P molar ratios, the N:P molar ratios are below unity, suggesting again the existence of a phosphate compound that does not contain nitrogen. Possible compounds include, but are not limited to, anapaite $\{\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ and vivianite $\{\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}\}$. The presence of vivianite crystals was confirmed, along with struvite, in the anaerobic digester at the Annacis Island WWTP (Brian Hystad, pers. comm., 2009).

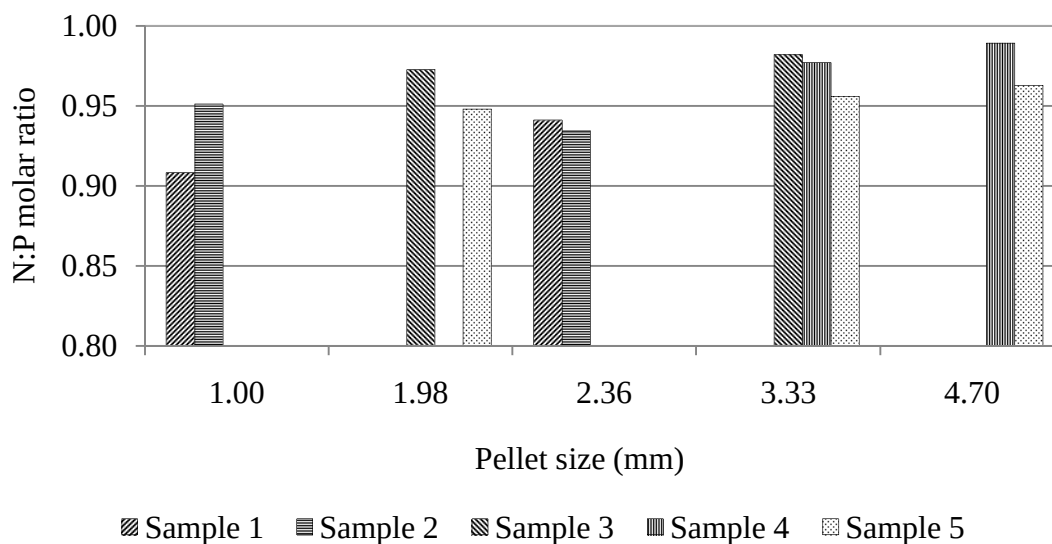


Figure 5.34. Measured ammonium-nitrogen to phosphate molar ratio of struvite samples.

5.14.3 Purity

Although the loss of ammonium from solution could be used as an indication of the amount of struvite precipitated, the purity (% struvite) in the present study was calculated based on the amount of magnesium present in the pellet. The reasoning for this is that there is less magnesium present in the pellet than required to fulfill the ammonium loss conversion to struvite (Mg:N molar ratio is not unity). However, it was assumed that no other magnesium-based phosphates were formed. Overall, based on magnesium concentration alone, the pellets were on average $90 \pm 2\%$ struvite. Table 5.6 provides details of the struvite analyses.

Table 5.6. Composition of struvite formed at LIWWTP

Sample number	Mass of sample (g)	P (mg/L)	N (mg/L)	Mg (mg/L)	Fe (mg/L)	Ca (mg/L)	Molar ratios			% Purity (based on Mg)
							Mg:P	N:P	Ca:Mg	
1	0.209	574	236	366	0.6	0.5	0.813	0.908	0.001	89
2	0.203	536	228	363	0.6	7.1	0.863	0.941	0.012	91
3	0.212	553	238	386	0.6	3.7	0.890	0.951	0.006	93
4	0.206	541	229	411	0.5	4.0	0.967	0.934	0.006	102*
5	0.238	583	242	394	0.5	5.6	0.861	0.916	0.009	85
6	0.209	516	222	344	0.7	9.2	0.851	0.953	0.016	84
7	0.224	580	255	391	1.4	7.5	0.859	0.973	0.012	89
8	0.218	552	245	373	1.5	8.3	0.860	0.982	0.013	87
9	0.213	525	216	357	0.8	9.0	0.866	0.909	0.015	86
10	0.218	560	237	370	0.6	7.7	0.840	0.935	0.013	87
11	0.212	539	238	359	1.6	7.6	0.850	0.977	0.013	87
12	0.209	530	237	373	1.5	5.8	0.897	0.989	0.009	91
13	0.207	550	237	360	1.4	15.5	0.835	0.953	0.026	89
14	0.203	529	229	358	1.2	6.9	0.861	0.958	0.012	90
15	0.214	562	244	369	1.6	5.3	0.837	0.960	0.009	88
16	0.205	550	239	368	1.7	5.2	0.853	0.961	0.008	91
17	0.135	364	156	257	1.1	15.2	0.899	0.948	0.036	97
18	0.200	516	223	361	1.4	8.3	0.892	0.956	0.014	92
19	0.222	563	245	385	1.5	7.7	0.871	0.963	0.012	88
Average							0.867	0.951	0.008	90
95 % confidence							± 0.02	± 0.01	± 0.00	± 2

*Possible analytical error

5.14.4 Shell formation – composition, SEM pictures

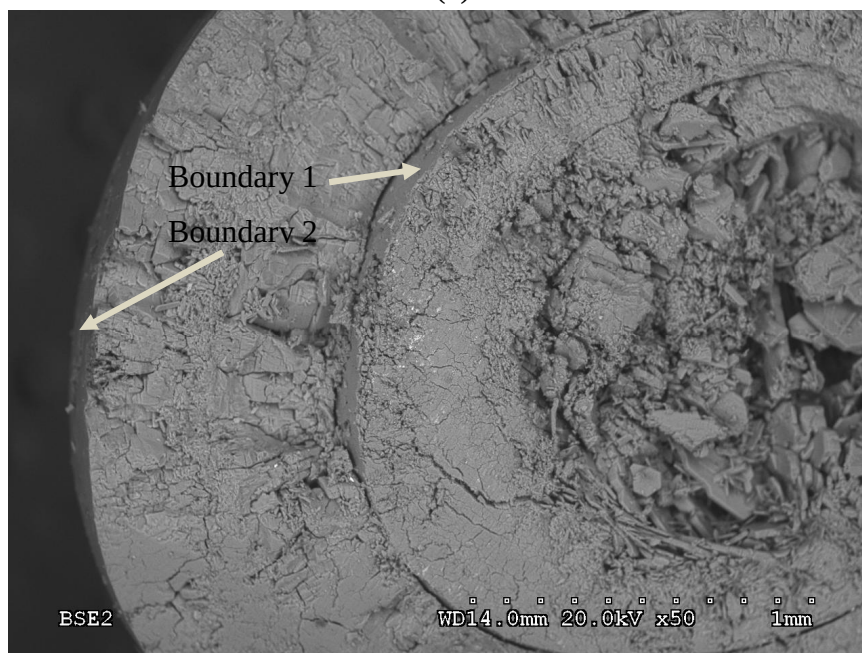
During one harvest of struvite, pellets with a distinct outer shell were formed (Figure 5.35). Visual inspection of these pellets showed that they had one dense inner part similar to other harvests, while a second outer shell was coated on top of the inner crystal. SEM pictures (Figure 5.35b) confirmed the two-layer structure, with a definite boundary between the two layers. However, the inner core was not as fused as the rest of the pellet. Although a detailed explanation could not be provided, it was thought that this abnormality may be due to changes in the operating conditions. During the few days preceding the harvest, the reactor SSR fluctuated considerably due to pH pump-related problems, resulting in an unstable reactor pH. In addition, the suspended solids content in the centrate was also very high during this period; normal total suspended solids (TSS) content in the centrate ranged from 600-800 mg/L, but during this particular event, the TSS increased to as high as 2500 mg/L. These fluctuations may have caused the inner pellet to act as a seed for the outer shell, hence showing the importance of operational stability, with respect to the growth of good quality pellets. In terms of composition, the two layers did not show significant variation (Table 5.7). The practical consequence of this shell-structured struvite pellets is explained in Section 5.16.5.

Table 5.7. Composition of shell-structured struvite pellet

	Mg:P	N:P
Inner part	0.861	0.916
Exterior shell	0.857	0.912



(a)



(b)

Figure 5.35. Shell formation of pellets (a) actual struvite and (b) SEM picture taken at x 50 magnification.

5.14.5 Compactness of struvite pellets

The compactness of struvite pellets was determined through SEM imagery (Figure 5.36). Figure 5.36a also shows the fusing of crystals in the pellet. It was observed that the compactness of the pellets was “different”, and depended on factors such as size and upflow velocity. Struvite crystals, which have a negative zeta potential in the pH ranges suitable for phosphorus recovery, tend to repel each other (Le Corre *et al.* 2007). It was found that metal salts, such as alum and ferric chloride, and cationic polymers, were efficient in growing struvite flocs. Although the probability of excess magnesium chloride in the reactor acting as a binding agent could not be determined conclusively, it is postulated that it may act as a destabilization agent in reducing the zeta potential of struvite crystals. This reduction in zeta potential would allow individual struvite crystals to come into contact with each other and allow increased compactness, and therefore density. The practical importance of this variety of struvite pellet is that they will contain greater nutrient per unit volume, and therefore reduce the space required for transportation and storage.

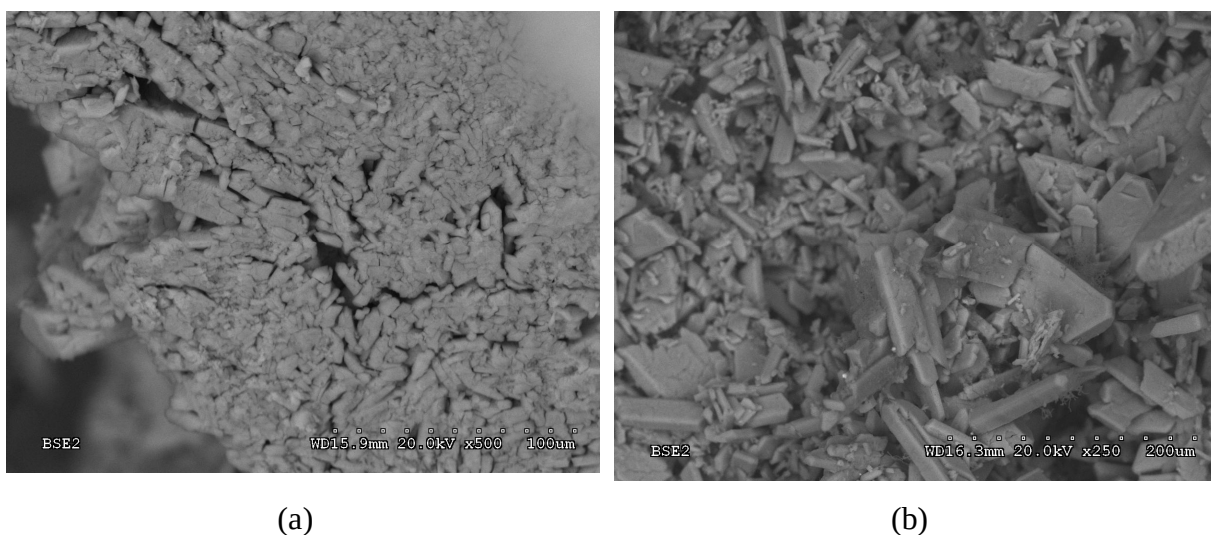


Figure 5.36. SEM pictures of struvite pellets: (a) illustrating the fusing of struvite crystals (500 magnification) and (b) compactness of the crystals (at 250 magnification).

5.14.6 Influence of upflow velocity on compactness

Higher flow, in a fully loaded crystallizer, allows for greater impacts and collisions between pellets, which, in turn, can be responsible for the compactness of the solids. A fully loaded crystallizer, that is, a crystallizer in which each section is filled with fluidized struvite pellets, can also allow individual crystals to come in close contact with each other, leading to higher collisions and agglomeration, or growth, of the particles. However, based on practical experience, there seems to be an upper limit to upflow velocity at which a crystallizer should be operated at, in order to produce good quality pellets. The present study operated the crystallizers at mainly two upflow velocities – 400 cm/min and 500 cm/min. An upper limit of 400 cm/min upflow velocity was found to be “efficient” for the crystallizer used. Operating the process at 500 cm/min caused too many strong inter-particle collisions that resulted in the formation of broken pellets. These broken pellets destroy the shape and reduce the crushing strength of the pellets, hence reducing the marketability of this product. Upflow velocity is discussed further in Section 5.15.2.

5.14.7 Struvite composition for presence of heavy metals

Struvite pellets were also analyzed, using inductively coupled plasma – mass spectrometry (ICP-MS), to determine the presence/absence of metals. The quantification of the metals is very important because it will ultimately determine if the product can be used as a fertilizer. The concentrations of some of the major metals of concern are given in Table 5.8. Detailed analytical composition is provided in Appendix K. Comparing the metal contents in the struvite formed in the present study to those found in literature, it can be seen that the those harvested at the LIWWTP is much richer (having higher percentages of constituent elements) in terms of quality. Therefore, from a heavy metal content perspective, the use of struvite formed at this treatment plant may not pose any health concerns, or at least have lower concerns than fertilizer formed from phosphate ore. However, it must be mentioned that the quality of struvite in Table 5.8 may not be representative of struvite grown at other treatment plants; similar analyses need to be conducted to determine suitability of the product for use as a local fertilizer. As mentioned above, calcium phosphate compounds are most likely to be present, in addition to struvite, in a pellet. The data show that, although little

(0.2%) calcium is present in the struvite pellet formed, part or all of calcium may be present as phosphate compounds.

Table 5.8. Concentration of heavy metals found in struvite pellets formed at LIWWTP and in nature

Element	Present study ^a (ppm)	Morocco ^b P-rocks (ppm)	Geestmerambacht ^b Ca ₃ (PO ₄) ₂ (ppm)
Aluminum (Al)	< 0.01 (as %)	200	950
Arsenic (As)	0.3	5	2
Cadmium (Cd)	< 0.01	40	<6
Calcium (Ca)	0.2 (as %)		
Copper (Cu)	5.3	23	17
Chromium (Cr)	4.2	357	8
Iron (Fe)	< 0.04 (as %)	1600	1260
Lead (Pb)	0.6		
Lithium (Li)	0.4		
Manganese (Mn)	236	10	560
Mercury	< 0.01		
Nickel (Ni)	0.32	67	8
Sodium (Na)	0.01 (as %)	1700	360
Tin (Ti)	9.1	108	8
Uranium	< 0.05		
Zinc (Zn)	4	880	310

^a Value indicates the average of six samples

^b values given in Jeanmaire (2001).

5.15 Influence of Parameters on Physical Structure of Struvite Pellets

In crystallization kinetics, two phases are generally considered – nucleation and growth. The increase in pellet size is a result of growth occurring due to the assimilation of ions in the lattice structure, established by the crystal embryo foundation (Ohlinger *et al.* 1999). Mass

transport from solution to the crystal surface and incorporation of material into a crystal lattice are two processes that dictate the growth of crystals. Among the various parameters that influence the particle size in a fluidized bed reactor, SSR, magnesium concentration in the reactor and fluid dynamics are among the most important (Fattah *et al.* 2008b) and will be discussed further.

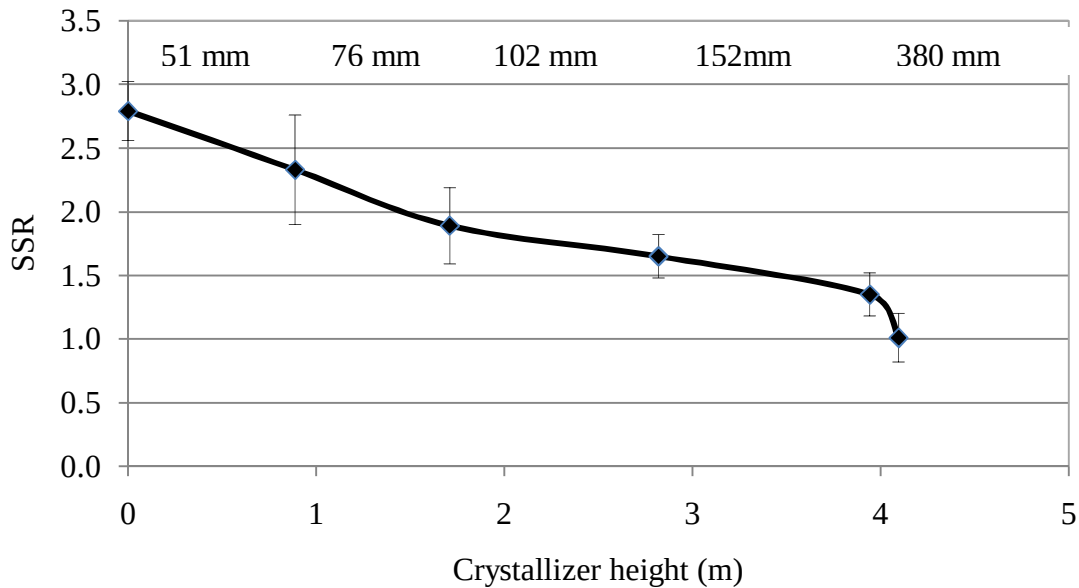
5.15.1 Possible influence of crystallizer supersaturation ratio

In a parallel study, Bhuiyan *et al.* (2007) suggested that, at high supersaturation ratios, the growth of smaller crystals was faster than that of larger ones. In addition to SSR, the growth of larger pellets is also strongly influenced by the upflow (fluidization) velocity, as discussed below. During the present study, it was determined visually that low reactor SSR (around 2.0) did not significantly reduce the size (around 3-5 mm) of pellets formed, as long as they were fluidized and the upflow velocity was in the range that provided collision-adherence of the particles, but not breakage.

Figure 5.37 illustrates a typical SSR profiling of UBC's second generation crystallizer. The difference between this crystallizer and the system used in the present study is that the former has six sections as opposed to five sections. Since the headspace in the pilot-scale setup in the present study was very low, it was not possible to sample inside the crystallizer and develop a profile of the SSR. However, the sections of the two reactors were approximately the same, and hence the data were used in this section to provide an explanation of the SSR impact on size and shape of struvite pellets formed. The objective of this section was to show, qualitatively, how the sectioning of the crystallizer used in the present study could be related to the growth of struvite pellets.

