

**Development of an aerated struvite crystallization reactor for
phosphorus removal and recovery from swine manure**

by

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Abstract

Declining phosphate reserves and stricter regulations regarding wastewater discharge have increased the need for phosphorus removal and recovery. Crystallization is a promising option since P would not only be removed from the waste stream, but could also be recovered as struvite, a potential fertilizer. The purpose of this research was to achieve effective P removal and recovery through struvite precipitation from agricultural wastewater with minimal chemical input. It was found that raw swine manure had the potential for P removal and recovery through struvite precipitation by raising the pH through aeration without any Mg^{2+} amendment. This led to the development of a side-stream continuous 12 L reactor design with a novel combination of fluidized seedbed and aeration for pH increase. Synthetic feed was used to optimize the operational parameters of the reactor system. It was found that for a 100 ml/min influent rate, an aeration and recycle rate combination of 4.5 – 7 LPM and 700 ml/min was sufficient for increasing and maintaining the reactor pH from 6.7 to between 7.6 and 8.0. Significant P removal was achieved in six h runs without a seedbed (91 – 92%), while neither the struvite nor sand seedbeds improved P removal (91 – 96%). Struvite was recovered in all runs, with additional Ca^{2+} precipitation in the seedbed runs. Long-term runs showed that operation of the reactor was possible for an extended period of time, up to 46 h without any major adjustment. The average P removal was 85 – 88%, and precipitate collected after 24 h was found to be mainly struvite, while the final precipitate also contained calcite. This study has demonstrated the technical feasibility of an aerated crystallization reactor system for struvite removal and recovery from synthetic swine wastewater. By avoiding chemical amendments this reactor system has eliminated a significant portion of the

operational costs found in comparable systems. The major obstacle for achieving system stability and consistency was scaling.

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Chapter 1 – Introduction

Phosphorus (P) has generated a great deal of interest in the research community, in part because it is a limited but essential resource. To a considerable extent this interest is focused on the removal and recovery of P from various waste streams where it is often seen as a nuisance – either clogging pipes in wastewater treatment plants or contributing to eutrophication through agricultural run-off (Morse *et al.*, 1998; Doyle and Parsons, 2002). A number of P removal and recovery methods are available, including precipitation of P by metal salts (iron, alum, calcium, magnesium), cultivation of microorganisms in wastewater (bacteria, microalgae), constructed wetlands, and crystallization (Morse *et al.*, 1998; de-Bashan and Bashan, 2004). Crystallization is of particular interest since it could accomplish both removal and recovery of P from waste streams through the precipitation of struvite, a promising slow-release fertilizer (Gaterell *et al.*, 2000; de Bashan and Bashan, 2004). Both municipal and agricultural wastewaters have been successfully treated to precipitate struvite and reduce the P concentration of the effluent (Ueno and Fujii, 2001; Nelson *et al.*, 2003; Suzuki *et al.*, 2005; Forrest *et al.*, 2008; Moerman *et al.*, 2009). The following sections will provide background on the issue of P, examine struvite chemistry, look at P removal and recovery processes, and discuss the P issue in Manitoba.

1.1 Phosphorus in the environment and industry

1.1.1 Phosphorus reserves

Phosphate rock is a finite resource with no known substitute in nature (Shu *et al.*, 2006), and although it is found worldwide, mining is focused in the United States, China, and Morocco (Forrest *et al.*, 2008). Estimates have placed the global reserve life of phosphate rock that can be mined economically somewhere between 50 and 100 years (Wang *et al.*, 2005; Forrest *et al.*, 2008; Cordell *et al.*, 2009). Although the exact extent of the global reserve life of high-quality phosphate is somewhat debatable, there is no doubt that it will be exhausted in the not too distant future. There are additional potential phosphate rock reserves of about 11 000 million tons, but currently these cannot be processed economically (Shu *et al.*, 2006). These reserves have lower phosphate rock quality, so as higher quality phosphate rock is being depleted, phosphorus industries have to deal with ore containing higher concentrations of metals such as cadmium, uranium, nickel, chromium, copper, and zinc (Driver *et al.*, 1999).

1.1.2 Phosphorus use

Phosphorus is used extensively in two main sectors: agricultural and industrial (non-fertilizer), the main distinguishing feature between the two sectors is the relative purity of their products. Agricultural use is mainly focused on manufacture of fertilizers, which requires little purification, but also includes certain animal feed supplements. The non-fertilizer sector manufactures high purity phosphates for a variety of industrial applications, including detergents, water treatment, flame retardants, paints,

pharmaceuticals, beverage and food uses (Morse *et al.*, 1998; Driver *et al.*, 1999; Gaterell *et al.*, 2000). Natural mineral phosphate rock is the primary source of raw material for both these sectors, although the agricultural sector is the greatest consumer of mined phosphate rock, using about 80% of the global production (Driver *et al.*, 1999; Gaterell *et al.*, 2000).

1.1.3 Sources and impact of excess phosphorus in water

Phosphorus can enter water bodies from industrial, human, and agricultural sources. These sources can be classified as either point or nonpoint sources. Point sources, such as wastewater effluents from municipal and industrial treatment plants, tend to have continuous discharge with little variation over time. This makes them easier to monitor and regulate, as well as to control discharge levels through treatment at the source (Carpenter *et al.*, 1998). Although nonpoint sources can also have continuous inputs, they are more often intermittent and linked to seasonal activities such as agriculture (excessive fertilizer use and high-density livestock operations), or to major construction. Since nonpoint sources can cover a large area and be transported overland or underground to receiving waters, they are difficult to monitor and control and consequently nonpoint inputs are the major source of water pollution in the United States (Carpenter *et al.*, 1998).

It is estimated that of the P used in animal feeding, 70% is directly excreted as waste (Wang *et al.*, 2005). Animal manure slurries high in nitrogen (N) and P are often land-applied to meet crop N needs (Miles and Ellis, 2001; Nelson *et al.*, 2003). Swine lagoon

liquid has higher levels of P than N relative to crop needs, so when swine manure is applied to meet crop N requirements, P can be over-applied by two to three times (Nelson *et al.*, 2003; Çelen *et al.*, 2007). The over-application of P can lead to an excess of the nutrient entering surface waters, and is seen as a major cause of eutrophication in water bodies (Greaves *et al.*, 1999).

Eutrophication is an extraordinary growth of algae as a result of excess nutrients (particularly N and P compounds) in water bodies, such as rivers, lakes, and seas (de-Bashan and Bashan, 2004). It can either be the result of over fertilization of aquatic environments due to human actions, or it can be a natural phenomenon where the seasonal increase in nutrients causes the organic load in a lake to increase (Doyle and Parsons, 2002). Generally, P is seen as the major nutrient responsible for eutrophication. There are many negative effects associated with eutrophication of aquatic environments, including (Carpenter *et al.*, 1998):

- increased biomass of phytoplankton
- shifts in phytoplankton to bloom-forming species (e.g. cyanobacteria) that may be toxic or inedible
- taste, odour, and water treatment problems (trihalomethanes)
- oxygen depletion
- increased incidence of fish kills
- loss of desirable fish species
- decreases in perceived esthetic value of the water body

Limiting the P and N input into water bodies can reverse eutrophication, but recovery rates are highly variable and often quite slow (Carpenter *et al.*, 1998).

1.1.4 Phosphorus regulations

In an effort to protect water quality, many countries have implemented nutrient management regulations that limit land application of substances containing N and P. Environmental Protection Agency (EPA) regulations regarding concentrated animal feeding operations will limit land application of manure to phosphorus-based rates. Consequently, producers will either need a much larger land base to dispose of all their manure, or need to transport manure off-site at great cost (Burns and Moody, 2002). These regulations are one of the main driving forces behind the development of P removal technologies from agricultural wastewater.

1.2 Struvite

1.2.1 Uses

As mentioned before, the phosphate industry is divided into the agricultural and industrial sectors. Substituting struvite for phosphate rock in the non-fertilizer sector has some technological barriers to overcome before it can be considered feasible. Struvite cannot be processed by the ‘wet’ route since it does not form an easily filterable crystal (due to magnesium interference), and the ammonia would pose major problems for processing by the ‘thermal’ route (increased N emission levels from the phosphorus furnace) (Driver *et al.*, 1999; Gaterell *et al.*, 2000). Struvite can, however, be used in the agricultural sector

since it does not face any of these processing obstacles to be used directly as a fertilizer. Struvite has often been described as a non-burning slow-release fertilizer (Gaterell *et al.*, 2000) with potential use with ornamentals, vegetables, forest out-plantings, turf, orchard trees, and potted plants (de-Bashan and Bashan, 2004). A study by Richards and Johnston (2001) found that recovered struvites as sources of P were just as effective as monocalcium phosphate (a source of water-soluble P generally considered to be fully plant available). Benefits of using struvite, as compared to other fertilizers, include low leach rates and prolonged release of nutrients throughout the growing season (Gaterell *et al.*, 2000).

1.2.2 Characterization and Solubility

Struvite is the common name for magnesium ammonium phosphate hexahydrate, or MAP ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), Table 1.1 lists some selected physical and chemical properties of struvite. Struvite crystals are usually stable, white, and orthorhombic (Le Corre *et al.*, 2005), precipitating as magnesium, ammonium, and phosphorus react in 1:1:1 molar ratios according to the simplified reaction Eq. (1):



The distinctive orthorhombic structure of struvite crystals allow them to be readily identifiable through X-ray diffraction (XRD), by matching the position and intensity of the peaks produced to a reference library of standard patterns (Doyle and Parsons, 2002).

Table 1.1 Physical and chemical properties of struvite.

Property	Struvite
Colour	White, yellowish white, or brownish white
Specific density	1.7 g.cm ⁻³
Solubility at 25°C	Very insoluble in water: 0.018 g.100ml ⁻¹ Soluble in acid: 0.178 g.100ml ⁻¹ in 0.01 N HCl
Formula weight	245.41 g.mol ⁻¹
ΔH°_f	-880.0 kcal.mol ⁻¹

Source: Wu and Bishop, 2004 and Le Corre *et al.*, 2009

Struvite crystals develop in two chemical stages: nucleation and crystal growth, yet various factors control this development, including solution pH, supersaturation, temperature, mixing energy, component molar ratios, reaction kinetics, and the presence of interfering ions (Doyle and Parsons, 2002; Le Corre *et al.*, 2005; Forrest *et al.*, 2008).

The key factor for determining crystallization is supersaturation, which is dependent upon solution pH and reactive solution concentration. The sum of the ionic concentrations of the free ions and complexes of the constituent ions (Mg^{2+} , NH_4^+ , and PO_4^{3-}) can be expressed as the following total soluble constituent species concentrations (Bouropoulos and Koutsoukos, 2000; Wu and Bishop, 2004; Ali and Schneider, 2008):

$$C_{T_{NH_4}} = [H_3PO_4] + [HPO_4^-] + [H_2PO_4^{2-}] + [PO_4^{3-}] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4^-] \quad (2)$$

$$C_{T_{Mg}} = [Mg^{2+}] + [MgOH^+] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4^-] \quad (3)$$

$$C_{T_{NH_4}} = [NH_3] + [NH_4^+] \quad (4)$$

To determine the activity coefficient (γ_i) of the constituent ions, the bulk fluid ionic strength is used in a variety of empirical relations, the most common being the Davies

equation, since it is applicable at high ionic strengths (Ali and Schneider, 2008). The ionization fractions of the constituent ions can be defined as follows:

$$\alpha_{Mg} = \frac{[Mg^{2+}]}{C_{TMg}} ; \quad \alpha_{PO_4} = \frac{[PO_4^{3-}]}{C_{TPO_4}} ; \quad \alpha_{NH_4} = \frac{[NH_3]}{C_{TNH_4}} \quad (5) - (7)$$

The solubility product, K_{SP} , for struvite can be derived from the total soluble concentration, ionization fraction, and activity of each constituent ion:

$$K_{SP} = (C_{TMg} \alpha_{Mg} \gamma_{Mg}) \cdot (C_{TPO_4} \alpha_{PO_4} \gamma_{PO_4}) \cdot (C_{TNH_4} \alpha_{NH_4} \gamma_{NH_4}) \quad (8)$$

There are a number of solubility products that have been published for struvite (Table 1.2), that cover quite a range of values. This is mostly because the inclusion of complexes formed in solution and the chemical speciation determined was different for various authors (Doyle and Parsons, 2002).

Table 1.2 Published values of struvite solubility product.

pK_{sp}	Reference
12.6	Stumm and Morgan, 1970
13.12	Burns and Finlayson, 1982
13.0	Mamais <i>et al.</i> , 1994
12.6	Loewenthal <i>et al.</i> , 1994
12.36	Buchanan <i>et al.</i> , 1994a, 1994b
12.94	Aage <i>et al.</i> , 1997
13.26	Ohlinger <i>et al.</i> , 1998
13.31	Pastor <i>et al.</i> , 2008

Adapted from Doyle and Parsons, 2002

Another solubility concept that is often reported is the conditional solubility product. The conditional solubility product, P_{CS} , and the equilibrium conditional solubility product, P_{CS}^{eq} , is defined as (Wu and Bishop, 2004; Forrest *et al.*, 2008):

$$P_{CS} = C_{T_{Mg}} \cdot C_{T_{NH_4}} \cdot C_{T_{PO_4}} \quad (9)$$

$$P_{CS}^{eq} = \frac{K_{SP}}{\alpha_{Mg} \gamma_{Mg} \alpha_{NH_4} \gamma_{NH_4} \alpha_{PO_4} \gamma_{PO_4}} \quad (10)$$

The conditional solubility product can simply be determined from the analytical measurement of the three component ions, while the equilibrium conditional solubility product relates to the solution properties, including ionization fraction, activity coefficients, and the struvite solubility product (Ali and Schneider, 2008; Forrest *et al.*, 2008). The P_{CS} can be calculated from the K_{SP} , but the P_{CS} will then only be valid for a specific pH value, while the K_{SP} is applicable at any pH (Doyle and Parsons, 2002). The advantage of using the conditional solubility product is that it is simply the product of the analytical concentrations of total magnesium, ammonium, and phosphate (or the concentrations of all soluble species), which can then be compared with the equilibrium solubility product (at system pH) to determine whether struvite will precipitate (Wu and Bishop, 2004).

The ratio of the conditional solubility product and the equilibrium conditional solubility product is known as the supersaturation ratio (SSR) (Ali and Schneider, 2008).

$$SSR = \left(\frac{P_{CS}}{P_{CS}^{eq}} \right)^{1/3} = \left(\frac{\{Mg^{2+}\} \{NH_4^+\} \{PO_4^{3-}\}}{K_{SP}} \right)^{1/3} = \left(\frac{IAP}{K_{SP}} \right)^{1/3} \quad (11)$$

Further simplification allows the supersaturation ratio to be expressed in terms of the ion activity product (IAP) and the solubility product. The saturation status of a solution (and possibility of struvite precipitation) can now be determined (Ali and Schneider, 2008; Forrest *et al.*, 2008):

Supersaturation – $P_{CS}^{eq} > P_{CS}$, or $SSR > 1 \rightarrow$ potential struvite precipitation

Saturation – $P_{CS}^{eq} = P_{CS}$, or $SSR = 1 \rightarrow$ equilibrium

Undersaturation – $P_{CS}^{eq} < P_{CS}$, or $SSR < 1 \rightarrow$ no potential struvite precipitation

Another way of looking at precipitation potential is that, when the concentration product of the component ions of struvite (Mg^{2+} , NH_4^+ , and PO_4^{3-}) exceeds the struvite solubility limit given by the solubility product (K_{SP}), precipitation will occur. The availability of Mg^{2+} , NH_4^+ , and PO_4^{3-} for forming struvite will depend on the system pH and on their total dissolved concentrations. Because the speciation of phosphate and ammonium is pH dependent, the solubility of struvite will also change with pH (Wu and Bishop, 2004).

The solubility of struvite generally decreases with increasing pH, but starts to increase at higher pH values since the ammonium ion concentration decreases while the phosphate ion concentration increases (Doyle and Parsons, 2002). Therefore, struvite will have a pH of minimum solubility, where the greatest amount of precipitation will occur. Various authors have suggested a range of values for this point as listed in Table 1.3.

Table 1.3 Reported values for pH of minimum struvite solubility.

pH values	Reference
9.0	Buchanan <i>et al.</i> , 1994a, b
8.9-9.25	Nelson <i>et al.</i> , 2003
8.0-10.6	Momberg and Oellermann, 1992
9.0-9.4	Booker <i>et al.</i> , 1999
9.0-9.5	Miles and Ellis, 2001
10.3	Booram <i>et al.</i> , 1975
10.3	Ohlinger <i>et al.</i> , 1998
10.7	Stumm and Morgan, 1970

Adapted from Doyle and Parsons, 2002

The determination of optimum pH for struvite precipitation has to take into account not only the maximum amount of precipitate, but also the highest purity of recovered product, if it is to be marketable as a fertilizer. The optimum pH is dependent on the composition of the wastewater. Different wastewater streams will have different values for optimum pH, mostly dependent on the Ca:Mg:P:NH⁴⁺ ratios (Wang *et al.*, 2005). One study found the optimum pH for struvite precipitation from anaerobic swine wastewater to be pH 8.7. This is lower than most published values for pH of minimum solubility, since there was a tendency for undesirable by-products to form at higher pH values, including brucite, Mg(OH)₂; hydroxyapatite, Ca₅(PO₄)₃OH; and calcium phosphates, Ca₄H(PO₄)₃•H₂O and CaHPO₄•2H₂O (Wang *et al.*, 2005).

Although supersaturation is a key factor in crystallization, it is not sufficient by itself to induce crystallization. In order for crystals to develop, there have to be a number of minute solid bodies, embryos, nuclei, or seeds in the solution that can act as centers of crystallization (Forrest *et al.*, 2008). Nucleation is the first stage of crystallization, and can be divided into primary nucleation, either homogeneous (spontaneous) or heterogeneous (induced by foreign particles), and secondary nucleation, which is induced by crystals (Forrest *et al.*, 2008). The second stage of crystallization is crystal growth, where the crystals are enlarged until equilibrium is reached (Le Corre *et al.*, 2005).

1.2.3 Seeding

A number of studies have investigated the potential of seeding materials to speed up the struvite crystallization reaction. One study found that both sand and struvite particles

used as seeding materials accelerated the reaction rate, with the 'seeds' acting as centers for secondary nucleation. The use of struvite seed was more effective at removing phosphate however, especially after magnesium addition, possibly because it could induce secondary nucleation faster. Adding more seeding material resulted in higher rates of crystallization (Wu and Bishop, 2004). This is contrary to the findings of Adnan *et al.* (2004) who studied the effect of the seeding technique (based on seed size and quantity) on phosphorus removal and crystal growth rate, and found that there was no significant difference between the techniques tested.

Seeding has also been used to produce larger struvite crystals in an effort to make them more acceptable as a direct fertilizer substitute and to enhance recovery of the precipitated crystals. Some success has been achieved, but the process requires a high energy input to keep the seed bed fluidized, which increases operational costs (Le Corre *et al.*, 2007a) As an alternative to seeding, some researchers have looked at metallic support structures for struvite recovery. Suzuki *et al.* (2005) developed an accumulation device made of stainless steel wire mesh for their demonstration reactor, which combines crystallization through aeration and separation through settling. Before deciding on the material for the recovery device, they tested struvite accumulation on various materials, and found that coarse steel surfaces had the highest accumulation efficiency while smooth rubber surfaces had very low accumulation efficiency. After the accumulation device was submerged in a reactor fed with swine wastewater, struvite cross-bridged and accumulated on its face. The accumulated struvite had a purity of 95% and was removed by simply brushing it off. Suzuki *et al.* (2005) concluded that the ease of use and robustness of this system makes this accumulation device a good contender for on-farm

use. Le Corre *et al.* (2007a) studied the efficiency of a stainless steel mesh system for struvite recovery in a crystallization reactor using synthetic wastewater. They found that the meshes were able to accumulate struvite by capturing crystals already formed in solution, thereby significantly reducing the amount of fine particles left in the solution.

1.2.4 Kinetics

The two phases of precipitation kinetics, nucleation and growth, are combined in the study of crystal formation. An important parameter for this study is the induction period, which is the time period between the mixing of solutions containing the precipitant components and the first measurable indication of the precipitant (Ohlinger *et al.*, 1999). Relatively few studies have investigated the kinetics of struvite precipitation, most of which relate to concentration decay and concentration related de-supersaturation (Ali and Schneider, 2008).

Ohlinger *et al.* (1999) found that nucleation is the controlling process for struvite formation during the induction period, with nucleation strongly dependent on (inversely proportional to) the struvite supersaturation level. In contrast, they found the crystal growth rate to be transport-controlled and a function of the mixing energy input. Nelson *et al.* (2003) assumed first-order reaction kinetics with respect to orthophosphate concentration to determine rate constants of 3.7, 7.9, and 12.3 h⁻¹ at pH 8.4, 8.7, and 9.0 respectively.

Nelson *et al.* (2003) used the modified expression in Eq. (12) for a first-order reaction:

$$-dC/dt = k(C - C_{eq}) \tag{12}$$

where: $-dC/dt$ = disappearance of a reactant (ppm/min).

k = rate constant (min^{-1}).

C = reactant concentration at time t (ppm).

C_{eq} = reactant concentration at equilibrium (ppm).

By integrating Eq. (12) the linear form of the first-order rate equation can be found, as shown in Eq. (13), where C_0 is the initial reactant concentration. A plot of $\ln(C - C_{\text{eq}})$ over time can then be used to determine the rate constant, since a first-order reaction should give a straight line with a slope of $-k$.

$$\ln(C - C_{\text{eq}}) = -kt + \ln(C_0 - C_{\text{eq}}) \quad (13)$$

Le Corre *et al.* (2007b) also adopted this first-order kinetics model in their study investigating the effect of magnesium on struvite kinetics, and found that the rate constants increased with increasing initial magnesium concentration.

Ali and Schneider (2008) proposed a different growth kinetics model for struvite, due to the limitation of using a single component concentration, ($[\text{Mg}^{2+}]$ or $[\text{PO}_4^{3-}]$ or $[\text{NH}_4^+]$) to determine supersaturation, which depends on all the reactive concentrations and the solution pH. They incorporated the SSR concept into their struvite kinetic modeling and combined it with a growth rate expression to create a growth kinetics model, which can be expressed as:

$$dL/dt = KSn \quad (14)$$

where: dL/dt = increase in mean particle size

K, n = growth kinetic parameters

S = relative supersaturation, $S = SSR - 1$

Understanding how struvite crystallization kinetics relates to the different component concentrations will greatly benefit the development and implementation of full-scale struvite crystallization reactors.

1.2.5 Component molar ratios

As mentioned above, struvite solubility is greatly dependent upon the SSR, which is based upon the concentration of the constituent ions of struvite – magnesium, ammonium, and phosphate. The molar ratio of these components in struvite is 1:1:1, so theoretically the amount of struvite precipitated will be limited by the component with the lowest molar concentration. In wastewater, both municipal and agricultural, the limiting constituent for struvite formation is most often magnesium (Burns and Moody, 2002; Yaffer *et al.*, 2002; Çelen *et al.*, 2007). Consequently a lot of research has focused on finding the optimum molar ratio of Mg:P for struvite precipitation, and the most effective source of magnesium amendment. A number of magnesium sources have been investigated, including magnesium chloride ($MgCl_2 \cdot 6H_2O$), magnesium oxide (MgO), magnesium hydroxide (MgOH), seawater, and bittern (Table 1.4).

Çelen *et al.* (2007) looked at the various amendments required to optimize struvite recovery from swine wastewater, in particular magnesium chloride addition ($MgCl_2 \cdot 6H_2O$) and pH adjustment (NaOH). They looked at three different Mg:P ratios, 1.0:1.0, 1.5:1.0, and 2.0:1.0, in combination with pH adjustment to 8.5. Their results

indicate that a 94% reduction in soluble phosphorus can be achieved with pH adjustment and an equal molar Mg:P ratio. Although additional magnesium did increase phosphorus removal, the small increase would not justify the additional magnesium cost. In a study by Nelson *et al.* (2003) similar results were obtained, where a 91-96% reduction in orthophosphate was achieved with a Mg:P ratio of 1.6:1 and at pH 8.9-9.25. The authors note that greater phosphorus removal with higher Mg:P ratios is significant because similar phosphorus removal could then be achieved with a smaller increase in pH, which would lower costs associated with pH adjustment. This could result in significant cost savings, since it has been estimated that 97% of the chemical costs associated with struvite precipitation is due to the large amount of NaOH needed to raise the pH (Yaffer *et al.*, 2002).

Table 1.4 Comparison of magnesium source and phosphate removal.

Wastewater source	Magnesium source	pH adjustment	Mg:P	P removal	Reference
Anaerobic swine lagoon liquid	MgCl ₂ •6H ₂ O	NaOH, 8.9-9.25	1.6:1	91-96%	Nelson <i>et al.</i> , 2003
Raw swine wastewater	MgCl ₂ •6H ₂ O	NaOH, 8.5	1:1	94%	Çelen <i>et al.</i> , 2007
Raw swine manure	MgCl ₂ •6H ₂ O	none	1.6:1	76%	Burns <i>et al.</i> , 2001
Raw swine manure	MgCl ₂ •6H ₂ O	NaOH, 9.0	1.6:1	91%	Burns <i>et al.</i> , 2001
Synthetic wastewater	MgCl ₂ •6H ₂ O	NaOH, 10.2	1NH ₄ :1P	75%	Lee <i>et al.</i> , 2003
Synthetic wastewater	Seawater	NaOH, 10.0	1NH ₄ :1P	81%	Lee <i>et al.</i> , 2003
Synthetic wastewater	Bittern	NaOH, 9.6	1NH ₄ :1P	76%	Lee <i>et al.</i> , 2003

The effect of magnesium feed concentration and the Mg:P molar ratio on the quality of harvested crystals (based mostly on brittleness) was investigated by Adnan *et al.* (2004). They found that there was no correlation between these parameters and the resultant struvite crystal quality. This is contrary to previous reports that suggested higher magnesium feed concentrations might improve struvite crystal quality (regular

orthorhombic shape and larger size) by favouring aggregation (Bouropoulos and Koutsoukos, 2000; Le Corre *et al.*, 2005). Magnesium feed concentration does seem to affect struvite purity, however. Çelen *et al.* (2007) found that without magnesium addition and with only pH adjustment, struvite, brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and monetite (CaHPO_4) were precipitated. For the Mg:P ratio of 2:1 trial struvite was the only precipitant detected. Therefore higher magnesium concentrations seem to increase struvite purity.

