THESIS

DAIRY FARM PHOSPHORUS RECOVERY AND RE-USE TO REDUCE WATER QUALITY RISK AND IMPROVE PHOSPHORUS CYCLING IN AGRICULTURE

Submitted by

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY MICHAEL STANLEY MASSEY ENTITLED DAIRY FARM PHOSPHORUS RECOVERY AND RE-USE TO REDUCE WATER QUALITY RISK AND IMPROVE PHOSPHORUS CYCLING IN AGRICULTURE BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT OF THESIS

DAIRY FARM PHOSPHORUS RECOVERY AND RE-USE TO REDUCE WATER QUALITY RISK AND IMPROVE PHOSPHORUS CYCLING IN AGRICULTURE

Phosphorus (P) is a limited natural resource, and its efficient use and cycling are important for the long-term sustainability of agricultural and industrial production. The over-application of P in dairy wastewater to fields, in addition to being inefficient, can lead to the degradation of water quality through P-induced eutrophication from agricultural runoff. This is especially true in areas where dairies and other livestock operations are increasingly concentrated around sources of fresh water such as rivers. Phosphorus recovery and re-use has the potential to reduce the amount of P applied to fields near the dairy while providing a useful, marketable, and easily transportable P fertilizer. This study evaluated the efficiency of magnesium (Mg) phosphate recovery on dairy farms using actual wastewater under field conditions, the nature of various recovered products including magnesium ammonium phosphate hexahydrate (struvite) and magnesium ammonium phosphate hydrate (dittmarite), and the feasibility of using Mg phosphates as fertilizers in slightly acidic and alkaline soil conditions.

Dairy wastewater was treated using a cone-shaped fluidized bed reactor and two treatment processes which differed in the chemicals used for pH manipulation. The "conventional" process made use of hydrochloric acid and anhydrous ammonia for pH adjustment, while the "new" process used acetic acid and potassium hydroxide. The

"new" process has the potential to produce a certified organic soil amendment with minimal modification to current organic production standards. After wastewater treatment, the recovered P products, along with other samples of recovered Mg phosphates including crystalline struvite and dittmarite, were examined with powder x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray spectroscopy. Finally, struvite, dittmarite, and a heterogeneous recovered product were applied in greenhouse fertilizer trials alongside commercial triple superphosphate (TSP) and certified organic rock phosphate (RP). The fertilizers' performance was tested at two application rates (45 kg ha^{-1} and 90 kg ha^{-1}) and two soil pH levels (6.5 and 7.6).

The "conventional" treatment method removed 14% of the total phosphorus (TP) in the dairy wastewater, while the "new" method removed 9% of TP, along with 12% and 9% of the Mg for the conventional and new methods, respectively. Detailed analysis and characterization of the products, as well as recovered struvite and dittmarite, showed great variation among the chemical, microscopic, and macroscopic characteristics of the different types of recovered Mg phosphates. Fertilizer trials found that TSP and recovered struvite and dittmarite crystals increased plant P concentration in spring wheat (*Triticum aestivum L.*) grown in slightly acidic soil. At high soil pH, the recovered Mg phosphates increased plant dry matter production over the control and also performed similarly to TSP.

The results of the current study indicate that P recovery through Mg phosphate precipitation is possible on dairy farms, but improvements must be made in removal efficiency and consistency of product characteristics. Furthermore, the resulting recovered phosphates may be useful as fertilizers in both acidic and alkaline soils.

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Abbreviations

Ca	Calcium
EDS	Energy dispersive x-ray spectroscopy
HRT	Hydraulic retention time
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
K	Potassium
Mg	Magnesium
N	Nitrogen
Na	Sodium
NH_4-N	Ammonium nitrogen (expressed as nitrogen)
NO_3-N	Nitrate nitrogen (expressed as nitrogen)
OP	Orthophosphate (PO_4^{3-})
P	Phosphorus
RP	Rock phosphate
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy and energy dispersive x-ray spectroscopy
TP	Total phosphorus
TSP	Triple superphosphate

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Chapter 1: Introduction

Rationale

There are two primary reasons to address phosphorus (P) cycling and recovery in agriculutural settings such as dairy farms. The most immediate concern is the gradual buildup of nutrients such as nitrogen (N) and P from manure application. If manure is applied to crops at agronomic rates for N fertilization, P can be over-applied (Greaves et al., 1999). Over time, the localized P surplus can lead to declining surface water quality and eutrophication from runoff (Carpenter et al., 1998). Eutrophication can have severe economic impacts, such as those associated with the collapse of fisheries (Randall, 2003). The localized P surplus is compounded by the concentration and intensification of livestock operations around water sources such as rivers, and the difficulty of transporting manure. The local P surplus associated with intensive livestock operations is documented by a variety of studies, including Spears et al. (2003). Phosphorus recovery from on-farm wastes can be used as a tool to address the nutrient imbalance, and can help to protect water quality in the process.

The second important concern in addressing P recovery is the anticipated worldwide decline in high-quality P reserves. At the current rate of extraction, high-quality P reserves will be depleted within a century (Driver et al., 1999). The current P cycle is unsustainable over the long-term, with a significant amount of extracted P being either eroded in to water bodies or fixed in marginally soluble, marginally useful forms in

wastewater treatment plants and soils. Recovery and re-use of P in a useful form from sources such as dairy manure have the potential to extend current P reserves by improving cycling and nutrient-use efficiency of P that has already been extracted. A further benefit could be realized if livestock producers could market and sell recovered P for an additional source of revenue. These two factors give P recovery from animal manures the potential to be economically attractive (Gaterell et al., 2000).

Phosphorus recovery from dairy manure has the potential to address both environmental issues by improving water quality and nutrient cycling, and economic issues by extending P reserves and generating additional revenue for livestock producers. The realization of these benefits, however, depends on finding suitable uses for recovered materials. Many recovered phosphates are magnesium (Mg) phosphates, which cannot be used by the current P industry (Schipper et al., 2001). Several studies have addressed the re-use of recovered phosphates as fertilizers in acidic or neutral soils (Bridger et al., 1962; Goto, 1998; Johnston and Richards, 2003; Li and Zhao, 2003; Bauer et al., 2007), but P fertilization in alkaline soils is often an equal or greater challenge. This is especially true for certified organic producers in arid and semi-arid regions where calcareous soils are common. Certified organic producers who farm calcareous soils have severely limited options for P fertility management, even more so than conventional producers with these conditions (Elliott et al., 2005).

Struvite ($MgNH_4PO_4 \bullet 6H_2O$) is one material of interest that has the advantage of being relatively easy to recover from waste streams, and of being tested as a potential P fertilizer. Bowers and Westerman (2005) have produced struvite by removing P and Mg from swine wastewater. In the current study, this process was evaluated for use on dairy

farms in the semi-arid western United States and modified to produce a potentially certifiable organic soil amendment. Recovered phosphates were examined and characterized, and also tested to determine their effectiveness as fertilizers in alkaline soil conditions common to this region of the United States.

Objectives

The objectives of this study were to: evaluate the performance of a fluidized bed reactor in recovering P from dairy wastewater; examine and characterize the recovered product; and test the effectiveness of recovered P as fertilizer in both acidic and alkaline soil conditions. Additionally, a wastewater treatment process that might produce a certified organic soil amendment was developed and became the focal point of reactor performance testing after initial proof-of-concept testing using an existing process.

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Chapter 2: Phosphorus removal from dairy wastewater using a fluidized bed reactor and an "organic" treatment process

Abstract

Recovery of phosphorus (P) through treatment of livestock wastewater can reduce water quality risks while creating a product that may be useful as a P fertilizer. This study was conducted to evaluate P recovery from dairy wastewater using two recovery methods, one of which resulted in a product that might one day be used in certified organic food production. Phosphorus was recovered as crystalline or amorphous magnesium ammonium phosphate hexahydrate (struvite) using a pilot-scale fluidized bed reactor and chemical additions to encourage phosphates to precipitate onto seed bed crystals. Hydrochloric acid and anhydrous ammonia were added in the "conventional" process, while the "new" process made use of acetic acid and potassium hydroxide addition. Mean total P removal of 14% was observed for the conventional method, and the new method resulted in 9% removal. The conventional and new methods also removed 12% and 9% of the wastewater magnesium, respectively. These removal rates were lower than laboratory and field studies conducted with swine wastewater, but were comparable to the limited field study data on dairy wastewater. Results indicated that P recovery from dairy wastewater can be accomplished, though improvements in P removal efficiency and further field testing using actual dairy wastewater are necessary.

Introduction

While there is some question regarding exactly how long existing rock P (RP) reserves will last, it is clear that P is a limited resource and that its recovery and re-use are necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Phosphorus recovery has the potential to become increasingly attractive, both commercially and environmentally, as the quality of RP reserves declines and energy prices rise (Gaterell et al. (2000).

Most P recovery efforts have focused on municipal wastewater treatment plants (WWTPs), where spontaneous precipitation of struvite (magnesium ammonium phosphate hexahydrate; $MgNH_4PO_4 \bullet 6H_2O$) inside infrastructure piping can be destructive to WWTPs, incurring downtime and cleaning expenses (Doyle et al., 2000; Doyle and Parsons, 2002; de-Bashan and Bashan, 2004; Shu et al., 2006). Spontaneous struvite precipitation can also be a problem for livestock operations by causing scaling in waste storage and treatment systems (Webb and Ho, 1992; Buchanan et al., 1994). Additionally, P releases from WWTPs and nonpoint pollution from farms can cause eutrophication of surface water bodies, resulting in substantial economic, environmental, and societal impact (Randall, 2003). In order to offset scaling and P discharge issues, chemical precipitation of P is often accomplished using iron or aluminum salts. Chemical P precipitation, however, causes large increases in sludge volume which leads to increased disposal costs for WWTPs (Doyle and Parsons, 2002). Given the scale and expense of a WWTP as compared to agricultural facilities, it is easier to justify capital investment in new P removal and recovery technologies, so these facilities have naturally been a focus of research to reduce scaling, sludge volume, and P discharge.

A substantial amount of laboratory-scale P recovery work has been conducted on real WWTP wastewater (Battistoni et al., 2000; Battistoni et al., 2002; Jaffer et al., 2002; Shimamura et al., 2003; Turker and Celen, 2007). These laboratory studies demonstrated the possibility of P recovery from municipal wastewater as Ca or Mg phosphates, and laid the foundation for larger scale work at WWTPs. Building on this body of work, Battistoni et al. (2001, 2005), Munch and Barr (2001), and Huang et al. (2006) have reported very successful pilot-scale work on actual WWTP effluent.