In the present study, the initial or starting SSR was higher in the injection zone than in the seed hopper (measured from effluent characteristics). Therefore, it can be assumed that the SSR decrease, as the water flows from the bottom to the top of the crystallizer. Therefore, it is reasonable to assume that, in the bottom section of the crystallizer, which has higher SSR and upflow velocity, tiny crystals are formed that are whisked away almost immediately to the top of the crystallizer; here the SSR and upflow velocity are lower and allow

agglomeration and growth of the pellets. Figure 5.38 illustrates the possible mechanism of pellet growth – from individual crystals that become fused, to being agglomerated into larger pellets with a smooth surface. Struvite pellets grown in the crystallizer with instrumentation and control (R #2) at the pilot-scale were measured for size with a scale and digital caliper. As illustrated in Figure 5.39, pellets as large as 6mm and above were consistently found.



Dimensions at the top indicate the crystallizer section diameter

Figure 5.37. Typical SSR profiling in UBC's crystallizer with crystallizer height (adapted from Forrest, 2004).

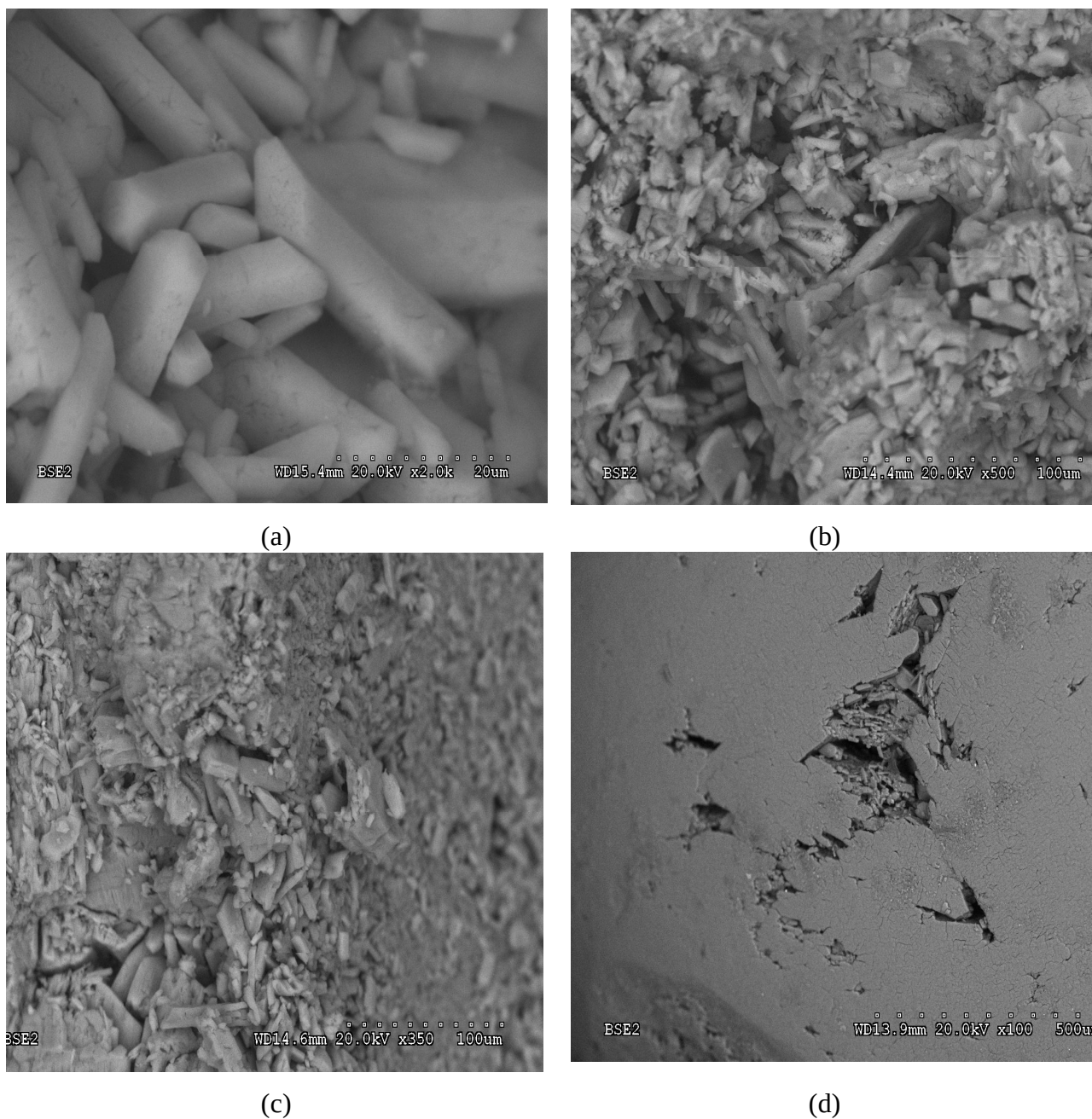


Figure 5.38. Formation of struvite pellets: individual crystals at (a) 2000 X magnification and (b) 500 X magnification, (c) agglomeration of crystals at 350 X magnification, (d) fused and smooth outer surface of pellet at 100 X magnification.



Figure 5.39. Struvite pellets harvested at LIWWTP in crystallizer with instrumentation.

5.15.2 Upflow velocity

Omar and Ulrich (2003) suggested that fluid dynamics has a great effect on the growth of particles in a fluidized bed reactor, with higher velocities resulting in higher mass transfer and consequently, bigger pellet size. A previous study (Fattah *et al.* 2008b) determined that an upflow velocity of about 400 cm/min was high enough to remove and recover phosphate, with a high degree of efficiency. During the course of the present study, the reactors were operated at a steady 400 cm/min upflow velocity. This value was increased to 500 cm/min to determine if upflow velocity had any effect on the quality of struvite pellets formed and to increase the treatment capacity of the reactors. Samples collected during the increased flow conditions were found to have broken structures – parts were missing from the parent pellet

(Figure 5.40). This could imply that agglomeration of crystals, resulting from collisions between particles, was overcome by destructive, colliding forces due to the higher upflow velocity. Therefore, there is a maximum upflow velocity that a crystallizer should be operated, in order to have good quality harvest. Upflow velocity also plays an important role in the operation of the process as it determines the mass loading of the reactor. As such, this operating limit should be confirmed at each full-scale installation.



Figure 5.40. Breakage of struvite pellets possibly due to high upflow velocity.

5.15.3 Flow patterns in the crystallizer

The development of struvite pellets can be described as a two-phase phenomenon – the formation of pure struvite crystals (nucleation) and the agglomeration, or growth, of these crystals through physical collision and particle bridging (Ohlinger *et al.* 1999). Previous pellets grown with the same crystallizer were mostly spherical in shape. However, during one episode of the operation, when part of the reactor was clogged due to struvite accumulation

(both by pellets and formation of a layer of struvite on the sides of the reactor), elongated pellets were formed (Figure 5.41a). This was attributed to the variation of hydrodynamics within the reactor and the existence of dead zones. The fluid hydrodynamics in such a system is important because it determines the local solids and ionic concentrations, mixing energies and the rate and intensity of particle collisions. Struvite pellets grown in Ostara's (Ostara Nutrient, Ltd.) reactors tend to be less spherical in nature (Figure 5.41b). One of the reasons for this may be the higher diameter to height ratio, producing a flow pattern that does not allow sufficient collisions and grinding/polishing of pellets. However, this hypothesis could not be verified in the present study.



(a)



(b)

Figure 5.41. (a) Elongated pellets possibly formed due to flow restrictions in the crystallizer and (b) pellets from Ostara's reactor.

5.16 Influence of Parameters on Crushing Strength of Struvite Pellets

Variations in the crushing strength of struvite pellets (Table 5.19 and 5.10) grown in the crystallizer show that they are strongly influenced by process parameters. In the present study, although detailed experiments were not possible to determine the exact impact of these parameters on the crushing strength, based on the observations and analytical data obtained during the pilot-scale operation of the two crystallizers, some probable relationships have been suggested. These relationships provide the background for further studies. Variations of size, shape and orientation of flaws, such as pores and defects, may result in differences in the crushing strengths of harvested pellets. The formations of fine crystals that fuse together, to form a tight internal structure, were probably what provided the high strength of struvite pellets formed in the present study. Although mechanical compaction can increase crushing strength, it can result in the formation of smaller pellet sizes. The following discussion is based on struvite formed in both crystallizers.

5.16.1 Influence of size on strength

Figure 5.42 illustrates the relationship between size of pellets and crushing strength. The crushing strength data are based on strengths obtained from crushing 100 or more pellets of each category. The strength initially increased with increase in the size of the pellets (till 2.5 mm); pellets in the 2.0-2.5 mm range had the greatest strengths. In a compression study using nitrogen-phosphorus-potassium (NPK) fertilizers, Walker *et al.*, (1997) found that, in the size range (2 mm to 4 mm) tested, the mechanical crush strength of granular fertilizer was linearly related to the increase in size of fertilizer granules. However, in the present study, beyond the 2.5 mm pellet size, the strength showed a decreasing pattern. This could be related to the lower denser structure found for larger pellets than for smaller ones. The consequence of this information is that, when larger and stronger pellets are required, it may be necessary to harden the outside of the pellet with other coating material, or soak the pellets in a liquid that will fill the inner pores of the pellets and provide higher crushing strength. The numerical crushing strength value also provides valuable information that can be used when the struvite is to be machine spread as fertilizer.

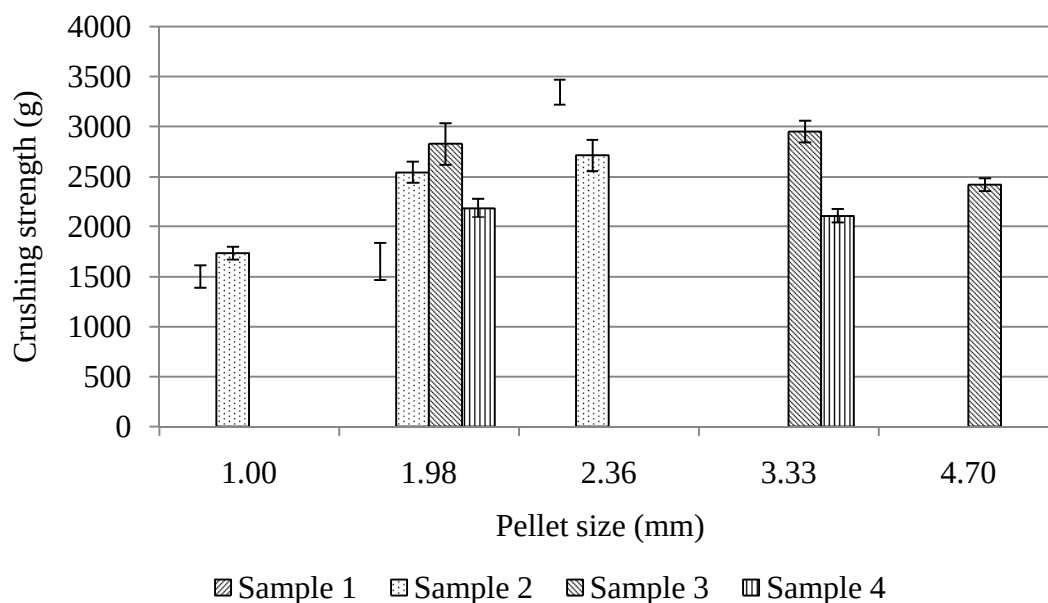


Figure 5.42. Influence of pellet size on crushing strength. Error bars: 95% confidence interval.

5.16.2 Influence of struvite composition on strength

Several samples of struvite were tested for their crushing strength and analyzed for composition. As illustrated in

Figure 5.43, the Mg:P molar ratio was not 1:1 at the highest strength, indicating that the strongest struvite pellet may contain material that is not struvite in nature, but one that has a higher crushing strength. However, it was not possible to isolate the compound(s) that may lead to the stronger pellets. Similar to the Mg:P molar ratio, the strongest struvite pellets were not 100% pure, with respect to the N:P molar ratio (Figure 5.44). However, the ratio is higher than the Mg:P molar ratio. Detailed analytical data are provided in Appendix L.

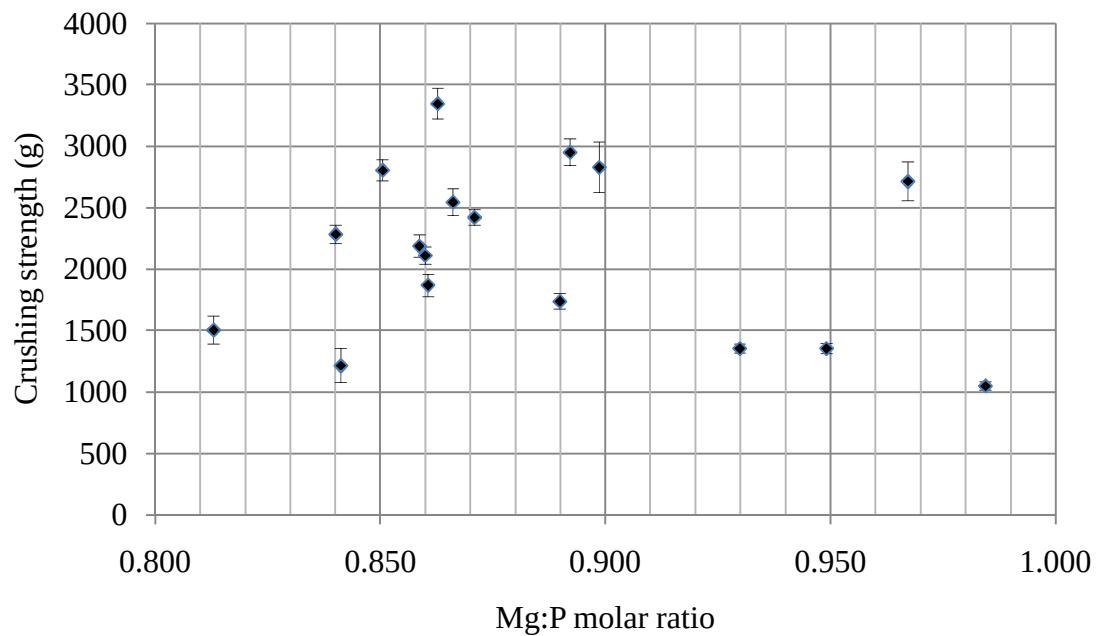


Figure 5.43. Relationship between Mg:P molar ratio and the crushing strength of struvite pellet. Error bars: 95% confidence interval.

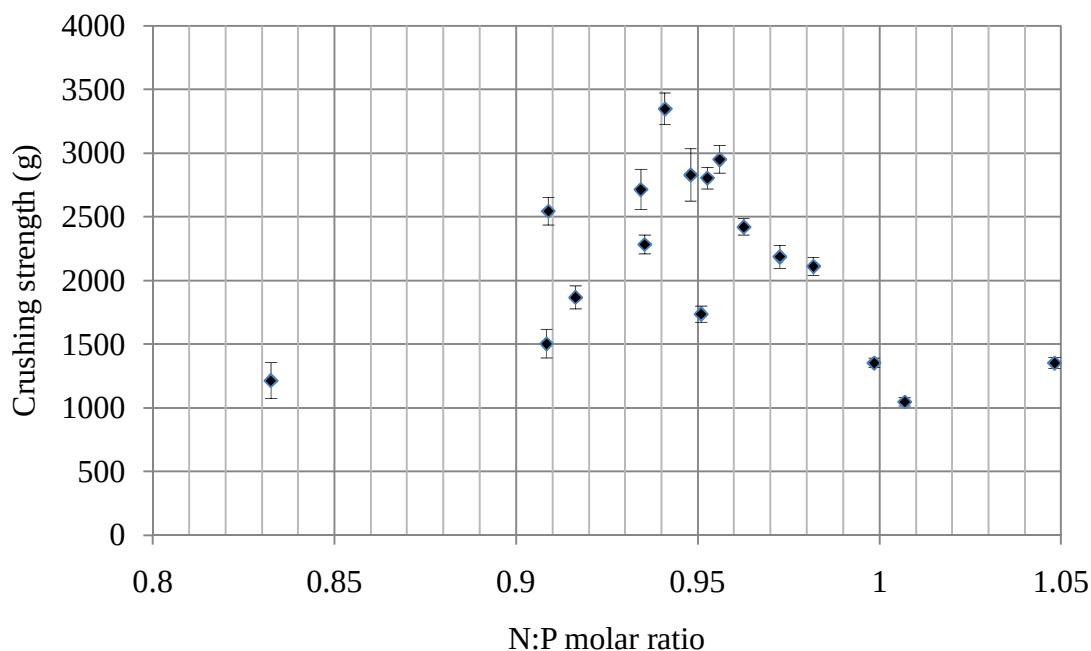


Figure 5.44. Relationship between N:P molar ratio and the crushing strength of struvite pellet. Error bars: 95% confidence interval.

5.16.3 Influence of SSR on strength

Various studies (Fattah *et al.* 2008b; Forrest *et al.* 2008a; Britton *et al.* 2005; Adnan *et al.* 2003; Ohlinger *et al.* 1998) have indicated the use of SSR as a control parameter in the removal- recovery of phosphorus from wastewater. However, there is little information on how this parameter affects the composition and quality of the product. In the range (1.5 – 7.1) covered in the present study, SSR did not appear to affect the crushing strength of struvite pellets. It is probable that the struvite pellets grow according to the SSR (as mentioned previously) and once formed, they maintain their integrity, as long as the SSR is above unity. Table 5.9 provides some evidence to support this hypothesis. The SSR value given in Table 5.9 was the actual value in the harvest section of the crystallizer (R#2) when the pellets, whose crushing strengths are given, were harvested. Although SSR does not have a huge impact on strength, it is critical to control the parameter in the crystallizer during the initial agglomeration process. Also, it is essential to maintain a profile similar to Figure 5.37

to produce a good quality product – with a high SSR in the bottom of the reactor, which then decreases in the top sections.