Alternative sources of magnesium ions for the struvite crystallization process include seawater and bittern. Bittern is the salt produced by evaporation of seawater during salt production; it consists mostly of magnesium chloride with some inorganic compounds. Its magnesium content is 27 times that of seawater, at 32 g/L (Lee *et al.*, 2003). Lee *et al.* (2003) found that as a magnesium source bittern performed just as well as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and seawater for phosphate removal from synthetic wastewater. Bittern was added to biologically treated swine wastewater and significant phosphorus removal was achieved (80%), with removal increasing up to a dosage of 0.3% bittern. Although seawater performed just as well as bittern, it is not as accessible as bittern in inland areas, and so transportation costs would be prohibitive.

Some magnesium sources, such as MgO or $\text{Mg}(\text{OH})_2$, can serve a dual purpose of magnesium addition and pH increase. Several authors have successfully used magnesium hydroxide to achieve phosphorus removal as struvite of up to 94% (Yaffer *et al.*, 2002). One deterrent to using such a dual-purpose chemical is that the magnesium dose and pH cannot be optimized independently of each other. Wu and Bishop (2004) found that both $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ help to speed up the struvite precipitation process, but

MgCl₂•6H₂O was more effective for phosphorus removal. This was attributed to the greater solubility of MgCl₂•6H₂O. Burns and Moody (2002) reported that of three possible magnesium amendments used (including magnesium hydroxide, magnesium oxide, and magnesium chloride) magnesium chloride, due to its solubility, was easier to handle and reduced the reaction time. Overall these characteristics seemed to outweigh the additional benefit of pH increase.

1.2.6 Competing ions

Crystal growth rate can be affected by impurities in the solution from which a compound may precipitate, since they could block the active growth sites, thereby preventing an increase in the crystal size (Le Corre *et al.*, 2009). Wastewater contains a large amount of foreign compounds, such as potassium, chloride, calcium, carbonates, and zinc, that could inhibit struvite formation and decrease the final product purity, and thereby the value of the product. If recovered struvite is to be used as a fertilizer the quality and size of the crystal have to be controlled (Le Corre *et al.*, 2005).

Calcium is a common ion in wastewater and an interfering ion in struvite formation, influencing struvite formation either by competing for phosphate ions, or by interfering with struvite crystallization. It has been shown that the presence of calcium or carbonate ions can increase the induction time and negatively affect the growth rate of struvite crystals (Le Corre *et al.*, 2005). Various compounds can be precipitated from wastewater with high calcium concentrations, including hydroxyapatite, calcium phosphate, and calcium carbonate (Le Corre *et al.*, 2005; Wang *et al.*, 2005):



Le Corre *et al.* (2005) investigated the influence of calcium and carbonate ions on struvite crystal formation and growth from synthetic wastewater at pH 9.0. It was determined that increasing the calcium concentration in the solution decreased the crystal size and inhibited struvite growth. They found that at low calcium concentrations in the solution (Mg:Ca ratio of 2:1), the struvite crystals could still be distinguished, although they were covered with a precipitate (containing both calcium and phosphate); while an increase in calcium concentration (Mg:Ca ratio of 1:1) inhibited the formation of struvite crystals and favoured the formation of amorphous matter, most likely calcium phosphate.

Wang *et al.* (2005) used synthetic anaerobic swine lagoon wastes to study the effect of interfering ions on struvite precipitation. They found that calcium concentration is the major factor that affects the composition of deposits when the molar concentrations of magnesium and ammonium were not limiting struvite formation. In particular, they determined that high Ca:P ratios caused the phosphorus to be removed as calcium precipitates, while inhibiting struvite formation; but when the Ca:P ratio is less than 0.5:1, relatively pure struvite can be produced if the pH is less than 9.2. It was also found that when the Mg:P ratio is less than 1:1, both magnesium and calcium concentrations impact the deposit composition. This is demonstrated by the finding that even if the Ca:P ratio is low (0.5:1), a calcium containing deposit will be formed at a pH of 8.7 when the Mg:P ratio is 0.5:1. Since a pH of 8.7 is close to published optimum pH values it suggests

that Mg is a critical parameter for optimizing struvite precipitation. The molar concentration of calcium should therefore be evaluated in relation to that of both phosphate and magnesium in order to create a more representative picture of which precipitates might form.

1.2.7 Other Factors

Temperature can also affect struvite solubility, with increasing temperature steadily increasing the solubility. One study found that the maximum solubility occurs at 50°C and thereafter solubility decreases again (Doyle and Parsons, 2002). A study by Adnan *et al.* (2004) found that lower temperatures (15°C) resulted in more effective struvite production, in terms of rate of crystal growth and phosphorus removal, than higher temperatures (25°C).

Struvite solubility increases in high strength wastes due to the presence of complexing agents, such as organics. It has been reported that total suspended solids concentrations above 1000 mg/L will interfere with precipitation (Burns and Moody, 2002).

1.3 Phosphorus removal and recovery

1.3.1 Phosphorus removal

There are several traditional phosphorus removal technologies currently being used by the wastewater industry that remove phosphorus by converting the ions into a solid fraction either chemically or biologically (Le Corre *et al.*, 2009). These phosphorus

removal technologies include precipitation of phosphorus by metal salts (iron, alum, calcium, magnesium), cultivation of microorganisms in wastewater (bacteria, microalgae), and constructed wetlands (Morse *et al.*, 1998; de-Bashan and Bashan, 2004). The removal product can take the form of insoluble salt precipitates, microbial mass in an activated sludge, or plant biomass in constructed wetland systems, none of which allow phosphorus to be recovered, since it is removed along with other waste products (de-Bashan and Bashan, 2004). Therefore, although these processes are efficient in removing P from wastewater, their disadvantages include increasing sludge volumes, accumulation of P in sludge, and inability to directly recycle precipitated P (Le Corre *et al.*, 2009).

1.3.2 Phosphorus recovery

Crystallization, in particular precipitation of struvite, has generated interest as a phosphorus recovery method, since struvite is a potentially valuable and sustainable slow-release fertilizer (Gaterell *et al.*, 2000; de Bashan and Bashan, 2004). The technologies that have been developed for struvite recovery can be broadly classified as selective ion exchange, precipitation in a stirred reactor, or most commonly precipitation in a fluidized bed or air-agitated reactor (Le Corre *et al.*, 2009). However, due to economic constraints imposed by the process and the product as well as technical difficulties, P recovery from wastewaters remains mainly experimental (Le Corre *et al.*, 2009). There are a number of wastewater streams that have the potential for implementing phosphorus removal and recovery through crystallization, since their chemical constituents have the potential to exceed the solubility product of struvite. Municipal and domestic waste streams that have been investigated focus mainly on

anaerobic digester centrate or sludge liquors (Ueno and Fujii, 2001; Wu and Bishop, 2004; Forrest *et al.*, 2008), but also include waste activated sludge liquors (Gaterell *et al.*, 2000), and landfill leachate (Doyle and Parsons, 2002). In the agricultural sector wastes from confined animal feeding operations have been targeted, in particular piggery wastes, either as raw liquid swine manure (Suzuki *et al.*, 2005; Çelen *et al.*, 2007), or as anaerobic digester or swine lagoon effluent (Miles and Ellis, 2001; Nelson *et al.*, 2003; Wang *et al.*, 2005). The benefit of anaerobic digestion as a pretreatment to crystallization is that it will decrease BOD and solids. It will also degrade organic nitrogen and phosphate to NH_4^+ and reactive phosphate (including H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}), respectively, thereby increasing the concentrations of struvite component ions and creating an environment favourable to struvite precipitation (Wang *et al.*, 2005).

1.3.3 Fluidized bed and air-agitated reactors

As mentioned above, fluidized bed reactors (FBR) or air-agitated reactors are the most commonly used processes for crystallizing struvite from wastewater. These reactors normally consist of a vertical column with seed material inside upon which struvite precipitates. The process usually makes use of chemical amendment to reach a desired Mg:P:N molar ratio, and while pH can be adjusted through aeration it is most often done through NaOH addition (Doyle and Parsons, 2002; Le Corre *et al.*, 2009). After these adjustments struvite particles can precipitate spontaneously, and growth in aerated reactors will occur due to interaction of particles (agglomeration), while in FBRs growth will take place by contact on seed materials making up the initial seedbed (Le Corre *et al.*, 2009). Fluidization of the particles is achieved through either the liquid flowrates

with feed entering the reactor column from the bottom (Mangin and Klein, 2004), or the up-flow circulation of air that keeps growing particles from settling down (Le Corre *et al.*, 2009). The geometry of these reactors is such that the flow velocity will decrease upwards, allowing treated effluent to flow out the top of the reactor, while the growing particles remain in the lower section.

The particles are recovered from the reactor when they reach an acceptable size for reuse, usually between 0.5 – 3 mm, which can take several days or weeks (Le Corre *et al.*, 2009). Therefore the reactor operates continuously for the liquid fraction, but in batches for the solids fraction (Mangin and Klein, 2004). Since particle size is a key factor in terms of recovery and reuse of struvite as fertilizer, seed materials can be used to provide nuclei on which struvite can attach to produce larger particles (Le Corre *et al.*, 2009). The initial particle bed is usually either sand, or pellets of the material to be precipitated (Mangin and Klein, 2004). According to Doyle and Parsons (2002) there are a number of reasons for using product as seed rather than introducing foreign particles, one being that this would decrease product purity and thereby its market value. In addition, providing seed material has inherent costs that could be avoided by recycling product as seed. Using product as seed may also influence the process kinetics, since crystal growth upon like materials requires less energy than growth on foreign particles.

Some of these processes have been hampered by the production of fines. This is a problem in high mixing energy reactors because an excess of fines usually leads to particle loss in the treated effluent, reducing the overall efficiency of the reactor. One method for limiting this problem is to recycle the fines as new seed material for the reactor (Le Corre *et al.*, 2009). In addition, a high recycling flow rate would induce

complete mixing and reduce the operating supersaturation thereby decreasing the risk of intensive primary and secondary nucleation leading to fines (Mangin and Klein, 2004). The production of fines has also been reported to detrimentally affect the operational consistency of crystallization reactor systems. Adnan *et al.* (2004) found that an increase in operational pH beyond a certain point resulted in the production of fines for a given set of experimental conditions. These fines often caused plugging and a reduction of the harvested product quality in terms of mechanical strength. Although operation below a certain pH limit resulted in lower P removal, it avoided fines production and allowed for smooth reactor operation. Further obstacles for implementation of these processes are the cost of raw materials as well as the energy requirements for keeping the seedbed fluidized (Le Corre *et al.*, 2009).

1.3.4 Existing recovery processes

A summary of operating parameters for various fluidized bed or air-agitated reactors for struvite recovery is given in Table 1.5. The following is a more detailed discussion of a select few recovery processes.

A struvite crystallization reactor has been developed in Japan, which uses anaerobic sludge centrate as a feed source as reported by Ueno and Fujii (2001). The feed was amended with magnesium hydroxide to a Mg:P ratio of 1:1, and the pH adjusted to 8.2-8.8 with sodium hydroxide, resulting in minimum P removals of 90%. They were able to produce struvite pellets 0.5-1.0 mm in diameter after a 10 day retention period, using an upward airflow to keep the particles suspended. Fines were recycled and used as new

Table 1.5 Struvite recovery in fluidized bed or air-agitated reactors.

References	Process	Seed material	Influent	Amendments		Fines	Recovered product size	P removal
				pH	Mg			
Adnan <i>et al.</i> (2003)	Pilot scale FBR	None	Synthetic water : Mg Cl ₂ •6H ₂ O + (NH ₄)H ₂ PO ₄ + NH ₄ Cl	NaOH		Very little generated	3.5 mm	21 – 98 %
Ueno and Fuji (2001)	Full scale FBR	Struvite	WWTP dewatered filtrate from anaerobic digestion	NaOH	Mg(OH) ₂	Return as seed material	0.5 – 1.0 mm	> 90 %
Suzuki <i>et al.</i> (2002)	Pilot scale aerated reactor	None	Screened swine wastewater	Aeration	none	Not mentioned	Sludge	65 %
Bowers and Westerman (2005)	Field scale cone-shaped FBR	Struvite	Swine lagoon liquid	NH ₃	Mg	Not mentioned	Not mentioned	70 – 82 %
Shepard <i>et al.</i> (2009)	Bench-scale aerated tank reactor	None	Swine wastewater	Aeration	MgCl ₂	Not mentioned	Not mentioned	78 – 95 %
Moerman <i>et al.</i> (2009)	Full scale stirred tank reactor	None	Anaerobic dairy effluent	Aeration and NaOH	MgCl ₂	Not mentioned	2 – 6 mm	38 – 91 %
Forrest <i>et al.</i> (2008)	Technical scale FBR	None	Municipal sludge digester supernatant and centrate	NaOH	MgCl ₂	Settled in seed hopper	2.0 – 3.3 mm	< 95 %

seed material in the reactor. The resultant product had relatively low heavy metal contamination and was sold as is to fertilizer companies, making it the only full-scale process that is economically reliable.

Researchers at the University of British Columbia have developed a novel fluidized bed reactor design and tested it at technical scale (four times larger than pilot scale) using sludge digester supernatant and centrate from municipal wastewater treatment (Forrest *et al.*, 2008). They found that ideal crystal growth was achieved at SSR values from 1 to 2.5, and Mg:P ratios from 1 to 2.5. The crystals generated had an average mean size 5 to 10 times greater than struvite currently on the market (2.0 to 3.3 mm). This large crystal size in combination with high struvite purity, dense crystal structure, and an average phosphate reduction of 80% gives this struvite recovery technology commercial potential.

Suzuki *et al.* (2007) reported the results of operating a demonstration crystallization reactor with a struvite accumulation device for struvite recovery using raw swine wastewater over a period of 3.5 years. Their reactor was dosed with bittern to increase the magnesium concentration and used aeration, to increase the pH of the wastewater. A stainless steel wire mesh column, with a total surface area of 3 m², was used as an accumulation device. They found that aeration (which increased the pH to 8.0-8.5) combined with magnesium addition was effective for reducing the soluble phosphate and total phosphorus concentration in the effluent. The accumulation device was submerged for 70 days during which it had an average struvite recovery rate of 171 g/m³ wastewater. The accumulated struvite was removed from the wire mesh with light brushing and needed only air-drying before use, since the resultant product had a purity of 95%. The authors feel that this crystallization reactor and accumulation device could be adapted,

with some modifications, to an existing primary settling tank, which would make it an economical method of struvite recovery for swine producers.

Moerman *et al.* (2009) described the performance of a full-scale stirred tank reactor for P recovery by struvite crystallization treating anaerobic dairy effluent. The reactor consists of an air stripper, crystallization reactor with a top-entry mixer and a setting zone, pH control using NaOH, and magnesium amendment with MgCl₂. Initial Ca interference resulted in the production of an amorphous precipitate, but a decrease in influent Ca/PO₄-P molar ratio from 2.69 to 1.36 resulted in the growth of 2-6 mm spherical particles. These were found to be mostly struvite, and were locally accredited for agricultural reuse. This reactor demonstrated that even at high flow rates (100-125 m³h⁻¹) phosphate removal of up to 78% is feasible.

1.4 Economic viability

In order to determine the cost-effectiveness of P recovery as struvite, the costs of production (chemicals, energy, and maintenance) as well as the market value of struvite as a fertilizer have to be taken into account (Le Corre *et al.*, 2009).

The cost of producing one tonne of struvite ranges from USD \$140 – 460 (Doyle and Parsons, 2002). Struvite production costs will be heavily dependent upon the chemical costs incurred by magnesium amendment and pH adjustment, as well as on the operational costs due to energy consumption (Le Corre *et al.*, 2009). The addition of NaOH for pH amendment was identified by Jaffer *et al.* (2002) as one of the principal sources of struvite production costs in their pilot scale study. Alternative methods for Mg

amendment that could help to reduce production costs include using brine or $\text{Mg}(\text{OH})_2$, which is cheaper than MgCl_2 and also increases pH, while air-stripping can be used to increase the pH (Le Corre *et al.*, 2009). Eliminating the use of seedbeds could reduce energy consumption by lowering the flow rates (liquid or air) needed to fluidize the particles (Le Corre *et al.*, 2009).

The market value of struvite remains largely unestablished, with a wide range of suggested values, including USD \$198-330, \$261, \$283, \$877, and \$1885 per tonne (Doyle and Parsons, 2002). Japan is one of the few countries where struvite has been sold to fertilizer companies at a price of approximately USD \$272 per tonne in 2001 (Ueno and Fujii, 2001). This has to compare with the cost of phosphate ore if struvite is to be a competitive alternative. The world price of phosphate rock, and consequently phosphate fertilizers, underwent a fourfold increase during 2007, from an average of USD \$40 - 51 per tonne to USD \$170 - 210 per tonne. This was attributed to a combination of increased world consumption, tighter supply of phosphate rock, high freight rates, rising energy costs, and a weaker dollar (USGS, 2008). Although fertilizer production from phosphate rock still seems to be more economical, if this trend continues, struvite could be an economically viable alternative phosphorus source for the fertilizer industry. In addition, the value of recovered phosphorus in the form of struvite tends to be higher than that of phosphate ore, since struvite has much lower heavy metal contamination (Forrest *et al.*, 2008). Gaterell *et al.* (2000) conducted a cost comparison of the production and distribution of struvite based products against existing fertilizers, showing that contingent upon high recovery rates and satisfying regional demand, struvite fertilizers could prove to be cost effective, especially if substituted for diammonium phosphate (DAP).

A study by Çelen (2009) looked at the economic feasibility of removing ortho-P by chemical precipitation in a continuous reactor before swine manure was land applied using an irrigation system. The cost of treatment included equipment, chemicals, and potential income from the fertilizer value of struvite. Treating the manure increased the cost of land application by 770%, with chemical expense making up 91% of the treatment cost. Although expensive, this method was technically feasible, and might be considered if land application was P-based.

1.5 Phosphorus and swine production in Manitoba

Swine production in Manitoba has increased and intensified dramatically in recent years, and as a result so has the volume and concentration of waste that has to be handled (Brewin *et al.*, 2007). Manure management on the Prairies generally does not include treatment; most manure is simply stored until it can be land-applied as fertilizer (PAMI and AFMRC, 1997; MAFRI, 2007). The total annual P content of pig manure in Manitoba has been estimated to range from 5000 to 7000 tonnes (Rawluk and Flaten, 2007), these figures are equivalent to 11 to 15% of the P removed by Manitoba crops. Therefore properly applied manure in conjunction with synthetic fertilizers should not lead to excess accumulation. However, only 2.5% of Manitoba's agricultural land is receiving this manure, much less than is required to apply P in balance with crop needs (Rawluk and Flaten, 2007). Consequently swine wastewater is a prime candidate for P removal and recovery in Manitoba.

1.5.1 Swine manure characteristics

The most common method of manure storage in Manitoba is the earthen manure storage (EMS), which can be either single, two, or three-cell storages (MAFRI, 2007; Sri Ranjan *et al.*, 2007). As mentioned above, although these storages are not designed for treatment, partial anaerobic treatment of the manure does occur during storage (Sri Ranjan *et al.*, 2007). A number of studies have been conducted to determine the nutrient content of hog manure storages, mostly to study some aspect of manure land-application (Racz, 2001; Malley *et al.*, 2002; Dick, 2003). One of the recurring observations of these studies is that the nutrient content of manure varies considerably, even within the same manure storage. Table 1.6 below shows the nutrient content of liquid swine manure storages as reported in four separate studies done in Manitoba.

Table 1.6 Nutrient concentrations of various liquid swine manure storages in Manitoba.

	Nutrient concentrations (g/L)				
	Liquid swine (n=133) ¹	Liquid swine (n=21) ²	Liquid swine (n=21) ²	Liquid swine ³	Liquid swine (n=64) ⁴
	avg (range)	single cell mean (SD)	two-cell mean (SD)	avg (range)	mean (range)
Total N	3.1 (0.4-6.8)	2.8 (0.9)	4.2 (1.3)	2.5 (0.2-6.9)	2.5 (1.2-4.8)
NH₄⁺-N	1.9 (0.2-5.2)	1.7 (0.2)	2.9 (0.3)	1.7 (0.1-5.2)	1.9 (1.1-2.7)
Total P	1.0 (0.0-5.1)	1.1 (0.8)	1.1 (1.0)	0.8 (0.0-5.1)	0.7 (0.1-3.0)
N:P	3.1	2.5	3.8	3.1	3.6
Dry matter (%)	3.4 (1.0-9.0)	3.7 (3.2)	4.1 (3.0)	2.8 (0.1-12.5)	

Sources: 1. PPCLDMM, 2003; 2. Dick, 2003; 3. Burton and Flaten, 1999; 4. Malley *et al.*, 2002

This table shows the wide range of nutrient concentrations that can be found in liquid manure storages. Although the average phosphorus content ranges only from 0.7 to 1.1 g/L, the overall range varies significantly from 0.0 to 5.1 g/L. The factors responsible for the high degree of variability in the phosphorus content of pig manure includes animal age, feed supplements, and manure storage and handling (MAFRI, 2007; Rawluk and

Flaten, 2007). Not only does the nutrient content vary between different storages, it varies with depth within a storage, as shown in Table 1.7. These samples were taken from several open earthen storages as they were emptied.

Table 1.7 Manure nitrogen and phosphorus content for different depths in earthen swine manure storages.

	Sample depth		
	Nutrient concentration (g/L)		
	Top (62)	Middle (30)	Bottom (53)
Total N	2.5	2.7	3.2
Total P	0.6	0.9	1.3
N:P	4.2	3.2	2.5
Dry matter (%)	2.3	3.7	4.6

Source: Rawluk and Flaten, 2007

The P content more than doubles from top to bottom, while the N content only increases by 28%. The total phosphorus concentration of hog manure increases with depth within a given liquid manure storage because most of the P is contained within solids that tend to settle to the bottom of the manure storage (PPCLDMM, 2003; MAFRI, 2007). These P values are representative of the TP in manure, and only part of this fraction, the dissolved reactive P (DRP), will be immediately available for crop uptake.

Pig manure has a highly variable phosphorus concentration, containing both organic and inorganic phosphorus forms (Buckley and Makortoff, 2004; MAFRI, 2007). Estimates of the inorganic phosphorus in swine manure vary somewhat, from 50 to 80% (MAFRI, 2007) and 45 to 90% (Buckley and Makortoff, 2004) of the total phosphorus, the rest is considered to be organic phosphorus. Pig manure contains mostly organic phosphorus (TUP) in the solid portion just after excretion, over time some of this organic phosphorus is converted to soluble inorganic phosphorus (or DRP) (PPCLDMM, 2003). In general,

pig feces will contain most of the excreted phosphorus; urine may contain 10 to 32% of ingested P as soluble phosphorus (Buckley and Makortoff, 2004). It has been found that of the TP in liquid swine manure, 10 to 50% can be present as soluble inorganic phosphate (DRP), the form which is immediately available to plants (PPCLDMM, 2003), and which could precipitate to form struvite. So, based on the values established above, the average amount of available P could be as low as 0.07 to 0.11 g/L or as high as 0.35 to 0.55 g/L.

1.6 Conclusion

The increasing levels of phosphorus in surface waters present a significant threat to surface water quality, due to the role that phosphorus plays in speeding up eutrophication. A considerable source of phosphorus entering the aquatic environment is land-applied manures, which usually have high phosphorus content. Of various P removal methods available for wastewaters, crystallization was seen as the most promising option since phosphorus would not only be removed from the waste stream, but could also be recovered as struvite, a potential fertilizer. There are various factors that influence struvite precipitation from a solution, including supersaturation, component-ion molar ratios, interfering ions, temperature, and pH of the solution. In general the supersaturation ratio is the controlling factor for struvite precipitation, it also plays a significant role in the reaction kinetics. Different ratios of magnesium and calcium can influence struvite precipitation by speeding up reaction, or by influencing the purity of the precipitated product. The solution pH is a very important factor when considering system optimization, since it significantly affects the solubility and purity of struvite. A number

of systems have been studied for recovering P from wastewater through struvite precipitation, often consisting of either a fluidized bed reactor or an aerated column reactor. These systems typically achieve struvite precipitation by inducing changes in the pH and/or the component concentrations, usually the magnesium concentration. The economic viability of this technology is not fully established, due to uncertainty regarding the market value of struvite. However, declining phosphate reserves and stricter regulations regarding wastewater discharge, could make phosphate removal and recovery through struvite precipitation a cost effective alternative.

1.7 Objectives of this research

The overall purpose of this research was to achieve effective phosphorus removal and recovery through struvite precipitation from agricultural wastewater with minimal chemical input. The main objective was to develop a robust, low-cost reactor system requiring minimal maintenance that would produce an agronomically valuable product. To realize these objectives, the following goals were identified: minimize cost, maximize removal, and increase product value. The specific objectives set to attain these goals were to:

1. Determine the optimal pH and Mg:PO₄-P ratio in terms of the amount of phosphorus removed/recovered from swine manure, the quality of recovered precipitate, and the need/cost of amendment.
2. Investigate aeration as a method of pH amendment, looking at different airflow rates and the extent of phosphorus removal.

3. Develop and evaluate a side-stream continuous reactor for phosphorus removal and recovery from swine lagoon supernatant. This will involve:
- optimizing operational parameters, such as aeration rate, overall throughput (HRT), recycle ratios, and particle size range for the struvite seedbed, for the purpose of achieving effective struvite recovery and purity
 - conducting long term precipitation runs to assess system stability and consistency (several days in length)

Ideally this type of reactor will be used on-farm to reduce phosphorus loading in manure slurries and to provide a revenue stream to the farmer in the form of phosphate fertilizer. Development and operation of this reactor will provide insight into the economic and technical viability of P recovery, ultimately addressing pressing problems of localized phosphorus overload and dwindling phosphate resources.