There also exist full-scale, working examples of WWTPs using crystallization processes for P removal. Depending on the process, the product is either calcium (Ca) phosphate (apatite) or magnesium (Mg) phosphate (struvite) (van Dijk and Braakensiek, 1984; Driver, 1998; Driver et al., 1999; de-Bashan and Bashan, 2004). Struvite from at least one WWTP is sold as part of a fertilizer mix (Ueno and Fujii, 2001). Still, even at WWTPs P recovery is very much an experimental and developing technology.

Phosphorus recovery from agricultural wastewater is even less developed. As compared to municipal examples, little field-scale or full-scale work has been done regarding on-site P removal from agricultural wastewater. Possibly the only reported full-scale P recovery process involved treatment of calf manure at a centralized treatment plant (Schuiling and Andrade, 1999). Of the laboratory-scale research that has been performed, some authors have examined P recovery from swine wastewater (Wrigley et al., 1992; Burns et al., 2003; Nelson et al., 2003; Bowers and Westerman, 2005b), while some have worked with dairy wastewater (Uludag-Demirer et al., 2005; Qureshi et al., 2006; Zeng and Li, 2006). The majority of field-scale studies, however, have been conducted on swine wastewater (Miles and Ellis, 2001; Suzuki et al., 2002; Vanotti et al.,

2003; Bowers and Westerman, 2005b; Suzuki et al., 2007), and have enjoyed reasonable success in Ca phosphate and Mg phosphate recovery. As outlined by Bowers and Harrison (2005) and Bowers et al. (2007), however, P recovery from dairy wastewater comes with its own substantial challenges. These unique challenges of dairy wastewater treatment, which include high Ca and solids concentrations, necessitate the separate, specific examination of P recovery from dairy waste streams.

Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure an ideal target for P recovery. According to the same review, while direct land application is the preferable method of P re-use from manure, the application of manure at a rate which meets crop nitrogen (N) needs results in a significant P surplus. In some cases, this surplus increases the risk of non-point pollution of surface waters through runoff (Carpenter et al., 1998).

Contributing to the situation are intensive livestock operations which are increasingly concentrated in certain regions, potentially overwhelming the capacity of the local land to absorb the quantity of manure generated by such operations. Spears et al. (2003) found that the average dairy in Utah and Idaho had a 6.6 t $year^{-1}$ surplus of imported P that was not accounted for in product outputs. Due to this local nutrient excess, manure must be transported greater distances for disposal or land application, at significant cost. Phosphorus recovery from agricultural wastewater as a crystalline, easily dried product has the potential to address some of these issues.

Significant constraints for on-site P removal processes must be overcome in order for the technology to be practical. Recovery technology must be relatively inexpensive and must be economical on a smaller scale than P removal at a typical WWTP.

Additionally, the system cannot require extensive monitoring, maintenance, or material inputs. Most importantly, treated effluent must remain suitable for application to crops (Greaves et al., 1999). This last requirement imposes the most stringent limitation on the process as it precludes the addition of certain chemicals, such as sodium hydroxide (NaOH), and the use of certain techniques such as raising wastewater pH to very alkaline levels. Though these are used in WWTP P recovery, high Na concentrations or pH would render agricultural effluent unsuitable for land application.

The cone-shaped fluidized bed reactor designed by Bowers and Westerman (2005a) is one such technology which could overcome the aforementioned obstacles. In laboratory- and field-scale experiments, P was recovered as crystalline struvite from wastewater generated in swine production. The reactor was used in combination with Mg and ammonia addition to increase pH and encourage struvite precipitation. Total phosphorus (TP) concentration in treated effluent was reduced by an average of up to 82% (Bowers and Westerman, 2005b). Even without Mg addition, pH manipulation alone resulted in TP removal as high as 64%. The crystalline product was confirmed to be struvite by x-ray diffraction (XRD) analysis.

Few applications for recovered struvite have been developed. Its chemical composition makes it impractical as a raw material in the modern P industry. Ammonium renders struvite unusable in the high-temperature process for the manufacture of phosphoric acid, and Mg interferes with the "wet" phosphoric acid manufacturing process (Driver et al., 1999; Schipper et al., 2001). Its potential for use as a slow-release fertilizer has been known for decades (Bridger et al., 1962), but few scientific studies have been published. According to the information currently available,

recovered struvite could be a useful fertilizer in acidic and neutral soils (Johnston and Richards, 2003; Li and Zhao, 2003).

The development of a sustainable, effective alternative for P fertilization on calcareous soils is especially important for organic agriculture in semi-arid environments. Manure and compost are the only viable options for P fertilization on organic farms with alkaline soils, which are common in the western United States. Rock phosphate and bone meal are other options available to organic producers with acid soils, but they are ineffective as fertilizers in calcareous soils. Phosphorus availability from manure and compost depends on mineralization of the organic phase, a process that can take weeks or months, and that is difficult to predict or manage (Elliott et al., 2005). Furthermore, manure or compost application may not be suitable for all situations, such as fields with high runoff risk or legume production with the goal of maximizing biological nitrogen fixation. An alternative for P fertilization in organic production on calcareous soils would be a welcome addition to any organic producer's fertility toolbox.

Recovered struvite has the potential to be this alternative. In this study, the technique outlined by Bowers and Westerman (2005a) was modified, and a new crystallization process was developed and tested that was more in accordance with the letter and spirit of the regulations for organic food production (USDA, 2007).

Materials and Methods

Wastewater treatment using the University of Idaho pilot-scale struvite crystallizer was performed in August and September 2006 at two separate dairies in northern Colorado. Both dairies used flush manure collection systems. One maintains a milking herd of approximately 1,200-1,400 head, while the other herd was 700 head. The

reactor setup used was similar to that used by Bowers and Westerman (2005b) and Bowers et al. (2007). Two different reactor processes were used: the "conventional" process which utilizes hydrochloric acid (HCl) and anhydrous ammonia for pH adjustment, and the "new" process which replaces these chemicals with acetic acid and potassium hydroxide (KOH). Acetic acid and KOH were used instead of HCl and anhydrous ammonia to adjust the pH since it was thought that the product of this treatment process could be certified for use in organic production with little or no modification to existing criteria. KOH was selected over NaOH since treated wastewater remains suitable for land application after KOH addition. The conventional method was tested as proof-of-concept at the first dairy, and the new method was tested at the second dairy.

The primary components of the fluidized-bed crystallizer system were a 1000 L acidification tank and a large, inverted conical reactor vessel with an approximately 30 L volume (Figure 2.1). The reactor cone was initially seeded with a bed of RP material to provide sites for the growth of struvite crystals. During operation, wastewater was pumped from the holding tank into the base of the reactor cone through a manifold. Inside the manifold, other substances such as Mg solution, hydroxide solution, or gaseous anhydrous ammonia can be combined with the wastewater stream, though in the current study Mg solution was not added. The wastewater entered the cone after pH adjustment in the manifold, passed through the bed of material at its base, eventually reaching the top of the reactor where treated effluent was allowed to drain back into the lagoon.

Wastewater was pumped from an anaerobic lagoon into the holding tank, and adjusted to an approximate pH of 5.2 by addition of acid. Acidification increases the

concentration of orthophosphate (OP) in the effluent by dissolving inorganic phosphate complexes already present in the wastewater. Liquid in the tank was continuously recirculated and mixed by a small pump at its base, and glass electrodes were used to monitor system pH. Once the target pH was reached, acidified wastewater was pumped at a rate of 410 to 456 L h^{-1} through the manifold, where a base (either gaseous ammonia or KOH solution) was added to rapidly increase the pH to between 7.5 and 8.3. This encouraged the precipitation of phosphates as the effluent passed through the bed of seed material. At the above flow rate, the hydraulic retention time (HRT) of the wastewater in the reactor was just over four minutes.

Wastewater samples were taken approximately hourly at three points in the process: prior to entering the holding tank, immediately prior to entering the manifold, and at the top of the reactor vessel near the outlet, referred to as "lagoon", "input", and "output" samples, respectively (Figure 2.1). Input and lagoon samples were taken by opening valves and draining wastewater directly into 1 L sample bottles, while output samples were obtained by transferring liquid from the top of the cone into sample bottles. Samples were refrigerated prior to analysis. Orthophosphate was evaluated using the ascorbic acid method (Kuo, 1996). Following digestion of samples with nitric and perchloric acid, TP, Mg, Ca, K, and Na were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Thermo Jarrell Ash IRIS Advantage, high resolution, dual view). Total N was measured using a LECO TruSpec C/N analyzer, and ammonium N was measured colorimetrically with an OI Analytical Flow Solution 3000 flow injection system.

Means were calculated using SAS 9.1 (SAS Institute, Inc., Cary, NC, USA) proc mixed, with sampling time as a random effect, and sample location (lagoon, input, output) and date as fixed effects. Means were compared using the lsmeans statement at a significance level of α=0.05. Standard deviations were calculated using SAS proc means.

Results

The different P removal processes were tested at separate dairies due to difficulties pumping the wastewater at the initial location. Magnesium and OP concentrations were greater in the lagoon effluent used for the new process, while TP concentration was greater in the wastewater used for the conventional process (Tables 2.1 and 2.2). Sampling date had a significant effect on the new method results due to a dilution event that occurred after the first day of reactor operation. All sample times (n=4) from a final day of new method operation were omitted from the statistical analysis due to confounding factors including major dilution events and weather/operating temperature differences from previous days of reactor operation.

Sampling location was the most important significant effect for all elements of interest (p-values < 0.01; Tables 2.1 and 2.2). Differences by sampling location demonstrate reactor performance.

Acidification had the expected effect, raising the OP concentration from the lagoon to the reactor input in both processes (Tables 2.1 and 2.2). A significant difference between lagoon and input samples was observed only for OP and TP in the new method, with the difference in TP attributable to settling in the acidification tank. Sodium (Na) concentration was used as an indicator of dilution throughout the system. A substantial dilution effect was observed in the reactor due to the addition of KOH

solution in the new method (Table 2.1). Dilution in the reactor was not observed in the conventional method since the pH increase was accomplished using gaseous ammonia rather than an alkaline solution (Table 2.2). Results showed a reduction in OP, TP, Mg, TN, and NH_4-N concentrations from reactor input to outlet for both the conventional and new processes. On a molar basis, an average of 2.8 and 1.8 times more Mg was removed than P using the new and conventional methods, respectively. Orthophosphate decreases were greater than TP decreases, and OP and TP reduction was greater in the conventional process than the new process after the effects of dilution were considered.

Ammonia addition for pH adjustment in the conventional method had a substantial effect on the N:P ratio of treated effluent (Table 2.3). Ammonium, Mg, and P were present in considerable excess of the stoichiometric ratio of 1:1:1 necessary for struvite precipitation (Table 2.4).