Table 5.9. Influence of SSR on crushing strength

SSR	Crushing Strength (g)
1.46	2460 ± 120
1.62	2640 ± 90
3.36	2660 ± 160
7.11	2340 ± 80

5.16.4 Influence of reactor magnesium concentration on strength

Although previous studies (Fattah *et al.* 2008b; Mavinic *et al.* 2007) hypothesized that the magnesium content in the crystallizer influences the quality of struvite pellets, no data were provided to support the theory. In the present study, magnesium concentrations in the crystallizer were correlated to the breaking strength of struvite (Table 5.10). An increase of 15% – 27% in crushing strengths were determined in the present study due to an increase of 7% (22.5 to 24.1 mg/L) and 132% (19 – 44 mg/L) of excess magnesium concentration in the crystallizer, respectively. Based on the data, it is possible that higher Mg concentrations may have been responsible for higher strengths. The hypothesis that magnesium concentration can influence crushing strength is backed by the fertilizer industry, which uses, among other things, magnesium sulphate to granulize mineral fertilizer pellets in order to develop larger and stronger material. It is important to note that the upflow velocities, when the samples were taken, were similar, to negate its influence. The average magnesium concentration in Table 5.10 represents the expected Mg concentration in the harvest zone of the crystallizer, based on the average of two days' concentration before the pellets were harvested. This value was calculated to allow for the fact that the pellets may not have grown in a day, and may have been exposed to this concentration before being harvested.

Table 5.10. Influence of reactor magnesium concentration on crushing strength of struvite

	Average* Mg concentration (mg/L)	Mg concentration on day of harvest (mg/L)	Strength (g)
System 1 (R #1; without instrumentation and control)	22.5 24.1	11.7 18.1	2145 ± 55 2460 ± 120
System 2 (R # 2; with instrumentation and control)	19.0 44.0	16.7 43.7	2637 ± 90 3345 ± 124

* Preceding two days before harvest

Error at 95% confidence interval.

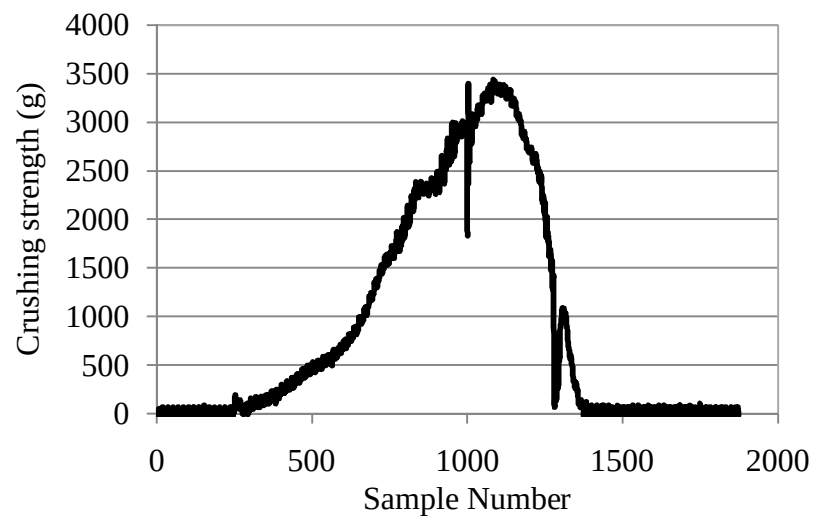
5.16.5 Shell formation and two peak strength

As mentioned previously, struvite with an outer shell also formed in this study. These pellets were tested for crushing strength and, unlike single pellets (Figure 5.45 a and b), these pellets did not have a distinct strength peak (Figure 5.45 c and d). The first peak corresponds to the breakage of the outer shell, while the second peak corresponds to the inner pellet. Given the higher crushing strength and compactness of the outer shell, the major implication of this pellet strength is that, if used with a mechanical spreader, there may be less loss of the material. Concurrently, when placed in a water matrix, the inner part, which had a lower dense structure and had lower crushing strength, may dissolve faster.

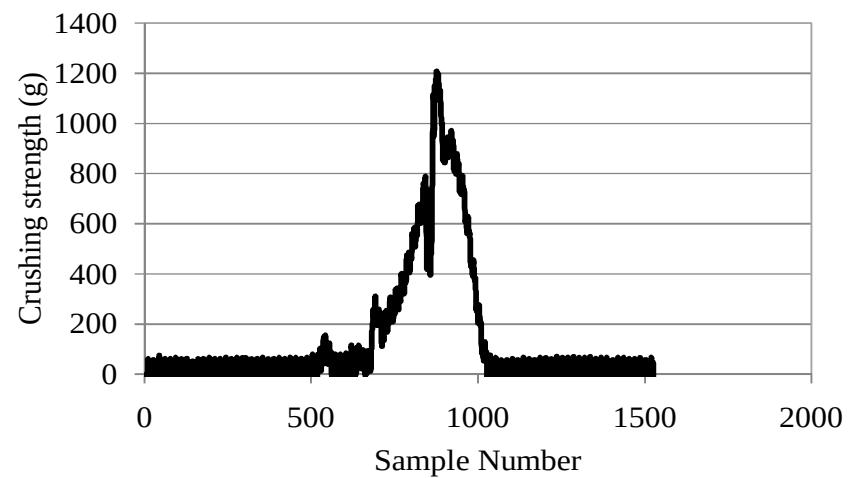
5.16.6 Conclusions on struvite quality

The composition of pellets is important and needs to be verified before being applied as a fertilizer. The product formed at LIWWTP had good struvite purity (in terms of magnesium content) and contained much lower heavy metals concentration than those found in ores used as a source of phosphate. The physical quality of the pellets formed is important for a number of reasons, such as, ease of transportability and applicability, lower loss of material and release rates. Pellets grown in the present study were as large as 6 mm; this size is among the largest formed from domestic wastewater. Supersaturation ratio and upflow velocity in the

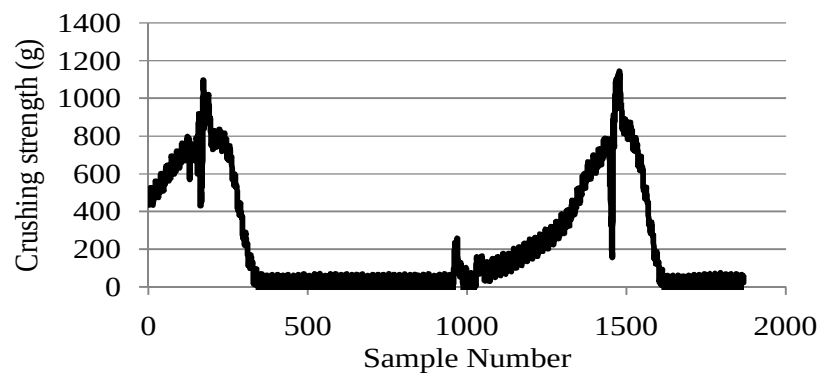
crystallizer were found to influence the size and shape of the pellets developed. Crushing strengths of struvite pellets were correlated to the size and composition of struvite, the reactor magnesium concentration and supersaturation ratio.



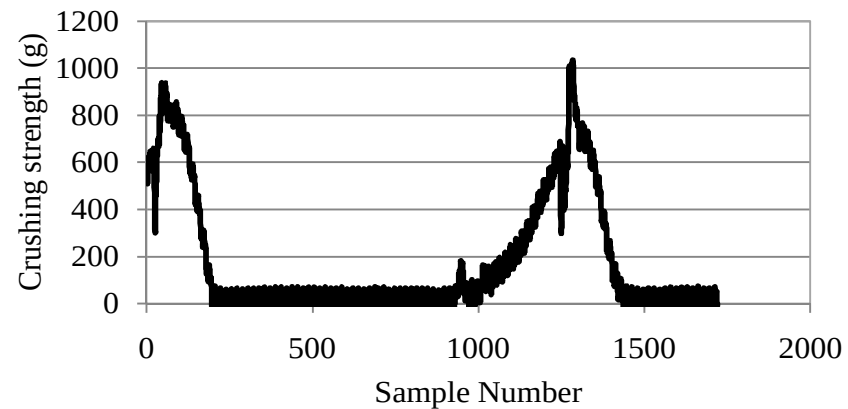
(a)



(b)



(c)



(d)

Figure 5.45. Crushing strength graphs showing formation of single peaks {(a) and (b)} for normal pellets and dual peaks for pellets with shell-structure {(c) and (d)}.

CHAPTER SIX: CONCLUSIONS

Based on experience in operating two struvite crystallization processes at the pilot-scale setup at Lulu Island Wastewater Treatment Plant, one with manual control and another with automated control (using the controlled program developed in the present study), and process data results, it was determined that the hypothesis on which the present study was based on was valid. As detailed in Chapter Five, and summarized below, changes in the process variables were detected, and actions were easily and timely taken in the controlled struvite crystallizer, which lead to the production of struvite of higher quality and decreased operation time. Supplementary studies carried out also proved to expand the knowledge of struvite crystallization process.

Based on the results from experiments carried out at both laboratory- and pilot-scale, and development of a control technology, the following conclusions can be drawn.

6.1 Development of Control Programs

- Laboratory and pilot-scale operation showed that the control program, developed to keep the SSR of a struvite crystallization system at the desired value was efficient, and could take into account various changes in process variables, such as ortho-phosphate concentration, temperature and conductivity.
- The automated crystallizer system (R#2) that had instrumentation and was controlled by the control programs developed in the present study exhibited better performance than the manual (uncontrolled) crystallizer system (R#1) in reducing the phosphate concentration. R#2 had an increase, with respect to R#1, of 40% and 15% in removing ortho-P and ammonium, respectively.
- In terms of purity (% struvite in pellets), compared to R#1, R#2 pellets were slightly higher (by 2%) in struvite content, and exhibited 13% higher average crushing strength.

- Analyses of the composition of struvite pellets formed at the Lulu Island Wastewater Treatment Plant showed that the pellets were never 100% pure with respect to struvite, as they contained different metal salts. However, the heavy metals content in the pellets were found to be much lower than reported in literature for phosphate ores.
- Struvite pellets harvested were, on average, 90% pure (based on magnesium content in the pellets).
- The models programmed in the present study can be used as a predictive tool for treatment plant operators to determine struvite formation potential due to changes in the process variables.
- A 5°C change in temperature can bring about an increase of more than 90% in the SSR value. The variation is enhanced at lower temperatures, where the SSR nearly doubles (between 15-20°C).
- The variation of SSR is more pronounced with limiting parameters than those present in excess. For example, at the lower concentration region (between 5-10 mg/L Mg), the SSR nearly doubles, whereas the rate of change is 50% at higher concentrations.
- Various graphical-user-interfaces developed provided visual and easier control of the struvite crystallization process.

6.2 Solubility Tests

- Within the working pH range (7.0-8.5) of a struvite crystallization process, the struvite solubility product, pK_{sp} , was determined to be independent of the working fluid matrix and pH.
- The struvite solubility product at 25°C was determined to be 13.26.
- An equation relating pK_{sp} to temperature was developed.

6.3 Carbon Dioxide Stripping Tests

- Over 90% of phosphorus was easily removed from the centrate at a pH of 8.1, with or without air stripping.

- With air and without air stripping, an average of 32% and 26% caustic savings was achieved using the cascade stripper, compared to the no-stripper condition, respectively.
- Both the compact media and cascade strippers were equally efficient (average 90% phosphate removal) in their application. However, due to ease of operation (lower plugging and easier cleaning), the cascade stripper proved to be more suitable.
- The cost of operating a struvite crystallization process could be significantly reduced by increasing the pH of the system through carbon dioxide stripping. The potential saving in caustic cost, due to CO₂ stripping, was calculated to be as high as 38 cents per thousand liters treated.

6.4 Magnesium Prediction Techniques

6.4.1 *Conductivity-pH measurements*

- For a struvite crystallization system, the combined use of pH and conductivity can be an easy and quick method to determine the amount of external magnesium that need to be added to a water sample. The amount required was determined by locating a bending point in the pH-conductivity-external magnesium added graph.
- At the bending point, for each mole of phosphate removed, the Mg:P molar ratio was 1.3-2.0. This ratio is important, because, although it does not signal the end of the reaction, it determines the quantity of magnesium chloride required to remove one mole of phosphate.
- Since the activity of an ion is responsible for actual reaction, and Mg determination by AA provides total concentration, the pH-conductivity method of determining magnesium addition provides a better estimate of the dosages required.

6.4.2 *Determination of magnesium concentration by hardness test method*

- Since phosphate interferes with hardness tests, removal of the ion by both PAC and alum was suitable in reducing phosphate concentrations (to lower than 20 mg/L) from the water matrix, prior to the hardness tests.
- Tests showed that there was a linear relationship between the amount of alum added and phosphate reduction. Although the relationship (rate of change) was different as the water matrices varied, by developing an equation for each matrix, the amount of alum required can be predicted.
- Determination of magnesium concentration by the hardness test method was found to be suitable for quick, on-site testing. The absolute average error between results from the hardness test and AA was only 2.0 mg/L.

6.5 Influence of Variables on Structure of Struvite Pellets

- Pellets grown in this study were as large as 6 mm; this size is among the largest formed from domestic wastewater. Upflow velocity in the crystallizer was found to influence the size and shape of the pellets.
- The compactness of struvite pellets is a function of size of the pellets and the upflow velocity. At an upflow velocity of above 400 cm/min, the surface smoothness and sphericity of the struvite pellets formed were lowered. Higher upflow velocity can possibly lead to the formation of denser, but smaller and less spherical pellets.
- Flow patterns in the crystallizer possibly influences the shape of the struvite pellets formed.

6.6 Determination of Crushing Strength

- Mid-sized pellets, in the 2.0-2.5 mm range, exhibited the highest crushing strengths. This could be related to the denser structural composition found for smaller pellets than larger ones.
- Within the range (SSR of 1.5 – 7.1) tested, supersaturation ratio did not appear to influence the crushing strength of pellets formed.

- A high concentration (above 20 mg/L) of unused magnesium in the crystallizer can lead to the formation of pellets having greater crushing strengths. An increase of 15% – 27% in crushing strengths were determined in the present study due to an increase of 7% (22.5 to 24.1 mg/L) and 132% (19 – 44 mg/L) of excess magnesium concentration in the crystallizer, respectively. However, it should be remembered that there is a limit to how much excess magnesium one should have in the crystallizer. High concentration of unused magnesium can lead to higher concentrations in the system's effluent, which can then increase struvite formation potential downstream of the treatment. In addition, inefficient use of magnesium leads to an increase in operating costs.

To summarize, the overall major contributions of the present study to the field of phosphorus removal-recovery as struvite were:

- The development of a process controller and graphical tools for use in operating a struvite crystallization process, and predicting struvite formation potential in wastewater treatment plants.
- The determination of a universal solubility product for struvite and the influence of temperature on the value.
- The applicability of a carbon dioxide stripper in reducing chemical costs, and development of program to determine operating stripping efficiency in increasing the pH of the system.
- The development of a protocol for quick and on-site measurement of external magnesium dosing requirements in struvite crystallization process.
- The development of a device that can be used as a quick means of measuring struvite pellet crushing strength.

CHAPTER SEVEN: RECOMMENDATIONS FOR FURTHER STUDY

- The prediction and equation developed in this study for struvite solubility product should be tested further with water matrices from more treatment plants, and should cover higher temperature ranges.
- The applicability of using gas stripping as a means of increasing the pH of the water matrix in a struvite crystallization process has been confirmed. The carbon dioxide stripping model developed should be tested at other pilot-scale setups, to increase its prediction power.
- The impact of operating pH on the degree and efficiency of carbon dioxide stripping should be tested.
- The presence of ammonium/ammonia in wastewater treatment plant effluent can increase the toxic effect of the gas in the water body into which it is discharged. Although struvite precipitation alone can reduce ammonium concentrations in the centrate/supernatant, the percentage removal is small (10-20%). Stripping of ammonia gas is another viable option to reduce the concentration. Therefore, the applicability of ammonia stripping, using the carbon dioxide cascade stripper, should be investigated.
- The application of indirect magnesium addition requirement (by using pH and conductivity) has been proposed and found to be useful in the laboratory in this study. The efficiency, and deficiencies, of this method should be tested at a larger pilot scale facility.
- Since the lack of instrumentation in this study could not utilize the full potential of the control program developed, it should be tested in a fully instrumented, full-scale struvite crystallization process.
- Tests should be carried out to determine the types of compounds, other than struvite, that are present in a struvite pellet, and conditions that increase their formation potential.

- Agglomeration studies, including formulation for struvite growth, should be investigated and incorporated into the model developed in this study.
- The application of the struvite crystallization process mentioned in this study should be investigated using dairy wastewater. At UBC, the application of peroxide and microwave (PM) to enhance solubility of phosphates and nitrogen from dairy wastewater has been studied. A treatment scheme that integrates PM technology with the crystallization process should be studied at a pilot scale.

REFERENCES

- Aage, H.K., Anderson, B.L., Blom, A. and Jensen, I. (1997). The solubility of struvite. *J Radioanal Nucl. Chem.* **223**, 213–215.
- Adnan, A., Mavinic, D.S. and Koch, F.A. (2003). Pilot-scale study of phosphorus recovery through struvite crystallization – examining the process feasibility. *J. Environ. Eng. Sci.* **2**, 315-324.
- Ali, M.I. (2005). Struvite crystallization from a nutrient rich wastewater. Ph.D. Thesis, Department of Chemical Engineering. Townsville, James Cook University, Australia.
- APHA, AWWA, WPCF (1995). Standard Methods for the Examination of Water and Wastewater, 19th Edition. American Public Health Association, Washington, D.C.
- Babić-Ivančić, V., Kontrec, J.Kralj, D. and Brečević, L. (2002). Precipitation diagrams of struvite and dissolution kinetics of different struvite morphologies. *Croatica Chemica Acta*, **75** (1), 89-106.
- Barnard, J.L. (2009) Elimination of eutrophication through resource recovery. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.
- Battistoni, P., Fava, G., Pavan, P., Musacco, A. and Cecchi, F. (1997). Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results. *Water Research*. **31** (11), 2925-2929.
- Berg, E. (1982). *Handbook for Sampling and Sample Preservation for Water and Wastewater*. United States Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, Ohio, U.S.A.