Chapter 2 – Experimental and analytical methods

2.1 Experimental organization

The specific objectives for this study were investigated through a series of batch tests. Objective 1 was evaluated for both anaerobically digested and raw swine manure, to determine the best source material for further experimentation (Chapter 3 and 4). Based on results, objective 2 was investigated using raw swine manure (Chapter 5). Objective 3 was completed as a proof of concept for the reactor using synthetic swine manure (Chapter 5 and 6).

2.2 Experimental methods

In several of the experiments performed, the Mg:P ratio of the supernatant had to be adjusted to a desired value by adding a certain mass of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Table 2.1). The following calculation was used to determine the amount needed in Chapter 3:

$$\text{Mass}_{\text{MgCl}_2}(\text{mg}) = \text{Vol}(\text{L}) \times M_{\text{MgCl}_2 \cdot 6\text{H}_2\text{O}}(\text{mg/mol}) \times \left(\frac{\text{Mg:P} \times [\text{PO}_4 - \text{P}](\text{mg/L})}{M_{\text{P}}(\text{mg/mol})} - \frac{[\text{Mg}](\text{mg/L})}{M_{\text{Mg}}(\text{mg/mol})} \right) \quad (18)$$

For Mg:P 1.0:1 $\text{Mass} = 2 \times 203310 \times (1.0 \times 41.5 / 30970 - 24.5 / 24310) = 135.1 \text{ mg}$

For the experiment in Chapter 4, a 10 g/ml $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution was made in order to ensure that the chemical would be completely dissolved prior to addition. The result from

the above equation was multiplied by $\frac{M_{Mg}}{M_{MgCl_2 \cdot 6H_2O}}$ to obtain the volume to be added to the supernatant.

Table 2.1 Amount of magnesium chloride hexahydrate added to effluent to achieve the desired Mg:P molar ratio.

Chapter 3		Chapter 4	
Mg:TP molar ratio	Mass of MgCl ₂ · 6H ₂ O (mg)	Mg:PO ₄ -P molar ratio	Volume of 10 g/ml MgCl ₂ · 6H ₂ O solution (ml)
1.0:1	135.1	1.3:1	4.5
1.2:1	244.1	1.6:1	7.8
1.4:1	353.0	1.9:1	11.1
1.6:1	462.0		

2.3 Liquid sample analysis

All samples were prepared and analyzed as described below, unless indicated otherwise for individual experiments.

Samples taken from the collected wastewater were centrifuged at 10 000 rpm for 5 min and then put through a series of vacuumed paper filters: 1.5, 0.8, and 0.45 µm (Whatman). The filtrate was then diluted 25/3 with a 0.02% HNO₃ solution for storage in the refrigerator until analysis. Samples taken from synthetic wastewater were directly diluted 25/3 with the 0.02% HNO₃ solution.

Orthophosphate, the dissolved reactive phosphorus fraction, was determined using the ascorbic acid method (Ultrospec 4300 Pro, University of Manitoba, Department of Biosystems Engineering).

Analysis of TP, Mg^{2+} , K^+ and Ca^{2+} was done using Inductively Coupled Plasma (ICP) spectrometry (Varian 700 ICP-OES, University of Manitoba, Department of Chemistry).

For the synthetic wastewater samples the TP was assumed to be equal to the orthophosphate concentration, and only ICP analysis was done. To test this assumption, one batch of 17 samples was tested for both PO_4 -P and TP and the results analyzed with a paired t-test. Since the P-value was found to be 0.07 there was no significant difference between the means of the two methods, and the assumption was valid.

Flow Injection Analysis (FIA) (LaChat QuikChem 8500, University of Manitoba, Department of Civil Engineering) was used to determine the NH_4^+ -N content after appropriate dilution.

2.4 Solid sample analysis

To determine the crystalline species present in the precipitate, samples of precipitate were analyzed using X-ray diffraction (XRD) (Philips PW1710, University of Manitoba, Department of Geological Sciences).

Samples of precipitate from supernatant experiments were prepared for ICP (Mg^{2+} , Ca^{2+} , and TP) and FIA (NH_4^+) analyses by dissolving 0.025 g of precipitate in 10 M HCl, diluting it with distilled water to 50 ml and filtering out organics.

Samples of precipitate from synthetic wastewater experiments were analyzed with ICP and FIA after dissolving 0.15 g in 1.0 M HCl and diluting it to 25 ml with DI water, then further diluting the sample 25/3 with DI water. Since the only phosphate species expected

in the precipitate is PO₄-P, the TP concentration was again assumed to be representative of the orthophosphate concentration.

2.5 Data analysis

The results from the colimetric, FIA, and ICP analyses were used to determine various parameters. Percentage removal of all constituents were calculated as shown for P:

$$P_{removal} = \frac{[P]_{influent} - [P]_{effluent}}{[P]_{influent}} \times 100 \quad (19)$$

The results from the colimetric, FIA, and ICP analyses were converted to molar concentrations through division by the molar mass, from which the molar ratios of Mg²⁺, NH₄⁺, and Ca²⁺ to TP or PO₄-P could be determined. The following example shows the molar ratio of Mg:P removed from solution:

$$Mg : P_{removed} = \frac{\frac{[Mg]_{influent}(mg/L) - [Mg]_{effluent}(mg/L)}{M_{Mg}(mg/mol)}}{\frac{[TP]_{influent}(mg/L) - [TP]_{effluent}(mg/L)}{M_P(mg/mol)}} \quad (20)$$

When evaluating the recovered precipitate from the synthetic supernatant tests, the maximum percentage of struvite recovered was calculated based on several different parameters. The recovered mass of precipitate was divided by the maximum mass of struvite that could possibly precipitate based on the moles of TP in solution and the total volume of synthetic feed prepared (21), as well as the average moles of TP and Mg²⁺ missing from solution after the run was completed (22).

$$\text{Struvite recovered} = \frac{\text{mass recovered}(g)}{\frac{[TP](g/L)}{M_P(g/mol)} \times M_{\text{struvite}}(g/mol) \times \text{Vol}(L)} \times 100 \quad (21)$$

$$\text{Struvite recovered} = \frac{\text{mass recovered}(g)}{\frac{([TP]_{\text{inf}} - [TP]_{\text{eff}})_{\text{avg}}(g/L)}{M_P(g/mol)} \times M_{\text{struvite}}(g/mol) \times \text{Vol}(L)} \times 100 \quad (22)$$

The precipitate was analyzed to determine the molar ratios of Mg^{2+} , NH_4^+ , and Ca^{2+} to TP, as shown here:

$$\text{Mg} : \text{P} = \frac{\frac{[Mg](mg/L)}{M_{Mg}(g/mol)}}{\frac{[TP](mg/l)}{M_P(g/mol)}} \quad (23)$$

After the recovered seed was dried it was sieved to separate the various particles sizes, which were evaluated separately. In order to quantify the amount of seed recovered, percentage seed recovery was determined as follows:

$$\text{seed recovered} = \frac{\text{mass seed recovered} (mg)}{\text{mass seed added} (mg)} \times 100 \quad (24)$$

Chapter 3 – The effect of magnesium and pH adjustment on phosphorus precipitation from anaerobically digested swine manure

3.1 Introduction

Confined animal feeding operation wastewaters have been targeted for P recovery, in particular piggery wastes, either as raw liquid swine manure (Suzuki *et al.*, 2005; Çelen *et al.*, 2007), or as anaerobic digester or swine lagoon effluent (Miles and Ellis, 2001; Nelson *et al.*, 2003; Wang *et al.*, 2005). The benefit of anaerobic biological treatment is that it will decrease BOD and solids. It will also degrade organic nitrogen and phosphate to NH_4^+ and reactive phosphate (including H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}), thereby increasing the concentrations of struvite component ions and creating an environment favourable to struvite precipitation (Wang *et al.*, 2005).

While struvite precipitation is enhanced between pH values 7 and 11 (Burns and Moody, 2002), there is a range of published values for the optimum pH for struvite precipitation, from 8.0 to 10.7 (Nelson *et al.*, 2003; Wang *et al.*, 2005; Pastor *et al.*, 2007). Magnesium is generally the limiting nutrient for struvite precipitation in animal manures (Burns *et al.*, 2001; Çelen *et al.*, 2007), and has been added as either MgCl_2 or MgO to wastewater to enhance precipitation (Burns and Moody, 2002; Wu and Bishop, 2004). Optimal molar ratios for magnesium to total phosphorus between 1.3:1 and 1.6:1 have been reported (Burns *et al.*, 2001; Wang *et al.*, 2005), despite studies indicating that an equal molar ratio is sufficient and the small additional removal achieved with more magnesium is not justified by the added cost (Çelen *et al.*, 2007). The level of calcium in wastewater effluent can be relatively high, and can affect struvite formation by interfering with

crystallization or by competing for phosphate ions and forming calcium phosphates (Le Corre *et al.*, 2005; Wang *et al.*, 2005).

The objective of this study was to determine the optimum conditions for struvite precipitation from anaerobically digested swine manure. Specific goals were to determine the effect of pH and the Mg:PO₄-P ratio on struvite precipitation. The recovered precipitate was examined to determine struvite quality and presence of co-precipitate.

3.2 Methods

3.2.1 Source and collection

Anaerobically digested swine manure effluent was collected from controlled experimental digesters over several weeks until there was a sufficient volume for testing. The effluent was screened and diluted four times with tap water after collection, then refrigerated and allowed to settle for several days. The effluent was then centrifuged at 4500 rpm for 5 min, and stored in the refrigerator until use without further alterations. Samples of the centrate were analyzed to determine the initial molar Mg:TP ratio, which was found to be 0.75.

3.2.2 Experimental setup

Based on the initial Mg:TP ratio of the centrate, appropriate amounts of MgCl₂ were added to four beakers containing 2 L centrate each to create Mg:P ratios of 1.0:1, 1.2:1,

1.4:1, and 1.6:1. After the chemical addition, the centrate was mixed on a magnetic stirrer for 10 min to dissolve the MgCl_2 . The four batches of adjusted effluent were divided between five glass beakers each so that there was 400 ml in every beaker. To adjust the centrate pH in a range from 7.5 to 9.5, either 1.0 M NaOH or 1.0 M HCl was added with a dropper as appropriate to each beaker, while monitoring the pH with a probe. Consequently there were four sets of five beakers with a similar pH range and different Mg:P ratios. The beakers were covered to prevent dust contamination, and left to equilibrate for 24 h at an average room temperature of 21°C.

After the equilibration period the final pH of each beaker was measured, then 5 ml samples were taken 2 cm below the surface from all the beakers, diluted ten-fold and acidified with a 0.05 M HCl, 0.01% HNO_3 solution. Multiple samples were prepared for ICP (TP, Mg^{2+} , and Ca^{2+}) and FIA ($\text{PO}_4\text{-P}$ and NH_4^+) analyses. Samples from all the beakers with similar pH values were combined to ensure that adequate precipitate would be collected through filtration (Whatman 1, 11 μm). The dried precipitate on the qualitative filter paper was weighed and homogenized before analysis.

3.3 Results and discussion

The objective of this study was to determine the optimum conditions for struvite precipitation from anaerobically digested swine manure. This was achieved by studying the effect of two factors, Mg:P ratio and pH. A secondary objective was to establish evidence of struvite precipitation, which was given by XRD analysis. The average

constituent concentrations shown in Table 3.1 were used as the baseline centrate concentrations for this study.

Table 3.1 Average constituent concentrations of original centrate, as given by FIA and ICP analysis.

Concentration (ppm)					Molar Mg:PO ₄ -P ratio	Molar Mg:TP ratio
TP	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	PO ₄ -P		
40.4 ± 3.9	94.9 ± 3.7	22.7 ± 3.0	1260 ± 208	32.4 ± 5.5	0.94:1	0.72:1

Figure 3.1 shows the residual concentration of total phosphorus (TP) in the centrate after 24 h. There is a distinct trend for all of the different Mg:P ratios: decreasing phosphorus concentration with increasing pH. For the lowest pH values, 7.5 and 8.0, there is little correlation between the Mg:P ratios and the TP concentration, however at pH 8.5 to 9.5 it is evident that more phosphorus was removed at the higher Mg:P ratios.

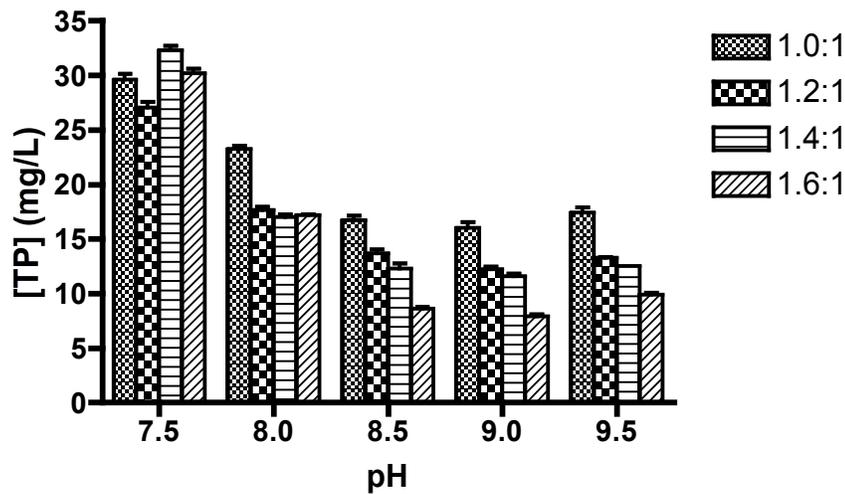


Figure 3.1 Comparison of TP concentration to centrate pH after 24 h equilibration for different Mg:P ratios.

Removing more phosphorus at higher Mg:P ratios would allow a given TP concentration to be achieved at lower pH values in the centrate, thereby minimizing the amount of pH adjustment needed. Wang *et al.* (2005) and Nelson *et al.* (2003) reported optimum Mg:P ratios between 1.3:1 and 1.6:1, similar to results from this experiment where the lowest phosphorus concentration was found in the Mg:P ratio of 1.6:1. It has to be kept in mind, however, that there will be a cost associated with increasing the Mg:P ratio, and so a balance has to be found between magnesium amendment and pH adjustment that will minimize cost and maximize removal.

As shown in Figure 3.1, the minimum TP concentrations were found to occur at pH 9.0 for all the Mg:P ratios. The increase in TP at pH 9.5 could be due to the solubility of struvite changing with pH, since the speciation of phosphate and ammonium is pH dependent (Wu and Bishop, 2004). The solubility of struvite generally decreases with increasing pH, but starts to increase at higher pH values because the ammonium ion concentration decreases while the phosphate ion concentration increases (Doyle and Parsons, 2002). Therefore, struvite will have a pH of minimum solubility, where the greatest amount of precipitation will occur. The greatest TP removal achieved was 80%, at pH 9.0 and a Mg:P ratio of 1.6:1, for a final phosphorus concentration of 7.9 ppm. The TP concentrations at the three highest pH values were very similar, suggesting comparable precipitation. This can be further illustrated by looking at the mass of recovered crystals for the various pH values, as shown in Table 3.2.

There is a dramatic increase in precipitate mass from pH 7.5 to 8.0 and from pH 8.0 to 8.5, almost doubling each time. However, the mass of precipitate recovered in pH 8.5, 9.0, and 9.5 does not differ as dramatically as the first two, they are in fact very similar.

These findings support the results presented in Figure 3.1, which shows that significant precipitation starts to occur around pH 8.5 and continues through to pH 9.5, with peak precipitation occurring close to pH 9. This agrees with the findings of Nelson *et al.* (2003), who found that maximum PO₄-P removal occurred between pH 8.9 and 9.25.

Table 3.2 Mass of precipitate recovered through filtration from combination of centrates with different Mg:P ratios but similar pH values.

pH	Mass (g)				
	7.5	8.0	8.5	9.0	9.5
	0.214	0.425	0.701	0.757	0.756

Another factor that should be taken into account when looking for the optimum pH is the purity of the recovered crystal. Studies done by Le Corre *et al.* (2005) and Wang *et al.* (2005) have indicated that high calcium concentrations in the centrate could lead to the formation of calcium phosphates or calcium carbonate. If calcium phosphates were formed, the amount of struvite recovered would decrease, along with the precipitant's value as fertilizer. If calcium carbonate was formed, it could interfere with struvite formation, but would not compete with struvite for phosphorus. It was found that the concentrations of struvite constituents all decreased with increasing pH, however, it was also evident that the calcium concentration dramatically decreased with increasing pH, suggesting that some form of calcium did precipitate. In order to determine if struvite was indeed recovered, and to assess the purity of any recovered struvite, XRD was used to analyze the recovered precipitate.

The XRD analysis (Appendix I-a) indicated that the purest struvite was recovered from the centrate with a pH of 7.5, since the intensity peaks of the analyzed substance correlate

well with those of pure struvite. Although struvite is still prominent for the pH 8.0 precipitate, it also has peaks consistent with calcium carbonate, or calcite. A similar trend can be observed for the pH 8.5, 9.0, and 9.5 precipitates. There was no evidence of an amorphous phase in any of the spectra, which would have suggested the presence of calcium phosphates. This seems to indicate that the calcium in the centrate precipitated mainly as calcium carbonate.

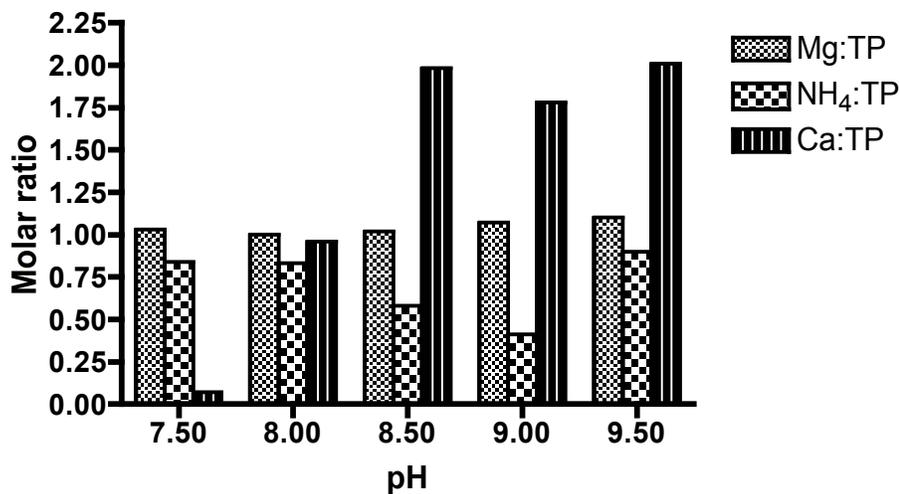


Figure 3.2 Molar ratio of constituent concentrations to TP as determined from recovered precipitate.

This decrease in struvite purity is also illustrated by the molar ratios of the precipitate component concentrations as shown in Figure 3.2. It was assumed, based on XRD analysis, that the majority of precipitate containing phosphorus was struvite, and therefore TP would be representative of PO₄-P. This figure confirms that while very little calcium is present in the pH 7.5 precipitate, its presence increases as the pH goes up. High concentrations of calcium at pH 8.5 – 9.5 is consistent with XRD results indicating

the presence of calcite at these pH values. The ratio of magnesium to TP remains very close to one for all pH values, and while the ammonium concentration is relatively close to one at pH 7.5, 8.0, and 9.5, it decreases for pH 8.5 and 9.0. Since struvite consists of an equal Mg:NH₄:P molar ratio, these similar ratios seem to confirm its presence at most pH values.

From this analysis it can be concluded that the precipitate at pH 7.5 contained the purest struvite, or the precipitate with the least calcite, and that increasing the pH resulted in decreased struvite purity due to the formation of calcite. Although this compound does not contain, and therefore compete with struvite, for phosphorus, it could interfere with struvite formation. At the higher pH values that gave rise to the greatest phosphorus removal, the struvite purity decreased along with the commercial value of the recovered precipitate as a fertilizer. This indicates that a balance exists between greatest phosphorus removal and the highest purity struvite recovered. The optimum pH will therefore depend on an acceptable trade-off between maximum phosphorus removal and greatest struvite purity.

3.4 Conclusion

The optimum conditions for maximum phosphorus removal from anaerobically digested swine manure were found to be pH 9.0 and a Mg:P ratio of 1.6, where 80% of TP was removed. Although struvite was recovered at all pH values, molar balances and XRD analysis showed that the purest struvite was recovered at pH 7.5, since at higher pH values the precipitate also contained calcite. Consequently the optimum pH for struvite

precipitation will depend on an acceptable trade-off between maximum phosphorus removal and greatest struvite purity. Overall it can be argued that, based on the amount of phosphorus removed and the quality of the recovered precipitate, struvite precipitation could be a viable method for phosphorus removal from anaerobically digested swine manure.

Chapter 4 – The effect of magnesium and pH adjustment on phosphorus precipitation from raw swine manure

4.1 Introduction

As mentioned in Chapter 3, a lot of research has been focused on finding the optimum molar ratio of Mg:PO₄ for struvite precipitation, and determining the effect of competing ions. Calcium is a common ion in wastewater and an interfering ion in struvite formation, influencing struvite formation either by competing for phosphate ions, or by interfering with struvite crystallization. Various compounds can be precipitated from a wastewater with high calcium concentrations, including hydroxyapatite, calcium phosphate, and calcium carbonate (Le Corre *et al.*, 2005; Wang *et al.*, 2005). The purpose of this experiment was to look at the effect of pH and Mg:PO₄ ratio on P removal from raw swine manure lagoon supernatant and the influence of Ca²⁺ on this process.

4.2 Method

4.2.1 Source and collection

Manure supernatant was collected in July from the primary lagoon at a commercial swine facility in Manitoba. The manure was taken to the lab and the experiment was conducted on the same day as collection.

4.2.2 Experimental setup

The manure was strained to remove large particles and divided into four batches of 1.6 L. One of these batches was not adjusted, while the others received a MgCl_2 addition to bring the $\text{Mg}:\text{PO}_4$ ratios to 1.3:1, 1.6:1, and 1.9:1 based on previous measurements from the same lagoon. These batches were then divided into four different pH categories: 8.0, 8.5, and 9.0 without stirring, and 8.5 with stirring. The stirring was done for 2 h after pH adjustment with 1.0 M NaOH. One batch of control centrate was also prepared with no pH or Mg^{2+} adjustment. The 1L beakers were then left to equilibrate at room temperature for 24 h.

After equilibration, the pH of each beaker was measured and samples were taken from all the beakers in triplicate. After pouring off the top portion of each batch the remaining supernatant was filtered through Whatman 1 filter papers to collect the precipitant. The dried precipitate on the qualitative filter paper was weighed and homogenized before analysis.

4.3 Results and discussion

The supernatant was analyzed before the experiment was conducted, as shown in Table 4.1. The addition of MgCl_2 was based on a previous sample from the same lagoon, however since the concentration ratios were different for this batch, the actual $\text{Mg}:\text{PO}_4$ ratios achieved were 1.2:1, 1.3:1, and 1.4:1. These values will therefore be used when discussing the results.

Table 4.1 Constituent concentrations of supernatant as sampled immediately prior to the experiment and in the control.

Concentration (mg/L)				pH	Mg:PO ₄	Ca:PO ₄
PO ₄ -P	TP	Mg ²⁺	Ca ²⁺			
213 ± 7	209 ± 7	168 ± 5	405 ± 7	6.84	1.0	1.47
Concentration in control (mg/L)				% PO ₄ -P removed	% Mg removed	
PO ₄ -P	TP	Mg ²⁺	Ca ²⁺			
155 ± 23	158 ± 23	133 ± 18	404 ± 4	27	21	

There is a dramatic increase in PO₄-P removal between the control and the lowest pH amendment for all the Mg:PO₄ ratios. However, as shown in Figure 4.1, there is little difference in terms of PO₄-P removal between either the pH values, the Mg:PO₄ ratios, or due to stirring. There seems to be a slight increase in PO₄-P removal with increasing Mg:PO₄ ratio and pH, ranging from 90 to 97% over all the trials, with a 27% removal in the control.

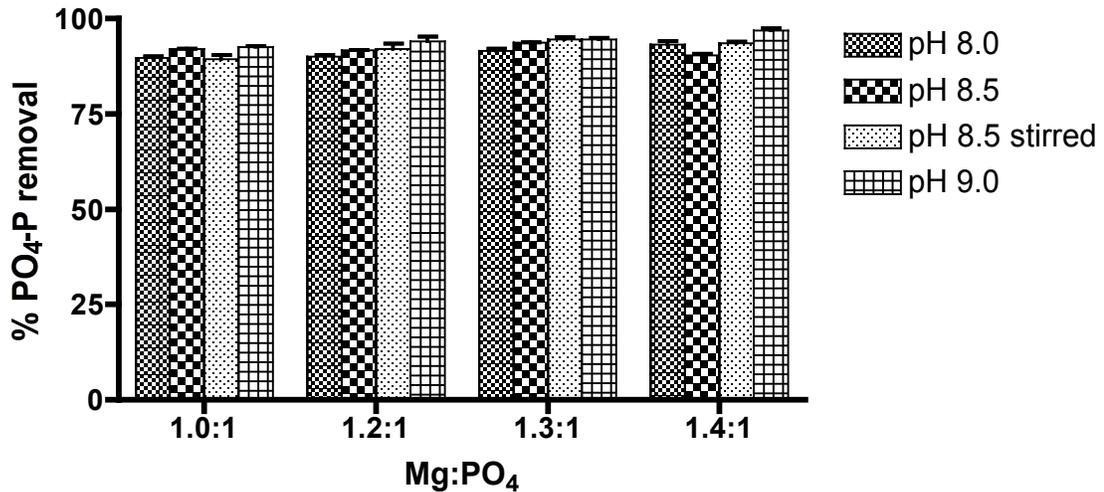


Figure 4.1 Percentage PO₄-P removal after 24 h for the various pH and Mg additions.