Discussion

The mean TP removal efficiency of 14% for the conventional method does not equal the 64% removal efficiency reported by Bowers and Westerman (2005b) in experiments using swine wastewater. However, it does compare more favorably to results obtained by Bowers and Harrison (2005) for treatment of dairy wastewater in Idaho (14%) and Washington (15%) using the conventional acidified process. Reported Mg and P concentrations in the Idaho dairy wastewater (Bowers and Harrison, 2005) were similar to the concentrations observed in this study. The swine wastewater used by Bowers and Westerman (2005b) had similar P concentrations and lower Mg concentration than dairy wastewater observed in the current study. Other important

physical and chemical features of the swine wastewater were not reported, but are likely related to the differences in performance.

One important factor not often considered in laboratory-scale work is the viscosity of dairy wastewater. Thick dairy wastewater tends to sweep particles out of the reactor. This phenomenon was observed in the current study, with sand and organic matter settling in the bed while fine bed particles were occasionally swept out of the reactor and observed in effluent samples. Wang et al. (2006) found that quartz sand was less effective as a seed material than struvite powder, and attributed this difference to the lower relative surface area and higher specific gravity of sand, resulting in fewer crystallization sites and reduced mixing. In the current study, ground RP was used, and the presence of phosphate binding sites would suggest that the RP would perform more similarly to struvite powder than sand particles. Loss of fines and contamination of the bed with sand as a result of the viscosity of the liquid could have contributed to reduced crystallization and P removal in the reactor.

According to Bowers and Westerman (2005a), all OP is theoretically available for recovery through struvite crystallization. The TP reduction Bowers and Westerman (2005a) observed was, in some instances, greater than this theoretical maximum. In the current study, however, mean TP reduction was notably lower than mean OP reduction on an absolute basis. This indicated that some potentially recoverable phosphate was being discharged in the treated effluent stream prior to crystallization or precipitation onto particles in the reactor bed, or that some of the bed particles themselves were being expelled from the reactor. A combination of these processes could have occurred; the net result was that decreased OP concentration in the treated effluent was reflected only

partially by the observed reduction in TP concentration. Bowers and Westerman (2005b) reported that slower flow rates resulted in greater P removal efficiency in field-scale experiments. In the current study, a flow rate between the 341 and 568 L h^{-1} rates used by Bowers and Westerman (2005b) was used, with a similar reactor size. With a larger reactor cone, Bowers et al. (2007) were able to reduce losses from the crystal bed by decreasing upflow velocity in the reactor for a given flow rate. This reduction in losses also reportedly increased TP removal from under 25% to approximately 50%. Though increased HRT is a consequence of the larger reactor, several investigators found that initial kinetics of struvite formation, as measured by concentration of ions in solution, are rapid (Stratful et al., 2001; Yoshino et al., 2003; Zeng and Li, 2006). Le Corre et al. (2007) found retention time to have a negligible effect on crystal size, but Stratful et al. (2001) noted that crystals grew larger with increasing HRT. Conflicting evidence exists, but it is possible that with a slower flow rate or larger reactor, a longer HRT would improve performance over that reported in the current study.

In addition to physical considerations, there are a number of chemical issues that have been shown to inhibit struvite crystal formation which could partially explain the poor P removal efficiency. One obvious complicating factor is the complex and concentrated nature of the organic suspended solids in dairy waste. A second is the Ca:Mg ratio of the wastewater, resulting in various competitive inhibition mechanisms with these ions. A third chemical consideration is the Mg:P ratio. There are conflicting reports on the effects of these last two parameters, but either one could explain part of the poor removal efficiency seen in the current study.

Schuiling and Andrade (1999) noted that high suspended solids concentrations (> 1000 mg L^{-1}) inhibited struvite formation at a full-scale calf manure treatment plant. Initial samples of the wastewater in the current study showed TSS values close to or substantially above 1000 mg L^{-1} in all cases (data not shown). van der Houwen and Valsami-Jones (2001) discussed the nature of organic ligands such as citrate and other ions that interfere with Ca phosphate precipitation through inhibition of bonding sites, but the same effects may indeed inhibit Mg phosphate precipitation as well.

Regarding optimal molar ratios, Wang et al. (2005) concluded that the ideal Ca:P molar ratio for struvite precipitation is 0.5 or less, and that a Ca:Mg ratio greater than one in wastewater can significantly inhibit struvite formation. Le Corre et al. (2005) also found high Ca concentrations to inhibit struvite formation, both by slowing the reaction and by increasing the precipitation of amorphous Ca phosphates and carbonates. The Ca:Mg ratio for the reactor influent in the current study ranged from 1.04 to 1.21 (data not shown).

Bowers and Westerman (2005b) found that excessively high Mg concentrations relative to P actually reduced P removal efficiency. They reported that a Mg:TP ratio greater than 1 may reduce P removal efficiency. The molar ratio of Mg:TP in the current study ranged from 2.0 to 3.8 (data not shown, averages shown in Table 2.4), so no supplemental Mg was added during wastewater treatment. Results are mixed regarding the impact of Mg:OP ratio on struvite recovery, with some investigators finding a ratio of 1.3-1.6:1 to be optimal (Munch and Barr, 2001; Burns et al., 2003; Nelson et al., 2003). It was possible that high concentrations of Mg inhibited struvite crystal formation or precipitation, likely from the production of fine particles that could not crystallize before

being swept from the reactor. However, Huang et al. (2006) found that Mg:TP ratios as high as 3.3:1 with Ca:Mg ratios of up to 6:1 were conducive to struvite production from WWTP effluent. Even with these various conflicting findings, it was possible that the Ca:Mg, Mg:OP, or Mg:TP ratios in the dairy lagoon wastewater may not have been optimal for struvite crystallization and could partially explain the low observed efficiency.

Even at decreased efficiency, the observed simultaneous reduction of effluent P, N, and Mg concentrations suggests that Mg phosphates were precipitated during treatment. On a molar basis, 1.6 to 3 times more Mg was removed than TP (data not shown), so other Mg compounds such as dolomite must have been produced in the reactor in addition to phosphates.

A major goal of P removal from dairy wastewater is to increase the N:P ratio of the treated effluent by decreasing P concentration. This will reduce the amount of P applied to fields when wastewater is applied to crops at agronomic N rates, decreasing the chance of water quality issues resulting from P runoff. In the current study, the conventional method substantially increased the average N:P ratio in the wastewater, primarily through ammonium addition, while the new method had no effect on the average N:P ratio of the treated effluent (Table 2.3). Increasing N concentration in the effluent through ammonium addition, however, would actually reduce the volume of wastewater that can ultimately be applied to fields at N-based rates. With process improvements, lower N inputs, and greater P removal efficiency, the new treatment method could increase the N:P ratio and thus also decrease the risk of over-application of P if a given volume of wastewater is applied at agronomic N-based rates. This would

make the new method an attractive alternative when compared to the conventional treatment method.

Conclusion

Low removal efficiency compared to that observed in Bowers and Westerman (2005b) suggests that further process optimization under field conditions, particularly with dairy wastewater, is important in order to increase the P removal efficiency of this struvite crystallization technology. Previous studies have shown that P can be recovered by producing struvite crystals in a cone-shaped fluidized bed reactor; the observed performance in the current study does not match that of previous work with swine wastewater, but was similar to that observed for dairy wastewater. Further research is needed to improve removal efficiency. The particular challenges of working with real wastewater underscore the importance of using actual wastewater under field conditions during testing.

Even though removal efficiencies were comparatively low, the data suggest that Mg phosphates were precipitated from the wastewater in the reactor. This new method, with optimization and improvement, could provide a useful alternative to existing organic and conventional P fertilizers. This method of P recovery also has the potential to protect water quality while simultaneously improving the sustainability of P cycling in agriculture.

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Tables

Table 2.1. Mean concentrations and removal efficiencies of selected elements of the untreated lagoon wastewater (lagoon), acidified influent (input), and treated effluent (output) using the new process (lagoon n=16, input and output n=30). Standard deviations are listed in parentheses. Means were separated using SAS proc mixed at a significance level of $\alpha = 0.05$. Na was used as an indicator ion for dilution in the reactor, and the relative change in Na concentration was taken into account in determining dilution-corrected removal rates.

element	lagoon	input	output	mean change in concentration, input to output	mean dilution-corrected removal rate[†]
	---------- mg L^{-1} ----------			---------- % ----------	
ortho P (as P)	41 (22)^{b‡}	61 (4)^{a}	31 (15)^{c}	-49	44
total P (as P)	86 (21)^{a}	81 (11)^{b}	69 (10)^{c}	-14	9
total Mg	184 (33)^{a}	179 (17)^{a}	155 (16)^{b}	-14	9
total N (as N)	1017 (243)^{ab}	1123 (171)^{a}	955 (190)^{b}	-15	10
NH_4-N (as N)	323 (30)^{a}	319 (31)^{a}	266 (29)^{b}	-16	12
total Ca	331 (60)^{a}	322 (37)^{a}	301 (37)^{b}	-7	2
total K	478 (92)^{b}	441 (73)^{b}	610 (112)^{a}	38	-43
total Na	285 (16)^{a}	285 (14)^{a}	272 (17)^{b}	-5	0

[†] Increases in concentration from input to output are expressed as negative removal rates.

[‡] Values followed by the same lower case letter in the row indicate that the means of those sampling locations are not significantly different (at $p \leq 0.05$).

Table 2.2. Mean concentrations and removal efficiencies of selected elements of the untreated lagoon wastewater (lagoon), acidified influent (input), and treated effluent (output) using the conventional process (lagoon n=3, input and output n=5). Standard deviations are listed in parentheses. Means were separated using SAS proc mixed at a significance level of $\alpha = 0.05$. Na was used as an indicator ion for dilution in the reactor, though no dilution was expected. Since there was a slight increase in Na concentration rather than a decrease that could be attributed to dilution, no adjustment was made for dilution when calculating mean removal rates.

element	lagoon	input	output	mean removal rate[†]
	---------- mg L^{-1} ----------			%
ortho P (as P)	12.2 (9.7)[b‡]	25.5 (3.0)[a]	4.77 (2.04)[b]	81
total P (as P)	99.8 (6.5)[a]	94.9 (1.9)[a]	81.0 (4.2)[b]	14
total Mg	161 (8)[a]	154 (7)[a]	136 (3)[b]	12
total N (as N)	718 (46)[b]	675 (74)[b]	1228 (78)[a]	-82
NH_4-N (as N)	379 (42)[b]	442 (29)[b]	889 (33)[a]	-101
total Ca	311 (8)[a]	299 (9)[a]	303 (6)[a]	-1
total K	357 (18)[a]	369 (43)[a]	422 (62)[a]	-14
total Na	307 (6)[a]	294 (8)[b]	297 (6)[ab]	-1

[†] Increases in concentration from input to output are expressed as negative removal rates.

[‡] Values followed by the same lower case letter in the row indicate that the means of those sampling locations are not significantly different (at $p \leq 0.05$).