Bhuiyan, M.I.H. and Mavinic, D.S. (2009). Temperature dependence on electrical conductivity and its relationship with ionic strength for struvite precipitation system. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

Bhuiyan, M.I.H., Mavinic, D.S. and Beckie, R.D. (2008). Nucleation and growth kinetics of struvite in a fluidized bed reactor. *J. Crystal Growth*. **210**, 1187-1194.

Bhuiyan, M. I. H., Mavinic, D. S. and Beckie, R. D. (2007). A solubility and thermodynamic study of struvite. *Environ Technol.* **28**(9), 1015-1026.

Bhuiyan, M. I. H., Mavinic, D. S. and Beckie, R. D. (2009). Determination of Temperature Dependence of Electrical Conductivity and Its Relationship with Ionic Strength of Anaerobic Digester Supernatant, for Struvite Formation. *Journal of Environmental Engineering-ASCE*. **135**(11), 1221-1226.

Booker, N. A., Priestley, A. J. and Fraser, I. H. (1999). Struvite formation in wastewater treatment plants: Opportunities for nutrient recovery. *Environ Technol.* **20**(7), 777-782.

Bouropoulos, N. C. and Koutsoukos, P. G. (2000). Spontaneous precipitation of struvite from aqueous solutions. *J Cryst Growth*. **213**(3-4), 381-388.

Britton, A., Koch, F. A., Mavinic, D. S., Adnan, A., Oldham, W. K. and Udala, B. (2005). Pilot-scale struvite recovery from anaerobic digester supernatant at an enhanced biological phosphorus removal wastewater treatment plant. *Journal of Environmental Engineering and Science*. **4**(4), 265-277.

Buchanan, J.R., Mote, C.R. and Robinson, R.B. (1994). Thermodynamics of struvite formations. *Transactions of the ASEA*. **37** (2), 617-621.

Burns, J.R. and Finlayson, B. (1982). Solubility products of ammonium magnesium phosphate hexahydrate at various temperatures. *The Journal of Urology*. **128**, 426-428.

CEEP (2001). *Phosphate Recovery: Where do we stand today?* Special issue of the Scope Newsletter, published in preparation to the 2nd International Conference on P-recovery from human and animal wastes. 12-14 march, 2001. Noordwijkerhout, The Netherlands.

Celen, I. and Turker, M. (2001). Recovery of ammonia as struvite from anaerobic digester effluents. *Environmental Technology*. **22**, 1263-1272.

Chambers, P.A., Guy, M., Roberts, E.S., Charlton, M.N., Kent, R., Gagnon, C., Grove, G. and Foster, N. (2001). Nutrients and their impact on the Canadian Environment. Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada and Natural Resources Canada. pp 241.

Childs, C. W. (1970). A potentiometric study of equilibria in aqueous divalent metal orthophosphate solutions. *Inorg. Chem.* **9**(11), 2465–2469.

Cohen, Y. and Kirchmann, H. (2004). Increasing the pH of wastewater to high levels with different gases- CO_2 stripping. *Water Air and Soil Pollution*. **159**(1-4), 265-275.

Cordell, D., Schmid-Neset, T., White, S. and Drangert, J.O. (2009). Preferred future phosphorus scenarios: a framework for meeting long-term phosphorus needs for global food demand. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

Demeestere, K., Smet, E., Van Langenhove, H. and Galbacs, Z. (2001). Optimisation of magnesium ammonium phosphate precipitation and its applicability to the removal of ammonium. *Environ Technol.* **22**(12), 1419-1428.

Dockhorn, T. (2009). About the economy of phosphorus recovery. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

doro, R., Bolzonella, D. and Pezzoli, S. (2001). Optimization of chemical and physical pretreatments in a platform for the treatment of liquid industrial wastes. *Ind Eng Chem Res.* **40**(21), 4506-4512.

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

Doyle, J. D., Philp, R., Churchley, J. and Parsons, S. A. (2000). Analysis of struvite precipitation in real and synthetic liquors. *Process Saf Environ Prot.* **78**(B6), 480-488.

Driver, J., Lijmbach, D. and Steen, I. (1999). Why recover phosphorus for recycling, and how? *Environ Technol.* **20**(7), 651-662.

Durrant, A. E., Scrimshaw, M. D., Stratful, I. and Lester, J. N. (1999). Review of the feasibility of recovering phosphate from wastewater for use as a raw material by the phosphate industry. *Environ Technol.* **20**(7), 749-758.

Fattah, K.P., Mavinic, D.S., Rahaman, M.S. and Koch, F.A. (2009). Development of a process control system for online monitoring and control of a struvite crystallization process. Proceeding of International Conference on Nutrient Recovery from Wastewater Streams, Vancouver, B.C., May 10-13, 2009.

Fattah, K. P., Zhang, Y., Mavinic, D. S. and Koch, F. A. (2008a). Application of carbon dioxide stripping for struvite crystallization - I: Development of a carbon dioxide stripper model to predict CO₂ removal and pH changes. *Journal of Environmental Engineering and Science.* **7**(4), 345-356.

Fattah, K. P., Mavinic, D. S., Koch, F. A. and Jacob, C. (2008b). Determining the feasibility of phosphorus recovery as struvite from filter press centrate in a secondary wastewater treatment plant. *Journal of Environmental Science and Health Part A-Toxic/hazardous Substances and Environmental Engineering*. **43**(7), 756-764.

Fattah, K.P. (2004). Pilot scale struvite recovery potential from centrate at Lulu Island Wastewater Treatment Plant. M.A.Sc. Thesis, Department of Civil Engineering, University of British Columbia, Vancouver, BC, Canada.

Forrest, A. L., Fattah, K. P., Mavinic, D. S. and Koch, F. A. (2008a). Optimizing struvite production for phosphate recovery in WWTP. *Journal of Environmental Engineering-Asce*. **134**(5), 395-402.

Forrest, A. L., Mavinic, D. S. and Koch, F. A. (2008b). The measurement of magnesium: A possible key to struvite production and process control. *Environ Technol*. **29**(6), 603-612.

Forrest, A. L., Fattah, K. P., Mavinic, D. S. and Koch, F. A. (2007). Application of artificial neural networks to effluent phosphate prediction in struvite recovery. *Journal of Environmental Engineering and Science*. **6**(6), 713-725.

Forrest, A. (2004). Process Optimization of a Technical Scale Phosphorus Recovery System Through Struvite Crystallization at the City of Penticton Advanced Wastewater Treatment Plant. Vancouver, BC: University of British Columbia, M.A.Sc. Thesis.

Gaddekar, S., Pullammanappallil, P. and Varshovi, A. (2009). Validation of a comprehensive chemical equilibrium model for predicting struvite precipitation. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

- Gaterell, M. R., Gay, R., Wilson, R., Gochin, R. J. and Lester, J. N. (2000). An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environ Technol.* **21**(9), 1067-1084.
- Gilbert, N. (2009). The disappearing nutrient. *Nature*. **461**, 8 October 2009.
- Gunzel, D. and Schlue, W. R. (2002). Determination of $[Mg^{2+}]$ - an update on the use of Mg^{2+} -selective electrodes. *Biometals*. **15**(3), 237-249.
- Gupta, V. K., Chandra, S. and Mangla, R. (2002). Magnesium-selective electrodes. *Sensors and Actuators B-Chemical*. **86**(2-3), 235-241.
- Hanhoun, M., Azzaro-PBiscans, B., Freche, M., Montastruc, L., Pibouleau, L. and Domenech, S. (2009). A thermochemical approach for struvite precipitation modeling from wastewater. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.
- Harada, H., Shimizu, Y., Miyagoshi, Y., Matsui, S., Matsuda, T. and Nagasaka, T. (2006). Predicting struvite formation for phosphorus recovery from human urine using an equilibrium model. *Water Science and Technology*. **54**(8), 247-255.
- Hirasawa, I., Nakagawa, H., Yosikawa, O. and Itoh, M. (1997). Phosphate recovery by reactive crystallization of magnesium ammonium phosphate: Application to wastewater. *Separation and Purification by Crystallization*. **667**, 267-276.
- Hiroyuki, H. and Toru, S. (2003). Nitrogen and Phosphorus recovery from a piggery waste water treatment facility. *Proc. 2003 Third International Symposium on Environmentally Conscious Design and Inverse Manufacturing*, Tokyo, Japan, 422-426.

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

Jeanmaire, N. (2001). Recycling of removed phosphorus: Analysis of the potential interest in wastewater treatment plants. Centre European d'Etudes des Polyphosphates (CEEP). World Wide Web. http://www.nhm.ac.uk/mineralogy/phos/Jeanmaire_report.doc

Jeanmaire, N. and T. Evans (2001). Technico-economic feasibility of P-Recovery from municipal wastewaters. *Environmental Technology.* **22**, 1355-1361.

Kumashiro, K., Ishiwatari, H. and Nawamura, Y. (2001). A pilot-scale study on using seawater as a magnesium source for struvite precipitation. In proceedings from Second International Conference on the recovery of phosphorus from sewage and animal wastes, Noodwijikerhout, Holland, March 2001.

Larkin, G.L. and Slaney, P.A. (1996). Trends in marine derived nutrient sources to south coastal British Columbia streams: impending implications to salmonid production. *Watershed Restoration Management Report No. 3, B.C. Ministry of the Environment, Lands and Parks.*

Le Corre, K. S., Valsami-Jones, E., Hobbs, P. and Parsons, S. A. (2007). Kinetics of struvite precipitation: Effect of the magnesium dose on induction times and precipitation rates. *Environ Technol.* **28**(12), 1317-1324.

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

Le Corre, K. S., Valsami-Jones, E., Hobbs P., Jefferson, B. and Parsons, S. A. (2007). Agglomeration of struvite crystals. *Water Res.* **41**(2), 419-425.

- Lee, G.F. (1970). *Eutrophication*. Prepared for the supplementation to the encyclopedia of chemical technology. John Wiley and Sons Inc. N.Y.
- Liao, P.H., Chen, A. and Lo, K.V. (1995). Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology*. **54** (1), 17-20.
- Liberti, L., Petruzzelli, D. and De Florio, L. (2001). REM NUT ion exchange plus struvite precipitation process. *Environ Technol*. **22**(11), 1313-1324.
- Lide, D. R. (1991). Handbook of chemistry and physics. 71st Edition. CRC Press.
- Loewenthal, R. E., Kornmuller, U. R. C. and Vanheerden, E. P. (1994). Modeling struvite precipitation in anaerobic treatment systems. *Water Science and Technology*. **30**(12), 107-116.
- Martell, A. E. and Smith, R. M. (1989) Critical Stability Constants. Plenum Press, New York
- MathWorks website. The MathWorks, Inc. (1994-2006)
<http://www.mathworks.com>
- Mavinic, D. S., Koch, F. A., Hall, E. R., Abraham, K. and Niedbala, D. (1998). Anaerobic co-digestion of combined sludges from a BNR wastewater treatment plant. *Environ Technol*. **19**(1), 35-44.
- Mavinic, D. S., Koch, F. A., Huang, H. and Lo, K. V. (2007). Phosphorus recovery from anaerobic digester supernatants using a pilot-scale struvite crystallization process. *Journal of Environmental Engineering and Science*. **6**(5), 561-571.
- Morel, F.M.M. (1983) Principles of Aquatic Chemistry. New York, NY: *John Wiley and Sons*.

- Munch, E. V. and Barr, K. (2001). Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Res.* **35**(1), 151-159.
- Musvoto, E. V., Ekama, G. A., Wentzel, M. C. and Loewenthal, R. (2000). Extension and application of the three-phase weak acid/base kinetic model to the aeration treatment of anaerobic digester liquors. *Water Sa.* **26**(4), 417-438.
- Neethling, J. B., Benisch, M. (2004). Struvite control through process and facility design as well as operation strategy. *Water Science and Technology.* **49**(2), 191-199.
- Ohlinger, K. N., Young, T. M. and Schroeder, E. D. (1999). Kinetics effects on preferential struvite accumulation in wastewater. *Journal of Environmental Engineering-Asce.* **125**(8), 730-737.
- Ohlinger, K. N., Young, T. M. and Schroeder, E. D. (1998). Predicting struvite formation in digestion. *Water Res.* **32**(12), 3607-3614.
- Omar, W. and Ulrich, J. (2003). Influence of crystallization conditions on the mechanism and rate of crystal growth of potassium sulphate. *Crystal Research and Technology.* **38**(1), 34-41.
- Owen, J., Stoven, H., Kowalski, J. and Phillips, K. (2009). Assessment of struvite containing controlled release fertilizer as a source of phosphorus for containerized ornamental crops. *Hortiscience.* **44** (4), 1131-1132.
- Parkhurst, D.L. and Appelo, C.A.J. (1998). User's guide to PHREEQC (Version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.
http://wwwbrr.cr.usgs.gov/projects/gwc_coupled/phreeqc/html/final.html
- Pitman A. R., Deacon, S. L. and Alexander, W. V. (1991). The Thickening and Treatment of Sewage Sludges to Minimize Phosphorus Release. *Water Res.* **25**(10), 1285-1294.

Ponce, R. G. and De Sa, M. E. G. L. (2007). Evaluation of struvite as a fertilizer: a comparison with traditional P sources. *Agrochimica*. **51**(6), 301-308.

Rahaman, M. S., Mavinic, D. S., Bhuiyan, M. I. H. and Koch, F. A. (2006). Exploring the determination of struvite solubility product from analytical results. *Environ Technol.* **27**(9), 951-961.

Rahman, M. J., Bozadjiev, P. and Pelovski, Y. (1994). Studies on the Effects of some Additives on the Physicomechanical Properties of Urea Ammonium-Sulfate (Uas) Pellets. *Fertilizer Research*. **38**(2), 89-93.

Sabrina, N. (2007) *Comparing the effectiveness of CO₂ strippers to reduce operating costs for struvite formation. M.A.Sc. Thesis, Department of Civil Engineering, The University of British Columbia Vancouver, B.C., Canada.*

Sasai, H., Kameyama, K. and Sugimori, N. (1995). An innovative option for nitrogen and phosphorus recovery in sludge treatment process. In *Proceedings of Water Environment Federation*. WEFTEC' 95.

Sawyer, C., McCarty, P and Parkin, G. (1994). *Chemistry for Environmental Engineering*. McGraw-Hill Series in water Resources and Environmental Engineering, New York, U.S.A.

Seckler, M.M., Bruinsma, O.S.L. and Van Rosmalen, G.M. (1996). Calcium phosphate precipitation in a fluidized bed in relation to process conditions: a black box approach. *Water Res.* **30** (7), 1677-1685.

Shepherd, T. A., Burns, R. T., Moody, L. B., Raman, D. R. and Stalder, K. J. (2009). Investigating Conductivity to Predict Magnesium Addition Requirements for Struvite Precipitation in Swine Manure Slurries. *Appl Eng Agric.* **25**(1), 103-108.

- Shimamura, K., Tanaka, T., Miura, Y. and Ishikawa, H. (2003). Development of a high-efficiency phosphorus recovery method using a fluidized-bed crystallized phosphorus removal system. *Water Science and Technology*. **48**(1), 163-170.
- Sterling, M.S. and Ashley, K. I. (2003). Evaluations of a slow-release fertilizer for rehabilitating oligotrophic streams. *American Fisheries Society Symposium*. **34**, 237-243.
- Stratful, I., Brett S., Scrimshaw, M. D. and Lester, J. N. (1999). Biological phosphorus removal, its role in phosphorus recycling. *Environ Technol*. **20**(7), 681-695.
- Stratful I., Scrimshaw M. D. and Lester J. N. (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Res*. **35**(17), 4191-4199.
- Slaney, T.L., Hyatt, K.D., Northcote, T.G. and Fielden, R.J. (1996). Status of anadromous salmon and trout in British Columbia and Yukon. *Fisheries*. **21**, 20-35.
- Snoeyink, V. and Jenkins, D. (1980). *Water Chemistry*. John Wiley and Sons, NY.
- Taylor, A.W., Frazier, A.W. and Gurney, E.L. (1963). Solubility products of magnesium ammonium and magnesium potassium phosphates. *Transactions of the Faraday Society*. **59**, 1580-1584.
- Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2003). *Wastewater engineering: treatment and reuse*. McGraw-Hill, New York, U.S.A.
- Thomas, M., vanderPoel, A. F. B. (1996). Physical quality of pelleted animal feed .1. Criteria for pellet quality. *Anim Feed Sci Technol*. **61**(1-4), 89-112.
- Ueno, Y and Fujii, M. (2001). Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology*. **22** (11), 1373-1381.

Vanotti, M. and Szogi, A. (2009). Technology for recovery of phosphorus from animal wastewater through calcium phosphate precipitation. International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

von Horn, J. and Sartorius, C. (2009). Impact of supply and demand on the price development of phosphate (fertilizer). International conference on nutrient recovery from wastewater streams. Vancouver, BC, Canada. IWA publishing, UK.

Wang, J., Burken, J. G. and Zhang, X. Q. (2006). Effect of seeding materials and mixing strength on struvite precipitation. *Water Environ Res.* **78**(2), 125-132.

Wierzbicki A., Sallis J. D., Stevens E. D., Smith M. and Sikes C. S. (1997). Crystal growth and molecular modeling studies of inhibition of struvite by phosphocitrate. *Calcif Tissue Int.* **61**(3), 216-222.