The Mg^{2+} concentrations shown in Figure 4.2 were adjusted for Mg^{2+} addition by subtracting the concentration added to achieve the various molar ratios. The Mg^{2+} removal remained fairly constant with increasing pH, and as with $\text{PO}_4\text{-P}$ removal there seems to be a slight increase in Mg^{2+} removal with increasing $\text{Mg}:\text{PO}_4$ ratio, ranging from 76 to 90%. The removal pattern is very similar to the $\text{PO}_4\text{-P}$ removal, which suggests struvite precipitation.

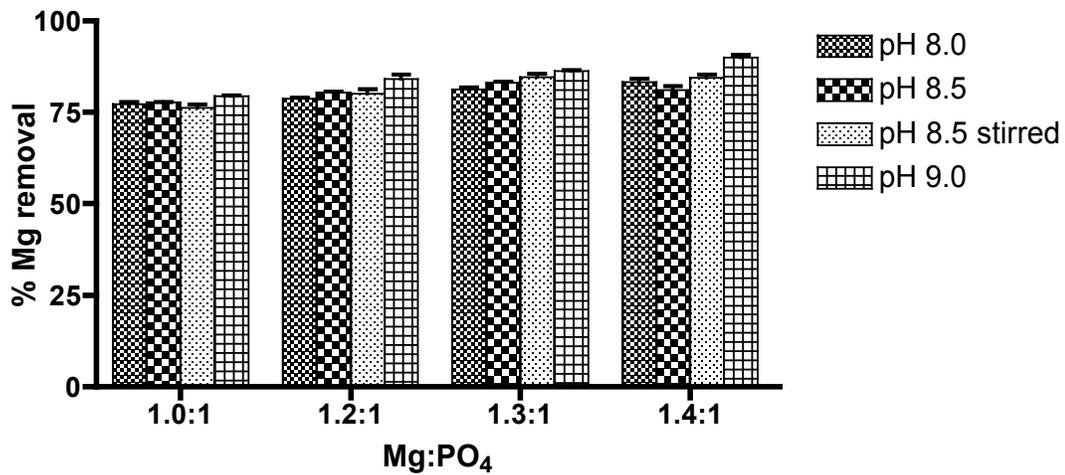


Figure 4.2 Percentage Mg^{2+} removal after 24 h for the various pH and Mg additions, with the added Mg subtracted.

A similar trend was observed in terms of Ca^{2+} removal for all the trials with added Mg^{2+} . Very little Ca^{2+} removal was observed at pH 8 and 8.5, while a minimum of 40% removal was observed at pH 9 (Figure 4.3). For the trials with no Mg^{2+} addition, the Ca^{2+} removal at the lower pH values are more pronounced, at around 10%, while the removal at pH 9 approaches 40%, as with the other trials. Although the $\text{Ca}:\text{PO}_4$ ratio is quite high, it does not seem that significant calcium phosphates were precipitated, since there is no

significant increase in PO₄-P removal or decrease in Mg²⁺ at pH 9. This seems to suggest that another form of Ca²⁺, such as calcium carbonate, was precipitated.

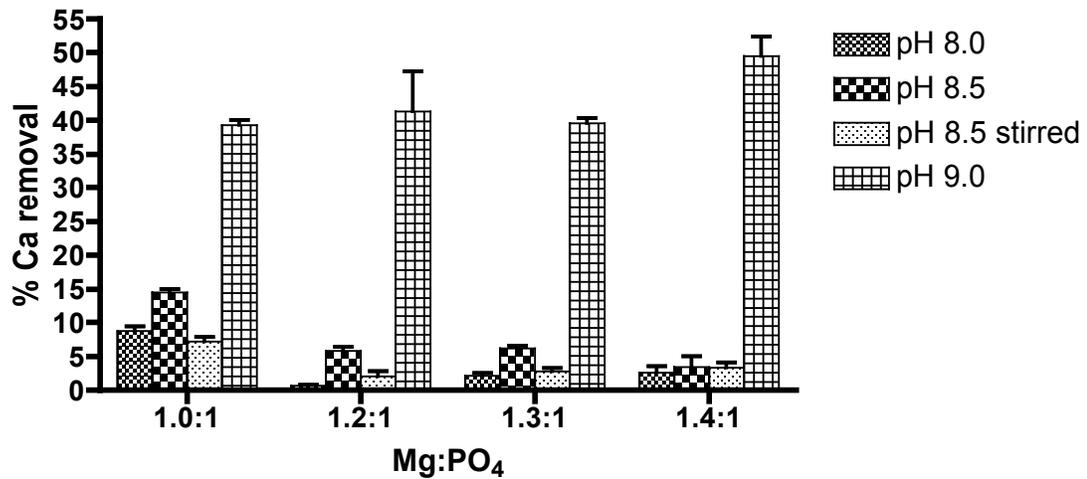


Figure 4.3 Percentage Ca²⁺ removal after 24 h for the various pH and Mg additions.

Although the increased Mg:PO₄ ratio did not significantly affect PO₄-P removal it did seem to suppress Ca²⁺ precipitation at pH 8.0 and 8.5. Stirring after pH adjustment did not significantly affect PO₄-P removal. The difference in PO₄-P removal between the trials is not really significant in terms of the increased cost necessary to achieve such small improvements in PO₄-P removal. These results agree with those of Celen *et al.* (2007) in terms of Mg²⁺ addition, who found that the small increase in PO₄-P removal with increased Mg:PO₄ ratio was not justified by the additional cost. The increase of supernatant pH to 8.0 without any Mg²⁺ adjustment resulted in a 90% PO₄-P removal, which seems to suggest that the Mg²⁺ content of the swine wastewater could be sufficient for significant PO₄-P removal. In addition, since the Ca²⁺ removal at this pH was relatively low, the resulting precipitate should be mainly struvite. Since the cost of raising

the pH to 8.0 will still be significant, a cost-effective method for raising the supernatant pH will be needed for this method to be feasible for farm-scale application.

These findings are further supported with the XRD analysis (Appendix I-b). The recovered precipitate from the Mg:PO₄ 1.4:1 trials and all the pH 8.0 trials as well as the control were analyzed. For all the samples struvite was the most probable match found. The only sample that had another likely match was the pH 9.0 trial, where calcite was also identified.

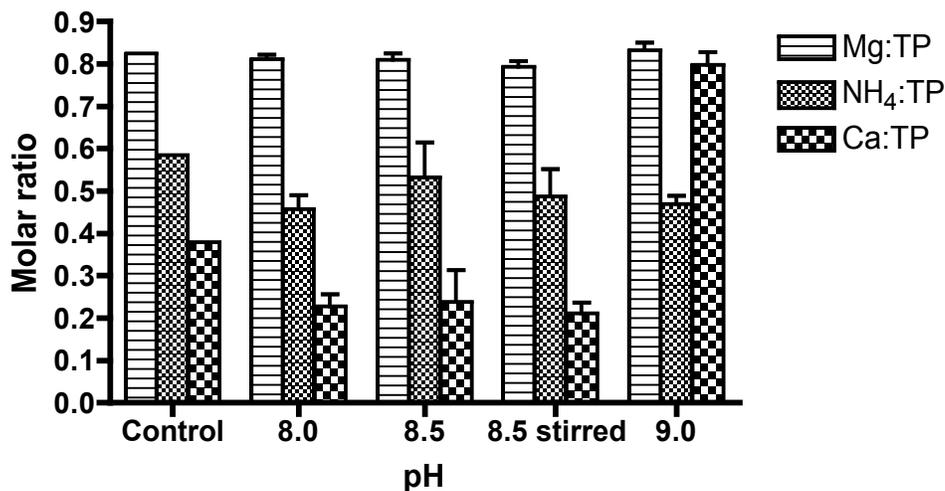


Figure 4.4 Molar ratio of constituent concentrations to TP averaged over the various Mg:PO₄ ratios from the recovered precipitate.

The ratio of moles in the recovered precipitate was determined to confirm XRD findings. As shown in Figure 4.4, the Mg:TP molar ratio is close to 0.8 for all the trials, including the control, while the NH₄:TP molar ratio ranges from 0.45 to 0.6. The expected molar ratio of Mg:TP and NH₄:TP for struvite precipitation would be 1.0. Therefore some PO₄-P could have been removed in a form other than struvite, but it was not detected on the

XRD and might be some amorphous form of calcium phosphate. Although very little Ca^{2+} was removed in the control, the Ca:TP molar ratio is close to 0.4, mainly because very little $\text{PO}_4\text{-P}$ was removed. The Ca:TP molar ratio for pH 8 and 8.5 is relatively low, ranging between 0.2 and 0.3. At pH 9, however, the range for the various Mg: PO_4 ratios is between 0.75 and 0.82. The significant amount of Ca^{2+} removed at pH 9 did not affect the NH_4 :Mg:TP molar ratio, supporting the XRD finding that it was precipitated as calcite. Unlike the findings by Le Corre *et al.* (2005) and Wang *et al.* (2005), the Ca^{2+} did not seem to interfere with struvite formation, since even at the high Ca: PO_4 ratio of the supernatant, struvite precipitated at all the pH values.

4.4 Conclusion

These tests revealed that struvite could be successfully precipitated from raw swine lagoon supernatant through chemical amendment of MgCl_2 (Mg: PO_4 ratios 1.2:1, 1.3:1, and 1.4:1) and NaOH (pH 8.0, 8.5, and 9.0). The XRD analysis confirmed struvite precipitation at all pH values, and indicated that calcite was mainly present at pH 9.0. The Mg^{2+} addition did not have a very notable effect on $\text{PO}_4\text{-P}$ removal and the small increase in $\text{PO}_4\text{-P}$ removal (90-97%) with increased Mg: PO_4 ratio would not be justified by the additional cost. However, the increase of supernatant pH to 8.0 without any Mg^{2+} adjustment resulted in a 90% $\text{PO}_4\text{-P}$ removal compared to a 27% removal in the control. This shows the potential of this waste stream for P recovery through struvite precipitation without any Mg^{2+} amendment. However, since the cost of raising the pH to 8.0 will still be significant, a cost-effective way for raising the supernatant pH will be needed for such a method to be feasible for farm-scale application.

Chapter 5 - Development of a crystallization reactor

5.1 Introduction

The main objective of this study was to develop a system for on-farm recovery of P as struvite from hog manure slurries that could provide farmers with a ready source of P fertilizer. For on-farm implementation the reactor would need to be robust and require little maintenance. The purpose of this reactor would be to recover P on an ongoing basis from swine lagoon supernatant. Supernatant would be taken from the lagoon, some of its P content recovered as struvite, and then returned to the lagoon. Because the reactor simply feeds back into the lagoon, it could be sized to optimize P removal, rather than to accommodate field application, which would involve large volumes and high flow-rates.

Based on the results from Chapter 4 the addition of Mg^{2+} could be eliminated, since the natural $Mg:PO_4-P$ molar ratios of local lagoon supernatant seem to be favourable for struvite precipitation. A possible low-cost method for increasing supernatant pH is aeration. Since aeration would only increase the pH slightly, it should also serve to prevent calcium precipitation, ensuring that the precipitant is mainly struvite and thereby maintaining its value as a fertilizer. The design calls for a combination of a fluidized-bed and air-agitated reactor. A struvite bed would be tested as seed material to encourage larger struvite crystal formation while aeration would be used to increase pH. The development of this reactor involved an investigation of aeration as a pH amendment, the interaction of aeration and a seedbed, and reactor operation set-up.

5.2 Aeration as a method for pH increase

A potential chemical-free method for pH increase is air sparging, where the main cost would be electrical. Sparging, or degasification, involves bubbling a solution with an inert gas to substitute the dissolved reactive gas, in this case CO₂, and results in a pH increase in CO₂-rich waste streams.

To determine whether aeration would result in a sufficient pH increase within a short time span a series of batch tests were conducted. The tests were conducted using supernatant collected from swine lagoons and refrigerated until use. Supernatant was placed in either a 1L beaker (#1-5) or a 5L flask (#6-9) and aerated at different rates through a cylindrical stone placed near the bottom of the beaker. The pH was continually monitored with a probe throughout the experiments. As shown in Table 5.1, the results for #1-3 were encouraging enough in terms of pH increase, around 0.5 pH units within 20 min, to warrant further testing and monitoring of nutrient concentrations. The results for #4-6 show that significant PO₄-P removal can be achieved in a relatively short period of time and with a pH increase of less than one unit. It also shows that the pH increases more rapidly with higher aeration rates, although excess aeration does not significantly increase PO₄-P removal. These findings are confirmed by the results from #7-9. These tests were only run for 5 min in order to determine whether aeration, and PO₄-P removal, occurs fast enough for the process to be used as a method for pH increase in an upflow reactor with a 5 min hydraulic retention time (HRT). The results indicated that aeration could sufficiently increase pH so that satisfactory PO₄-P removal is possible within the desired time.

Table 5.1 Summary of results for the aerated batch tests.

Supernatant source: Starlite primary lagoon								
#	Storage time (days)	Volume (ml)	TS/TSS (g/L)	Aeration rate (LPM)	Normalized aeration (LPM per L)	Initial pH	pH at 20 min	% PO₄-P removal
1	1	300	na/23	4.1	13.7	6.53	7.21	na
2	3	300	na/25	1.5	5.0	6.59	7.00	na
3	3	300	na/23	2.5	8.3	6.52	7.12	na
4	60	400	12.4/2.9	3.1	7.75	7.24	8.11	81.7
5	90	300	12.3/2.9	7.2	24	7.34	8.27	87.6
6	120	850	15.7/2.8	1.6	1.88	7.52	7.9	7.9
Supernatant source: Glenlea conventional barn wetwell								
#	Storage time (days)	Volume (ml)	TS/TSS (mg/L)	Aeration rate (LPM)	Normalized aeration (LPM per L)	Initial pH	pH at 5 min	% PO₄-P removal
7	0*	1000	9.5/4.2	3.1	3.1	7.3	7.71	34.4
8	0*	1000	9.5/4.2	9.5	9.5	7.3	7.99	62.8
9	0*	1000	9.5/4.2	19.5	19.5	7.3	8.13	68.8

*Tests conducted on same day as collection
na = not available

5.3 Aeration and seedbed interaction

The preliminary reactor design, shown in Figure 5.1, consists of a cone bottom and cylindrical top with an influent line, aeration port, and drainage port at the bottom, fitted with effluent lines at 3, 4, and 5L. An additional aeration line was also placed inside the reactor. The interaction of a seedbed with the proposed aeration was observed to determine the effect of volume, flow rate, and aeration rate.

The 20 g seedbed used for all the tests consisted of struvite powder collected from previous experiments. After the seedbed was poured in, the reactor was filled with tap water to the appropriate effluent line and the influent was started at a rate of 200 ml/min. Flow rates were measured with a graduated cylinder and stopwatch. The effluent was collected in separate containers every five min, and after it settled the clear water was

poured off and the seed air-dried. Table 5.2 shows the various combinations of volume, aeration rate, and aerator position tested.

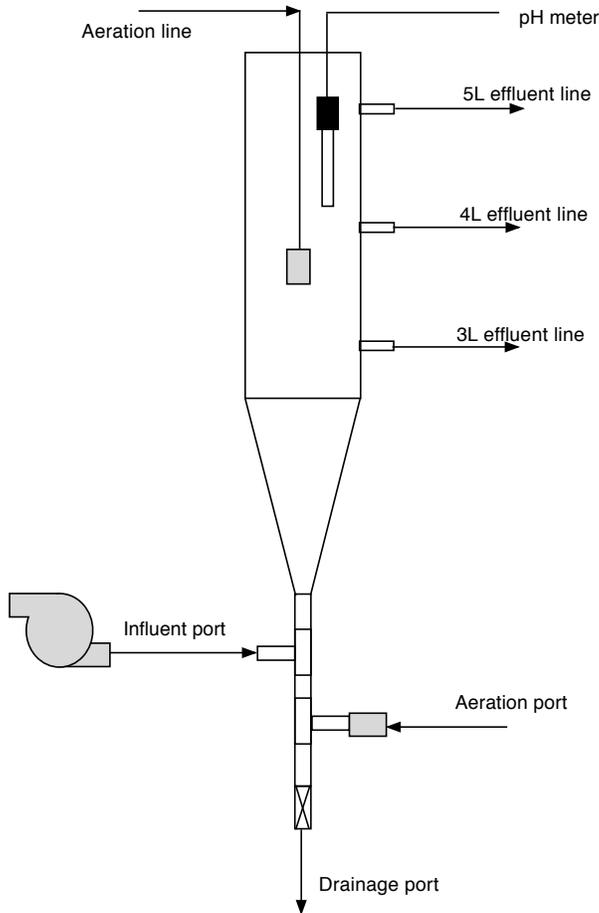


Figure 5.1 Schematic of cone reactor set-up used for preliminary testing.

Table 5.2 Summary for the preliminary testing of the interaction between the seedbed and aeration in the cone reactor.

Test #	1	2	3	4
Aeration location	Bottom	Bottom	Top	Top
Aeration rate (LPM)	1.3	1.3	1.3	4.1
Volume (L)	3	5	4	4
% Seedbed left in reactor	26	46	69	53

As can be seen from Figure 5.2, a significant amount of seed initially overflowed during test #1, then gradually decreased until only 5.2 g was left in the reactor. The larger volume of test #2 allowed for almost twice the seed retention. These tests were aerated from the bottom, which meant that large bubbles continually disturbed the seedbed, causing a lot of fines to be suspended in the reactor and eventually leave through the overflow. The rationale for placing the aerator at the bottom is to increase the pH of the incoming supernatant before it reaches the seedbed so that it is ready to precipitate onto the existing particles. However, moving the aeration to the top of the reactor resulted in better seedbed retention (#3), even with a higher aeration rate (#4). Aerating above the seedbed means that precipitant will form above the seedbed and then settle down, making no allowance for interaction with the seedbed. Changing the location of aeration in the reactor will therefore require further design changes to overcome this problem.

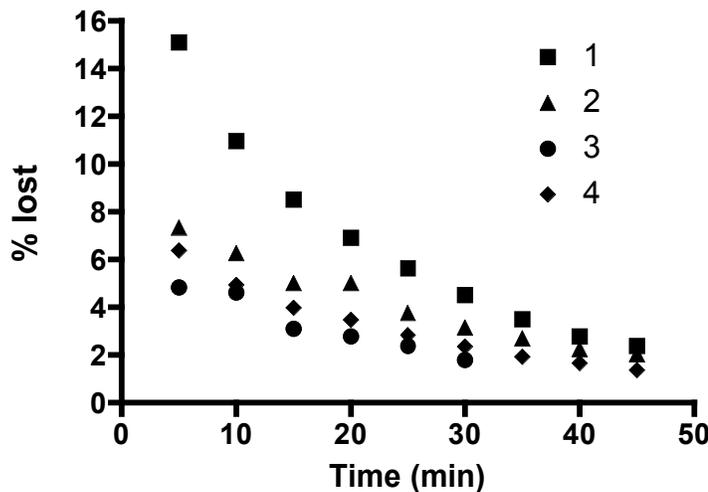


Figure 5.2 Percentage of the reactor seedbed lost through the overflow for successive five-min periods.

5.4 Preliminary reactor testing

The next step was to test the top-aerated reactor with supernatant to determine the pH and nutrient concentration changes. The reactor was filled to 3 L with supernatant from a low-pH anaerobic reactor (Table 5.3), and the influent set at 600 ml/min for a 5 min HRT. From t=0 to t=28 min the reactor was constantly aerated at 9 LPM (3 LPM per L) from the top, while the influent was started at t=5 min and stopped at t=18. The aeration rate was chosen based on the aeration tests described in Chapter 5.2, specifically #7-9.

Table 5.3 Reactor supernatant characteristics and PO₄-P concentration.

pH	TS/TSS (g/L)	VS/VSS (g/L)	PO ₄ -P t=0/t=28 (mg/L)	% Removal
6.38	12.85/8.2	8.99/6.0	185.4/158.3	14.6

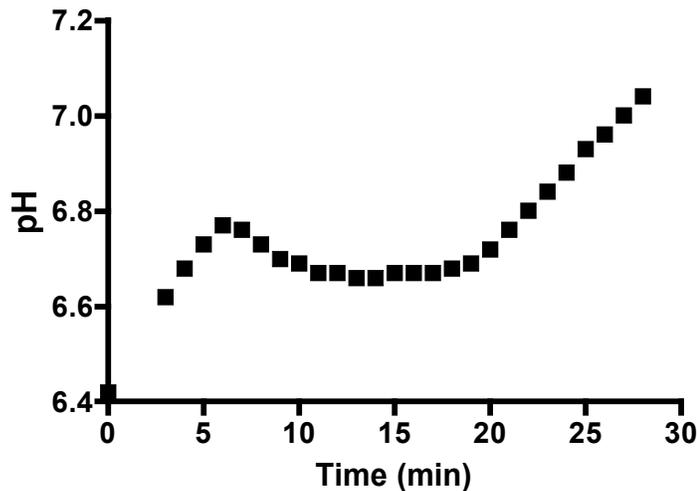


Figure 5.3 Reactor pH during aerated run with a 5 min HRT.

This test demonstrated that the pH of supernatant can be raised through aeration and maintained at an elevated level while running through a reactor. The PO₄-P concentration decreased by 14.6%, which was not very significant, but it has to be taken into account

that the pH was below 7 for the bulk of the test. In order to affect an overall pH increase, the dip in pH due to the low pH influent was addressed by incorporating a recycle loop that will boost the pH at the bottom of the reactor and ideally help maintain a higher, stable pH. This would also allow the seedbed to see supernatant with a sufficiently high pH to allow for precipitation and interaction with the bed particles.

5.5 Reactor design and operation

The data gathered from these tests aided in the creation of a new and modified reactor design with a novel combination of fluidized seedbed, aeration for pH increase, and an internal recycle. The reactor, shown in Figure 5.6, consisted of a long cylinder, 1.9 cm in diameter connected through a funnel to a 15.1 cm wide cylinder with a total volume of 12 L. All the parts and equipment used for the reactor system are listed in Table 5.4.

Table 5.4 Description of components used to construct and operate reactor.

Component	Location, #	Description
Top section	1	6" clear PVC pipe
Bottom section	1	¾" clear PVC pipe
Funnel	1	6" wide, 5" tall clear polyethylene
Ports	Top, 3	Polypropylene, Sch. 40 (std), 1/4" MPT × 3/8" HB adapter
	Bottom, 6	Polypropylene, Sch. 40 (std), 1/8" MPT × 5/16" HB adapter
Tubes	Recycle pump	3/8 ID × 1/16 Wall, clear PVC
	All other	7/16 DD × 5/16 ID, clear PVC
Valves	Reactor	¾" S × S Ball valve, PVC
	Settling cone	¼" FPT PVC Ball valve
Pumps	Influent, fine return	Masterflex L/S digital std drive, 2 × easyload head II
	Recycle	Masterflex L/S economy drive, easyload head II
Overflow cone	1	Imhoff cone, 1L
pH meter	2	Acorn pH 5, with Oakton epoxy body pH electrode
Air pumps	2	Elite 801 and 803 Air pump
Air stones	2	½" × 1" cylindrical stone

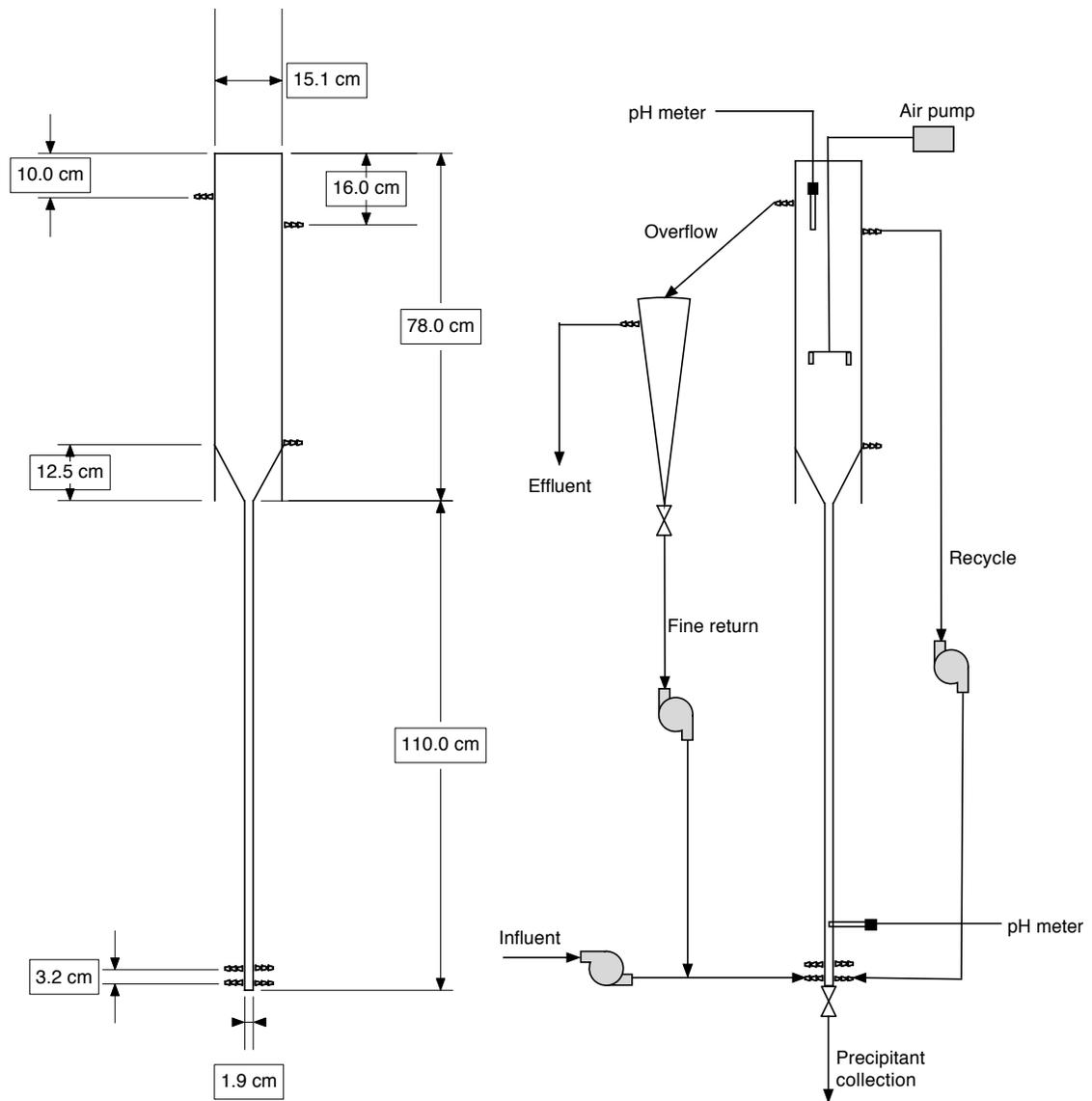


Figure 5.4 Schematic of reactor dimensions and operational set-up.