Table 2.3. Molar ratios of N:P in the wastewater showing the effect of each treatment. Ammonia added for pH adjustment in the conventional process has a noticeable effect on the N:P ratio. Calculations were performed using total N and total P concentrations from Table 2.1 and Table 2.2.

treatment method	N:P ratio before treatment (mol/mol)	N:P ratio after treatment (mol/mol)
new	31 : 1	31 : 1
conventional	16 : 1	34 : 1

Table 2.4. Molar ratios of mean concentrations of OP, TP, Mg^{2+}, and Ca^{2+} for reactor influent in the two treatment processes. It is evident that neither Mg^{2+} nor NH_4^+ is stoichiometrically limiting.

ratio	new	conventional
Mg^{2+} : NH_4^+ : OP	3.8 : 12 : 1	7.7 : 38 : 1
Mg^{2+} : TP	2.8 : 1	2.1 : 1
Ca^{2+} : Mg^{2+}	1.1 : 1	1.2 : 1

Figures

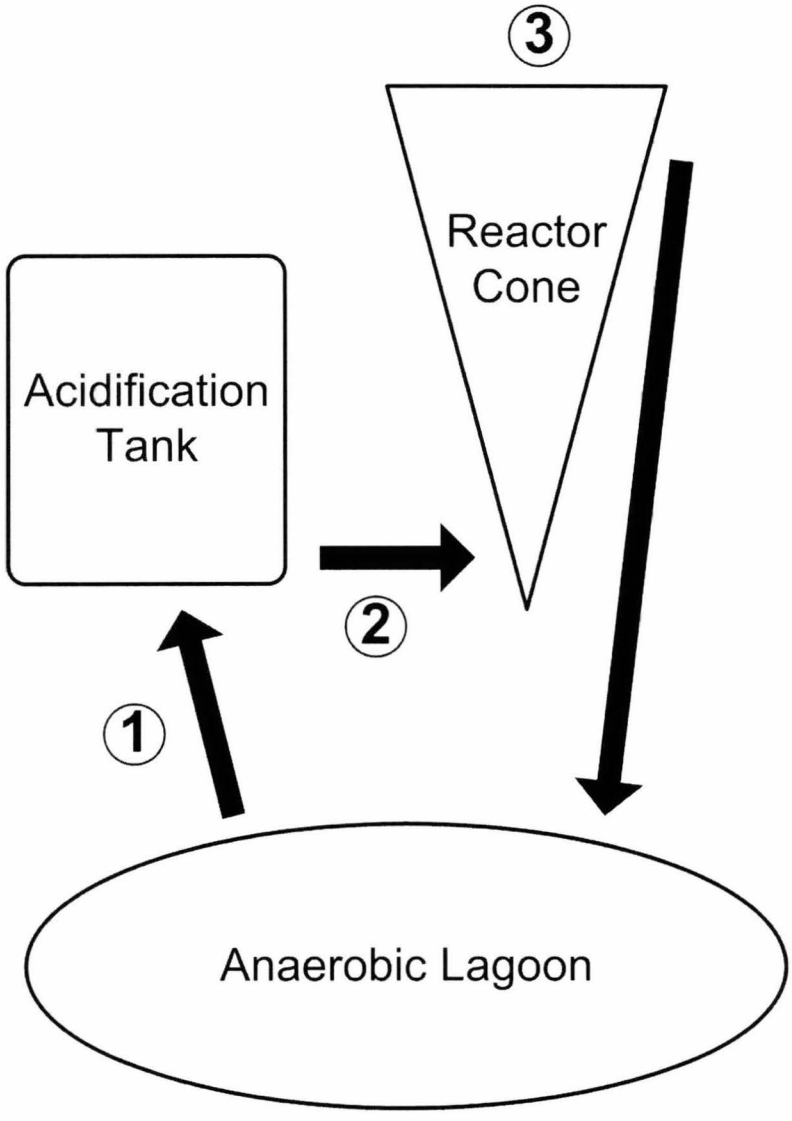

Figure 2.1. Simplified diagram of the wastewater treatment process. Black arrows show the flow of wastewater from the lagoon into the acidification tank, then into the reactor vessel, and finally back to the lagoon. Numbers denote sample locations: (1) lagoon (untreated wastewater), (2) input (acidified wastewater), and (3) output (treated effluent).

Chapter 3: Macroscopic and microscopic variation in recovered magnesium phosphate materials: Implications for phosphorus removal processes and product re-use

Abstract

Phosphorus (P) recovery and re-use will become increasingly important for water quality protection and sustainable nutrient cycling as environmental regulations become stricter and global P reserves decline. The objective of this study was to examine and characterize several magnesium phosphates recovered from actual wastewater under field conditions. Three types of particles were examined including crystalline magnesium ammonium phosphate hexahydrate (struvite) recovered from dairy wastewater, crystalline magnesium ammonium phosphate hydrate (dittmarite) recovered from a food processing facility, and a heterogeneous product also recovered from dairy wastewater. The particles were analyzed using "wet" chemical techniques, powder x-ray diffraction (XRD), and scanning electron microscopy in conjunction with energy dispersive x-ray spectroscopy (SEM-EDS). The struvite crystals had regular and consistent shape, size, and structure, and SEM-EDS analysis clearly showed the struvite crystals as a surface precipitate on calcium phosphate seed material. In contrast, the dittmarite crystals showed no evidence of seed material, and were not regular in size or shape. The XRD analysis identified no crystalline magnesium phosphates in the heterogeneous product and indicated the presence of sand particles. However, magnesium phosphate

precipitates on calcium phosphate seed material were observed in this product under SEM-EDS examination. These substantial variations in the macroscopic and microscopic characteristics of magnesium phosphates recovered under field conditions could affect their potential for beneficial re-use and underscore the need to develop recovery processes that result in a uniform, consistent product.

Introduction

Existing rock phosphate (RP) reserves are projected to last approximately another 75 to 100 years, making the recovery and re-use of phosphorus (P) necessary for the long-term sustainability of agricultural production (Driver et al., 1999). In addition to agriculture, P is used in products such as detergents, matches, and grenades and flares. As quality RP reserves continue to decline and energy prices rise, P recovery from various sources will likely become increasingly economical (Gaterell et al., 2000). Many P recovery efforts have focused on the precipitation of struvite ($MgNH_4PO_4 \bullet 6H_2O$) using "heterogeneous nucleation" crystallization processes, which precipitate phosphates onto seed particles such as sand or Ca/Mg phosphate.

Several studies (Battistoni et al., 2001; Munch and Barr, 2001; Battistoni et al., 2005; Le Corre et al., 2007) have focused on struvite, as a method for P recovery at wastewater treatment plants (WWTPs). Some studies have examined struvite recovery from swine or dairy wastewater (Bowers and Westerman 2005a; Bowers and Westerman 2005b; Zeng and Li, 2006), or in other environments (e.g., Schuiling and Andrade, 1999; Yi and Lo, 2003). Phosphorus recovery from manure is particularly attractive, as it can correct manure nutrient imbalances and help preserve water quality in agricultural areas (Greaves et al., 1999). Off-site P movement into surface waters can cause eutrophication,

making P recovery important for reducing some environmental impacts of agriculture (Randall, 2003).

In addition to struvite crystallization, some processes involve the recovery of calcium (Ca) phosphates (van Dijk and Braakensiek, 1984; Driver et al., 1999; de-Bashan and Bashan, 2004). Calcium phosphates may be more useful to the current phosphate industry, since the presence of Mg and nitrogen (N) in struvite causes problems in the manufacturing process (Schipper et al., 2001). These issues include Mg interference during P purification in the "wet" process, and nitrogenous emissions during heating in the "dry" P manufacturing process. Struvite can spontaneously precipitate in agricultural, industrial, and municipal wastewater systems (Webb and Ho, 1992; Buchanan et al., 1994; Doyle et al., 2000; Doyle and Parsons, 2002; de-Bashan and Bashan, 2004), which can be very costly in terms of downtime, cleaning, and waste disposal (Shu et al., 2006). Struvite is regarded as being more easily recovered than Ca phosphates, but due to its chemical composition, the potential for struvite re-use is currently limited to utilization as an agricultural fertilizer (Schipper et al., 2001). Recent studies have focused on the P recovery process rather than the uses of recovered P, though some evidence exists that struvite might be a useful fertilizer (Bridger et al., 1962; Rothbaum and Rohde, 1976; Lindsay, 1979; Goto, 1998; Johnston and Richards, 2003; Li and Zhao, 2003). Struvite has recently been sold as a commercial product in at least one fertilizer mixture (Ueno and Fujii, 2001).

Studies of P recovery processes tend to perform some product characterization, including x-ray diffraction (XRD) analysis (Quintana et al., 2004; Bowers and Westerman, 2005a; Le Corre et al., 2005; Wang et al., 2005), and scanning electron

microscope (SEM) examination sometimes coupled with energy dispersive x-ray spectroscopy (EDS; Battistoni et al., 2001; Wu and Bishop, 2004; Battistoni et al., 2005; Wang et al., 2005; Huang et al., 2006; Le Corre et al., 2007). These studies, however, show significant variations in the microscopic and macroscopic features of recovered products, even when one only considers studies which examine recovered Mg phosphates. Furthermore, studies generally only examine the surface layer of recovered product, even though most practical recovery processes make use of heterogeneous nucleation crystallization processes with seed particles. The recovered P products, therefore, are usually physically and chemically heterogeneous, and that heterogeneity is not always reflected in x-ray diffractograms or surface precipitate EDS analysis.

The objective of the current study was to thoroughly characterize both the exterior and interior of recovered P products made from real wastewater under field conditions.

Materials and Methods

Recovered Phosphate Materials

Four recovered phosphate materials were examined: struvite crystals manufactured in a fluidized-bed reactor at a dairy in northern Washington as described in Bowers et al. (2007); dittmarite ($MgNH_4PO_4 \bullet H_2O$) crystals recovered from the clean-up of a food processing facility pump; and a heterogeneous product manufactured at dairies in Colorado using the conventional and new processes described in chapter 2, hereafter referred to as "Colorado product". Finely ground Ca phosphate and sand material, used to seed the reactor bed, was also examined to evaluate the effects of the treatment process on the bed material (Table 3.1).

Chemical Analysis

Chemical analysis of the materials was performed at Ward Laboratories, Inc. (Kearney, NE, USA). After digestion with nitric and perchloric acid, P concentrations were measured colorimetrically (Padmore, 1990). Magnesium and Ca concentrations were measured according to the method outlined by Isaac (1990).

X-ray Diffraction Analysis

Samples of reactor seed material, struvite, dittmarite, and Colorado product were examined using XRD analysis at the Colorado School of Mines. The samples were examined using powder XRD techniques and a Scintag, Inc. (USA) model 2400 x-ray diffractometer (Cu x-ray tube, fixed slits, theta-theta design) and a scan rate of 2.00 degrees min^{-1}. Diffractograms were analyzed using the software package DMSNT (Scintag, Inc.) and the JCPDF library of diffraction patterns (International Centre for Diffraction Data).

Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy

Samples from the various products were sprinkled on a fine coat of C paint applied to a 10 x 10 mm Al stub, and the system was allowed to dry for > 24 h prior to analysis. Samples were then analyzed at an accelerating voltage of either 15 or 20 kV and a working distance between 9.9 and 10.4 mm using a JEOL-JSM 6500F Thermal Assist Emission Scanning Electron Microscope (Peabody, MA). To identify solid phase elemental associations, multivariate component and phase analysis was performed using EDS with a Thermo Scientific NORAN System SIX x-ray microanalysis system equipped with a NanoTrace Si(Li) detector (Waltham, MA).

For exterior examination and chemical characterization, particles were sprinkled on carbon paint. While this enabled the examination of the particles' three-dimensional shape, generally only very small particles could be analyzed using EDS due to the limitations of maintaining electrical ground in the microscope. For interior particle examination and chemical characterization, particles were placed in a very thin layer in the bottom of individual 0.7-cm by 1.6-cm by 1-cm deep plastic boats. Next, Acrylimet epoxy (South Bay Technology, Inc., San Clemente, CA) was gently poured over the samples and then cured for 24 h at room temperature and approximately 138 kPa of pressure. After curing, the epoxy-coated samples were removed from the plastic boats and wet wheel-polished with an Exakt 400CS microgrinder (Exakt Technologies, Inc., Oklahoma City, OK) using 1200-grit polishing paper to expose the interior of the particles. Finally, the samples were carbon coated in a vacuum evaporator (Kinney vacuum evaporator Model KDTG-3P) and analyzed as previously described.

Results

Chemical Analysis

Struvite crystals recovered from dairy wastewater contained larger and lesser amounts of Ca and Mg, respectively, than ideal struvite (Table 3.2). Dittmarite recovered from the food processing facility had slightly less Mg than ideal dittmarite. Other elements, such as Fe and Al, were not measured, so the cationic constituents of other phosphate compounds were not identified. Treatment unexpectedly lowered the concentration of P, Mg, and Ca in the Colorado product relative to the seed material due to dilution with sand and other material from the waste storage and treatment system.

X-ray Diffractograms

Samples were analyzed with XRD, and diffractograms were compared with the JCPDF library of diffraction patterns database. The diffractogram of the product recovered from dairy lagoon wastewater by Bowers et al. (2007) matched well with struvite ($MgNH_4PO_4 \bullet 6H_2O$; Figure 3.1), and the deposit recovered from the food processing facility was an excellent match with dittmarite ($MgNH_4PO_4 \bullet H_2O$; Figure 3.2). The "new" Colorado product (Figure 3.3) and RP seed material (Figure 3.4) were heterogeneous, a mixture of quartz, carbonate fluorapatite, calcite, and dolomite. No Mg phosphate crystalline phases were identified in the Colorado product samples by XRD.

SEM Images

Since no crystalline Mg phosphates were identified in the Colorado product analyzed by XRD, but wastewater analysis indicated that Mg and P were being removed from the wastewater during treatment (see chapter 2), Colorado product samples, and the other samples as well, were examined using SEM. The struvite crystals recovered from dairy wastewater had a crystalline, large, and homogeneous nature (Figure 3.5). Examination of "conventional" method Colorado product found smaller, less crystalline particles (Figure 3.6). Though the recovery methods and setup were very similar between the struvite crystals and Colorado product, the product differences were striking. Examination of dittmarite crystals found regions exhibiting a dendritic crystalline structure (Figure 3.7), and other particles (not shown) had blocky crystalline features. Particles of Mg phosphate in the Colorado product made with the "new" treatment process were generally very small and irregular in nature (Figure 3.8).

EDS Analysis

Energy dispersive x-ray spectroscopic analysis of the Colorado product was important to finding non-crystalline phases of Mg phosphates or crystalline phases in concentrations too low for XRD identification. The EDS also yielded structural information regarding the recovered struvite and dittmarite. The EDS interior images of the struvite manufactured by Bowers et al. (2007) showed Mg phosphate crystals precipitated on the Ca phosphate seed material surface (Figure 3.9). No evidence of heterogeneous nucleation (seed material) was found using EDS analysis of the crystalline dittmarite from the food processing plant (Figure 3.10). In Figures 3.11 and 3.12, one can see partial coverage of the surface of several Ca phosphate seed particles with a Mg phosphate phase, which may or may not be crystalline. The EDS component analysis demonstrated several different possibilities for the form of recovered Mg phosphates: heterogeneous nucleation with crystals completely surrounding seed particles (Figure 3.9); homogeneous nucleation or heterogeneous nucleation on pipe surfaces rather than seed particles (Figure 3.10); or as a crystalline or amorphous precipitates partially covering seed materials (Figure 3.11 and 3.12). Precipitated Mg phosphates were only observed on Ca phosphate seeds, rather than Si oxide seeds, in the Colorado product materials. However, this does not preclude the presence of Mg phosphate precipitates on Si oxide mineral phases in these samples. Such a case was simply not observed during SEM-EDS examination.

Discussion

Along with the fine Mg phosphate particles in Figures 3.6 and 3.8, the Mg phosphate precipitates depicted in Figures 3.11 and 3.12 provide microscopic evidence

that helps explain the macroscopic performance of the process outlined in chapter 2. Magnesium and P were removed in the reactor as Mg phosphate precipitates, either as fine Mg phosphate particles formed by homogeneous nucleation or a surface precipitate on a seed particle formed by heterogeneous nucleation. However, the Mg phosphate phases were neither regular nor did they completely cover the seed material, as in the large, physically homogeneous material depicted in Figures 3.5 and 3.9.

Formation of the Different Materials

The physical and chemical differences in the different materials can be linked to the conditions of their formation. The crystalline struvite precipitated by heterogeneous nucleation on Ca phosphate seed particles by Bowers et al. (2007) was an example of the "successful" application of a P recovery process on a field-scale. Particles were relatively large and were homogeneous in size, external and internal structure. Experimental evidence suggests that in order to achieve this, chemical conditions, physical conditions, and retention time must be adequate for crystals to grow to a sufficient size. Stratful et al. (2001) found that increased retention time was associated with larger recovered crystals. This was especially true for complex wastewater matrices where organic matter or other ions could interfere with crystallization by blocking crystal growth sites and delaying crystal formation (Schuiling and Andrade, 1999; Valsami-Jones, 2001; van der Houwen and Valsami-Jones, 2001; Le Corre et al., 2005).

In contrast, the Colorado product particles showed a combination of homogeneous nucleation resulting in the formation of fine particles (Figure 3.6, Figure 3.8), and seed particles incompletely covered by precipitate (Figure 3.11, Figure 3.12). These Mg phosphates cannot be confirmed as struvite by the methods of this study, but

ammonia removal was observed in the water treatment process, as reported in chapter 2. Additionally, Babic-Ivancic et al. (2006) found that struvite, rather than newberyite ($MgHPO_4 \bullet 3H_2O$), formed at a higher pH and high ammonium phosphate concentration, such as the concentrations and pH measured in chapter 2. Thus, strong evidence supports the contention that Mg phosphates observed in the Colorado product were Mg ammonium phosphates rather than Mg phosphates such as newberyite.

Regardless of which Mg phosphate phase formed in the reactor, with a longer retention time the fine particles could have become larger crystals just as the layer of Mg phosphate precipitate (Figures 3.11 and 3.12) could have grown if conditions were more conducive. Short retention times, excessive mixing velocities in the reactor, and interference from ions and organic ligands could have influenced product formation with these irregular characteristics.

A further difficulty stemming from the field-scale nature of this study was that sand was most likely swept up into the crystal bed in the Colorado product, diluting the useful nutrients in the recovered material and possibly reducing the effectiveness of the reactor. Wang et al. (2006) noted that the effectiveness of struvite powder was greater than that of sand as a seed material. The presence of Mg phosphate precipitate on Ca phosphate seed material but not on sand (Figure 3.11) supports the contention that Mg phosphates preferentially precipitated onto the surface of other phosphates over that of sand grains.

The crystalline dittmarite was unique in this study in that it was not recovered from an engineered P recovery process, but rather as a true waste product from the cleaning of an industrial facility. Le Corre (2006) provided an excellent review of

locations and conditions likely to cause scaling in wastewater treatment. These conditions include high concentrations of the component ions of struvite and a motivating force for precipitation such as pH change associated with turbulence in pumps and turns in pipes. Dittmarite could have formed as a result of high temperatures either during operation or cleaning. Sarkar (1991) and Bhuiyan et al. (2008) found that struvite loses five of its water molecules when boiled with excess water, becoming dittmarite. This, along with SEM-EDS analysis confirming the lack of seed particles in the dittmarite sample, supports the notion that this sample formed as a scale deposit. Crystal growth likely began through heterogeneous nucleation on pipe or pump surfaces, and high temperature water (either during normal operation or cleaning) made conditions ideal for the monohydrate, rather than hexahydrate, crystal.

Practical Implications of Material Characteristics

The most common use usually suggested for recovered struvite is as an agricultural fertilizer. Le Corre et al. (2007) identified the size, purity, and morphology of recovered materials as critical factors in the materials' successful recovery and re-use as fertilizer. All of the materials examined in this study were easily handled, but the quantity and form of useful nutrients varied greatly among materials. Only one material examined in this study, dittmarite, was relatively pure, but chemical analysis showed that even it contained impurities. The crystalline struvite was pure, but the seed material was also a major component of the recovered material. The Colorado product contained substantial amounts of sand, and no crystalline Mg phosphate was identified by XRD. Struvite and dittmarite both showed regular morphology, but the form of Mg phosphate

in the Colorado product was unclear. These inconsistencies may limit some recovered P materials' potential for use as a fertilizer.

More importantly, material differences could affect their fertilizer effectiveness. Although chemically identical, different struvite morphologies, including dendritic and rod-like crystals, have been shown to have different dissolution kinetics linked to differences in surface area (Babic-Ivancic et al., 2002). Chemical differences, such as the Mg phosphate layer surrounding the Ca phosphate seed material shown in Figure 3.9, will also affect solubility and phosphorus availability over time as the materials dissolve in soil solution.

Though the solubility of amorphous Mg phosphate materials has not been studied, Valsami-Jones (2001) noted that amorphous Ca phosphates were generally more soluble than crystalline forms, and Bauer et al. (2007) found recovered amorphous Ca phosphate to be an effective fertilizer in a greenhouse study. Similarly, amorphous or semi-crystalline Mg phosphates such as those observed in the Colorado product samples may be more plant-available than crystalline forms. Lindsay (1979) stated that Mg phosphates can be discounted as permanent P fixation products in soils, and thus Mg phosphates should constitute useful fertilizers for supplying readily plant-available P.