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

Yoshino, M., Yao, M., Tsuno, H. and Somiya, I. (2003). Removal and recovery of phosphate and ammonium as struvite from supernatant in anaerobic digestion. *Water Science and Technology.* **48**(1), 171-178.

Zhang, Y. (2006). Struvite crystallization from digester supernatant – reducing caustic chemical addition by CO₂ stripping. M.A.Sc. Thesis, Department of Civil Engineering, University of British Columbia, Vancouver, BC, Canada.

APPENDICES

**APPENDIX A: SUMMARY OF PROGRAM CODE TO DETERMINE
REQUIRED pH OF A STRUVITE CRYSTALLIZER SYSTEM
(solvepH.m)**

Ionic species Considered.

1. Mg^{2+}
2. NH_4^+
3. PO_4^{3-}
4. MgOH^+
5. NH_3
6. H_3PO_4
7. H_2PO_4^-
8. HPO_4^{2-}
9. MgPO_4^-
10. MgHPO_4
11. $\text{MgH}_2\text{PO}_4^+$

Equilibrium	Constant
$\text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$	K_1
$\text{H}_2\text{PO}_4^- \rightarrow \text{H}^+ + \text{HPO}_4^{2-}$	K_2
$\text{HPO}_4^{2-} \rightarrow \text{H}^+ + \text{PO}_4^{3-}$	K_3
$\text{MgH}_2\text{PO}_4^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{PO}_4^-$	K_{Mg}
$\text{MgHPO}_4 \rightarrow \text{Mg}^{2+} + \text{HPO}_4^{2-}$	K_{Mg1}
$\text{MgPO}_4^- \rightarrow \text{Mg}^{2+} + \text{PO}_4^{3-}$	K_{Mg2}
$\text{NH}_4^+ \rightarrow \text{H}^+ + \text{NH}_3$	K_{N}
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	K_{w}

$Z(n)$ = ionic charge of n^{th} species

$A(n)$ = activity coefficient of n^{th} species

$AW(n)$ = atomic weight of the n^{th} species

The following formulae for the coefficients have been derived based on thermodynamic equilibrium relationships between species.

$$a = \text{totalMg}/\text{AWMg}/1000 * A(1)*A(4)*A(9)*A(11);$$

$$b = A(4)*A(9)*A(11);$$

$$c = K_w/\text{KMgOH} * A(1)*A(9)*A(11);$$

$$d = 1/\text{KMg3} * A(1)*A(4)*A(11);$$

$$e = 1/\text{K3}/\text{KMg2} * A(1)*A(4)*A(9)*A(11);$$

$$f = 1/\text{K2}/\text{K3}/\text{KMg1} * A(1)*A(4)*A(9);$$

$$g = \text{totalN}/\text{AWN}/1000 * A(2);$$

$$h = K_n * A(2);$$

$$i = \text{totalP}/\text{AWP}/1000 * A(3)*A(7)*A(8)*A(9)*A(11);$$

$$j = A(7)*A(8)*A(9)*A(11);$$

$$k = 1/\text{K1}/\text{K2}/\text{K3} * A(3)*A(7)*A(8)*A(9)*A(11);$$

$$l = 1/\text{K2}/\text{K3} * A(3)*A(8)*A(9)*A(11);$$

$$m = 1/\text{K3} * A(3)*A(7)*A(9)*A(11);$$

$$n = 1/\text{KMg3} * A(3)*A(7)*A(8)*A(11);$$

$$o = 1/\text{K3}/\text{KMg2} * A(3)*A(7)*A(8)*A(9)*A(11);$$

$$p = 1/\text{K2}/\text{K3}/\text{KMg1} * A(3)*A(7)*A(8)*A(9);$$

Quadratic Formula coefficients

$$a_{\text{quad}} = ((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2));$$

$$b_{\text{quad}} = ((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i);$$

$$c_{\text{quad}} = (-i * (b + c/H));$$

The following equation solves the quadratic equation for activity of phosphorus based on equation derived above.

Solves quadratic for activity of P

$$P1 = (-b_quad + \sqrt{b_quad^2 - 4*a_quad*c_quad}) / (2*a_quad);$$

$$P1 = @ (H) (-((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - ... \\ (d + e*H + f*H^2)*i) + \sqrt{ ((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - ... \\ (d + e*H + f*H^2)*i)^2 - 4*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))*(-i * (b + c/H))) } / (2*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2)));$$

$$P2 = (-b_quad - \sqrt{b_quad^2 - 4*a_quad*c_quad}) / (2*a_quad);$$

pH calculation; Takes the SSR as a function of H and solves for H

$$C1 = a/(b + c/H + (d + e*H + f*H^2)*C3);$$

$$C2 = g / (1 + h/H);$$

$$C3 = P1;$$

Equation for struvite formation - $MgNH_4PO_4 \cdot 6H_2O \rightleftharpoons Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$

$$SSR = \{Mg^{2+}\} * \{NH_4^+\} * \{PO_4^{3-}\} / KMAP$$

$$SSR * KMAP = MAP_{product};$$

$$MAP_{product} = C1 * C2 * C3;$$

$$H_{function} = @ (H) ... (function of H)$$

$$... \% C1:$$

$$a/(b + c/H + (d + e*H + f*H^2) * ...$$

$$(-((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i) + ...$$

$$\sqrt{ ((n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H + f*H^2)*i)^2 - ...$$

$$4*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))*(-i * (b + c/H))) ... \\ / (2*((j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2))) ...$$

$$... \% C2:$$

```

* g / (1 + h/H ) ...
...% C3:
* ( -( (n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H +
f*H^2)*i ) + ...
      sqrt( ( (n + o*H + p*H^2)*a + (b + c/H)*(j + k*H^3 + l*H^2 + m*H) - (d + e*H
+ f*H^2)*i )^2 - ...
      4*( (j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2) )*( -i * (b + c/H) ) ) ) ...
/ (2* ( (j + k*H^3 + l*H^2 + m*H) * (d + e*H + f*H^2) ) ) ...
...% SSR * KMAP:
- SSR * KMAP;

```

**APPENDIX B: VALUES OF PARAMETERS TO DETERMINE
THEIR INFLUENCES ON THE SUPERSATURATION RATIO**

Sample Number	Influence of	Cond. mS/cm	SSR	Temp. °C	PO ₄ mg/L	NH ₄ mg/L	Mg mg/L
0	Temp.	3500	8.65	15	70	800	10
1800	Temp.	3500	8.65	15	70	800	10
3600	Temp.	3500	4.33	20	70	800	10
5400	Temp.	3500	4.33	20	70	800	10
7200	Temp.	3500	1.15	30	70	800	10
9000	Mg	3500	1.15	30	70	800	10
10800	Mg	3500	1.70	30	70	800	15
12600	Mg	3500	3.24	30	70	800	30
14400	PO ₄	3500	1.15	30	70	800	10
16200	PO ₄	3500	1.27	30	80	800	10
18000	PO ₄	3500	1.39	30	90	800	10
19800	PO ₄	3500	1.56	30	105	800	10
21600	PO ₄	3500	1.71	30	120	800	10
23400	PO ₄	3500	1.75	30	125	800	10
25200	PO ₄	3500	1.85	30	135	800	10
27000	PO ₄	3500	1.89	30	140	800	10
28800	PO ₄	3500	1.97	30	150	800	10
30600	PO ₄	3500	2.02	30	155	800	10
32400	PO ₄	3500	2.05	30	160	800	10
34200	NH ₄	3500	1.60	30	100	850	10
36000	NH ₄	3500	1.88	30	100	1000	10
37800	NH ₄	3500	2.16	30	100	1150	10
39600	NH ₄	3500	2.44	30	100	1300	10
41400	Cond.	3500	1.88	30	100	1000	10
43200	Cond.	4500	1.61	30	100	1000	10
45000	Cond.	3000	1.04	30	100	1000	10

APPENDIX C: EQUATIONS USED IN DERIVING STRIPPER MODEL

Coefficient	Expression
A	$(6.72 \ln(\text{BN}) + 69.36)/76.74^{\text{Note*}}$
B	$(-0.57(\text{ERR})^2 + 5.76(\text{ERR}) + 74.98)/74.98$
C	$(-6.27(\text{IFR}) + 92.96)/78.53$
D	$(-8 \times 10^{-6} (\text{ASR})^3 + 0.003(\text{ASR})^2 - 0.168(\text{ASR}) + 64.64)/78.19$
E	$(0.67 \times (\text{IT} - 18) + 59.22)/59.22$
F	$(20.21 \ln([\text{CO}_2]_{\text{inf}}) - 67.14)/55.85$
G	$(-8 \times 10^{-10} (\text{IBC})^3 + 9 \times 10^{-6} (\text{IBC})^2 - 0.029(\text{IBC}) + 96.67)/73.07$

Note*: the expression for coefficient A is obtained from $(6.72 \ln(\text{BN}) + 69.36) / (6.72 \ln(\text{BN}^0) + 69.36)$, where $\text{BN}^0 = 3$. Equations for B~ G are obtained in the similar way.

APPENDIX D: PERFORMANCE OF CONTROLLER – EFFLUENT DATA

Sample Number	Reactor 1(without instrumentation and control)			Reactor 2 (with instrumentation and control)		
	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1	26.9	387.5	85.7	47.2	432.5	10.1
2	30.2	195.0	11.7	24.0	184.5	7.2
3	35.1	381.0	47.9	28.3	281.0	39.3
4	34.4	321.0	57.0	39.1	344.0	12.5
5	13.4	54.6	72.3	9.7	49.3	54.0
6	18.0	54.1	14.7	15.0	50.1	58.0
7		291.0	57.6		296.0	43.5
8		281.5	64.5		244.5	41.7
9	33.8	331.5	53.2			39.1
11	27.5	466.0	49.0			32.8
12	15.6	416.5	17.4			18.4
14	8.2	110.5	31.9			28.6
15	14.2	292.0	21.8			
16	12.8	117.5	33.7			
18	13.6	133.0	32.2			
19			33.7			
20	15.0	218.5	26.8	14.0	199.0	21.6
21	10.5	333.0	34.5	12.8	310.0	25.5
22	9.1	274.5	41.6	5.2	273.0	27.3
23	12.2	504.0	40.9	25.3	440.0	42.8
24	34.6	395.0	44.3	6.3	262.5	30.3
25	13.3	400.5	27.8	8.0	396.5	15.2
26	61.6	552.5	6.1	50.4	529.5	0.9

Sample Number	Reactor 1(without instrumentation and control)			Reactor 2 (with instrumentation and control)		
	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
27	53.2	656.5	3.8	9.8	546.5	6.5
28	27.3	730.5	8.1	9.2	693.5	6.7
29				13.0	727.0	23.6
30		720.5	2.2	18.3	795.0	6.1
31	37.7	779.0	18.1	22.2	746.5	10.4
32	42.1	796.5	10.4	26.6	787.5	4.3
33						
34	6.8	705.0	14.1	8.3	713.5	10.3
35	34.5	705.50	10.9	18.2	655.5	21.5
36	9.4	687.0	5.9	10.5	708.0	9.1

APPENDIX E: SOLUBILITY TESTS

Table E.1. Centrate at 15°C

	Sample	pH	NH ₄ -N (mg/L)	Average N mg/L	PO ₄ -P mg/L	Average P mg/L	Mg mg/L	Average Mg mg/L	Cond. ms/cm
S0 initial day 1	1.00		1120.0		468.0		295.8		
	2.00	4.80	1100.0	1103.3	465.0	464.7	295.9	293.6	10.25
	3.00		1090.0		461.0		288.9		
	4.00		963.0		312.0		252.0		
S1	5.00	5.95	977.0	980.0	310.0	323.0	254.6	247.0	10.15
	6.00		1000.0		347.0		234.3		
	7.00		925.0		193.0		175.7		
S2	8.00	6.26	903.0	922.0	177.0	178.7	174.1	174.4	9.85
	9.00		938.0		166.0		173.4		
	10.00		875.0		88.1		113.0		
S3	11.00	6.52	885.0	883.7	83.5	85.2	113.2	112.4	9.75
	12.00		891.0		83.9		111.0		
	13.00		922.0		55.6		80.8		
S4	14.00	6.73	939.0	912.7	50.4	51.3	80.4	80.2	9.65
	15.00		877.0		47.9		79.2		
	16.00		876.0		33.6		67.6		
S5	17.00	6.88	899.0	885.3	33.9	33.2	67.6	67.5	9.65
	18.00		881.0		32.1		67.3		
	19.00		908.0		28.0		62.2		
S6	20.00	7.02	909.0	906.7	27.4	27.4	61.9	61.7	9.60
	21.00		903.0		26.8		60.7		
	22.00		543.0		13.6		84.5		
S7	23.00	7.15	717.0	684.3	9.4	10.7	84.8	85.1	8.75
	24.00		793.0		9.0		86.0		
	25.00		857.0		7.6		83.6		
S8	26.00		876.0		7.0		88.1		
							82.6		
	27.00	7.28	883.0	872.0	6.8	7.1		84.8	8.83

Appendix E

	Sample	pH	NH ₄ -N (mg/L)	Average N mg/L	PO ₄ -P mg/L	Average P mg/L	Mg mg/L	Average Mg mg/L	Cond. ms/cm
	28.00		833.0		5.5		81.4		
S9	29.00	7.46	831.0	821.7	5.3	5.3	81.2	81.3	8.80
	30.00		801.0		5.1		81.141		
	31.00		744.0		5.1		81.842		
S10	32.00	7.55	752.0	748.0	4.9	5.0	81.6035	81.9	8.65
	33.00		748.0		4.8		82.1335		
	34.00		650.0		4.2		80.439		
S11	35.00	7.72	647.0	648.3	4.0	4.2	79.287	79.5	8.55
	36.00		648.0		4.2		78.812		
	37.00		537.0		3.0		76.219		
S12	38.00	8.21	537.0	540.0	3.4	3.2	76.024	80.2	8.40
	39.00		546.0		3.1		88.417		
S0-2	40.00		1060.0		373.0		351.4		
initial for second set	41.00	5.93	1030.0	1043.3	362.0	377.7	340.2	343.4	9.40
	42.00		1040.0		398.0		338.7		
	43.00		895.0		17.6		89.5032		
S13	44.00	7.32	866.0	872.0	17.8	16.5	89.3148	89.1	10.40
	45.00		855.0		14.0		88.6218		
	46.00		875.0		12.3		87.8658		
S14	47.00	7.42	854.0	870.3	10.6	11.1	89.895	88.6	10.20
	48.00		882.0		10.4		87.8892		
	49.00		829.0		8.4		85.8546		
S15	50.00	7.59	857.0	849.3	7.8	7.9	85.7814	86.1	10.50
	51.00		862.0		7.5		86.514		
	52.00		777.0		6.2		83.7954		
S16	53.00	7.71	774.0	773.0	6.0	6.1	85.2294	84.6	10.40
	54.00		768.0		6.0		84.9228		
	55.00		700.0		5.3		83.6244		
S17	56.00	8.00	698.0	693.3	4.7	4.7	83.0964	83.1	9.80
	57.00		682.0		4.1		82.5468		
	58.00		625.0		5.1		80.7192		
S18	59.00	8.34	873.0	691.0	3.8	4.2	79.7058	80.4	9.90
	60.00		575.0		3.6		80.6688		

Table E.2. Distilled water at 10°C.

	Sample	pH	NH ₄ -N (mg/L)	Average N mg/L	PO ₄ -P mg/L	Average P mg/L	Mg mg/L	Average Mg mg/L	Cond ms/cm
Initial for set 1	1		295.0		397.0		210.9		
	2	2.64	297.0	295.0	404.0	400.3	213.3	214.1	3.35
	3		293.0		400.0		218.1		
	4		312.0		437.0		252.0		
S1	5	6.14	314.0	312.3	433.0	436.0	258.9	256.1	3.20
	6		311.0		438.0		257.4		
	7		289.0		388.0		214.4		
S2	8	6.25	286.0	286.3	379.0	381.0	214.4	215.7	3.00
	9		284.0		376.0		218.3		
	10		241.0		275.0		122.9		
S3	11	6.50	241.0	241.0	277.0	276.0	123.3	123.7	2.80
	12		241.0		276.0		124.9		
	13		216.0		204.0		46.9		
S4	14	6.90	213.0	215.0	199.0	201.3	50.1	49.0	2.90
	15		216.0		201.0		50.0		
	16		194.0		176.0		26.0		
S5	17	7.20	192.0	192.3	174.0	174.3	26.2	26.4	2.90
	18		191.0		173.0		26.9		
	19		182.0		166.0		9.4		
S6	20	7.32	182.0	182.0	168.0	167.3	10.1	9.9	2.8/
	21		182.0		168.0		10.2		
	22		189.0		161.0		10.2		
	23		192.0		159.0		10.3		
S7	24	7.30		350.0		159.0		10.3	2.95
	25		182.0		157.0		10.4		
	26	7.50	185.0		155.0		6.7		
S8	27		191.0	187.7	154.0	154.3	6.8	6.8	3.03
	28		190.0		154.0		7.0		
	29	7.70	180.0		151.0		4.3		
S9	30		181.0	188.7	153.0	152.0	4.4	4.4	2.90
	31		179.0		152.0		4.6		
	32		160.0		154.0		4.6		
S10	33	7.74	161.0	180.0	155.0	154.7	4.7	4.7	2.88
	34		157.0		155.0		4.8		
	35		147.0		152.0		1.6		
S11	36	8.30	142.0	159.3	151.0	151.3	1.6	1.6	2.91
	37		143.0		151.0		1.6		
	38		124.0		150.0		1.1		
S12	39	8.60	123.0	144.0	146.0	146.7	1.2	1.2	2.85
	40		127.0		144.0		1.2		
	41		346.0		534.0		261.2		178
initial for set 2	42	5.90	353.0	350.0	544.0	539.3	262.9	263.0	3.30
S13			351.0		540.0		264.8		