The seedbed was placed in the bottom section and aeration was introduced 2/3 from the top of the reactor above the seedbed. A recycle stream was used to elevate the pH at the bottom of the reactor. The overflow entered a settling cone for capturing fines that were periodically returned to the feed tank, while the effluent flowed out from the top of the overflow cone. The pH was monitored at the top and bottom of the reactor. In order to

hold the pH probe in the bottom section pipe, it was pushed through a rubber stopper and then plugged into a T-connection, where it remained throughout the run. Peristaltic pumps were used to control the flow rates for the influent, recycle, and fine return lines. A number of extra ports were added to the bottom of the reactor to accommodate any future changes in operation that might be needed. Ports not in use were equipped with a crimp and rubber stopper to allow for easy line change during operation. A picture of the reactor system set-up is shown in Appendix II-a.

5.5.1 Synthetic feed solution

In order to conduct a number of tests with comparable results, a synthetic feed was developed based on several samples taken from a secondary swine lagoon, as shown in Table 5.5. The synthetic feed was made in 12 L batches by mixing KH_2PO_4 , NH_4Cl , and CaCl_2 in DI water, adding NaHCO_3 and Na_2CO_3 for the alkalinity, bubbling through CO_2 until the solution reaches 6.67, and then adding $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Bubbling CO_2 into a solution containing carbonate buffers will decrease the pH as the CO_2 dissolves into solution:



The amount of carbonate buffers needed was determined by trial and error until the desired alkalinity was attained. All the chemicals were obtained from Fisher Scientific or Sigma Aldrich as ACS reagent grade, except $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which was obtained in bulk as a 90% Mg salt. Therefore the mass added for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is 10% greater than stoichiometrically required to reach its target concentration to compensate for impurities.

Table 5.5 Average concentration of ions in the swine lagoon supernatant and compounds used to create a synthetic feed.

Compound	Target ion	Molar ratio target:PO ₄	Target concentration (mg/L)	Mass added (g/12L)
KH ₂ PO ₄	PO ₄ -P	1	160	8.43
NH ₄ Cl	NH ₄ ⁺	34.6	2500	114.64
MgCl ₂ ·6H ₂ O	Mg ²⁺	1.2	150	18.83
CaCl ₂	Ca ²⁺	1.2	250	8.31
Na ₂ CO ₃	Bicarbonate alkalinity, mg/L CaCO ₃		3000	38.30
NaHCO ₃	Carbonate alkalinity, mg/L CaCO ₃		3000	61.02

5.5.2 Struvite seedbed

To produce struvite particles for the seedbed, a highly concentrated synthetic solution (MgCl₂, NH₄Cl, and KH₂PO₄) was made and the pH increased with 1M NaOH to 8.5, resulting in struvite precipitation. Once the precipitate was dried somewhat, a repeated process of forced air-drying, crushing, and shaking produced pellets of sufficient hardness and size to undergo the sieving process. The pellets were hand sieved with a standard US sieve series numbers 10-50, with sieve openings from 2.00 to 0.297 mm. The bed consisted of approximately 100g struvite, ranging in size from 0.6 to 2 mm in diameter, with about half between 0.6 and 0.8 mm.

The analysis of synthetic struvite made for the seedbed pellets show that although struvite is the main precipitate based on equal molar ratios of Mg²⁺, TP, and NH₄⁺, there are significant amounts of K⁺ and Na⁺ present (Figure 5.5). This is evidenced by the diffractogram peak intensity not conforming completely to the standard struvite pattern (Appendix I-c). This suggests that there is another precipitate present, but its identity could not be confirmed by the XRD analysis.

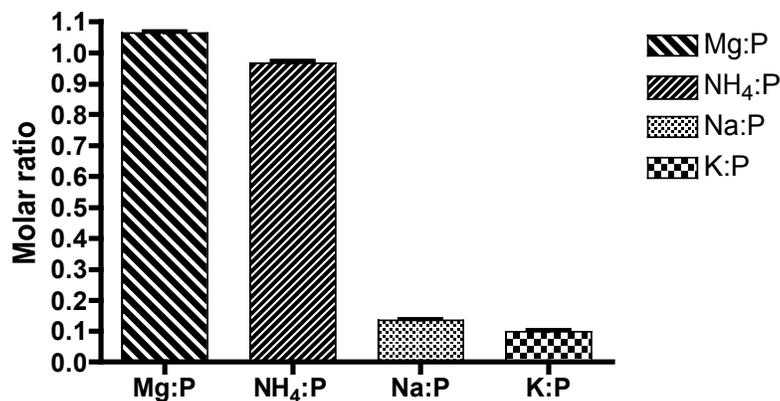


Figure 5.5 Molar analysis of synthetic struvite made for seedbed.

During the initial testing of the reactor to determine seedbed behaviour, the precipitate produced during the runs were recycled and reused as seedbed material. However, as it became clear that some additional precipitation was taking place, fresh seedbed particles were used for each run. Of the runs described in Chapter 6, only the test run had recycled particles. The composition of the seedbed particles used in the test run (Figure 5.6) was slightly different than the synthetic struvite, with lower proportions Na⁺ and K⁺ and some Ca²⁺ contamination.

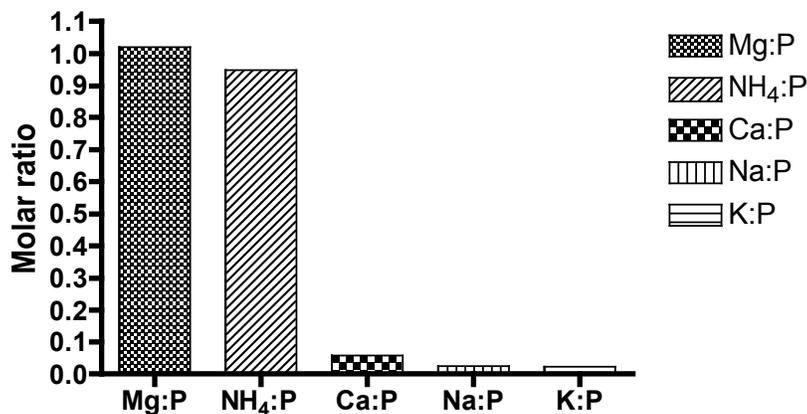


Figure 5.6 Molar analysis of seedbed particles used for the test run.

Chapter 6 – Reactor testing with synthetic supernatant

6.1 Introduction

The performance of the aerated struvite crystallization reactor was evaluated and refined using synthetic feed. Based on samples taken from hog lagoon supernatant, a synthetic feed was made to reflect the average concentration of constituent and competing ions for struvite formation (phosphate, magnesium, ammonium, and calcium). Alkalinity was added in the form of carbonate species and the appropriate pH was achieved through CO₂ bubbling. Various runs were done using this feed in order to test and optimize the reactor operation. Adjustments were made to influent flow rate, recycle rate, seedbed volume and particle size, fines management, and run time.

Some of the main goals for testing with the synthetic solution were to develop a mass balance around the reactor, establish an acceptable aeration rate, optimize influent and recycle flow rates, and to achieve long-term, consistent operation. Initial tests aimed to determine the optimum flow and aeration rates for pH increase as well as an appropriate seedbed volume and particle size distribution.

6.2 Methods

Unless otherwise indicated in Table 6.1, the basic procedure for the tests was as follows:

- Seed was poured into the top of the reactor
- The reactor was filled with the feed solution and a recycle flow was established

- Aeration was initiated at 7 LPM for 20 min before the influent feed was started
- The pH was monitored at the top and bottom throughout
- Fines were collected in the overflow cone and returned through the influent port once every h
- Effluent from the overflow cone including some fines was collected by hourly composites
- Hourly samples were taken for analysis from the influent and effluent reservoirs

Following this basic procedure the influence of various parameters on the reactor operation was investigated in a series of tests (Table 6.1) looking at the effects of aeration, seedbed size and material, and the recycle ratio.

Table 6.1 Summary of reactor test parameters during short-term runs.

	Test run	Recycle rate	Struvite bed	Sand bed
Influent (ml/min)	200	100	100	100
Recycle (ml/min)	600	700 - 300	700	700
HRT (min)	60	120	120	120
Seedbed (g)	struvite	none	struvite	sand
2-0.8 mm	10	-	50	30
0.8-0.6 mm	40	-	50	40
0.6-0.4 mm	20	-	0	30
<0.4 mm	0	-	0	100
Aeration (LPM)	7	7	7	7
Start-up time (min)	20	20	20	20
Run time (hrs)	3	6	6	6
Fines recycle period	-	1 hr	1 hr	1 hr
Sampling	Grab	Composite	Composite	Composite

This was followed by long-term runs, which were planned for a continuous five-day operation. The planned flow rates were the same as the last three runs described in Table 6.1, but no seedbed was added to the reactor. The aeration rate was decreased to 4.3 LPM because the pH observed in previous runs was more than sufficient for struvite

precipitation, and a lower aeration rate would decrease fine losses. Fine recycling and reactor drainage was planned for once per day, sampling for once per day from the feed and from the effluent after collecting overflow for an hour, and pH measurement every hour from 8:00 to 17:00. Feed would be continually prepared during the day and stored in a drum to last overnight. The actual operation of the reactor necessitated some modification of these plans to accommodate changes. The actual timetables for the two long-term runs are given in Table 6.2 below.

Table 6.2 Experimental timetables for long-term runs.

Long-term run 1			
Day	Time	Run time (hrs)	Event/Action
Tuesday	10:40	20 min start-up	Start run Collect influent sample
	17:00	6	Reduce flow rates to 50 ml/min influent and 350 ml/min recycle Collect influent/effluent samples
Wednesday	11:00	24	Return flow rates to 100 ml/min influent and 700 ml/min recycle Return fines to reactor
	17:00	30	Collect precipitate from reactor Collect precipitate from reactor
Thursday	8:00	45	Collect influent/effluent samples Stop run Collect precipitate
Long-term run 2			
Day	Time	Run time (hrs)	Event/Action
Monday	9:40	20 min start-up	Start run Collect influent sample
	16:00	6	Collect influent/effluent samples
Tuesday	10:00	24	Replace aeration stones Collect precipitate from reactor
	16:00	30	Collect influent/effluent samples
Wednesday	8:00	46	Stop run to replace influent port and aeration stones Collect precipitate
	11:00	46	Restart run without aeration
	11:45		Restart aeration
Thursday	16:00	51	Collect influent/effluent samples
	8:00	67	Stop run Collect precipitate

6.2.1 Experimental development

For every run, the following aspects were monitored to establish reactor performance:

- The extent of TP removal
- The mass and composition of precipitate produced

The test run was planned to verify that the reactor would operate as assumed. The main aspects that were of interest were:

- The ability of aeration and recycle ratio to effect and maintain pH change in the reactor
- The fluidization of the seedbed

Having established these aspects, various runs were completed to investigate specific aspects of reactor operation and so determine optimal performance conditions.

- Recycle rate
 - Effect of recycle ratio on pH gradient in reactor
 - Fluidization of fines
- Seedbeds – struvite and sand
 - Effect of seedbeds on reactor operation and performance

Using the results from these runs, the reactor operation was adjusted for optimal performance in the duration run in order to establish the operational stability and performance of the reactor over time.

6.3 Results and discussion

6.3.1 Test run

With the main focus on establishing flow rates, evaluating seedbed distribution, and determining the extent of pH increase due to aeration, fines were not recycled for this test. Based on some preliminary work to establish which particle sizes would be fluidized in the reactor, a suitable seedbed range was found. During the test run the seedbed particles were well distributed through the bottom section, fluidizing up to the bottom of the funnel, although some fines collected in the top section of the funnel. For further tests, a seedbed consisting of only the larger seed particles (> 0.6 mm) would probably be sufficient for filling the bottom section of the reactor, where they will be most available to serve as struvite nuclei.

The pH measurement during the test run revealed a relatively large difference between the top and bottom pH (Figure 6.1). This would suggest that the recycle flow rate should be increased and/or the influent decreased to minimize the difference and optimize the reactor operation. The pH at the top of the reactor is relatively stable, and stays below 8, this is ideal for avoiding calcite precipitation (Chapter 4). An aeration rate of 7 LPM should therefore be sufficient for increasing the pH to an acceptable level.

The ICP results in Table 6.3 show that the TP and Mg^{2+} concentrations decrease significantly within the first hour, and remain relatively constant thereafter, while the Ca^{2+} concentration does not change significantly. The slight increase in K^+ could be due to seed dissolving, since the seed was found to have some K^+ content.

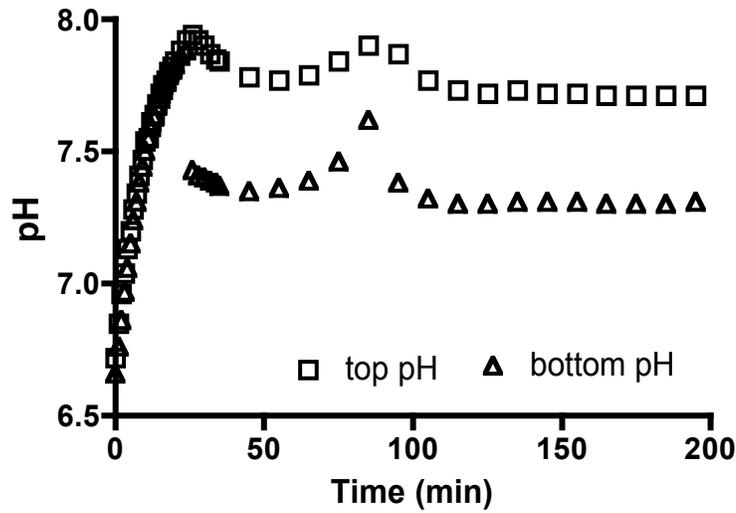


Figure 6.1 The pH profile during the test run.

Note: The influent bucket was initially stirred which caused CO₂ release, some precipitation, and the pH rise around 80 min; the subsequent buckets were not stirred continuously, and much more constant influent pH was achieved.

Table 6.3 ICP results for effluent grab samples during reactor test run.

Time (min)	Concentration (mg/L)				Mg:TP moles missing	Ca:TP moles missing
	TP	Mg ²⁺	Ca ²⁺	K ⁺		
0	119.1 ± 38.1	126.6 ± 22.0	296.4 ± 14.7	209.6 ± 7.9	1.36	1.93
50	16.9	64.3	271.1	217.7	0.78	0.19
110	17.2	62.4	248.2	205.7	0.80	0.37
170	39.2	67.6	281.6	228.1	0.94	0.14

Note: Initial values are average of samples taken throughout the test with standard deviation. Difference between initial concentrations and concentration at given time used to calculate ratio of moles missing from solution. Moles missing at time 0 indicates initial molar ratio.

Samples were taken from the effluent line every hour, while the top section of the reactor was sampled more frequently. The ICP results shown in Figure 6.2 indicate that with a few exceptions the concentrations quickly reach a steady state. On average, the TP and Mg²⁺ concentrations are significantly higher than those found in the effluent, while the Ca²⁺ and K⁺ is very similar. This may be due to the fact that fine struvite particles were

suspended in the reactor and included in the sample, while it was able to settle out of solution in the settling cone. Consequently, samples in future tests were taken from the effluent to prevent fines entering the sample. In addition, to take more representative samples, effluent was collected for an hour so that composite samples could be taken.

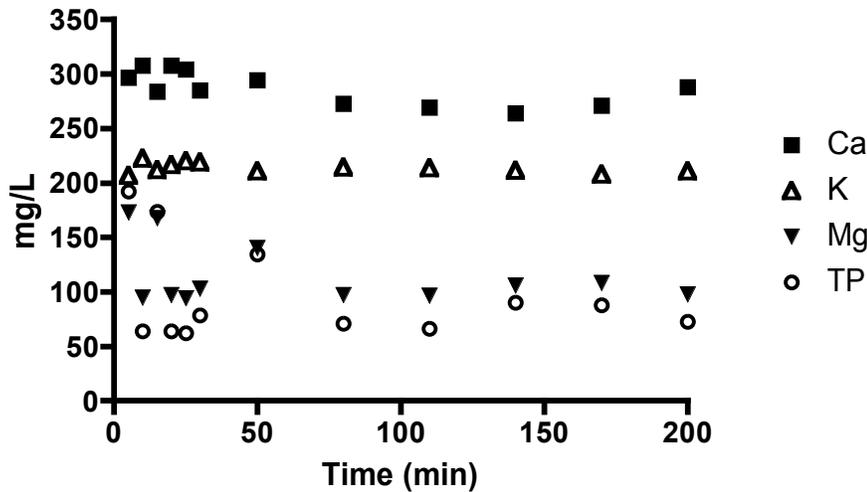


Figure 6.2 Constituent concentrations in the top section of the reactor during test run.

The results for precipitation recovery is shown in Table 6.4. The seedbed lost some mass, probably due to particles disintegrating, which would account for the increased K^+ concentration in the effluent. Longer run times may allow the seedbed to grow and increase its mass. Very little mass was lost to the effluent reservoir, indicating that the overflow cone was successful in retaining the majority of fines lost through the overflow. The recovered precipitate is less than the maximum possible struvite based on the TP concentration of the feed, but more than the maximum possible struvite based on moles of TP and Mg^{2+} missing from solution. The excess precipitate with respect to moles missing from solution may be due to errors in the sampling method. The grab samples

could have included fine struvite particles that would make removal seem lower than it actually was, thereby underestimating maximum struvite possible. It may also indicate that some precipitate other than struvite is present.

Table 6.4 Summary of precipitation recovery for reactor test run.

		Test run
Mass recovered (g):	in overflow cone	16.0
	in effluent reservoir	3.2
Total mass precipitated (g)		52.7
% seed recovered:	2-0.8 mm	89
	0.8-0.6 mm	91
	0.6-0.4 mm	90
% of total mass recovered as fines:	in reactor	33
	in overflow cone	13
	in effluent reservoir	3
% of max struvite possible:	Feed [TP]	87
	Effluent [TP]	146 ± 22
	Effluent [Mg]	176 ± 8

Note: Precipitant collected from reactor, cone, and effluent bucket drained and dried separately; then sieved to determine particles sizes recovered.

An analysis of the recovered precipitate indicated that the molar ratios of Mg^{2+} and NH_4^+ to TP were consistent with struvite, being very close to one. There was some Ca^{2+} precipitation, which could account for some of the additional precipitation observed with respect to moles removed. Insignificant amounts of K^+ and Na^+ were found in the recovered precipitate.

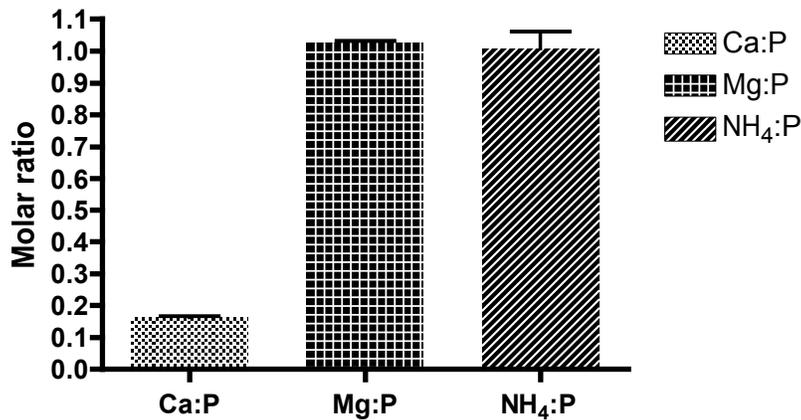


Figure 6.3 Component molar ratios to TP found in the recovered precipitate from the test run.

This run has demonstrated that an aeration rate of 7 LPM is sufficient to increase the pH to just below 8, minimizing the possibility of calcite precipitation, while resulting in significant TP removal. This was confirmed by ICP analysis which showed little Ca^{2+} decrease in the effluent and a low Ca:TP molar ratio in the precipitate. The precipitate analysis also confirmed the presence of struvite. The recycle/influent ratio should be adjusted to minimize the difference between top and bottom pH, ensuring that incoming feed encounters sufficiently high pH to induce struvite precipitation in the seedbed. The finer seedbed particles were suspended in the funnel, therefore, to increase the seedbed density in the bottom section, the proportion of larger particles should be increased and the finer seeds removed.

6.3.2 Recycle rate

To establish a base of comparison for future tests, this test was run without any seedbed, putting the focus on system operation and recycle rates. Based on the results from the first test run, initial recycle and influent rates were adjusted to 700 and 100 ml/min respectively, with the aim of narrowing the difference between top and bottom pH. The recycle rate was decreased by 100 ml/min after 2 h, and then every hour from 700 to 300 ml/min. Systematically decreasing the recycle rate would show how pH is affected and also indicate at which flow rate the fines observed in the funnel entered the tube where they have the potential to interact with the seedbed.

The pH values in the reactor increased rapidly during the start-up period as shown in Figure 6.4. The top pH continued to increase slightly before stabilizing around pH 7.98, while the bottom pH dropped steeply with the influent starting after 20 min of operation but recovered up to pH 7.75. Increasing the recycle-influent ratio narrowed the difference between top and bottom pH. With each successive drop in recycle flow rate, the bottom pH decreased noticeably, while the top pH gradually decreased to 7.91.

This pH rise should be sufficient to induce significant struvite precipitation from the feed solution in the bottom section. Visually a precipitation reaction was confirmed during the start-up period, with increasing precipitant accumulating and remaining in the funnel throughout the test. The precipitate remained in the funnel throughout the test, even at the lowest combined flow rate of 400 ml/min (Appendix II-b). This demonstrated that the fines produced quickly moved through the bottom section and did not have time to interact with any seed (i.e. potential for growth was limited). Very little fines were captured in the overflow, especially at the lower recycle rates.

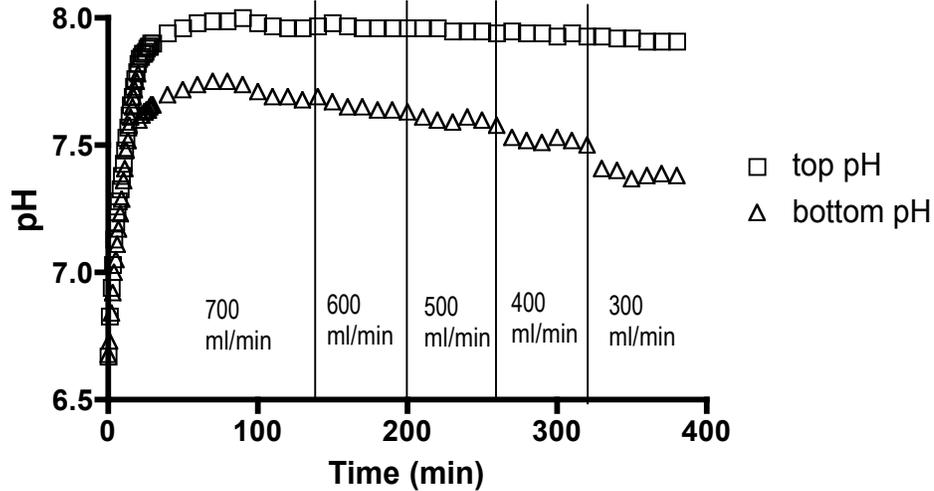


Figure 6.4 The pH profile at the top and bottom of the reactor during the recycle rate test.

From the precipitate recovery shown in Table 6.5, it can be seen that the majority of precipitate remained within the system, with only 2% lost to the effluent. Overall recovery was 88% of the maximum possible struvite formation based on TP concentration in the feed, very similar to the test run. The recovery based on moles missing from the effluent is a bit higher, and indicate that there might have been some additional precipitation.

Table 6.5 Summary of precipitate recovery during recycle rate test.

	Mass recovered (g)	% of total mass recovered
Reactor	52.1	98
Effluent reservoir	1.1	2
Total precipitate produced	53.2	100
% of max struvite possible:	Feed [TP]	88
	Effluent [TP]	94 ± 1
	Effluent [Mg]	107 ± 1

Analysis of the effluent samples (Table 6.6) showed that significant TP and Mg^{2+} removal occurred during the test, while the Ca^{2+} concentration remained fairly unchanged. The lower pH due to the decreasing recycle did not seem to affect nutrient removal, except for a slight decrease in TP removal at the lowest flow rates. Little change in the Ca^{2+} concentration indicates that the low pH in the reactor was successful in preventing Ca^{2+} precipitation, and therefore the precipitate should be mainly struvite. The Mg:TP molar ratio of moles lost is very stable at around 0.89 throughout, close to the equal molar ratio of struvite. The NH_4^+ concentration in the feed is in excess to what is needed for struvite precipitation and should not have any limiting effect on the process.

Table 6.6 Analysis of effluent samples taken during the recycle rate test.