Several authors (Bridger et al., 1962; Sarkar, 1991; Bhuiyan et al., 2008) noted that dittmarite gradually re-hydrates to struvite at environmentally relevant temperatures and in the presence of water. Dittmarite is a more economical form of P to transport since it has a greater P concentration, but difficulties in manufacturing or differences in solubility and dissolution kinetics could ultimately impact its usefulness as a P fertilizer.

Indeed, at present no process exists for its manufacture, limiting the practical viability of dittmarite crystals as fertilizer.

Conclusion

Though most P recovery research to date has focused on the wastewater treatment phase of P recovery and re-use, this examination of various recovered P materials indicated that macroscopic reactor performance does not guarantee that the resulting product is chemically or physically desirable as a P fertilizer. Even if macroscopic analysis indicated the presence of Mg phosphates, the microscopic and chemical properties of actual recovered Mg phosphate materials could vary quite widely. These microscopic and chemical properties could have a significant impact on the potential for beneficial re-use of the product. Furthermore, the possibility for recovery and beneficial re-use of other Mg phosphates, such as scale deposits, may be similarly hampered by uncertainty linked to the chemical and thermal transformation of struvite, dittmarite, and newberyite, all of which have different mineralogical characteristics.

In this study, both the exterior and interior of recovered P products made from real wastewater under field conditions were characterized. X-ray diffraction analysis identified crystalline struvite in a product recovered from dairy wastewater, and dittmarite in a material from a food processing plant, but could not identify crystalline Mg phosphates in a third sample, the Colorado product, also from dairy wastewater. Wastewater analysis, however, suggested that Mg phosphates were indeed precipitating on to the Colorado product sample, which SEM-EDS examination confirmed. The SEM-EDS analysis also clearly showed chemical and physical differences in all of the recovered materials. These differences may affect the eventual usefulness of the

recovered P materials as fertilizers, underscoring the importance of microscopic examination and consistent product characteristics in any commercially viable recovered P fertilizers eventually developed.

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Tables

Table 3.1. Qualitative physical description of recovered struvite, dittmarite, Colorado product, and seed material examined in this study.

material	physical description
struvite	brown in color, regularly shaped sand-sized particles, some small pieces of cellulosic organic material
dittmarite	pure white, irregular shapes and sizes ranging from large pebbles to extremely fine powder
Colorado product (both methods)	heterogeneous mixture of sand, small pieces of organic matter, sand-sized white particles, and fine powder
seed material	tan in color, finely ground particles, some heterogeneity

Table 3.2. Mass percentages of recovered and pure phosphates, and seed material used for Colorado product (n=3 for recovered phosphates and seed material). Standard deviations are shown in parentheses for recovered materials. Composition of pure substances from Bridger et al. (1962).

material	P (% by mass, as P)	Mg (% by mass)	Ca (% by mass)
struvite (dairy wastewater)	12.3 (0.2)	4.2 (0.3)	17.9 (0.9)
struvite (ideal)	12.62	9.91	0.0
dittmarite (food processing plant)	19.8 (0.1)	12.2 (0.6)	< 0.1
dittmarite (ideal)	19.94	15.65	0.0
Colorado product (dairy wastewater)	7.1 (0.3)	0.41 (0.01)	18.3 (1.0)
Seed material for Colorado product	7.94 (0.04)	0.73 (0.02)	22.2 (1.0)

Figures

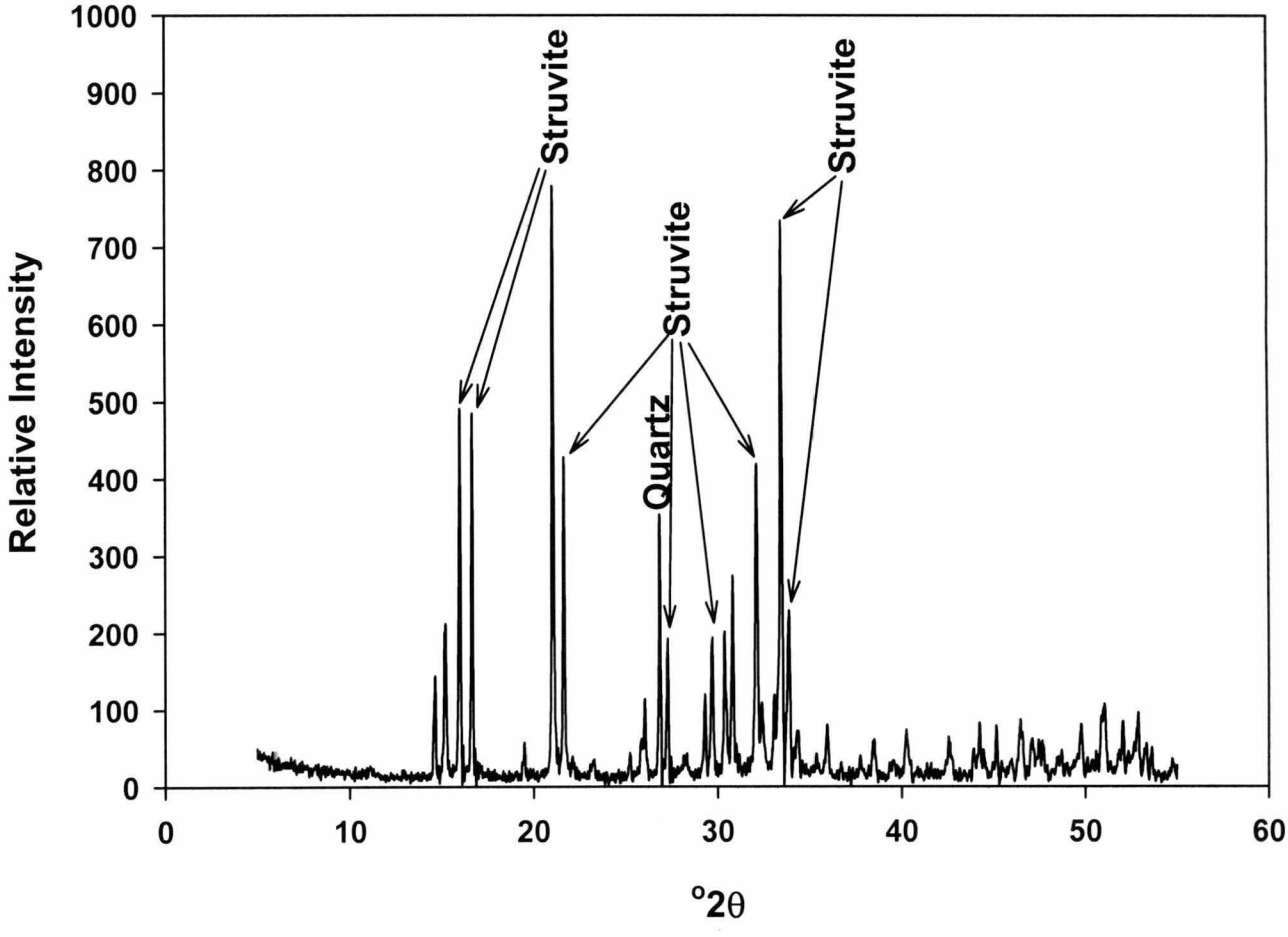

Figure 3.1. X-ray diffractogram of struvite crystals (JCPDF #15-0762) recovered from dairy wastewater using a fluidized bed reactor seeded with ground calcium phosphate. Differences from a pure struvite diffraction pattern are likely attributable to the presence of seed material such as quartz (JCPDF #46-1045).

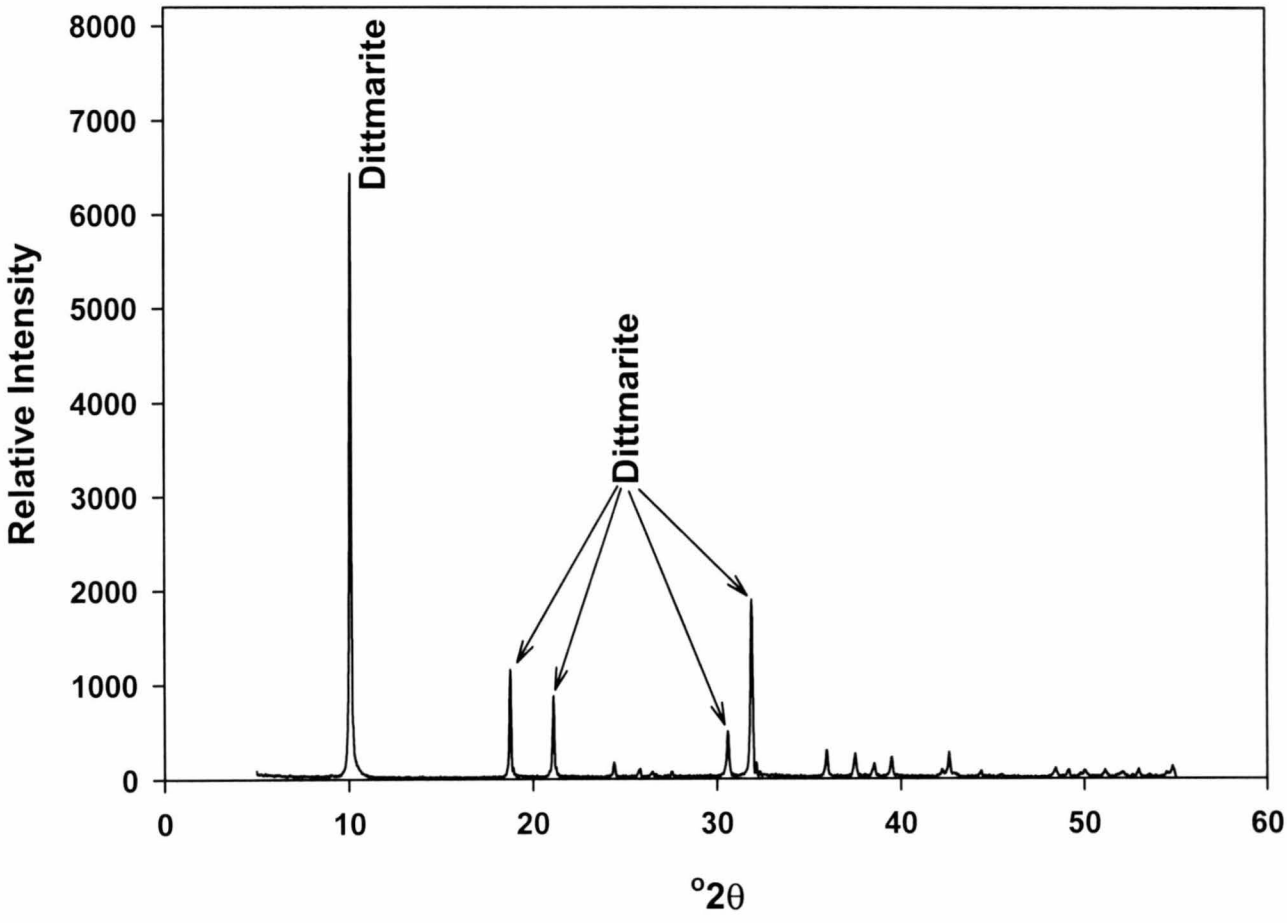

Figure 3.2. X-ray diffractogram of dittmarite crystals (JCPDF #20-0663) recovered from a food processing plant during cleaning.