Table E.3. Distilled water at 20°C

Sample	pH	NH ₄ -N (mg/L)	Average N (mg/L)	PO ₄ -P (mg/L)	Average P (mg/L)	Mg (mg/L)	Cond (mS/cm)
1.00	initial - 5.92	536.0	539.3	468.0	479.7	245.0	7.19
2.00		544.0		488.0			
3.00		538.0		483.0			
4.00		424.0		130.0			
5.00	7.46	420.0	420.0	122.0	123.7	12.5	7.14
6.00		416.0		119.0			
7.00		441.0		222.0			
8.00		421.0		185.0			
9.00	7.53	407.0	423.0	158.0	188.3	11.9	7.10
10.00		380.0		125.0			
11.00		376.0		120.0			
12.00		378.0		121.0			
13.00	7.67	353.0	378.0	114.0	122.0	7.5	7.14
14.00		345.0		111.0			
15.00		351.0		114.0			
16.00		296.0		108.0			
17.00	7.88	289.0	349.7	106.0	113.0	5.2	6.98
18.00		287.0		106.0			
19.00		233.0		108.0			
20.00		233.0		110.0			
21.00	8.13	236.0	290.7	110.0	106.7	3.3	7.00
	8.33		234.0		109.3	2.4	7.02

Table E.4. Tap water at 15°C

	Sample	pH	NH ₄ -N (mg/L)	Average N (mg/L)	PO ₄ -P (mg/L)	Average P (mg/L)	Mg (mg/L)	Average Mg (mg/L)	Cond (ms/cm)
	1.00		294.0		492.0		302.8		
	2.00	4.44	288.0	289.7	490.0	486.3	305.5	305.8	4.24
S0	15.00		287.0		477.0		309.2		
	3.00		355.0		533.0		325.4		
	4.00	6.00	352.0	354.3	524.0	526.3	321.2	322.1	5.37
S1	16.00		356.0		522.0		319.6		
	5.00		307.0		394.0		210.5		
	6.00	6.30	297.0	300.3	397.0	397.3	209.5	211.0	5.01
S2	17.00		297.0		401.0		213.1		
	22.00		175.0		223.0		76.8		
	23.00	6.75	175.0	175.0	225.0	224.0	77.4	77.2	4.20
S7	36.00						77.3		
	7.00		203.0		251.0		69.3		
	8.00	6.80	195.0	198.7	237.0	239.3	70.9	70.0	4.55
S3	18.00		198.0		230.0		69.9		
	24.00		138.0		175.0		37.5		
	25.00	7.10	139.0	138.5	175.0	175.0	37.6	37.5	4.00
S8	37.00						37.2		
	9.00		171.0		183.0		21.8		
	10.00	7.30	173.0	171.0	176.0	177.7	21.9	21.9	4.51
S4	19.00		169.0		174.0		22.1		
	11.00		150.0		154.0		17.7		
	12.00	7.50	151.0	152.0	157.0	155.7	17.5	17.5	4.25
S5	20.00		155.0		156.0		17.3		

	Sample	pH	NH ₄ -N (mg/L)	Average N (mg/L)	PO ₄ -P (mg/L)	Average P (mg/L)	Mg (mg/L)	Average Mg (mg/L)	Cond (ms/cm)
	26.00		118.0		150.0		17.1		
	27.00	7.51	118.0	118.0	147.0	148.5	17.1	17.0	4.00
S9	38.00						16.8		
	28.00		111.0		141.0		12.6		
	29.00	7.66	111.0	111.0	140.0	140.5	12.5	12.5	4.10
S10	39.00						12.5		
	13.00		134.0		145.0		10.8		
	14.00	7.70	128.0	131.3	139.0	142.0	10.8	10.8	4.18
S6	21.00		132.0		142.0		10.7		
	30.00		102.0		148.0		10.5		
	31.00	7.80	99.9	101.0	146.0	147.0	10.7	10.6	4.20
S11	40.00						10.7		
	32.00		91.9		137.0		6.1		
	33.00	8.10	91.1	91.5	138.0	137.5	6.2	6.1	4.10
S12	41.00						6.2		
S0-2	34.00		308.0		509.0		302.8		
initial	35.00		320.0		504.0		305.5		
for		3.81		314.0		506.5		305.8	4.82
second	42.00								
set							309.2		

Table E.5. Tap water at 20°C

	Sample	pH	NH ₄ -N (mg/L)	Average N (mg/L)	PO ₄ -P (mg/L)	Average P (mg/L)	Mg (mg/L)	Average Mg (mg/L)	Cond (ms/cm)
Initial	1		260.0		491.0		399.2		
for set	2	5.50	269.0	263.3	534.0	515.0	381.2	386.1	4.50
1 S0	3		261.0		520.0		377.8		
	4		266.0		522.0		381.2		
	5	6.06	273.0	270.0	514.0	516.7	380.9	380.0	4.75
S1	6		271.0		514.0		377.8		
	7		213.0		380.0		279.7		
	8	6.26	214.0	213.7	381.0	380.7	271.3	275.3	4.40
S2	9		214.0		381.0		274.9		
	10		152.0		228.0		167.2		
	11	6.59	154.0	153.3	225.0	223.3	165.5	165.3	4.05
S3	12		154.0		217.0		163.2		
	13		107.0		127.0		94.3		
	14	6.93	109.0	108.7	127.0	127.3	93.7	93.5	3.00
S4	15		110.0		128.0		92.6		
	16		88.0		97.0		72.0		
	17	7.20	87.2	87.6	99.0	98.2	71.8	70.8	3.90
S5	18		87.7		98.5		68.5		
	19		69.6		80.8		72.9		
	20	7.21	72.7	72.0	80.6	81.0	60.5	64.8	3.95
S6	21		73.8		81.5		61.1		
	25		74.9		79.4		58.8		
	26	7.36	76.6	76.3	79.1	79.3	61.7	60.7	4.70
S7	27		77.4		79.3		61.5		

	Sample	pH	NH ₄ -N (mg/L)	Average N (mg/L)	PO ₄ -P (mg/L)	Average P (mg/L)	Mg (mg/L)	Average Mg (mg/L)	Cond (ms/cm)
	28		68.1		63.8		52.9		
	29	7.55	68.2	76.3	64.5	64.3	51.7	52.2	4.75
S8	30		67.4		64.5		52.1		
	31		55.8		64.1		50.6		
	32	7.69	57.2	67.9	63.9	63.8	51.7	51.4	5.50
S9	33		56.9		63.4		51.9		
	34		47.1		49.5		42.0		
	35	7.89	47.9	56.6	50.0	48.5	40.1	40.6	4.65
S10	36		48.1		46.1		39.7		
	37		31.6		43.4		32.1		
	38	8.18	31.5	47.7	12.3	32.8	33.2	32.7	4.60
S11	39		31.2		42.6		32.8		
	40		27.8		34.0		25.4		
	41	8.45	29.2	31.4	34.9	34.3	25.6	25.5	4.85
	42		29.5		34.0		25.4		
	22		335.0		690.0		508.6		
initial for set 2 S13	23	5.24	333.0	335.0	688.0	688.0	494.1	497.4	5.45
	24		337.0		686.0		489.3		

APPENDIX F: CARBON DIOXIDE TESTS

Table F.1. Run #1.

Total feed: 2.5 L/min, Recycle Ratio R = 6, Operating pH = 8.1

R #1	Inflow to reactor					Effluent					Molar P removal	Caustic use	Molar NaOH usage
Day	pH	Cond	Mg	PO ₄ -P	NH ₃ -N	pH	Cond	Mg	PO ₄ -P	NH ₃ -N			
		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(kg/day)	
1	7.53	6.9	99.4	90.4	878	8.15	6.9	5.5	21	819	2.24E-03	2.91	72.8
2	7.61	7.2	84.5	85.8	838	8.22	7.53	33.2	5.3	810	2.60E-03	1.66	41.5
3	7.68	7.5	83.7	81.1	797	8.40	7.27	13.3	10.5	741	2.28E-03	2.30	57.5
4	7.63	7.4	81.0	81.6	800	8.20	7.76	74.9	2.7	736	2.55E-03	1.93	48.3
5	7.58	7.36	60.4	82.0	802	8.29	7.13	2.4	12.3	723	2.25E-03	2.93	73.3

R #2	Influent to reactor					Effluent					Molar P removal	Caustic use	Molar NaOH usage
Day	pH	Cond	Mg	PO ₄ -P	NH ₃ -N	pH	Cond	Mg	PO ₄ -P	NH ₃ -N			
		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(kg/day)	
1	7.53	6.9	82.1	90.4	878	8.16	7.11	10	16.2	841	2.40E-03	0.43	10.8
2	7.61	7.2	86.1	85.8	838	8.3	7.81	57.6	3.3	787	2.66E-03	0.81	20.3
3	7.68	7.5	82.3	81.1	797	8.1	7.39	24.2	16.1	734	2.10E-03	1.65	41.3
4	7.63	7.4	81.0	81.6	800	8.3	8.48	31.2	2.0	649	2.57E-03	2.14	53.5
5	7.58	7.36	76.0	82.0	802	8.4	7.0	18.3	5.9	703	2.46E-03	1.12	28.0

Table F.2. Run # 2.

Total feed: 2.61 L/min, Recycle ratio: 6, Operating pH: 8.1
Harvest zone up flow velocity: 400 cm/min, With air

R #1	Influent to reactor					Effluent					Molar P removal	Caustic use	Molar NaOH usage
Day	pH	Cond	Mg	PO₄-P	NH₃-N	pH	Cond	Mg	PO₄-P	NH₃-N			
		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(kg/day)	
1	7.8	7.62	81.8	88.3	826	8.29	7.13	15.2	9.56	740	2.54E-03	0.92	23.0
2	7.75		87.9	78.0	814	8.3		21.8	7.5	780	2.28E-03	1.55	38.8
3	7.78	7.22	90.0	84.1	845	8.41	6.73	20.5	6.5	791	2.51E-03	1.65	41.3
4	8.4	7.4	78.8	82.2	775	8.42	7.04	30.2	8.5	761	2.38E-03	1.53	38.3

R # 2	Inflow to reactor					Effluent					Molar P removal	Caustic use	Molar NaOH usage
Day	pH	Cond	Mg	PO₄-P	NH₃-N	pH	Cond	Mg	PO₄-P	NH₃-N			
		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(mS/cm)	(mg/L)	(mg/L)	(mg/L)		(kg/day)	
1	7.8	7.62	91.3	88.3	826	8.2	7	21.0	9.1	772	2.56E-03	0.61	15.3
2	7.75		87.9	78.0	814	8.1		24.3	8.6	790	2.24E-03	0.34	8.5
3	7.78	7.22	90.0	84.1	845	8.3	7.11	22.1	7.8	779	2.46E-03	0.93	23.3
4	8.4	7.4	92.0	82.2	775	8.5	7.13	72.0	7.1	752	2.42E-03	1.46	36.5

Table F.3. Run # 3

Total feed: 2.61 L/min, Recycle ratio: 6, Operating pH: 8.1

Harvest zone upflow velocity: 400 cm/min, No air

R # 1	Inflow to reactor					Effluent					Molar P removal	Caustic use (kg/day)
Date	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)		
1	8.3		78.3	69.3	634	8.51	7.21	55.9	7.1	370	2.01E-03	1.69
2	7.78	7.16	77.1	50.6	827	8.44	7.26	26.2	6.9	761	1.41 E-03	1.64
3	8	6.83	75.0	29.7	698	8.49	5.18	54.4	3.1	573	0.86 E-03	1.02
4	7.82	7.15	72.4	63.1	760	8.45	7.09	27.0	5.0	718	1.88 E-03	1.7

R # 2	Inflow to reactor					Effluent					Molar P removal	Caustic use (kg/day)
Day	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)		
1	8.3		78.3	69.3	634	8.46		33.7	6.9	600	2.01E-03	0.57
2	7.78	7.16	82.7	50.6	827	8.48	7.5	76.0	7.0	672	1.41E-03	0.94
3	8	6.83	69.7	29.7	698	8.36	8.09	46.8	2.4	505	8.81E-04	0.48
4	7.82	7.15	72.4	63.1	760	8.3	7.14	31.7	4.5	713	1.89E-03	1.17

Table F.4. Run # 4.

Total feed: 2.05 L/min, Recycle ratio:9, Operating pH: 8.1

Harvest zone up flow velocity: 450 cm/min, With air

R #1	Inflow to reactor					Effluent					Molar P removal	Caustic use (kg/day)
Day	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)		
1	8	6.99	100.2	67.3	799	8.42	7.04	44.4	4.6	696	2.03E-03	0.87
2	8.1	12.48	80.7	38.2	553	8.45	5.25	16.9	4.5	483	1.09 E-03	1.05
3	7.86	5.09	81.7	42.6	575	8.48	5.33	44.4	4.9	525	1.22 E-03	1.15
4	7.93	5.99	59.8	49.0	670	8.46	5.94	32.5	6.3	652	1.38 E-03	1.40
5	7.92	5.68	75.2	52.6	696	8.25	5.8	38.5	9.0	637	1.41 E-03	2.29

R # 2	Inflow to reactor					Effluent					Molar P removal	Caustic use (kg/day)
Day	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)	pH	Cond (mS/cm)	Mg (mg/L)	PO₄-P (mg/L)	NH₃-N (mg/L)		
1	8	6.99	75.58	67.3	799	8.42	6.98	34.29	4.42	732	2.03E-03	0.38
2	8.1	12.48	80.71	38.2	553	8.54	8.61	77.7	2.47	545	1.15E-03	0.53
3	7.86	5.09	83.55	42.6	575	8.23	8.47	76	2.96	221	1.28E-03	0.48
4	7.93	5.99	78.54	49	670	8.22	6.14	52.6041	5.94	653	1.39E-03	0.08
5	7.92	5.68	99.49	52.6	696	8.31	5.94	49.1331	5.13	624	1.53E-03	0.55

**APPENDIX G: INDIRECT METHOD (USING pH AND
CONDUCTIVITY) TO DETERMINE EXTERNAL Mg ADDITION
REQUIREMENTS FOR STRUVITE CRYSTALLIZATION**

Table G.1. Synthetic water

Run 1				
ml of MgCl ₂ added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	8.21	1.886		
0.5	8.2	1.916	0.02	0.06
1	8.2	1.944	0	0.056
1.5	7.76	1.919	0.88	-0.05
2	7.82	1.933	0	0.028
2.5	7.72	1.949	0.2	0.032
3	7.61	1.952	0.22	0.006
3.5	7.55	1.967	0.12	0.03
4	7.49	1.981	0.12	0.028
4.5	7.43	2.02	0.12	0.078
5	7.38	2.03	0.1	0.02
5.5	7.34	2.05	0.08	0.04
6	7.29	2.07	0.1	0.04
6.5	7.26	2.1	0.06	0.06
Run 2				
ml of MgCl ₂ added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	8.25	2.01		
0.5	8.23	2.05	0.04	0.08
1	8.23	2.08	0	0.06
1.5	7.86	2.05	0.74	-0.06
2	7.78	2.06	0.16	0.02
2.5	7.71	2.08	0.14	0.04
3	7.56	2.08	0.3	0
3.5	7.49	2.1	0.14	0.04
4	7.44	2.13	0.1	0.06
4.5	7.38	2.15	0.12	0.04
5	7.33	2.18	0.1	0.06

Run 3

ml of MgCl_2 added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	8.23	2.03		
0.5	8.23	2.07	0	0.08
1	8.22	2.1	0.02	0.06
1.5	7.88	2.06	0.68	-0.08
2	7.79	2.08	0.18	0.04
2.5	7.69	2.09	0.2	0.02
3	7.58	2.1	0.22	0.02
3.5	7.52	2.12	0.12	0.04
4	7.44	2.13	0.16	0.02
4.5	7.38	2.16	0.12	0.06
5	7.32	2.18	0.12	0.04

Table G.2. Centrate matrix

Run 1				
ml of MgCl ₂ added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	7.92	7.18		
0.5	7.91	7.21	0.01	0.03
1	7.91	7.25	0	0.04
1.5	7.91	7.3	0	0.05
2	7.91	7.34	0	0.04
2.5	7.9	7.38	0.01	0.04
3	7.9	7.4	0	0.02
3.5	7.87	7.42	0.03	0.02
4	7.8	7.42	0.07	0
4.5	7.8	7.43	0	0.01
5	7.78	7.46	0.02	0.03
5.5	7.77	7.48	0.01	0.02
6	7.76	7.5	0.01	0.02
6.5	7.76	7.52	0	0.02
7	7.75	7.54	0.01	0.02
7.5	7.75	7.56	0	0.02
8	7.74	7.58	0.01	0.02
8.5	7.74	7.6	0	0.02
9	7.73	7.62	0.01	0.02
9.5	7.73	7.65	0	0.03
10	7.72	7.68	0.01	0.03

Run 2				
ml of MgCl ₂ added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	7.78	6.09		
0.5	7.78	6.12	0	0.06
1	7.78	6.14	0	0.04
1.5	7.75	6.14	0.06	0
2	7.7	6.12	0.1	-0.04
2.5	7.69	6.13	0.02	0.02
3	7.66	6.15	0.06	0.04
3.5	7.66	6.16	0	0.02
4	7.65	6.17	0.02	0.02
4.5	7.63	6.19	0.04	0.04
5	7.62	6.2	0.02	0.02
5.5	7.61	6.22	0.02	0.04
6	7.6	6.24	0.02	0.04
6.5	7.59	6.25	0.02	0.02
7	7.58	6.27	0.02	0.04
7.5	7.57	6.29	0.02	0.04
8	7.57	6.32	0	0.06
8.5	7.56	6.33	0.02	0.02
9	7.55	6.36	0.02	0.06
9.5	7.56	6.38	-0.02	0.04