Time (hr)	Concentration (mg/L)					Mg:TP moles missing
	Ca^{2+}	K^+	Mg^{2+}	TP	NH_4^+	
0	291.2 ± 1.4	222.0 ± 1.8	163.1 ± 3.2	161.4 ± 5.5	2536 ± 26	1.25
1	264.0 ± 4.5	218.0 ± 7.4	61.6 ± 2.2	13.5 ± 0.2	2514 ± 12	0.88
2	272.5 ± 5.9	217.4 ± 1.4	61.1 ± 2.1	13.5 ± 0.6	2458 ± 75	0.88
3	281.3 ± 1.8	220.7 ± 2.4	60.8 ± 0.6	12.5 ± 0.1	2493 ± 43	0.88
4	258.5 ± 0.5	223.4 ± 1.7	60.4 ± 0.3	13.5 ± 0.8	2507 ± 32	0.89
5	279.0 ± 1.2	223.2 ± 1.3	60.6 ± 0.3	14.4 ± 0.8	2521 ± 42	0.89
6	267.1 ± 11.7	216.9 ± 3.9	60.3 ± 1.6	15.4 ± 0.1	2514 ± 24	0.90

Note: Initial values are average of samples taken throughout the test. Difference between initial concentrations and concentration at given time used to calculate ratio of moles missing from solution. Moles missing at time 0 indicates initial molar ratio.

Analysis of the precipitate indicated that the Mg:TP and NH_4 :TP molar ratios were 1.03 and 1.01 respectively, while the Ca:TP molar ratio was 0.07, suggesting that the precipitant is mainly struvite with negligible amounts of calcium. The precipitant was also analyzed using XRD and was found to be consistent with struvite (Appendix I-d). No other compound was identified, and since the pattern was a very good match to

struvite it can be assumed that the precipitate is highly pure struvite, which is consistent with the results of the precipitate analysis and mass recovery.

This run has shown that changing the system recycle flow resulted in pH changes within the reactor, yet did not significantly affect the nutrient removal capability of the system. Although the lower flow rates would not be able to fluidize a seedbed, the fines produced in the reactor were kept suspended in the funnel while less were lost to the overflow. The recovered precipitate, which was mainly struvite with very little Ca^{2+} contamination, was very close to the expected amount of recovery based on influent and effluent moles.

6.3.3 Seedbed material

In order to investigate the effect of a seedbed on the reactor operation, tests were run using the same procedure, but with different seed material, as shown in Table 6.7 below.

The recycle rate test will be used for a comparison without any seedbed. One test was run with a 100 g struvite seedbed, while another test was run with sand as a seedbed.

Although the sand test was started with a 100 g seedbed, the particles were only filling the bottom section up to the pH port so additional fines were added. Appendix II-c to II-e shows pictures of the reactor operation during the struvite bed run.

During the struvite seedbed run the seed particles seemed to break apart and became fines, resulting in very low seed recovery (Table 6.7). The disintegration of seed happened almost immediately – visually the amount of particles in the bottom section did not change significantly after the first 30 min of operation. Based on previous tests, this amount and size of seed should have filled most of the tube. Instead, particles were only

visible below the pH port while fines collected in the funnel. The high precipitate recovery may indicate the presence of a precipitate other than struvite. As described in Chapter 5, the struvite seedbed used in this run was slightly different than in the test run, where the particles did not disintegrate as much. This might be due to the specific contaminants present in the particles or be a reflection of variations in the production method. Attempts to determine the relative integrity of the different particles were not conclusive. For the sand run the increased mass of sand particles recovered seems to indicate that some struvite attached to the sand, especially the larger particles. Overall the sand precipitate recovery is lower than previous runs.

Table 6.7 Seedbed composition and precipitate recovery.

		Struvite	Sand
Seedbed mass (g)	2-0.8 mm	50	30
	0.8-0.6 mm	50	40
	0.6-0.4 mm	0	30
	<0.4 mm	0	100
Total mass precipitated (g)		60	49
% seed recovered:	2-0.8 mm	9	142
	0.8-0.6 mm	24	116
	0.6-0.4 mm	-	104
	<0.4 mm	-	123
% of total mass recovered as fines:	in reactor	83	-
	in effluent reservoir	5	2
% of max struvite possible:	Feed [TP]	99	81
	Effluent [TP]	103 ± 1	89 ± 1
	Effluent [Mg]	119 ± 12	92 ± 1

Note: Precipitant collected from reactor and cone drained and dried separately; then sieved to determine particles sizes recovered.

The pH in the struvite run was slightly higher than the sand run, and showed less difference between the top and bottom of the reactor (Figure 6.5). For the last several hours the struvite bed run pH remained between 7.77 and 7.96, while the sand run pH remained between 7.61 and 7.87.

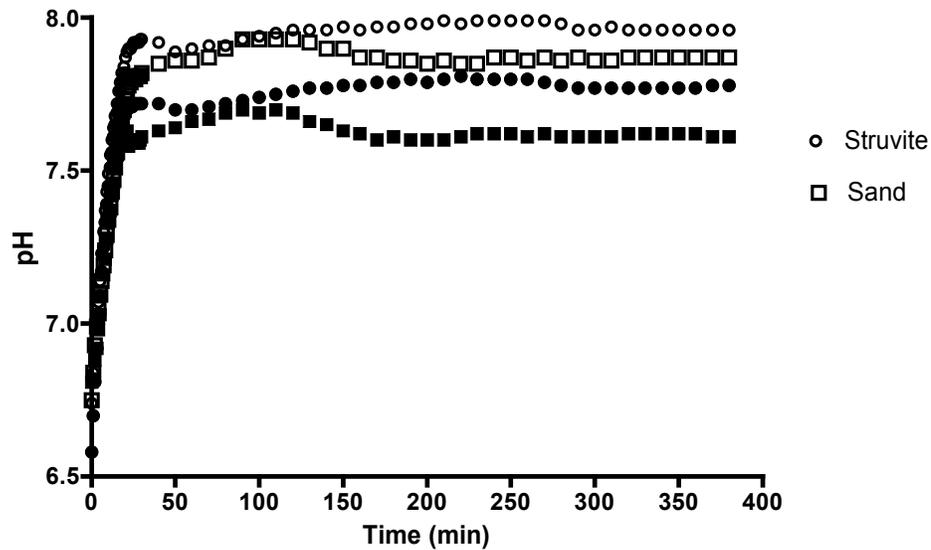


Figure 6.5 The pH profile of runs with different seedbed materials.

Note: Hollow symbols indicate top pH, solid symbols indicate bottom pH.

The sample analysis in Table 6.8 shows that for the struvite run an increasingly large amount of Ca^{2+} was removed from the feed, while some K^+ was introduced to the solution and subsequently removed. This is probably because the seed contained K^+ and upon contact with the feed was dissolved into solution and then precipitated again. The TP and Mg^{2+} concentrations decreased significantly in the first hour and continued to decrease slightly throughout the run. The high Ca^{2+} removal could account for the higher than expected mass that precipitated. In previous tests, high pH (8.0 and higher) resulted in calcite precipitation; however the low pH conditions during this test should not have been favorable for this to occur, so it is possible that another form of Ca^{2+} precipitated. The sand run sample analysis showed that a relatively constant small amount of Ca^{2+} was removed, while Mg^{2+} and TP were removed in an almost equal molar ratio from the first hour, similarly to the recycle rate run. This would suggest that the struvite seedbed

slightly inhibited Mg^{2+} and TP removal, although the effect wore off gradually, as the Ca^{2+} and K^+ concentrations stabilized.

Table 6.8 Results of the sample analysis for reactor tests with different seeded materials.

Struvite						
Time (hr)	Concentration (mg/L)					Mg:TP moles missing
	Ca^{2+}	K^+	Mg^{2+}	TP	NH_4^+	
0	289.9 ± 13.4	218.4 ± 9.7	172.0 ± 10.3	160.0 ± 4.3	2586 ± 66	1.37
1	134.0 ± 1.8	315.2 ± 2.0	83.1 ± 1.4	9.3 ± 1.1	2521 ± 29	0.75
2	99.7 ± 1.3	288.8 ± 4.3	73.3 ± 0.8	5.8 ± 0.6	2542 ± 42	0.82
3	83.5 ± 1.3	262.6 ± 4.0	68.0 ± 1.3	5.9 ± 1.0	2514 ± 48	0.86
4	76.9 ± 1.2	246.8 ± 6.2	63.1 ± 1.0	6.2 ± 0.3	2542 ± 55	0.90
5	72.6 ± 1.4	232.6 ± 5.5	59.0 ± 1.5	6.5 ± 0.3	2514 ± 52	0.94
6	79.6 ± 0.4	228.5 ± 1.9	56.9 ± 0.8	6.3 ± 0.3	2500 ± 21	0.96
Sand						
Time (hr)	Concentration (mg/L)					Mg:TP moles missing
	Ca^{2+}	K^+	Mg^{2+}	TP	NH_4^+	
0	303.9 ± 1.5	210.4 ± 3.7	178.3 ± 1.5	157.9 ± 1.7	2607 ± 25	1.44
1	288.8 ± 2.1	208.8 ± 0.7	69.6 ± 0.3	12.5 ± 0.8	2576 ± 12	0.95
2	277.1 ± 1.8	208.9 ± 0.5	67.4 ± 0.2	11.5 ± 0.7	2549 ± 24	0.97
3	286.4 ± 0.8	209.7 ± 2.6	68.7 ± 0.3	13.4 ± 0.4	2535 ± 12	0.97
4	287.3 ± 1.5	208.5 ± 1.3	69.7 ± 0.1	14.4 ± 0.9	2549 ± 12	0.97
5	287.9 ± 2.4	209.0 ± 2.0	69.6 ± 0.7	14.9 ± 0.7	2486 ± 32	0.97
6	284.9 ± 0.4	209.1 ± 1.4	67.4 ± 0.6	13.2 ± 0.1	2486 ± 32	0.98

Note: Initial values are average of samples taken throughout the test. Difference between initial concentrations and concentration at given time used to calculate ratio of moles missing from solution. Moles missing at time 0 indicates initial molar ratio.

The precipitate analyses of both runs showed that the molar ratios of $\text{Mg}:\text{NH}_4:\text{P}$ were consistent with that of struvite (Figure 6.6). There was significant Ca^{2+} precipitation in both runs, as well as some Na^+ . There was a little K^+ in the struvite run, which was probably contributed by the seedbed, which is why the sand precipitate did not have a K^+ component. The XRD analysis (Appendix I-e) was only done on the struvite run precipitate, and confirmed struvite precipitation. The resulting pattern was very similar to

that observed for the synthetic struvite, with skewed intensities. This indicated the presence of some other unidentified precipitate, most likely a Ca^{2+} compound, but not calcite as that would have been recognized.

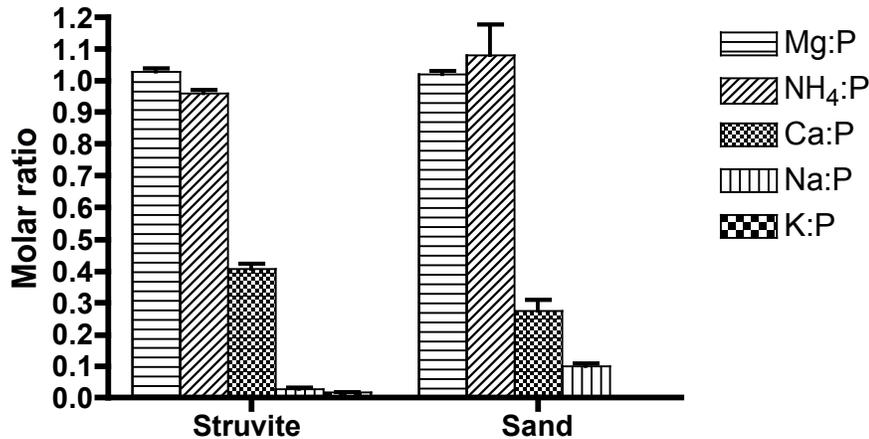


Figure 6.6 Molar ratios of components to P found in precipitate of runs with different seedbed materials.

Note: The concentration of K^+ in the sand precipitate was negligible.

In comparison with the recycle rate test where no seedbed was used, the precipitate recovery was slightly higher for the struvite run, and lower for the sand run. However, the precipitate analysis revealed that the purest struvite was recovered during the recycle rate run, where no seedbed was used. The struvite and sand seedbeds seemed to induce Ca^{2+} precipitation in an unidentified form, which would increase the mass precipitated. The TP removal was slightly higher in the struvite run, 96% as compared to 92% and 93% in the recycle rate and sand run respectively. The struvite seedbed did not contribute to crystal growth since the particles seemed to disintegrate. This was most likely a fault of the particle production, and struvite from another source might maintain the seedbed and allow for particle growth. Struvite did seem to attach to the sand, since the seedbed mass increased. However, having sand as seed would decrease the percentage of struvite in the

recovered mass, thereby decreasing the overall value. Therefore, since the seedbeds decreased the precipitate purity and did not significantly increase TP removal, future long-term tests were attempted without any seedbed.

6.3.4 Duration

The long-term runs were planned to test the performance consistency of the reactor. Compared to the 6hr runs in previous tests, the duration of testing was extended to 120 hrs (5 days). Although the runs were planned for five days, several issues came up that cut short both runs. The flow rates in long-term test 1 (L1) were halved after 6 h of operation to save feed because the new CO₂ gas canister had not yet arrived, and there was not enough feed to last through the night. The flow rates were returned to normal 22 h after they were reduced. The precipitate collecting on the tube walls was manually loosened after 30 h, resulting in an accumulation of flakes at the reactor port that caused the recycle line to become plugged. Therefore the reactor had to be stopped and partially drained to clear the line before operation could resume. At some time during the night the influent line became plugged at the reactor port and the pressure in the line increased until a tube came loose from its fitting. Feed was pumped onto the floor, and an unknown volume was lost. Since the influent port was plugged the reactor volume remained intact and the recycle flow and aeration continued for several hours. Because the exact volume of feed used in the reactor is unknown, a mass balance could not be performed for the recovered precipitate (Table 6.9).

Table 6.9 Precipitate collected during L1.

Time (hrs)	24	30	45	Total
Mass (g)	34.9	20.5	92.2	147.6

The pH profile in the reactor is shown in Figure 6.7, as measured during the first two days of operation. The top pH is relatively stable around 7.91 and the bottom pH around 7.65. As soon as the flow rates are decreased, the pH increases. After 15 h the pH is still around 7.91 – 7.69, but when the flow rates are returned to normal, the pH decreases dramatically. The following morning the pH had increased to 8.8 because the influent had been cut off, and the reactor was just recycling and aerating.

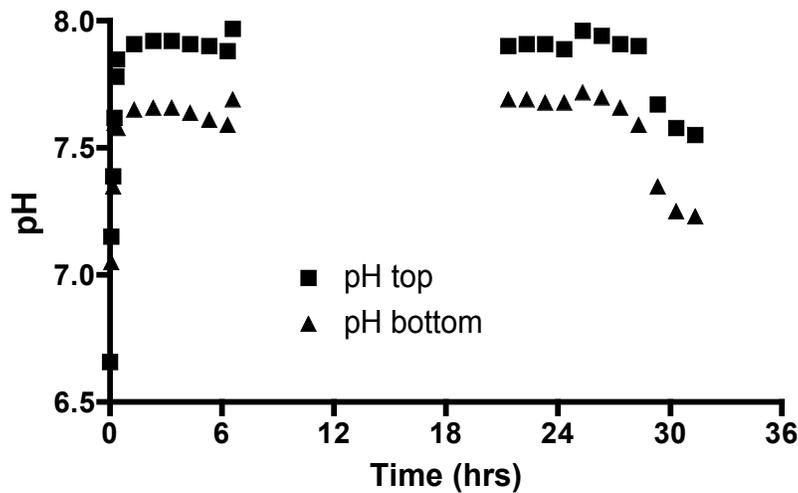


Figure 6.7 The pH in the reactor during L1.

The sample analysis for this run in Table 6.10 showed that TP and Mg^{2+} decreased significantly, and in a molar ratio consistent with struvite. Calcium decreased slightly during the first six h, and then a greater portion was removed after another 24 h.

Table 6.10 Results of sample analysis for L1.

Time (hr)	Concentration (mg/L)					Mg:TP moles missing
	Ca ²⁺	K ⁺	Mg ²⁺	TP	NH ₄ ⁺	
0	303.7 ± 4.4	204.8 ± 3.8	171.2 ± 3.6	151.5 ± 6.0	2532 ± 21	1.44
6	284.7 ± 5.1	203.0 ± 4.7	69.5 ± 2.0	17.9 ± 0.6	2486 ± 12	0.97
30	248.3 ± 2.0	207.0 ± 2.0	74.7 ± 0.6	22.3 ± 0.9	2500 ± 0	0.96

Note: Concentrations at time 0 are the average of all influent samples. Difference between influent and effluent concentration at given time used to calculate ratio of moles missing from solution. Moles missing at time 0 indicates initial molar ratio.

The analysis of precipitate collected after 24 h of operation confirmed struvite precipitation and showed little Ca²⁺ or Na⁺ contamination (Figure 6.8). The precipitate collected at 30 and 45 h showed significant Ca²⁺ precipitation. It was possible that the precipitate collecting in the tubes contained a high proportion of Ca²⁺, and cleaning the tubes allowed it to be collected at the second draining. The final precipitate collection occurred after the pH in the reactor had increased significantly, which greatly increased the possibility of Ca²⁺ precipitation as calcite.

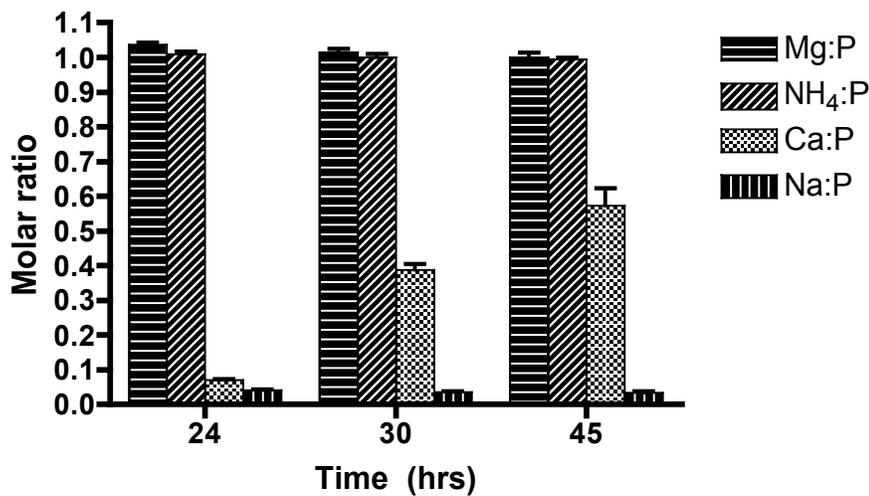


Figure 6.8 Molar ratio of components to P found in precipitate from L1 collected at various times.

The XRD analysis confirmed struvite precipitation at 24 h along with an unknown precipitate (Appendix I-f), while the precipitation collected after 45 h (Appendix I-g) contained both struvite and calcite, which would account for the high proportion of Ca^{2+} in the precipitate.

After the reactor was drained, the ports at the bottom were examined, and it was found that the influent port was completely plugged with precipitate. The recycle port was significantly plugged, with only a small hole left in the middle. The overflow port also had significant scaling. The aeration stones were found to be severely scaled, which could account for the decreasing pH when the flow rates were increased since aeration must have been greatly reduced.

The reactor was thoroughly cleaned with an acidic solution to remove any scaling build-up. All unnecessary connections were removed from the tubes, and the equipment set-up was adjusted to minimize tube length. The long-term run 2 (L2) was run similarly to L1 but without any fine return since the fine recycle seemed to create additional plugging issues, instead the fines were collected separately. The run continued for 24 h without interruption, when the aeration stones were replaced. After another 22 h the reactor was stopped because the pH was significantly elevated and a large volume of feed was left. It was found that the influent port was practically plugged. The influent port was replaced, and the recycle line moved to a higher port, and then the reactor was restarted after 3 h without aeration to decrease the pH. When the pH was sufficiently reduced after 45 min the aeration was started with new aeration stones. The aeration stones were again replaced after 6 h. The next morning the recycle line was found to have disconnected due to a blockage of the reactor port. Since the fines were stuck on the pH probe and plugged

the bottom section, very little precipitate was lost, and the reactor volume was still mainly intact. Since only effluent was lost, the volume used could still be calculated to complete the mass balance. As in L1, the reactor ports showed significant scaling in both the influent and recycle ports.

The precipitation recovery was relatively low compared to the shorter runs (Table 6.11), although the relative proportions of recovered precipitate is very similar to the previous runs. Scaling on aeration stones and ports were not recovered and may represent a significant portion of the precipitate.

Table 6.11 Precipitate collected during L2.

Run time (hrs)	Fines	Mass (g)	
		Reactor	Total
6	5.3		
24	2.4	92.8	95.2
46	3.0	83.1	86.1
51	2.6		
67	4.2	112.8	119.6
			300.9
Volume feed prepared (L)			390
Volume feed left (L)			40.4
Volume used (L)			349.6
% of max struvite possible:		Feed [TP]	68
		Effluent [TP]	79 ± 4
		Effluent [Mg]	86 ± 9

Note: Precipitant collected from reactor and cone drained and dried separately.

The pH in the reactor remained fairly steady for the first 6 h, after which a slight decrease is visible (Figure 6.9). At steady state the pH in the top and bottom ranged from 7.93 – 7.74. It seems as though the pH continued to decrease until the aeration stones were replaced, when the pH jumped back to the 7.93 – 7.74 range, and then slightly decreased

again. Due to the plugging of the influent port, the pH in the reactor increased overnight to around 8.8. After the reactor was restarted the pH returned to the 7.92 – 7.67 range.

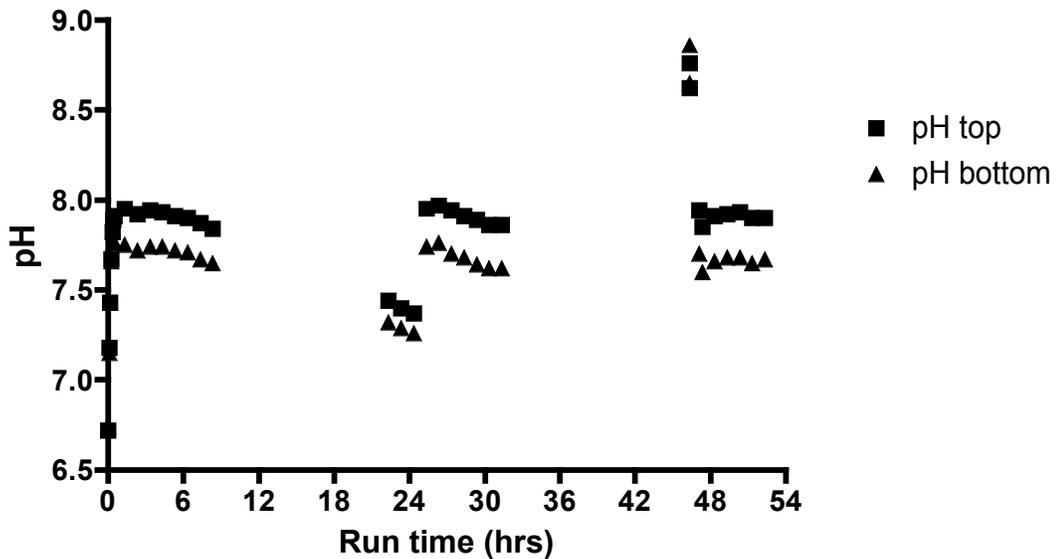


Figure 6.9 The pH in the reactor during L2.

The sample analysis in Table 6.12 shows that the Mg^{2+} and TP removal remained fairly constant throughout the run, with relatively equal molar ratios. The Ca^{2+} removal was minimal for the first 30 h, but had increased slightly at the last sampling. Samples taken from the reactor when it was stopped show a significant decrease in the Ca^{2+} concentration, as well as a slight decrease in Mg^{2+} and TP concentration compared to the effluent samples. Each of these samples was taken after an extended period of high pH in the reactor, which probably resulted in calcite precipitation.

The analysis of the recovered precipitate confirmed the trends seen in the effluent and reactor samples (Figure 6.10). Equal molar ratios of $Mg:P:NH_4$ were found, along with increasing amounts of Ca^{2+} over time. The XRD analysis confirmed struvite in the

precipitate collected after 24 h (Appendix II-VIII), while the final precipitate contained both struvite and calcite (Appendix II-IX).

Table 6.12 Results of sample analysis for L2.

Concentration (mg/L)						
Time (hr)	Effluent					Mg:P moles missing
	Ca ²⁺	K ⁺	Mg ²⁺	TP	NH ₄ ⁺	
0	314.2 ± 7.7	195.9 ± 4.8	158.2 ± 14	144.3 ± 14	2559 ± 18	1.40
6	292.0 ± 3.1	202.5 ± 2.2	71.2 ± 1.3	18.5 ± 0.6	2486 ± 12	0.83
30	290.0 ± 0.4	197.2 ± 1.0	66.9 ± 0.9	18.1 ± 2.1	2507 ± 12	1.00
51	259.1 ± 1.8	198.1 ± 1.2	68.0 ± 0.4	15.0 ± 0.8	2507 ± 32	0.92
Time (hr)	Reactor					Mg:P moles missing
	Ca ²⁺	K ⁺	Mg ²⁺	TP	NH ₄ ⁺	
46	7.4 ± 10.5	194.3 ± 5.2	54.7 ± 2.4	2.0 ± 0.6	2417 ± 21	1.00
67	48.9 ± 1.1	198.0 ± 2.6	59.9 ± 0.4	4.5 ± 0.5	2521 ± 21	0.92

Note: Concentrations at time 0 are the average of all influent samples. Difference between influent and effluent concentration at given time used to calculate ratio of moles missing from solution. Moles missing at time 0 indicates initial molar ratio.