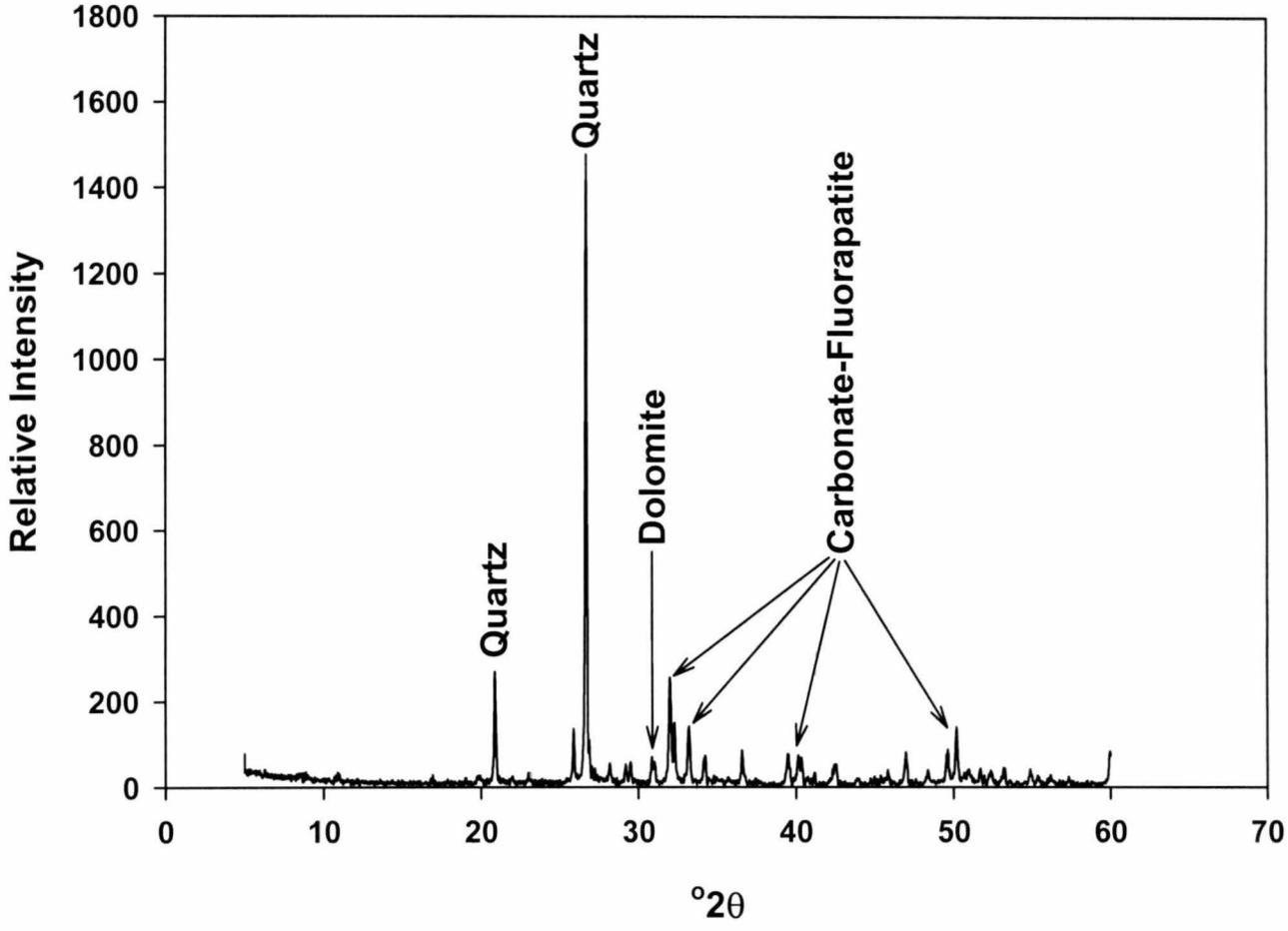

Figure 3.3. X-ray diffractogram of Colorado product material using the "new" method. Analysis of diffractogram showed crystalline phases of quartz (sand, JCPDF #46-1045), carbonate fluorapatite (JCPDF #31-0267), and dolomite (JCPDF #36-0426). The conventional method diffractogram was similar, but with a small, unidentified peak at low 2-theta angle.

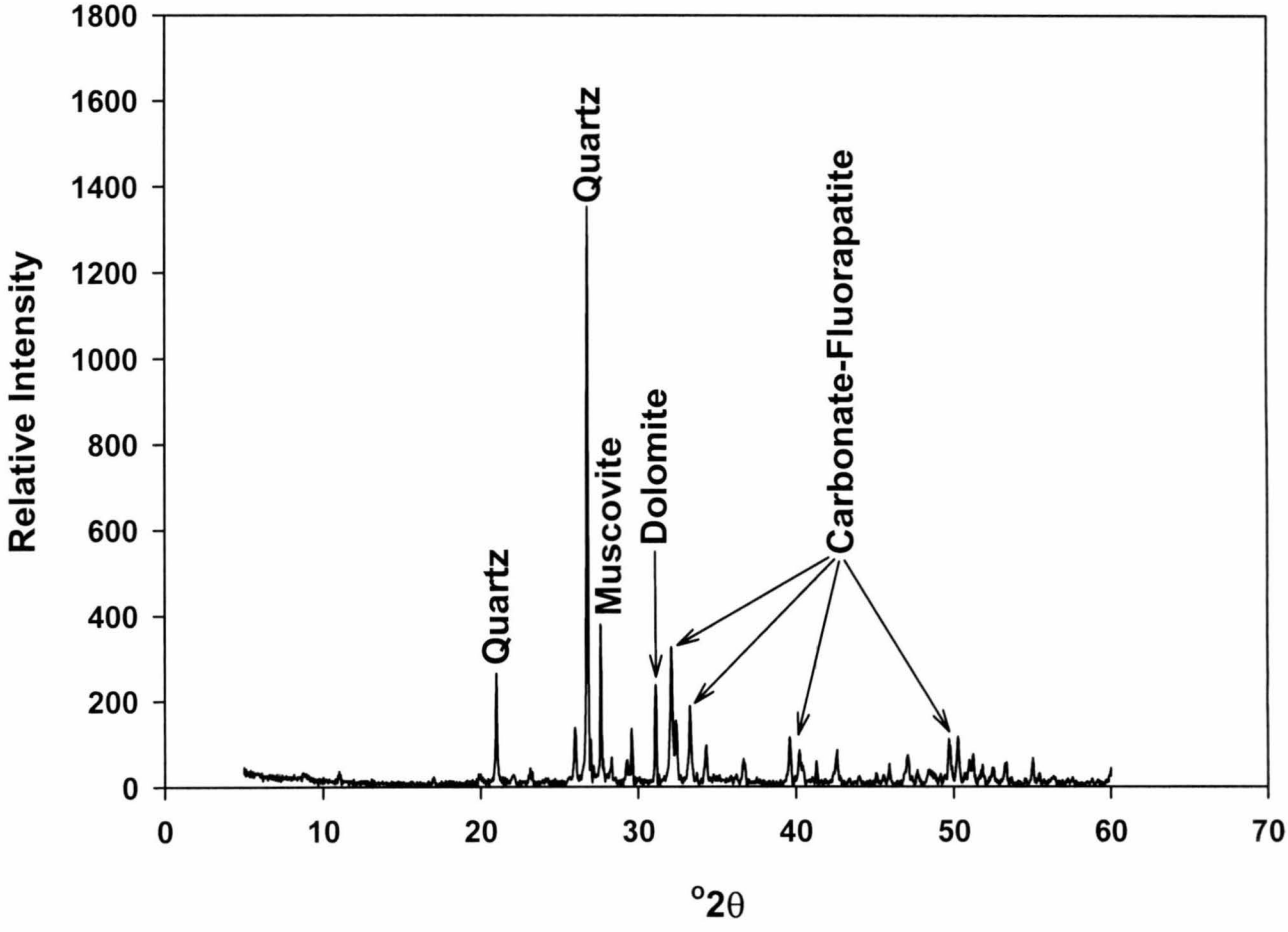

Figure 3.4. X-ray diffractogram of reactor seed material used in making Colorado product. Analysis of diffractogram showed crystalline phases of quartz (sand, JCPDF #46-1045), carbonate fluorapatite (JCPDF #31-0267), dolomite (JCPDF #36-0426), calcite, whitlockite, and traces of muscovite (JCPDF #46-1409) and illite.