Run 3				
ml of MgCl ₂ added	pH	Conductivity (mS/cm)	dpH/dml	dcon/dml
0	8.65	6.92		
0.5	8.66	6.94	-0.02	0.04
1	8.66	6.95	0	0.02
1.5	8.65	6.95	0.02	0
2	8.64	6.96	0.02	0.02
2.5	8.63	6.96	0.02	0
3	8.62	6.95	0.02	-0.02
3.5	8.62	6.96	0	0.02
4	8.61	6.97	0.02	0.02
4.5	8.61	6.98	0	0.02
5	8.6	6.99	0.02	0.02
5.5	8.59	7	0.02	0.02
6	8.59	7.02	0	0.04
6.5	8.58	7.04	0.02	0.04
7	8.58	7.05	0	0.02
7.5	8.57	7.11	0.02	0.12
8	8.57	7.13	0	0.04
8.5	8.56	7.18	0.02	0.1

APPENDIX H: APPLICATION OF CHEMICALS FOR THE REDUCTION OF PHOSPHATE CONCENTRATION IN WATER MATRIX

Table H.1. Effects on phosphate concentrations due to PAC addition to centrate

Test Number	PAC (mL added)	Phosphate (mg/L)
1	0.1	91.7
	0.2	74.6
	0.3	71.2
	0.4	61.7
	0.5	32.5
	0.6	38.3
	0.8	9.93
	1.0	2.88
2	0.0	106
	0.1	90.9
	0.2	63.7
	0.3	38
	0.4	9.71
	0.5	56.5*
	0.6	7.69
	0.8	9.68
3	0.0	108
	0.2	48.8
	0.4	11.3
	0.6	1.35
	0.8	1.03
	1.0	1.04

* Possible outlier

Table H.2. Effects on pH, phosphate and aluminum concentrations due to alum addition to centrate

	Alum added	PO₄-P	pH	Al
	(ml)	(mg/L)		(mg/L)
Test 1	0	196	8.26	0.66
	2	157	8.28	1.94
	4	119	8.22	1.91
	6	94.9	8.13	14.76
	8	67.1	8.13	12.95
	10	45.5	8.06	13.79
Test 2				
	0	199	8.3	1.07
	2	151	8.26	0.67
	4	116	8.19	5.34
	6	87.4	8.13	15.57
	8	62.8	8.07	16.03
	10	43	7.99	15.97

APPENDIX I: HARDNESS TEST RESULTS

Table I.1. Comparison of calcium concentrations in LIWWTP centrate between samples tested by AA and by hardness test method

Ca by hardness test	Ca by AA	Absolute error
(mg/L)	(mg/L)	(mg/L)
44.0	35.9	8.1
36.0	33.3	2.7
28.0	33.0	4.9
28.0	31.4	3.4
44.0	30.5	13.5
40.0	52.8	12.8
40.0	37.2	2.9
36.0	32.3	3.7
32.0	34.8	2.8
32.0	32.8	0.7
32.0	33.6	1.6
31.3	33.9	2.6
14.4	14.8	0.3
11.2	10.1	1.1
10.4	8.7	1.7
10.4	7.6	2.8
8.4	8.3	0.1

Table I.2. Comparison of magnesium concentrations in LIWWTP centrate between samples tested by AA and by hardness test method

Mg by hardness test	Mg by AA	Absolute error
(mg/L)	(mg/L)	(mg/L)
18.8	16.3	2.6
13.7	12.7	1.0
13.7	12.3	1.4
15.2	12.5	2.7
15.2	12.1	3.1
9.7	13.9	4.2
14.6	13.7	0.9
14.6	13.0	1.6
4.9	7.8	2.9
7.3	5.2	2.1
9.7	6.2	3.5
6.3	5.5	0.8
5.3	5.7	0.3
4.6	5.8	1.2
4.6	6.2	1.6

APPENDIX J: OPERATIONAL DATA – REACTOR 1

Date		Flows						
		Mg inflow	Centrate	Total influent	Recycle	Total	Upflow	RR
		mL/min	L/min	L/min	L/min	L/min	cm/min	
1-Jul	Wednesday	0.0	2.70	2.70	18.30	21.00	461	6.8
2-Jul	Thursday	0.0	2.40	2.40	-2.40			
3-Jul	Friday	0.0	2.80	2.80	18.80	21.60	474	6.7
7-Jul	Tuesday	84.0	2.52	2.60	15.40	18.00	395	5.9
8-Jul	Wednesday	90.0	2.41	2.50	15.50	18.00	395	6.2
9-Jul	Thursday	84.0	2.52	2.60	15.40	18.00	395	5.9
10-Jul	Friday	90.0	2.41	2.50	15.50	18.00	395	6.2
11-Jul	Saturday	90.0	2.51	2.60	14.80	17.40	382	5.7
12-Jul	Sunday	90.0	2.54	2.63	14.47	17.10	375	5.5
13-Jul	Monday	90.0	2.41	2.50	15.80	18.30	401	6.3
14-Jul	Tuesday	54.0	2.65	2.70	15.60	18.30	401	5.8
15-Jul	Wednesday	54.0	2.87	2.92	15.80	18.72	411	5.4
16-Jul	Thursday	54.0	2.45	2.50	14.50	17.00	373	5.8
17-Jul	Friday	54.0	2.85	2.90	14.10	17.00	373	4.9
19-Jul	Sunday	54.0	2.75	2.80	14.90	17.70	388	5.3
20-Jul	Monday	54.0	2.45	2.50	15.50	18.00	395	6.2
21-Jul	Tuesday	54.0	2.60	2.65	16.25	18.90	414	6.1
22-Jul	Wednesday	54.0	2.55	2.60	15.40	18.00	395	5.9
23-Jul	Thursday	54.0	2.55	2.60	16.00	18.60	408	6.2
								5.9
24-Jul	Friday	54.0	2.61	2.66	15.64	18.30	401	

		Flows						
Date		Mg inflow	Centrate	Total influent	Recycle	Total	Upflow	RR
		mL/min	L/min	L/min	L/min	L/min	cm/min	
25-Jul	Saturday	68.0	2.43	2.50	16.10	18.60	408	6.4
26-Jul	Sunday				16.10	16.10	353	recycle mode
27-Jul	Monday	62.0	2.41	2.47	14.93	17.40	382	6.0
28-Jul	Tuesday		3.30	3.30	15.40	18.70	410	4.7
29-Jul	Wednesday		2.50	2.50	15.80	18.30	401	6.3
30-Jul	Thursday	0.0	2.50	2.50	15.20	17.70	388	6.1
31-Jul	Friday	0.0	2.60	2.60	-2.60			
1-Aug	Saturday	60.0	2.59	2.65	15.05	17.70	388	5.7
11-Aug	Tuesday	60.0	-0.06		0.00			
12-Aug	Wednesday	60.0	2.60	2.66	26.74	29.40	645	10.1
13-Aug	Thursday	60.0	2.54	2.60	15.40	18.00	395	5.9
17-Aug	Monday	66.0	1.08	1.15	14.15	15.30	336	12.3
18-Aug	Tuesday	0.0	1.70	1.70	14.80	16.50	362	8.7
19-Aug	Wednesday				16.00	16.00	351	recycle mode
28-Aug	Friday	78.0	2.47	2.55	15.75	18.30	401	6.2
29-Aug	Saturday	60.0	2.34	2.40	16.20	18.60	408	6.8
30-Aug	Sunday							
31-Aug	Monday	80.0	1.47	1.55	14.95	16.50	362	9.6
1-Sep	Tuesday	102.0	3.15	3.25	15.95	19.20	421	4.9
2-Sep	Wednesday	102.0	3.45	3.55	16.05	19.60	430	4.5

Centrate								Influent					
pH	Conductivity	Temp	PO ₄ -P	NH ₄ -N	Mg	Mg:P	N:P	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	mS/cm	C	mg/L	mg/L	mg/L			mg/L	mg/L	mg/L	moles/L	moles/L	moles/L
7.35	1.26	23.1	13.6	105.0	5.4	0.51	17.08	13.6	105.0	5.4	4.39E-04	7.50E-03	2.22E-04
7.50	1.37	24.7	16.2	120.5	4.4	0.35	16.45	16.2	120.5	4.4	5.23E-04	8.61E-03	1.81E-04
7.44	3.38	27.8								0.0			
7.30	0.95	24.7	9.3	63.5	4.8	0.66	15.10	9.0	61.4	67.6	2.91E-04	4.39E-03	2.78E-03
7.30	0.94	25.3		69.1	5.8			0.0	66.6	75.8	0.00E+00	4.76E-03	3.12E-03
7.44	3.99	28.0		402.0	12.6			0.0	389.0	75.2	0.00E+00	2.78E-02	3.09E-03
7.34	2.84	31.0		233.0	8.8					78.7			
7.47	4.36	30.0	53.6	357.0	11.4	0.27	14.73	51.7	344.6	78.5	1.67E-03	2.46E-02	3.23E-03
7.45	3.84	29.0	48.7	396.0	9.8	0.26	17.99	47.0	382.4	76.1	1.52E-03	2.73E-02	3.13E-03
7.52	4.84	26.5	59.1	513.0	12.4	0.27	19.20	57.0	494.5	82.1	1.84E-03	3.53E-02	3.38E-03
7.49	4.85	30.0	67.0	481.5	12.9	0.24	15.90	65.7	471.9	51.6	2.12E-03	3.37E-02	2.12E-03
7.50	3.07	26.5	36.1	317.0	8.4	0.30	19.43	35.4	311.1	44.3	1.14E-03	2.22E-02	1.82E-03
7.30	1.12	38.9	9.2	84.3	2.4	0.33	20.27	9.0	82.5	44.4	2.91E-04	5.89E-03	1.83E-03
7.45	2.89	34.5	15.6	109.3	6.4	0.52	15.50	15.3	107.3	42.5	4.94E-04	7.66E-03	1.75E-03
7.20	1.03	36.3			5.4			0.0	0.0	42.9	0.00E+00	0.00E+00	1.77E-03
7.5	2.17	34.0	21.8	173.5	4.2					46.2			1.90E-03
7.4	2.47	33.7	24.7	198.0	6.1	0.31	17.73	24.2	194.0	45.7	7.81E-04	1.39E-02	1.88E-03
								0.0	0.0	40.5	0.00E+00	0.00E+00	1.67E-03
7.5	2.29	29.6	32.7	246.0	5.5	0.21	16.64	32.0	240.9	45.9	1.03E-03	1.72E-02	1.89E-03
7.5	4.22	28.2	52.7	442.5	9.6	0.23	18.57	51.6	433.5	49.0	1.67E-03	3.10E-02	2.02E-03
7.54	3.00	26.8	44.4	361.0	9.1	0.26	17.99	52.4	690.2	61.9	1.69E-03	4.93E-02	2.55E-03
											0.00E+00	0.00E+00	0.00E+00
7.63	4.90	27.7	60.4	565.5	11.7	0.25	20.71	58.9	551.3	60.3	1.90E-03	3.94E-02	2.48E-03
7.48	4.87	28.4	48.6	408.5	11.5	0.30	18.59	48.6	408.5	11.5	1.57E-03	2.92E-02	4.73E-04

Centrate								Influent					
pH	Conductivity	Temp	PO ₄ -P	NH ₄ -N	Mg	Mg:P	N:P	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	mS/cm	C	mg/L	mg/L	mg/L			mg/L	mg/L	mg/L	moles/L	moles/L	moles/L
7.59	4.61	30.3	53.5	514.0	11.1	0.26	21.25	53.5	514.0	11.1	1.73E-03	3.67E-02	4.57E-04
7.5	4.85	29.7	71.3	604.0	8.5	0.15	18.74	71.3	604.0	8.5	2.30E-03	4.31E-02	3.50E-04
7.65	5.91	29.8	70.5	559.5	4.4	0.08	17.56	70.5	559.5	4.4	2.28E-03	4.00E-02	1.81E-04
7.6	5.80	30.0	58.0	682.0	3.6	0.08	26.01	56.7	666.6	47.7	1.83E-03	4.76E-02	1.96E-03
7.84	6.95	32.3	83.5	800.5	19.1								
7.1		28.5	83.5	900.5	16.2	0.25	23.86	81.6	880.2	59.8	2.64E-03	6.29E-02	2.46E-03
8.08	6.90	27.4	101.0	920.0	17.4	0.22	20.15	98.7	898.8	62.0	3.19E-03	6.42E-02	2.55E-03
8.2	7.28	29.6	91.5	904.0	22.0	0.31	21.86	86.2	852.1	135.5	2.78E-03	6.09E-02	5.58E-03
8.26	6.69	28.7	75.0	796.5	8.3	0.14	23.49	75.0	796.5	8.3	2.42E-03	5.69E-02	3.42E-04
8.2	6.60	28.0	95.7	880.0	12.3	0.16	20.34				0.00E+00	0.00E+00	0.00E+00
8.36	7.05	30.1	92.1	867.0	8.1	0.11	20.82	89.3	840.5	69.0	2.88E-03	6.00E-02	2.84E-03
		26.0	88.0	840.0	2.3	0.03	21.12	85.8	819.0	52.2	2.77E-03	5.85E-02	2.15E-03
			.										
8.35	6.39	28.7	67.0	762.5	14.9	0.28	25.18	63.5	723.1	117.4	2.05E-03	5.17E-02	4.83E-03
		29.5	81.3	745.0	9.6	0.15	20.27	78.7	721.6	72.1	2.54E-03	5.15E-02	2.97E-03
8.3	6.96		66.4	690.0	8.4	0.16	22.99	64.5	670.2	65.6	2.08E-03	4.79E-02	2.70E-03

Effluent							Expected In reactor Conditions					
pH	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg	pH	Temp	Conductivity	PO ₄ -P	NH ₄ -N	Mg
	mg/L	mg/L	mg/L	moles/L	moles/L	moles/L		°C	mS/cm	mg/L	mg/L	mg/L
8.1							8.1	25.0	3.10	1.7	13.5	0.7
8.2							8.2	25.0	1.23			
8.1							8.1	26.0	3.39			0.0
8.2	13.4	54.6	72.3	4.33E-04	3.90E-03	2.98E-03	8.2	25.0	1.50	12.8	55.6	71.6
8.4	18.0	54.1	14.7	5.81E-04	3.86E-03		8.4	25.0	0.90	15.5	55.8	23.2
8.1		291.0	57.6	0.00E+00	2.08E-02		8.1	25.0	3.92		305.2	60.1
7.9		281.5	64.5		2.01E-02		7.9	30.2	3.67			66.5
8.0	33.8	331.5	53.2	1.09E-03	2.37E-02	2.19E-03	8.0	32.0	4.46	36.5	333.5	56.9
8.0	33.5	278.5	63.3	1.08E-03	1.99E-02	2.60E-03	8.0	25.7	3.39	35.6	294.5	65.3
8.1	27.5	466.0	49.0	8.88E-04	3.33E-02	2.02E-03	8.1	24.2	4.90	31.5	469.9	53.5
8.0	15.6	416.5	17.4	5.04E-04	2.98E-02	7.14E-04	8.0	18.5	4.62	23.0	424.7	22.4
8.0	10.4	217.0	19.8	3.36E-04	1.55E-02	8.15E-04	8.0	26.0	2.86	14.3	231.7	23.6
8.0	8.2	110.5	31.9	2.65E-04	7.89E-03	1.31E-03	8.0	37.8	1.74	8.3	106.4	33.7
8.0	14.2	292.0	21.8	4.59E-04	2.09E-02	8.95E-04	8.0	27.8	3.25	14.4	260.5	25.3
7.3							7.3	27.7	1.94			6.8
	13.6	133.0	32.2				8.0	27.7	1.78			34.1
			33.7			1.39E-03	7.9	27.5	2.15	3.4	27.2	35.4
							7.9	27.0	1.56			5.9
	15.0	218.5	26.8	4.84E-04	1.56E-02	1.10E-03	7.9	28.7	2.65	17.4	221.6	29.5
	10.5	333.0	34.5	3.39E-04	2.38E-02	1.42E-03	7.9	26.0	4.37	16.5	347.6	36.6
	9.1	274.5	41.6	2.94E-04	1.96E-02	1.71E-03	8.0	26.1	3.21	13.7	284.8	44.3
							8.0	26.1	3.21			
	12.2	504.0	40.9	3.94E-04	3.60E-02	1.68E-03	8.0	28.8	5.22	18.8	510.7	43.7
	34.6	395.0	44.3	1.12E-03	2.82E-02	1.82E-03	7.4	27.0	3.85	37.1	397.4	38.5

Effluent							Expected In reactor Conditions					
pH	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg	pH	Temp	Conductivity	PO ₄ -P	NH ₄ -N	Mg
	mg/L	mg/L	mg/L	moles/L	moles/L	moles/L		°C	mS/cm	mg/L	mg/L	mg/L
	13.3	400.5	27.8	4.29E-04	2.86E-02	1.14E-03	8.0	32.6	4.75	18.8	416.0	25.5
	61.6	552.5	6.1	1.99E-03	3.95E-02	2.51E-04	8.1	29.8	4.88	63.0	559.8	6.4
	53.2	656.5	3.8	1.72E-03	4.69E-02	1.56E-04	8.1	28.1	5.96			
	27.3	730.5	8.1	8.81E-04	5.22E-02	3.33E-04	8.1	27.7		31.7	720.9	14.0
8.4	22.5	795.0	11.4	7.27E-04	5.68E-02	4.69E-04	8.0		7.58	27.8	802.7	15.8
8.3	23.8	800.5	25.7	7.68E-04	5.72E-02	1.06E-03	7.2	26.6	6.45	34.6	814.7	30.9
9.1	21.9	818.0	14.1	7.07E-04	5.84E-02	5.80E-04	7.9	28.8	7.12	26.7	820.6	23.2
	79.7	916.5	4.6	2.57E-03	6.55E-02	1.89E-04	7.9			79.2	904.1	5.0
9.8				0.00E+00	0.00E+00	0.00E+00	8.0	33.7	5.36			
8.5	37.7	779.0	18.1	1.22E-03	5.56E-02	7.45E-04	7.3	29.9	7.09	44.9	787.6	25.2
	42.1	796.5	10.4	1.36E-03	5.69E-02	4.28E-04	7.2		6.70	47.7	799.4	15.8
							8.0					
	6.8	705.0	14.1	2.57E-03	6.55E-02	2.98E-03	7.9	28.9		12.1	706.7	23.8
	34.5	705.5	10.9	2.57E-03	6.55E-02	2.98E-03		28.3		42.0	708.2	21.3
	9.4	687.0	5.9	6.28E-04	2.35E-02	8.67E-04		24.0	3.34	19.4	684.0	16.7