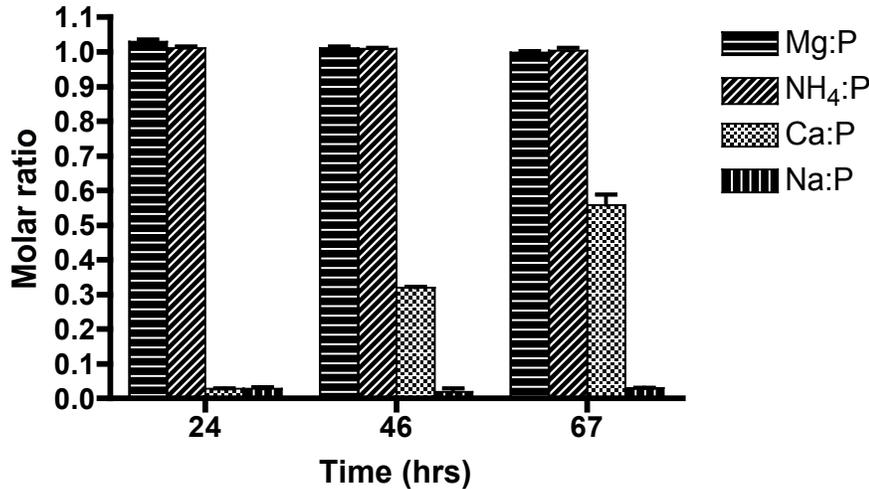


Figure 6.10 Molar ratio of components to P found in precipitate from L2 collected at various times.

These runs showed that operation of the reactor is possible for an extended period of time, up to 46 h without any major adjustment. Relatively pure struvite was recovered after 24 h, while calcite was present in the precipitate collected later. Removal of TP and Mg^{2+} was relatively stable throughout and comparable to the 6hr runs. The low Ca^{2+} removal was very similar to the recycle run without any seedbed, yet there were periods of high pH that caused Ca^{2+} precipitation as calcite. This was not reflected in the samples taken from the effluent, probably because the reactor experienced phases, evidenced by the changing pH, during which its removal behavior might have changed based on conditions. More frequent sampling would have given a better indication of how such changes affected effluent concentrations, and thereby overall removal. This might also be the reason why precipitate recovery seems low, since there could have been periods where removal was not as high as assumed.

6.4 Conclusions

A number of runs were done using the reactor system to optimize its operational parameters in order to achieve effective struvite recovery and purity, including aeration rate, overall throughput, recycle ratios, seedbed material and particle size. Long-term runs were also conducted to assess the stability and consistency of the reactor system. A summary of results for the tests run with synthetic feed in the reactor system is given in Tables 6.13 and 6.14.

The initial test runs showed that the recycle/influent ratio should be increased to minimize the difference between top and bottom pH, and that the proportion of larger

particles in the seedbed should be increased to fill the bottom section. Phosphorous removal rates of up to 87% were achieved, with low Ca^{2+} precipitation. The subsequent runs demonstrated that for a 100 ml/min influent rate, an aeration and recycle rate combination of 4.5 – 7 LPM and 700 ml/min was sufficient for increasing and maintaining the reactor pH to between 7.6 and 8. Keeping the pH low suppressed the precipitation of calcite, which was only detected in the precipitate from L1 and L2 after the pH was elevated due to plugging issues. Significant P removal was achieved in all runs, 91 – 96% in the short-term runs and 85 – 88% in the long-term runs. The seedbeds did not seem to have much effect on the extent of TP removal. X-ray diffraction analysis of precipitate identified struvite in all samples tested. The struvite run indicated the presence of an unidentified precipitate, possibly some form of calcium precipitation that seemed to have been induced by the struvite seedbed. The purest struvite was found in the recycle rate run, L1, and L2, none of which had a seedbed. These findings were confirmed by comparing molar ratios of compounds found in precipitate. The struvite seedbed did not contribute to crystal growth since the particles seemed to disintegrate. This was most likely due to the process of particle production, and struvite from another source might maintain the seedbed and allow for particle growth. Struvite did seem to attach to the sand, since the seedbed mass increased. However, having sand as seed would decrease the percentage of struvite in the recovered mass, thereby decreasing the overall value. The long-term runs showed that operation of the reactor was possible for an extended period of time, up to 46 h without any major adjustment. The major obstacle for the long-term runs was scaling on aeration stones and in reactor ports.

Table 6.13 Summary of results for short-term reactor runs.

	Test run	Recycle rate	Struvite	Sand	
Seedbed behaviour	Filled bottom section	n.a.	Disintegration	Low fluidization	
Fines behaviour	Fines in funnel	Fines in funnel	Fines in funnel	Fines in bottom section and funnel	
Top pH (min – max)	7.71 – 7.87	7.91 – 8.0	7.90 – 7.99	7.86 – 7.93	
Bottom pH (min – max)	7.30 – 7.38	7.37 – 7.75	7.70 – 7.81	7.60 – 7.70	
% removal (min – max)					
	TP	67 – 86	91 – 92	94 – 96	91 – 93
	Mg	47 – 51	62 – 63	52 – 67	61 – 62
	Ca	5 – 16	3 – 11	54 – 75	5 – 9
% seed recovered	90	n.a.	19	122*	
% maximum struvite possible					
	Feed [TP]	87	88	99	81
	Effluent [TP]	146	94	103	89
	Effluent [Mg]	176	107	119	92
Precipitate molar ratio					
	Mg:TP	1.02	1.03	1.03	1.02
	NH₄:TP	1.01	1.01	0.96	1.08
	Ca:TP	0.16	0.07	0.41	0.27
XRD	-	Struvite	Struvite Unidentified	-	

Note: pH range reported after 1 h of operation.

n.a. = not applicable

* % seed recovered for sand run excludes fines added to seedbed

Table 6.14 Summary of results for long-term reactor runs.

		Long-term test 1		Long-term test 2	
Longest continuous operational period (hrs)		30		46	
Top pH (min – max)		7.55 – 8.81		7.37 – 8.76	
Bottom pH (min – max)		7.23 – 8.84		7.26 – 8.86	
% removal (min – max)		Effluent		Effluent	
	TP	85 – 88		88	
	Mg	55 – 60		54 – 60	
	Ca	6 – 19		6 – 18	
% maximum struvite possible					
	Feed [TP]	-		68	
	Effluent [TP]	-		79	
	Effluent [Mg]	-		86	
		24 hrs	45 hrs	24 hrs	67 hrs
Precipitate molar ratio					
	Mg:TP	1.04	1.0	1.03	1.0
	NH₄:TP	1.01	0.99	1.01	1.0
	Ca:TP	0.07	0.57	0.03	0.56
XRD		Struvite	Struvite Calcite	Struvite	Struvite Calcite

6.5 Engineering significance

Manure from lagoons is generally land-applied in Manitoba, and due to the high concentration of swine farms in certain areas, localized over-application of P is a significant problem. Consequently swine wastewater is a prime candidate for P removal and recovery in Manitoba. The main objective of this study was to develop a robust, low-cost system for on-farm removal and recovery of P as struvite from hog manure slurries. This could not only reduce the P content of swine lagoons, but could also provide farmers with a ready source of P fertilizer.

A number of other continuous reactor systems that have been tested were designed to accommodate field application. It was found that although P removal and recovery in such a system is technically feasible, the cost of treatment, in particular the chemical cost due to Mg^{2+} and NaOH amendment, is very high (Çelen, 2009). The reactor design described in this study is a combination of a fluidized-bed and air agitated reactor that uses aeration to increase supernatant pH, thereby reducing the chemical cost. In addition, since the natural $Mg:PO_4\text{-P}$ molar ratios in supernatant from local swine lagoons were favourable for struvite precipitation, the need for costly Mg^{2+} addition could be eliminated. The reactor would continuously feed back into the lagoon while recovering P from swine lagoon supernatant, which would allow for a smaller volume and lower flow rate than needed for land-application systems. Therefore, what makes this reactor system so promising is that the only operational costs would be the energy required to run the pumps and aerator. Some maintenance costs might also be required, such as periodical cleaning of the reactor with an acid rinse. By eliminating the need for chemical amendment the economical viability of this system could be increased. It has been

suggested by Westerman *et al.* (2010) that for a continuous-flow fluidized bed crystallizer the chemical costs would be about 26% of the operational costs, and 17.4% of the overall net cost.

This study has shown that an aerated struvite crystallization reactor system can successfully remove and recover P as struvite from synthetic wastewater without chemical input. The system operation over time was less successful due to scaling in the reactor ports and on the aeration stones. Since the reactor could not be operated for an extended period of time, the ability of the system to produce struvite particles could not be established. Production of particles would be preferable to a fine sludge, since sludge would need to be processed to prepare it for use as fertilizer, while particles can simply be dried. If these issues can be resolved, the high P removal achieved in this reactor could contribute to reducing the P levels in swine lagoons. In addition, the precipitate produced could be a valuable product, since indications were that struvite was the main precipitate when the pH was kept below 8.

If further testing revealed that the P removal was not as high with real supernatant, the reactor performance would not be compromised, since it would operate continuously and not be land-applied but discharged back into the lagoon. The main focus for the reactor would be to recover high purity struvite that was agronomically valuable to the farmer, while over time slowly lowering the P content of the lagoon.

Chapter 7 – Conclusion

The overall purpose of this research was to achieve effective phosphorus removal and recovery through struvite precipitation from agricultural wastewater with minimal chemical input. The main objective was to develop a robust, low-cost reactor system requiring minimal maintenance that would produce an agronomically valuable product. A number of experiments were conducted to establish the technical and economic viability of a side-stream continuous reactor system for P removal and recovery from swine lagoon supernatant.

The first step was to determine the optimal pH and Mg:PO₄-P ratio for struvite precipitation from swine manure. In terms of the amount of P removed/recovered, pH 9.0 and a Mg:TP ratio of 1.6 resulted in an 80% TP removal from anaerobically digested swine manure, while pH 9.0 and a Mg:PO₄-P ratio of 1.4 resulted in a 97% PO₄-P removal from raw swine manure. The quality of precipitate recovered was significantly different at various pH values. The highest purity struvite was recovered at the lowest pH values (7.5 and 8.0 for anaerobic and raw swine manure respectively), with calcite precipitating at higher pH values. Consequently the optimum pH for struvite precipitation will depend on an acceptable trade-off between maximum phosphorus removal and greatest struvite purity. At pH 9.0, the TP removal in the anaerobic manure ranged from 61 – 80% for the various Mg²⁺ additions, while the tests with raw swine manure revealed that the Mg²⁺ addition increased PO₄-P removal from 93 – 97%. However, the increase of raw swine supernatant pH to 8.0 without any Mg²⁺ adjustment resulted in a 90% PO₄-P removal compared to a 27% removal in the control. This shows the potential of raw

swine manure for phosphorus removal and recovery through struvite precipitation without any Mg^{2+} amendment. Overall it can be argued that, based on the amount of phosphorus removed and the quality of the recovered precipitate, struvite precipitation could be a viable method for phosphorus removal from swine manure.

However, since the cost of raising the pH to 8.0 will still be significant, a cost-effective way for raising the supernatant pH of raw swine manure will be needed for such a method to be feasible for farm-scale application. A potential chemical-free method for pH increase is air sparging, where the main cost would be electrical. To determine whether aeration would result in sufficient pH increase and PO_4 -P removal within a short time span, a series of batch tests were conducted. The results indicated that aeration rates of 3.1 – 19.5 LPM could sufficiently increase pH so that PO_4 -P removal of 34 – 69% was possible within five min. The data gathered from these tests were used to develop a side-stream continuous reactor design with a novel combination of fluidized seedbed and aeration for pH increase.

Several runs were conducted using synthetic feed to optimize the operational parameters of the reactor system. It was found that for a 100 ml/min influent rate, an aeration and recycle rate combination of 4.5 – 7 LPM and 700 ml/min was sufficient for increasing and maintaining the reactor pH to between 7.6 and 8. The effect of the struvite seedbed on reactor operation was hard to determine, since the particles seemed to disintegrate. There was little difference in P removal between the runs with (91 – 96%) or without a seedbed (91 – 92%), while the effect on Ca^{2+} removal was significant, 54 – 75% with a struvite seedbed and 3 – 11% without a seedbed. X-ray diffraction of the precipitate from the struvite run indicated the presence of an unidentified precipitate, which, based on the

precipitate molar ratios, was some form of calcium precipitation. It seemed to have been induced by the struvite seedbed, since the precipitate from the run without a seedbed was found to be highly pure struvite. When sand was tested as a seedbed material, struvite did seem to attach to the sand particles, but although the P removal was similar to the other runs, the P recovery as struvite was lower, 81% as compared to 88% for the run without a seedbed. In addition, having sand as seed would decrease the purity of the recovered precipitate, thereby decreasing the overall agronomic value. Therefore, since the seedbeds did not improve P removal, and only served to decrease the purity of the recovered precipitate, the long-term runs were conducted without a seedbed.

The long-term runs showed that operation of the reactor was possible for an extended period of time, up to 46 h without any major adjustment. The average P removal was slightly lower than the short-term runs ranging from 85 – 88%, while the P recovery as struvite was 68%. During the runs the reactor experienced significant scaling that clogged the aeration stones thereby decreasing the aeration rate, and also plugged the bottom ports resulting in increased reactor pH and eventual line failure. Precipitate collected after 24 h was found to be mainly struvite, while the final precipitate also contained calcite, probably precipitated due to the increased pH resulting from the scaling.

This study has demonstrated the technical feasibility of an aerated crystallization reactor system for struvite removal and recovery from synthetic swine wastewater. By avoiding chemical amendments, this reactor system has eliminated a significant portion of the operational costs found in comparable systems. The major obstacle for achieving system stability and consistency was scaling on aeration stones and in reactor ports.

Chapter 8 – Recommendations

The following recommendations are aimed at improving the reactor performance and conducting further system testing at pilot or full-scale.

The narrow ports were a vulnerable point in the reactor operation, prone to scaling and the cause of failure for both long-term runs. For future tests these small ports should be avoided and tubes connected to the reactor through rubber stoppers and T-connections, similarly to the bottom pH probe. Scaling on aeration stones also present a challenge for maintaining a constant pH in the reactor. Different aeration heads should be examined to determine the type least prone to plugging. Long-term runs with this new configuration should be conducted to establish system stability and consistency. A method for isolating part of the bottom section would help to facilitate harvesting. A second valve above the pH port would allow the reactor volume to remain intact while product is removed from the bottom. It would also allow for cleaning of the ports during a run.

After the scaling issues have been addressed, the reactor should be tested with real swine lagoon supernatant to evaluate its performance with a complex wastewater. A pilot or full-scale version of the reactor could then be taken to a lagoon to test its performance on a continuous basis. The agronomic value of the recovered struvite should be evaluated by comparing it to commercial grade fertilizer (mono ammonium phosphate) and pure, laboratory grade struvite. An economic and life cycle analysis of an on-farm recovery system should be conducted to fully establish the economic feasibility of the reactor.

Chapter 9 – References

- Aage, H.K., Anderson, B.L., Blom, A., Jensen, I. (1997). The solubility of struvite. *Journal of Radioanalytical and Nuclear Chemistry*, 223: 213-215.
- Adnan, A., Dastur, M., Mavinic, D.S., and Koch, F.A. (2004). Preliminary investigation into factors affecting controlled struvite crystallization at the bench scale. *Journal of Environmental Engineering and Science*, 3: 195-202.
- Adnan, A., Mavinic, D.S., and Koch, F.A. (2003). Pilot-scale study of phosphorus recovery through struvite crystallization - examining the process feasibility. *Journal of Environmental Engineering and Science*, 2: 315-324.
- Ali, I., and Schneider, P.A. (2008). An approach of estimating struvite growth kinetic incorporating thermodynamic and solution chemistry, kinetic and process description. *Chemical Engineering Science*, 63: 3514-3525.
- Booker, N.A., Priestly, A.J., Fraser, I.H., (1999). Struvite formation in wastewater treatment plants: opportunities for nutrient recovery. *Environmental Technology*, 20: 777-782.
- Booram, C.V., Smith, R.J., Hazen, T.E. (1975). Crystalline phosphate precipitation from anaerobic animal waste treatment lagoon liquors. *Transactions of the American Society of Agricultural Engineering*, 18: 340-343.
- Bouropoulos, N.C., and Koutsoukos, P.G. (2000). Spontaneous precipitation of struvite from aqueous solutions. *Journal of Crystal Growth*, 213: 381-388.
- Bowers, K.E., and Westerman, P.W. (2005). Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. *Transactions of the American Society of Agricultural Engineering*, 48: 1227-1234.
- Brewin, D., Honey, J., and Ryan, J. (2007). Chapter 1 Statistics for Manitoba Pork Industry in A Report on Current Knowledge of Key Environmental Issues Related to Hog Production in Manitoba commissioned by Clean Environment Commission. Retrieved December 1, 2009, from the National Center for Livestock and the Environment web site: <http://www.umanitoba.ca/afs/nclc/ResearchProjects.html>
- Buchanan, J.R., Mote C.R., Robinson, R.B. (1994a). Struvite control by chemical treatment. *Transactions of the American Society of Agricultural Engineers*, 37: 1301-1308.
- Buchanan, J.R., Mote, C.R., Robinson, R.B. (1994b). Thermodynamics of struvite formation. *Transactions of the American Society of Agricultural Engineers*, 37: 617-621.

- Buckley, K. and Makortoff, M. (2004). Phosphorus in Livestock Manures. Retrieved December 1, 2009, from the farmwest.com web site: <http://www.farmwest.com/index.cfm?method=library.showPage&librarypageid=137>
- Burns, J.R., and Finlayson, B. (1982). Solubility of magnesium ammonium phosphate hexahydrate at various temperatures. *Journal of Urology*, 128: 426-428.
- Burns, R.T., and Moody, L.B. (2002). Phosphorus Recovery from Animal Manures using Optimized Struvite Precipitation. Coagulants and Flocculants: Global Market and Technical Opportunities for Water Treatment Chemicals, Chicago, Illinois.
- Burton, D.L. and Flaten, D.N. (1999). The Role of Hog Manure Application in Maintaining Air, Water, and Soil Quality. Retrieved December 1, 2009, from Banff Pork Seminar web site: <http://www.banffpork.ca/proc/1999.shtml>
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., and Smith, V.H. (1998). Nonpoint pollution of surface water with phosphorus and nitrogen. *Ecological Applications*, 8(3): 559-568.
- Çelen, I. (2009). Effect of HRT in a continuous flow reactor on orthophosphate removal from swine wastewater and economic evaluation for the land application. *Water, Science and Technology*, 60(9): 2271-2279.
- Çelen, I., Buchanan, J.R., Burns, R.T., Robinson, R.B., and Raman, D.R. (2007). Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research*, 41(8): 1689-1696.
- Cordell, D., Drangert, J.O., and White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change*, 19, 292-305.
- de-Bashan, L.E., and Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*, 38: 4222-4246.
- Doyle, J.D., and Parsons, S.A. (2002). Struvite formation, control and recovery. *Water Research*, 36: 3925-3940.
- Dick, S. (2003). Fluctuations in Manure Nutrient Concentration During Swine Storage Pump-outs. Retrieved December 1, 2009, from Manitoba Livestock Manure Management Initiative web site: <http://www.manure.mb.ca/projects/viewproject.php?id=23>
- Driver, J., Lijmbach, D., and Steen, I. (1999). Why recover phosphorus for recycling, and how? *Environmental Technology*, 20(7): 651-662.
- Forrest, A.L., Fattah, K.P., Mavinic, D.S., and Koch, F.A. (2008). Optimizing struvite production for phosphate recovery in WWTP. *Journal of Environmental Engineering-Asce*, 134(5): 395-402.
- 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. *Environmental Technology*, 21: 1067-1084.

- Greaves, J., Hobbs, P., Chadwick, D., and Haygarth, P. (1999). Prospects for the recovery of phosphorus from animal manures: A review. *Environmental Technology*, 20(7): 697-708.
- Jaffer, Y., Clark, T.A., Pearce, P., and Parsons, S.A. (2002). Potential phosphorus recovery by struvite formation. *Water Research*, 36: 1834-1842.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., and Parsons, S.A. (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth*, 283: 514-522.
- Le Corre, K. S., Valsami-Jones, E., Hobbs, P., Jefferson, B., and Parsons, S.A. (2007a). Struvite crystallisation and recovery using a stainless steel structure as a seed material. *Water Research*, 41(11): 2449-2456.
- Le Corre, K. S., Valsami-Jones, E., Hobbs, P., and Parsons, S.A. (2007b). Kinetics of struvite precipitation: effect of the magnesium dose on induction times and precipitation rates. *Environmental Technology*, 28: 1317-1324.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., and Parsons, S.A. (2009). Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology*, 39: 433-477.
- Lee, S.I., Weon, S.Y., Lee, C.W., Koopman, B. (2003). Removal of nitrogen and phosphate from wastewater by addition of bittern. *Chemosphere*, 51: 265-271.
- Loewenthal, R.E., Kornmuller, U.R.C., van Heerden, E.P. (1994). Modeling struvite precipitation in anaerobic treatment systems. *Water Science and Technology*, 30: 107-116.
- Malley, D.F., Yesmin, L., and Eilers, R.G. (2002). Rapid analysis of hog manure and manure-amended soils using near-infrared spectroscopy. *Soil Science Society of America Journal*, 66: 1677-1686.
- Mamais, D., Pitt, P.A., Yao Wen Cheung, Loicano, J., Jenkins, D. (1994). Determination of ferric chloride dose to control struvite precipitation in anaerobic digesters. *Water Environment Research*, 66: 912-918.
- Mangin, D., and Klein, J.P. (2004). Fluid dynamic concepts for a phosphate precipitation reactor design. In Valsami-Jones, E. (ed.). *Phosphorus in environmental technologies: Principles and applications*. London: IWA Publishing, pp. 358-400.
- Manitoba Agriculture, Food and Rural Initiatives. (2007). Farm Practices Guidelines for Pig Producers in Manitoba. Retrieved December 1, 2009, from the MAFRI web site: <http://www.gov.mb.ca/agriculture/crops/cropproduction/gaa01d04.html>
- Miles, A., and Ellis, T.G. (2001). Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Water Science and Technology*, 43(11): 259-266.
- Moerman, W., Carballa, M., Vandekerckhove, A., Derycke, D., and Verstraete, W. (2009). Phosphate removal in agro-industry: Pilot- and full-scale operational

- considerations of struvite crystallization. *Water Research*, 43: 1887-1892.
- Momberg, G.A., and Oellermann, R.A. (1992). The removal of phosphate by hydroxyapatite and struvite crystallization in South Africa. *Water, Science and Technology*, 26: 987-996.
- Morse, G. K., Brett, S.W., Guy, J.A., and Lester, J.N. (1998). Review: Phosphorus removal and recovery technologies. *Science of the Total Environment*, 212(1): 69-81.
- Nelson, N.O., Mikkelsen, R.L., and Hesterberg, D.L. (2003). Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. *Bioresource Technology*, 89: 229-236.
- Ohlinger, K.N., Young, T.M., Schroeder, E.D. (1998). Predicting struvite formation in digestion. *Water Research*, 32: 3607-3614.
- Ohlinger, K.N., Young, T.M., and Schroeder, E.D. (1999). Kinetics effects on preferential struvite accumulation in wastewater. *Journal of Environmental Engineering*, 125(8): 730-737.
- Pastor, L., Mangin, D., Barat, R., Seco, A. (2008). A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process. *Bioresource Technology*, doi:10/1016/j.biortech.2007.12.003.
- Prairie Agricultural Machinery Institute and Alberta Farm Machinery Research Centre. (1997). A Guide to Swine Manure Management Methods. Retrieved December 1, 2009, from the Government of Alberta Agriculture and Rural Development web site: [http://www1.agric.gov.ab.ca/\\$department/deptdocs.nsf/all/eng9870](http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/eng9870)
- The Prairie Provinces' Committee on Livestock Development and Manure Management. (2003). Tri-Provincial Manure Application and Use Guidelines. Retrieved December 1, 2009, from the MAFRI web site: <http://www.gov.mb.ca/agriculture/crops/cropproduction/gaa01d39.html>
- Racz, G.J. (2001). Long-term Effects of Hog Manure on Soil Quality and Productivity. Retrieved December 1, 2009, from MAFRI web site: <http://www.gov.mb.ca/agriculture/research/ardi/projectsresultsindex.html#manure>
- Rawluk, C. and Flaten, D. (2007). Chapter 2 Manure Nutrient Management and Water Quality in A Report on Current Knowledge of Key Environmental Issues Related to Hog Production in Manitoba commissioned by Clean Environment Commission. Retrieved December 1, 2009, from the National Center for Livestock and the Environment web site: <http://www.umanitoba.ca/afs/ncle/ResearchProjects.html>
- Richards, I.R., Johnston, A.E. (2001). The effectiveness of different precipitated phosphates as sources of phosphorus for plants. Report undertaken for CEEP, published online, and accessible via CEEP Website: <http://www.nhm.ac.uk/mineralogy/phos/>, accessed 2009.
- Shepherd, T.A., Burns, R.T., Moody, L.B., Raman, D.R., and Stalder, K.J. (2009). Development of a bench-scale air sparged continuous flow reactor for struvite

- precipitation from two different liquid swine manure storage systems. *Applied Engineering in Agriculture*, 25: 425-430.
- Shu, L., Schneider, P., Jegatheesan, V., and Johnson, J. (2006). An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresource Technology*, 97(17): 2211-2216.
- Sri Ranjan, R., Cordeiro, R., and Robinson, B. (2007). Chapter 5 Manure Storage in A Report on Current Knowledge of Key Environmental Issues Related to Hog Production in Manitoba commissioned by Clean Environment Commission. Retrieved December 1, 2009, from the National Center for Livestock and the Environment web site: <http://www.umanitoba.ca/afs/ncle/ResearchProjects.html>
- Stumm and Morgan. (1970). *Aquatic Chemistry*. New York: Wiley.
- Suzuki, K., Tanaka, Y., Osada, T., and Waki, M. (2002). Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. *Water Research*, 36: 2991-2998.
- Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., and Fukumoto, Y. (2005). Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology*, 96: 1544-1550.
- Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. (2007). Removal and recovery of phosphorus from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology*, 98: 1573-1578.
- Ueno, Y., and Fujii, M. (2001). Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology*, 22: 1373-1381.
- US Geological Survey (2008). 2007 Minerals Yearbook: Phosphate Rock, 56.1-56.11.
- Wang, J., Burken, J.G., Zhang, X.Q., and Surampalli, R. (2005). Engineered struvite precipitation: Impacts of component-ion molar ratios and pH. *Journal of Environmental Engineering-Asce*, 131: 1433-1440.
- Westerman, P.W., Bowers, K.E., Zering, K.D. (2010). Phosphorus recovery from covered digester effluent with a continuous-flow struvite crystallizer. *Transactions of the American Society of Agricultural and Biological Engineers*, 26(1): 153-161.
- Wu, Q., and Bishop, P.L. (2004). Enhancing struvite crystallization from anaerobic supernatant. *Journal of Environmental Engineering and Science*, 3: 21-29.
- Yaffer, Y., Clark, T.A., Pearce, P., and Parsons, S.A. (2002). Potential phosphorus recovery by struvite formation. *Water Research*, 36: 1834-1842.