APPENDIX J: OPERATIONAL DATA – REACTOR 2

		Flows						
Date		Mg inflow	Centrate	Total influent	Recycle	Total	Upflow	RR
		mL/min	L/min	L/min	L/min	L/min	cm/min	
1-Jul	Wednesday		3.0	3.0	13.2	16.2	355	4.4
2-Jul	Thursday		2.5	2.5	15.5	18.0	395	6.2
3-Jul	Friday		2.7	2.7	18.3	21.0	461	6.8
7-Jul	Tuesday	102.0	2.5	2.6	15.4	18.0	395	5.9
8-Jul	Wednesday		2.5	2.5	14.9	17.4	382	6.0
9-Jul	Thursday	84.0	2.5	2.6	15.4	18.0	395	5.9
10-Jul	Friday	84.0	2.0	2.1	15.3	17.4	382	7.3
11-Jul	Saturday	84.0	2.0	2.1	15.9	18.0	395	7.6
12-Jul	Sunday	84.0	2.4	2.5	14.7	17.1	375	6.0
13-Jul	Monday	84.0	2.3	2.4	15.6	18.0	395	6.5
14-Jul	Tuesday	60.0	2.1	2.2	-2.2		0	-1.0
15-Jul	Wednesday	60.0	2.8	2.9	16.6	19.5	428	5.7
16-Jul	Thursday	54.0	2.4	2.5	16.2	18.6	408	6.6
17-Jul	Friday				16.0	16.0	351	
18-Jul	Saturday				16.0	16.0	351	recycle mode
19-Jul	Sunday				16.0	16.0	351	recycle mode
20-Jul	Monday				16.0	16.0	351	recycle mode
21-Jul	Tuesday				13.0	13.0	285	recycle mode
22-Jul	Wednesday	42.0			13.0	13.0	285	recycle mode
23-Jul	Thursday	54.0	2.7	2.8	15.3	18.0	395	5.5

		Flows						
Date		Mg inflow mL/min	Centrate L/min	Total influent L/min	Recycle L/min	Total L/min	Upflow cm/min	RR
24-Jul	Friday	54.0	2.8	2.8	15.2	18.0	395	5.4
25-Jul	Saturday	56.0	2.6	2.7	15.4	18.0	395	5.8
26-Jul	Sunday	0.0	0.0	0.0	15.4	15.4	338	recycle mode
27-Jul	Monday	62.0	2.0	2.1	15.1	17.2	378	7.2
28-Jul	Tuesday	48.0	2.2	2.3	15.4	17.7	387	6.8
29-Jul	Wednesday	48.0	2.3	2.3	15.7	18.0	395	6.8
30-Jul	Thursday	0.0	2.5	2.5	15.5	18.0	395	6.2
31-Jul	Friday	48.0	2.6	2.6	15.4	18.0	395	5.9
11-Aug	Tuesday							recycle mode
12-Aug	Wednesday	48.0	2.7	2.7	16.8	19.5	428	6.2
13-Aug	Thursday	48.0	1.9	2.0	14.0	15.9	349	7.2
16-Aug	Sunday	0.0	0.0					
17-Aug	Monday	48.0	0.0	0.0	0.0			
18-Aug	Tuesday							
19-Aug	Wednesday	102.0	2.2	2.4	15.4	17.7	388	6.5
20-Aug	Thursday	48.0	2.6	2.6	15.4	18.0	395	5.9
28-Aug	Friday	48.0	2.0	2.0	15.7	17.7	388	7.9
29-Aug	Saturday	48.0	2.4	2.4	15.2	17.6	386	6.3
30-Aug	Sunday							recycle mode
31-Aug	Monday	50.0	2.7	2.7	14.9	17.6	386	5.5
1-Sep	Tuesday	96.0	2.5	2.6	15.7	18.3	401	6.0
2-Sep	Wednesday	96.0	2.5	2.6	17.8	20.4	447	6.9

Centrate								Influent					
pH	Cond	Temp	PO ₄ -P	NH ₄ -N	Mg	Mg:P	N:P	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	mS/cm	C	mg/L	mg/L	mg/L			mg/L	mg/L	mg/L	moles/L	moles/L	moles/L
7.35		23.1	13.6	105.0	5.4	0.51	17.08	13.6	105.0	5.4	4.39E-04	7.50E-03	2.22E-04
7.50		24.7	16.2	120.5	4.4	0.35	16.45	16.2	120.5	4.4	5.23E-04	8.61E-03	1.81E-04
7.44	3.38	27.8						0.0	0.0	0.0			
7.30		24.7	9.3	63.5	4.8	0.66	15.10	8.9	61.0	83.1	2.89E-04	4.36E-03	3.42E-03
7.30		25.3		69.1	5.8				69.1	5.8		4.94E-03	2.39E-04
7.44	3.99	28.0		402.0	12.6				389.0	76.8		2.78E-02	3.16E-03
7.34	2.84	31.0		233.0	8.8				223.7	88.4			
7.47	4.36	30.0	53.6	357.0	11.4	0.27	14.73	51.5	342.7	90.9	1.66E-03	2.45E-02	3.74E-03
7.45	3.84	29.0	48.7	396.0	9.8	0.26	17.99	47.0	382.4	78.0	1.52E-03	2.73E-02	3.21E-03
7.52	4.84	26.5	59.1	513.0	12.4	0.27	19.20	57.0	495.0	81.9	1.84E-03	3.54E-02	3.37E-03
7.49	4.85	30.0	67.0	481.5	12.9	0.24	15.90	65.2	468.4	67.0	2.10E-03	3.35E-02	2.76E-03
7.50	3.07	26.5	36.1	317.0	8.4	0.30	19.43	35.4	310.4	49.6	1.14E-03	2.22E-02	2.04E-03
7.30		38.9	9.2	84.3	2.4	0.33	20.27	9.0	82.4	46.4	2.91E-04	5.89E-03	1.91E-03
7.45	2.89	34.5	15.6	109.3	6.4	0.52	15.50						
7.20		36.3			5.4								
7.45	2.17	34.0	21.8	173.5	4.2								
7.41	2.47	33.7	24.7	198.0	6.1	0.31	17.73						
7.51	2.29	29.6	32.7	246.0	5.5	0.21	16.64	32.1	241.2	43.7	1.04E-03	1.72E-02	1.80E-03
7.54	4.22	28.2	52.7	442.5	9.6	0.23	18.57	51.7	434.1	46.6	1.67E-03	3.10E-02	1.92E-03
7.54	3.00	26.8	44.4	361.0	9.1	0.26	17.99	43.5	353.4	50.1	1.40E-03	2.52E-02	2.06E-03

Centrate								Influent					
pH	Cond	Temp	PO ₄ -P	NH ₄ -N	Mg	Mg:P	N:P	PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg
	mS/cm	C	mg/L	mg/L	mg/L			mg/L	mg/L	mg/L	moles/L	moles/L	moles/L
7.63	4.90	27.7	60.4	565.5	11.7	0.25	20.71	58.6	548.8	68.9	1.89E-03	3.92E-02	2.83E-03
7.48	4.87	28.4	48.6	408.5	11.5	0.30	18.59	47.6	399.8	52.8	1.54E-03	2.86E-02	2.17E-03
7.59	4.61	30.3	53.5	514.0	11.1	0.26	21.25	52.4	503.3	51.5	1.69E-03	3.59E-02	2.12E-03
7.50	4.85	29.7	71.3	604.0	8.5	0.15	18.74	71.3	604.0	8.5	2.30E-03	4.31E-02	3.50E-04
7.65	5.91	29.8	70.5	559.5	4.4	0.08		69.2	549.2	40.3			
7.84	6.95	32.3	83.5	800.5	19.1								
7.10		28.5	83.5	900.5	16.2	0.25	23.86	82.0	884.5	50.6	2.65E-03	6.32E-02	2.08E-03
8.08	6.90	27.4	101.0	920.0	17.4	0.22	20.15	98.5	897.4	64.9	3.18E-03	6.41E-02	2.67E-03
8.20	7.28	29.6	91.5	904.0	22.0	0.31	21.86	0.0	0.0	1949.0	0.00E+00	0.00E+00	8.02E-02
8.26	6.69	28.7	75.0	796.5	8.3	0.14	23.49						
8.20	6.60	28.0	95.7	880.0	12.3	0.16	20.34	91.5	841.8	96.4	2.96E-03	6.01E-02	3.97E-03
8.21	6.90	28.5	88.0	866.5	8.8	0.13	21.78	86.4	850.5	44.6	2.79E-03	6.08E-02	1.84E-03
8.36	7.05	30.1	92.1	867.0	8.1	0.11	20.82	89.9	846.2	54.7	2.90E-03	6.04E-02	2.25E-03
		26.0	88.0	840.0	2.3	0.03	21.12	86.2	823.2	41.2	2.78E-03	5.88E-02	1.70E-03
8.35	6.39	28.7	67.0	762.5	14.9	0.28	25.18	65.8	748.4	50.7	2.12E-03	5.35E-02	2.09E-03
		29.5	81.3	745.0	9.6	0.15	20.27	78.3	717.5	81.2	2.53E-03	5.12E-02	3.34E-03
8.34	6.96		66.4	690.0	8.4	0.16	22.99	63.9	664.2	80.9	2.06E-03	4.74E-02	3.33E-03

Effluent						Expected In reactor Conditions					
PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₄ -N	Mg	pH	Conductivity	Temp	PO ₄ -P	NH ₄ -N	Mg
mg/L	mg/L	mg/L	moles/L	moles/L	moles/L		mS	C	mg/L	mg/L	mg/L
						8.15	2.76	24.7	13.6	105.0	1.0
						8.04	1.30	24.4	16.2	120.5	0.6
						7.81	1.78	26.4			0.0
9.7	49.3	54.0	0.00031	0.00352	0.00222	8.15	2.28	24.1	66.4	353.0	58.2
15.0	50.1	58.0	0.00048	0.00358	0.00239	7.86	2.02	24.0	89.4	367.7	50.5
	296.0	43.5	0.00000	0.02114	0.00179	7.66	2.12	25.0		2142.2	48.3
	244.5	41.7		0.01746	0.00172	7.98	2.29	25.0		2005.0	47.3
		39.1			0.00161	8.06	2.53	25.4	51.5	342.7	45.1
		54.0			0.00222	8.1	2.71	26.2	47.0	382.4	57.4
		32.8			0.00135	8.13	3.49	25.7	57.0	495.0	39.3
		18.4			0.00076	8.09	4.60	24.2	65.2	468.4	
		30.7			0.00126	7.6	2.62	24.5	35.4	310.4	33.5
		28.6			0.00117	8.1	1.67	26.3	9.0	82.4	30.9
						8.07	2.96	27.8			
						8.13		27.7			
		194.8			0.00802	8.14	2.79	27.5			194.8
						8.14					6.3
14.0	199.0	21.6	0.00045	0.01421	0.00089	8.12	2.14	28.2	16.8	205.4	25.0
12.8	310.0	25.5	0.00041	0.02214	0.00105	8.15	2.32	26.0	18.9	329.5	28.8
5.2	273.0	27.3	0.00017	0.01950	0.00112	8.18	2.7	26.1	10.8	284.8	30.7
						8.21	2.47	26.2			

Effluent						Expected In reactor conditions					
PO ₄ -P	NH ₄ -N	Mg	PO ₄ -P	NH ₃ -N	Mg	pH	Conductivity	Temp	PO ₄ -P	NH ₄ -N	Mg
mg/L	mg/L	mg/L	moles/L	moles/L	moles/L		mS/cm	C	mg/L	mg/L	mg/L
25.3	440.0	42.8	0.00082	0.03143	0.00176	8.3	3.08	27.4	29.4	453.3	46.0
6.3	262.5	30.3	0.00020	0.01875	0.00125	8.17	3.5	27.2	11.6	280.0	33.2
8.0	396.5	15.2	0.00026	0.02832	0.00063	7.57	4	29.7	13.7	410.1	19.8
50.4	529.5	0.9	0.00163	0.03782	0.00004	8.15	4.85	26.5	53.3	539.8	2.0
9.8	546.5	6.5	0.00032	0.03904	0.00027	8.13		28.0	18.4	546.9	11.4
29.1	825.5	14.9	0.00094	0.05896	0.00061	7.89	2.15	26.0	36.4	833.7	19.8
44.7	862.5	15.1	0.00144	0.06161	0.00062	7.66	3.39	25.6	51.3	866.8	21.2
13.0	727.0	23.6	0.00042	0.05193	0.00097	8.27	6.05	26.5	23.4	742.2	33.3
18.3	795.0	6.1	0.00059	0.05679	0.00025	7.6	5.46	26.4	28.1	803.0	11.7
22.2	746.5	10.4	0.00072	0.05332	0.00043	8.14	4.1	27.2	29.8	757.8	15.4
26.6	787.5	4.3	0.00086	0.05625	0.00018	8.15	4.16	25.0	34.7	792.4	9.3
						8.5	3.2	26.0			
8.3	713.5	10.3	0.00163	0.06161	0.00802	8.13	3.72	25.6	17.1	718.9	16.5
18.2	655.5	21.5	0.00000	0.00000	0.00000	7	6.28	28.3	26.7	664.3	30.0
10.5	708.0	9.1	0.00035	0.01748	0.00082	8			17.2	702.5	18.1

APPENDIX K: COMPOSITION OF STRUVITE PELLETS – ICP-MS TEST RESULTS

Sampling date	Unit	MDL	2-Sep 4.7mm	2-Sep 3.33mm	2-Sep 1.98mm	21-Aug 3.33mm	21-Aug 1.98mm	20-Aug 1.98mm
Aluminum (Al)	%	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Arsenic (As)	ppm	0.1	0.3	0.3	0.6	0.3	0.3	0.4
Barium (Ba)	ppm	10	<10	<10	<10	<10	<10	<10
Beryllium (Be)	ppm	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bismuth (Bi)	ppm	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium (Cd)	ppm	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Calcium (Ca)	%	0.01	0.19	0.19	0.2	0.2	0.19	0.2
Cerium (Ce)	ppm	0.02	0.17	<0.02	0.03	<0.02	<0.02	<0.02
Cesium (Cs)	ppm	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cobalt (Co)	ppm	0.1	<0.1	0.4	<0.1	<0.1	<0.1	<0.1
Copper (Cu)	ppm	0.2	16.4	3.2	4.3	2.5	2.9	2.3
Cromium (Cr)	ppm	1	4	4	5	4	4	4
Gallium (Ga)	ppm	0.05	0.8	0.69	0.73	0.65	0.71	0.7
Germanium (Ge)	ppm	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Indium (In)	ppm	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Iron (Fe)	%	0.01	0.04	0.04	0.04	0.04	0.04	0.04
Lanthanum (La)	ppm	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Lead (Pb)	Ppm	0.2	0.7	0.5	1.5	0.2	0.3	0.2
Lithium (Li)	ppm	0.1	0.6	0.3	0.6	0.3	0.2	0.2
Manganese (Mn)	ppm	5	218	216	229	240	248	266

Sampling date	Unit	MDL	2-Sep 4.7mm	2-Sep 3.33mm	2-Sep 1.98mm	21-Aug 3.33mm	21-Aug 1.98mm	20-Aug 1.98mm
Mercury (Hg)	ppm	0.01	<0.01	<0.01	<0.01	<0.01	0.12	<0.01
Molybdenum (Mo)	ppm	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Nickle (Ni)	ppm	0.2	0.6	<0.2	0.4	0.2	0.2	0.2
Potassium (K)	%	0.01	0.03	0.03	0.03	0.03	0.03	0.03
Rhenium (Re)	ppm	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Rubidium (Rb)	ppm	0.1	0.9	0.9	1	1	1	1
Scandium (Sc)	ppm	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Selenium (Se)	ppm	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Silver (Ag)	ppm	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sodium (Na)	%	0.01	0.01	0.01	0.01	<0.01	<0.01	0.01
Strontium (Sr)	ppm	0.2	1.1	1.4	1.4	1.3	1.6	1.7
Sulphur (S)	%	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Thalium (Tl)	ppm	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Tin (Sn)	ppm	0.2	28	5.1	9.3	4.4	5.4	2.5
Titanium (Ti)	%	0.005	0.025	0.025	0.023	0.025	0.022	0.023
Tungsten (W)	ppm	0.05	0.19	2.66	0.16	0.12	0.08	0.06
Uranium (U)	ppm	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Vanadium (V)	ppm	1	<1	<1	<1	<1	<1	<1
Zinc (Zn)	ppm	2	4	4	5	3	4	4
Zirconium (Zr)	ppm	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

APPENDIX L: CRUSHING STRENGTH DATA

Sample Number	P (mg/L)	N (mg/L)	Mg (mg/L)	Fe (mg/L)	Ca (mg/L)	Average Strength		Std. Dev g
						g	N	
1	573.5	235.5	365.8	0.6	0.5	1503	14.7	305.5
2	536	228	362.8	0.6	7.1	3346	32.8	636.2
3	552.5	237.5	385.8	0.6	3.7	1736	17.0	325.4
4	541	228.5	410.6	0.5	4.0	2714	26.6	745
5	583	241.5	393.7	0.5	5.6	1868	18.3	464
6	515.5	222	344.0	0.7	9.2	2804	27.5	433
7	580	255	390.77	1.4	7.5	2187	21.5	370
8	552	245	372.48	1.5	8.3	2110	20.7	329
9	524.5	215.5	356.5	0.8	9.0	2544	25.0	557
10	560.5	237	369.5	0.6	7.7	2283	22.4	379
11	364	156	256.65	1.1	15.2	2828	27.7	620.7
12	516	223	361.22	1.4	8.3	2950	28.9	493.7
13	563	245	384.73	1.5	7.7	2420	23.7	289