Appendix I - XRD analysis results

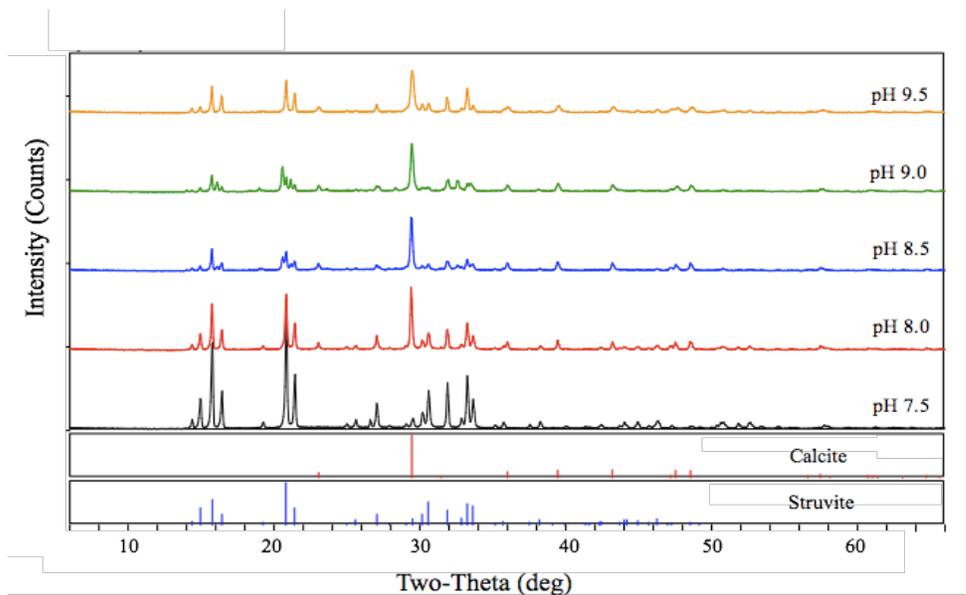


Figure I-a. X-ray diffractograms of precipitate at all pH values. The struvite pattern shown on the bottom can be seen in all the diffractograms, but the strongest correlation is with pH 7.5. The other pH values all exhibit a distinct calcite peak.

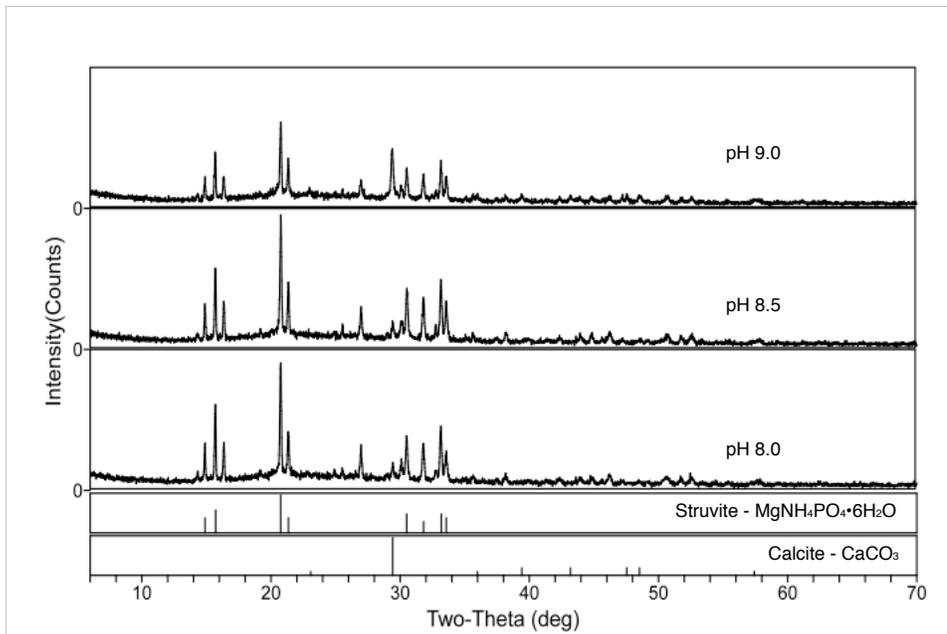


Figure I-b. X-ray diffractograms for Mg:PO₄ 1.4:1 at all pH values. Struvite was identified for all pH values, while calcite was also detected at pH 9.0.

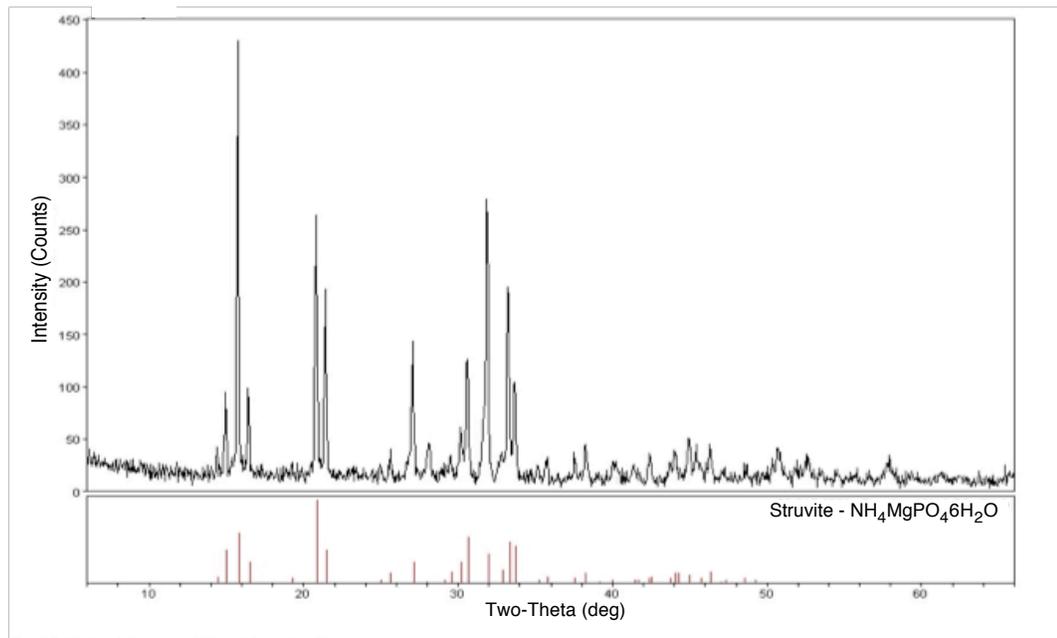


Figure I-c. X-ray diffractogram of synthetic struvite prepared for seedbed particles. Skewed intensity of peaks compared to pure struvite under the graph indicates presence of unknown precipitate.

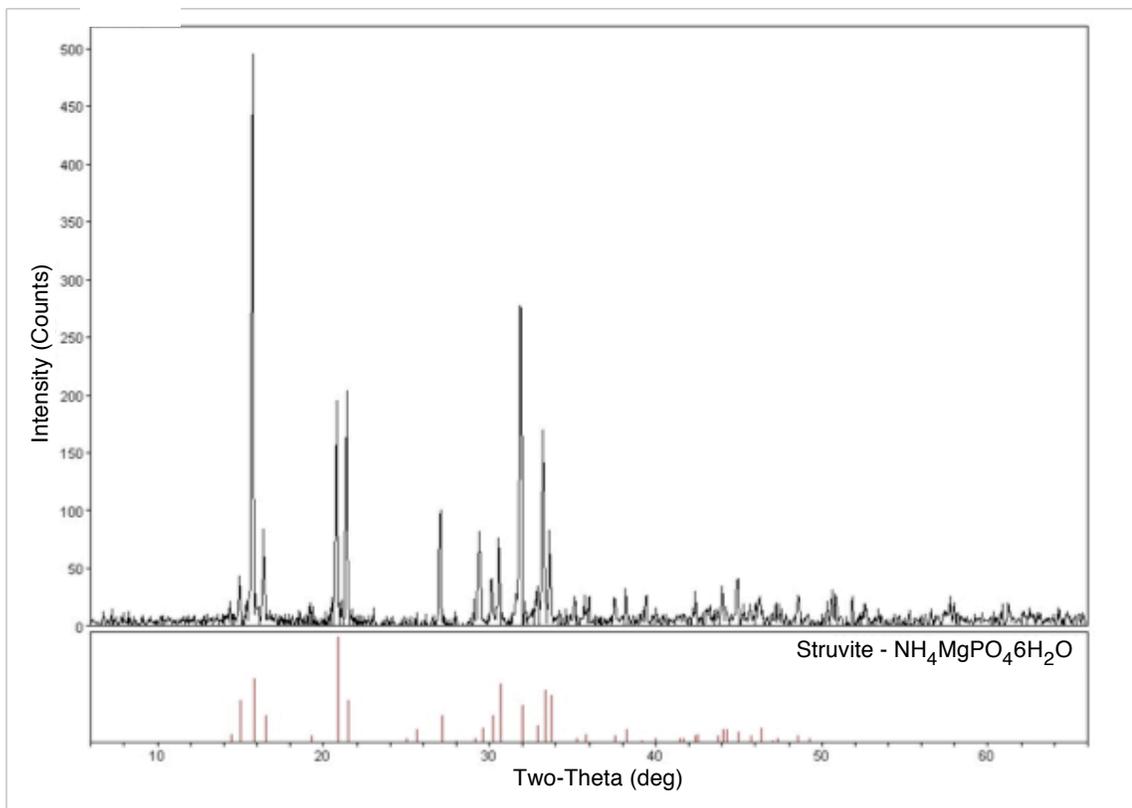


Figure I-d. X-ray diffractogram of precipitate recovered from S1. Skewed intensity of peaks compared to pure struvite under the graph indicates presence of unknown precipitate.

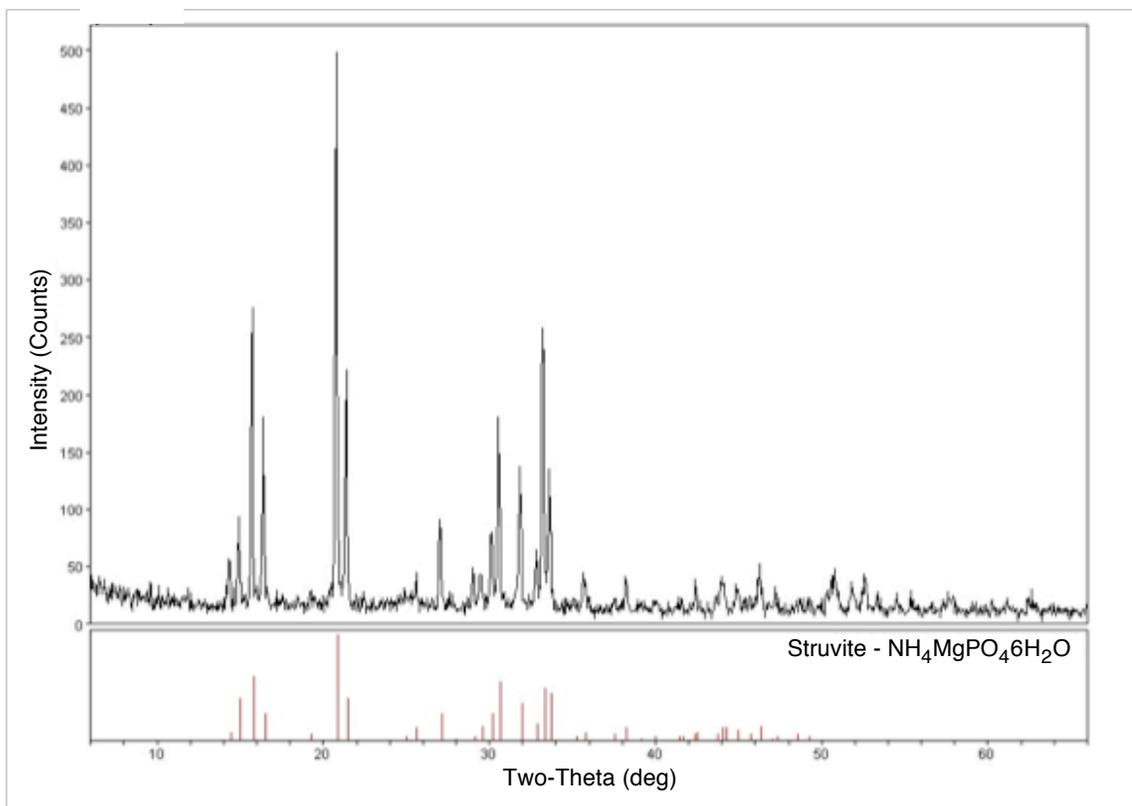


Figure I-e. X-ray diffractogram of precipitate recovered from recycle rate run. Good correlation with pure struvite peaks under the graph indicates high struvite purity.

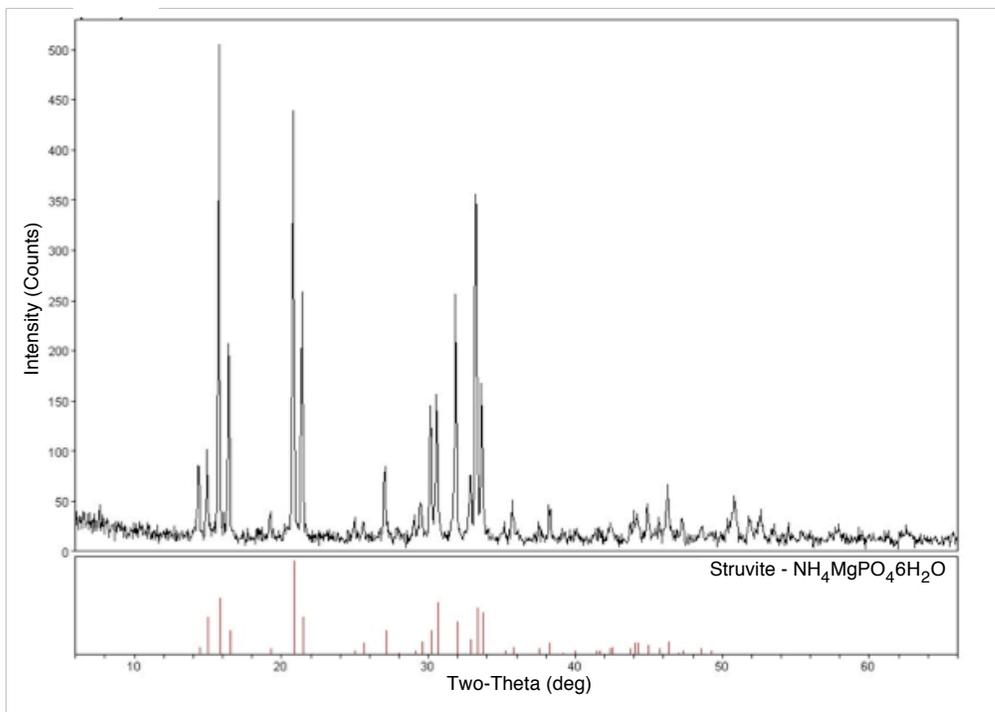


Figure I-f. X-ray diffractogram of precipitate collected after 24 h during L1. Skewed peak intensities indicate presence of unknown precipitate.

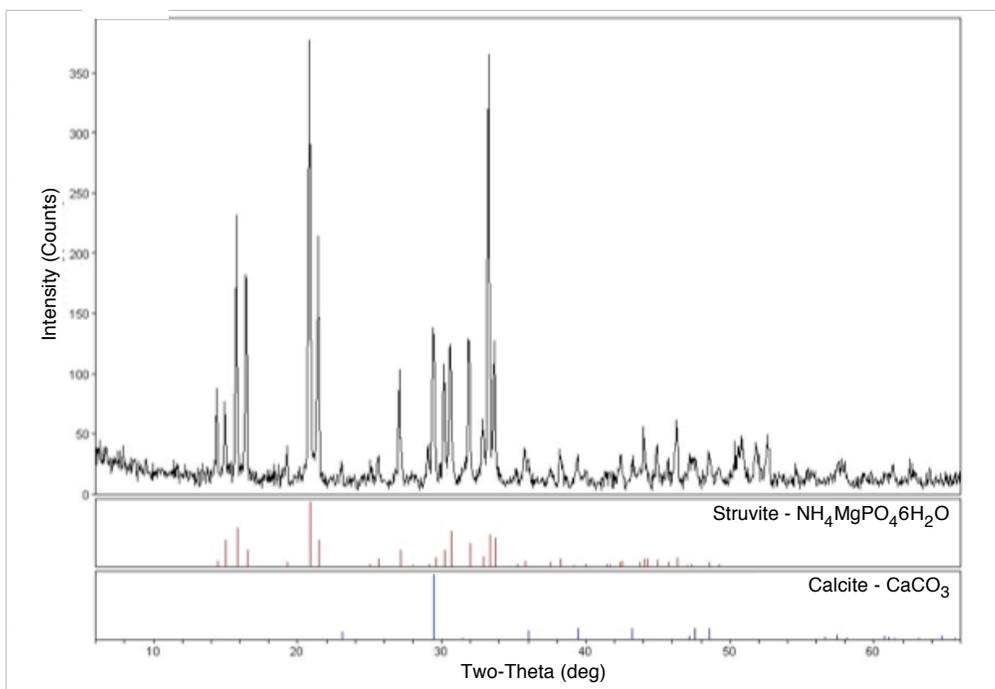


Figure I-g. X-ray diffractogram of precipitate collected after 45 h during L1. Relatively good comparison to struvite intensity with additional calcite peak.

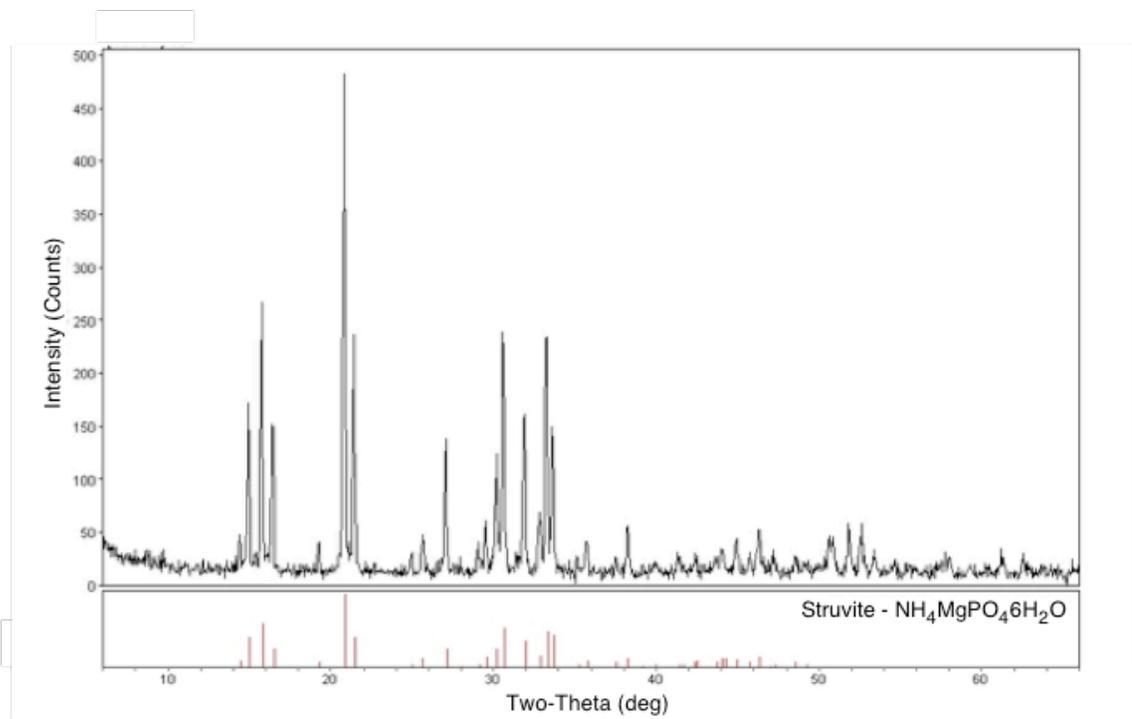


Figure I-h. X-ray diffractogram of precipitate collected at 24 h during L2. Good comparison to struvite peaks indicates high struvite purity.

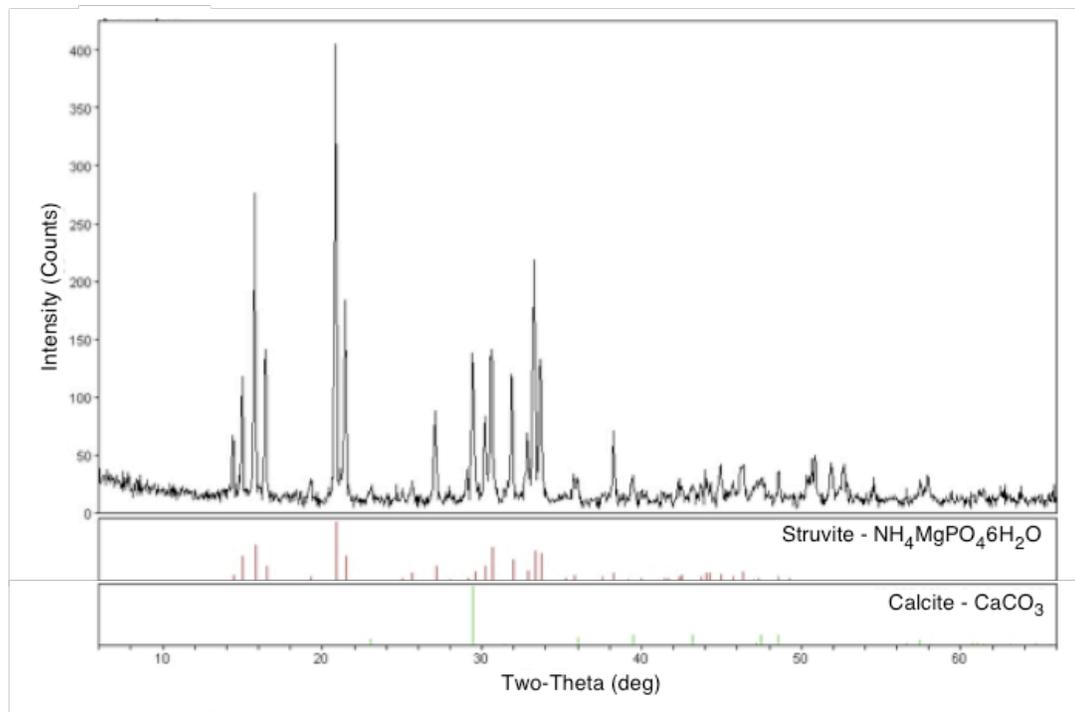


Figure I-i. X-ray diffractogram of precipitate collected at 67 h during L2. Both struvite and calcite peaks found.

Appendix II – Pictures



Figure II-a. Picture of reactor system set-up showing main reactor with aeration stones and overflow cone.



Figure II-b. Picture of the reactor during recycle run. Fines can be seen in the funnel, while the top section is relatively clear.



Figure II-c. Picture showing reactor during struvite run. Note fines in funnel. The top section is much more opaque than during the recycle run due to seedbed disintegration and higher flowrates.

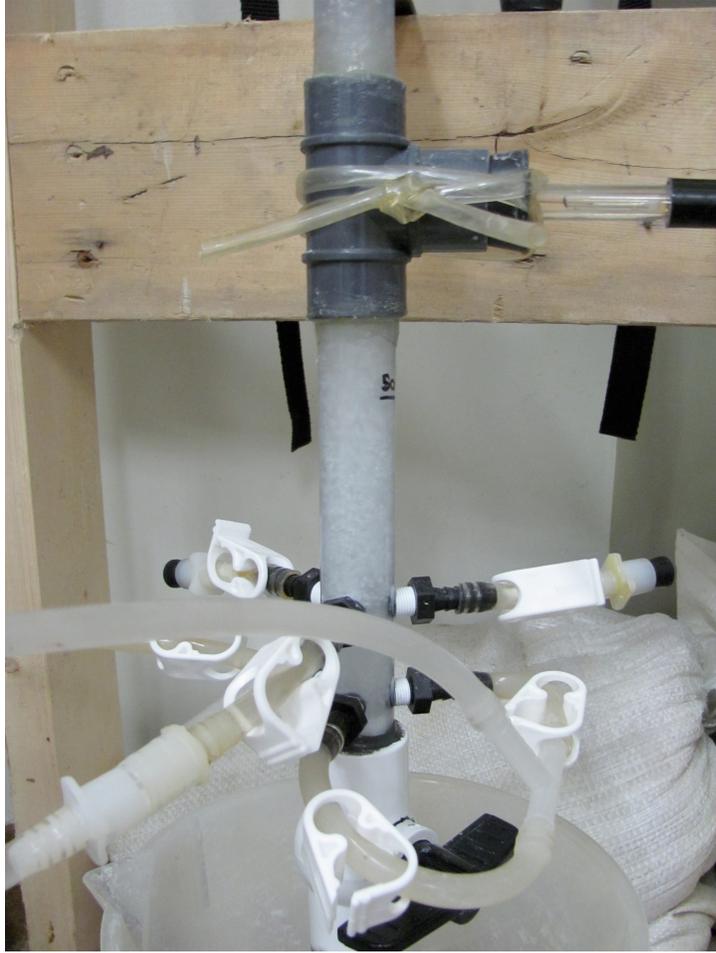


Figure II-d. Picture of the bottom section of the reactor during the struvite run. The seedbed particles can be seen, mostly below the pH port.



Figure II-e. Picture of overflow cone during struvite run before fine recycle.