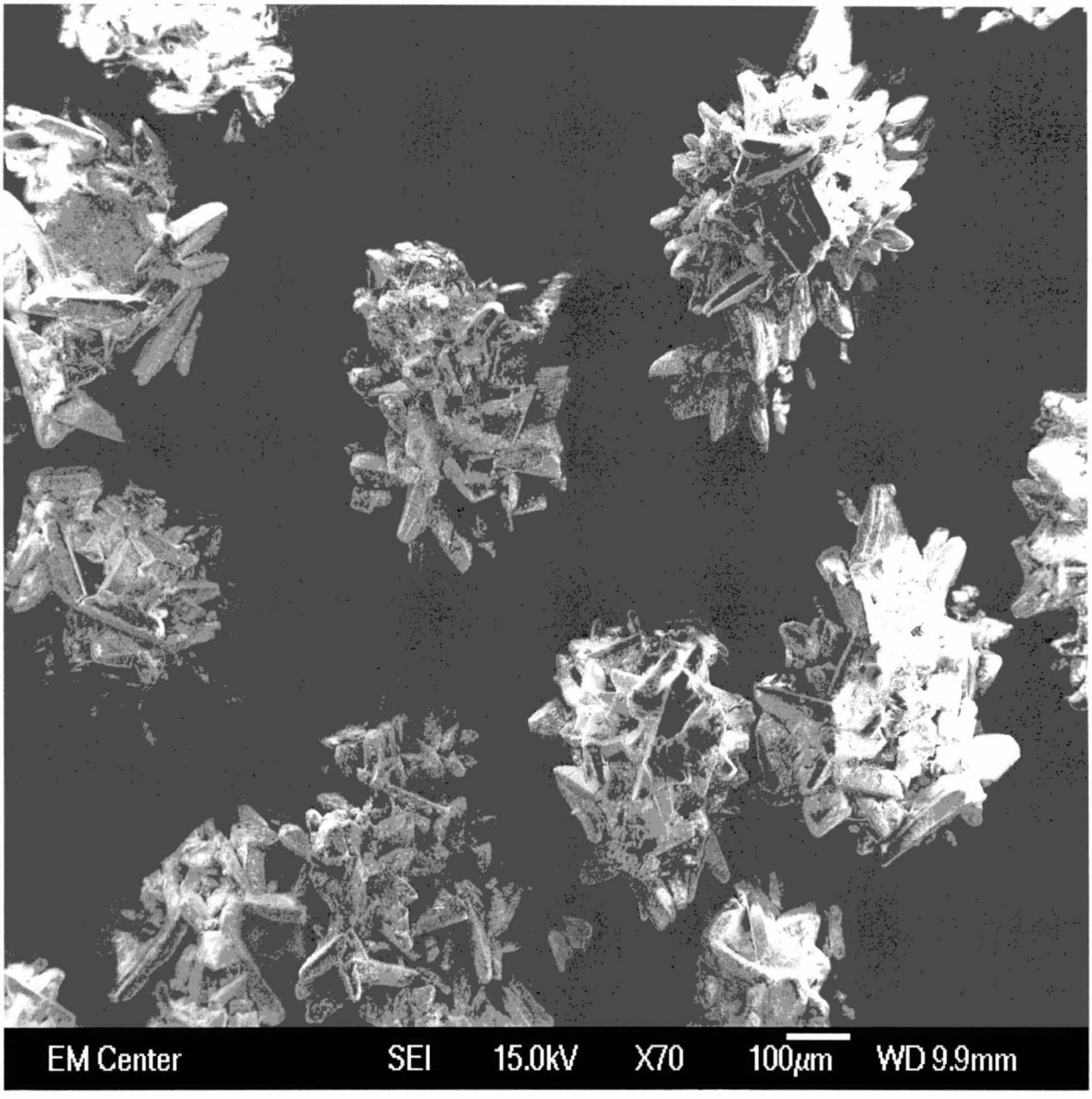

Figure 3.5. Scanning electron micrograph of struvite crystals recovered from dairy wastewater by Bowers et al. (2007) using the "conventional" method. The energy dispersive x-ray analysis of the exterior layer of a single particle showed an approximate 1:1 molar ratio of Mg:P, with a molar composition of 11.78% P, 12.65% Mg, 0.38% Ca, 70.44% O, 2.18% S, and 1.89% Fe.

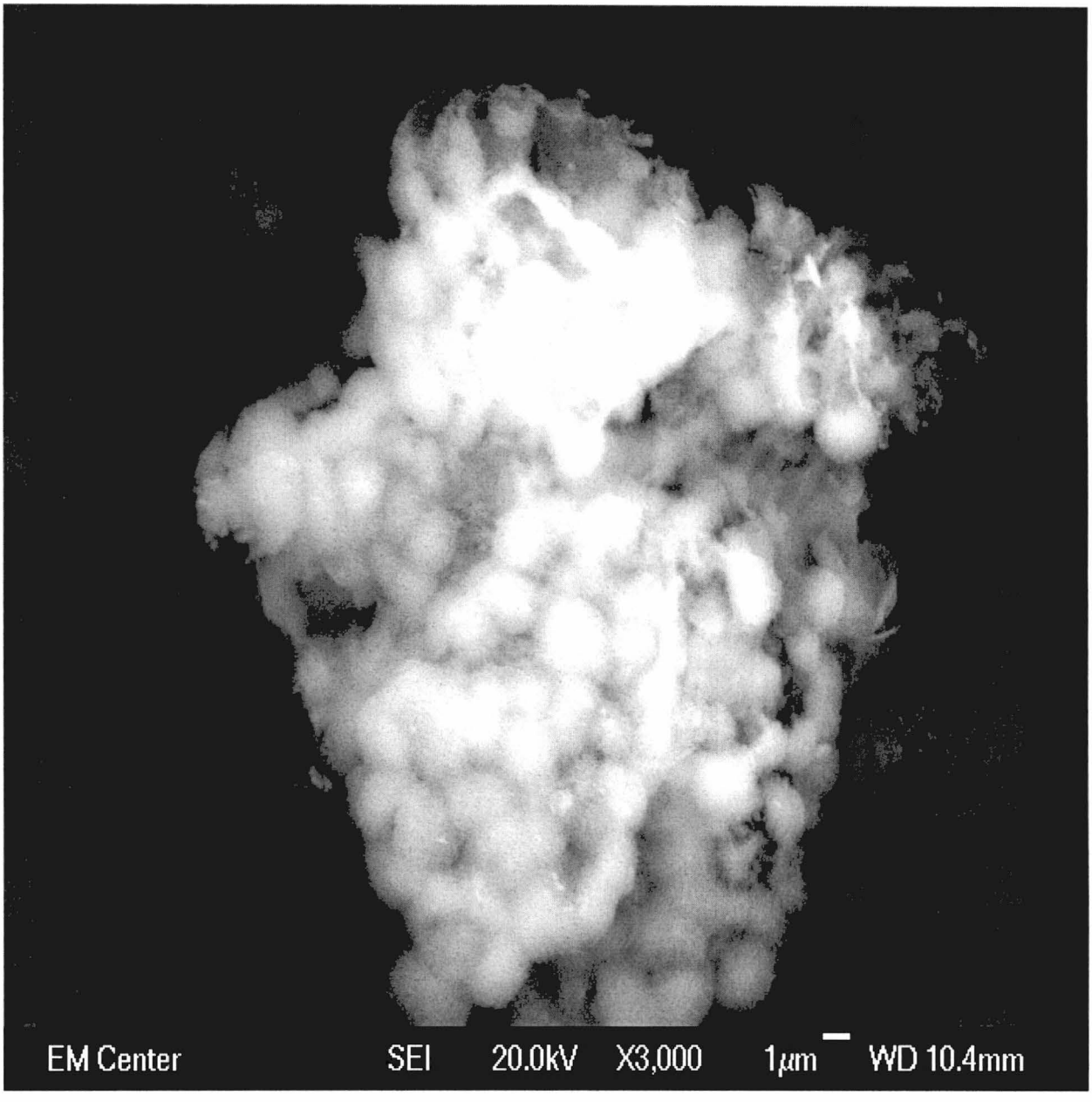

Figure 3.6. Scanning electron micrograph of a Colorado product particle produced using the same method as the particle in Figure 3.5 (the "conventional" method). The energy dispersive x-ray analysis showed a molar composition of 12.91% P, 9.99% Mg, 5.17% Ca, 66.18% O, 2.02% Si, and small amounts of Fe, K, and Cu. Note the small size and semi-crystalline nature of the particle.

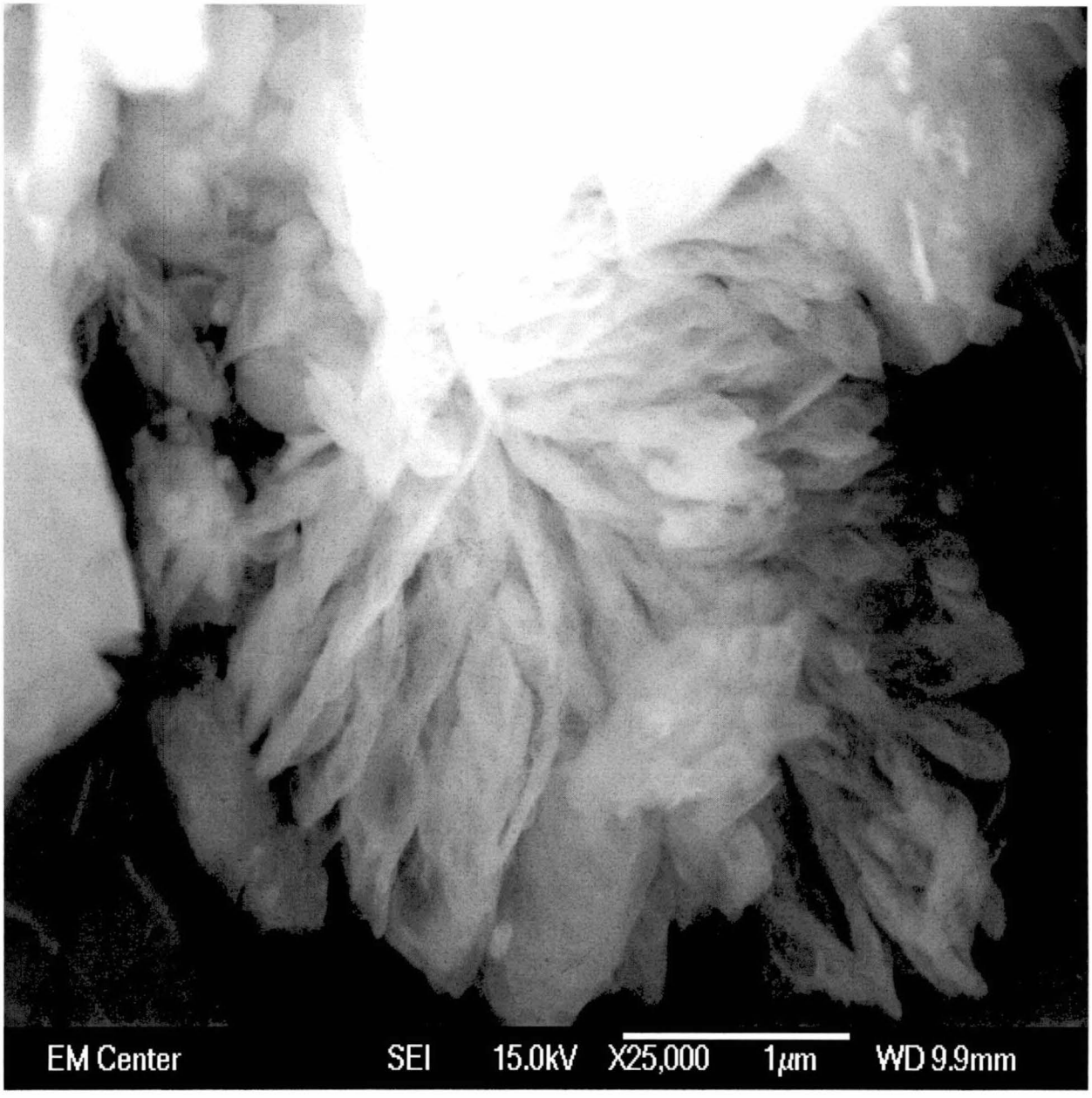

Figure 3.7. Scanning electron micrograph of a small region of dittmarite crystals recovered from a food processing facility. This region is notable for its dendritic ("tree-like") crystalline structure. The energy dispersive x-ray analysis showed a molar composition of 18.55% P, 16.86% Mg, 63.57% O, and 1.02% Fe.

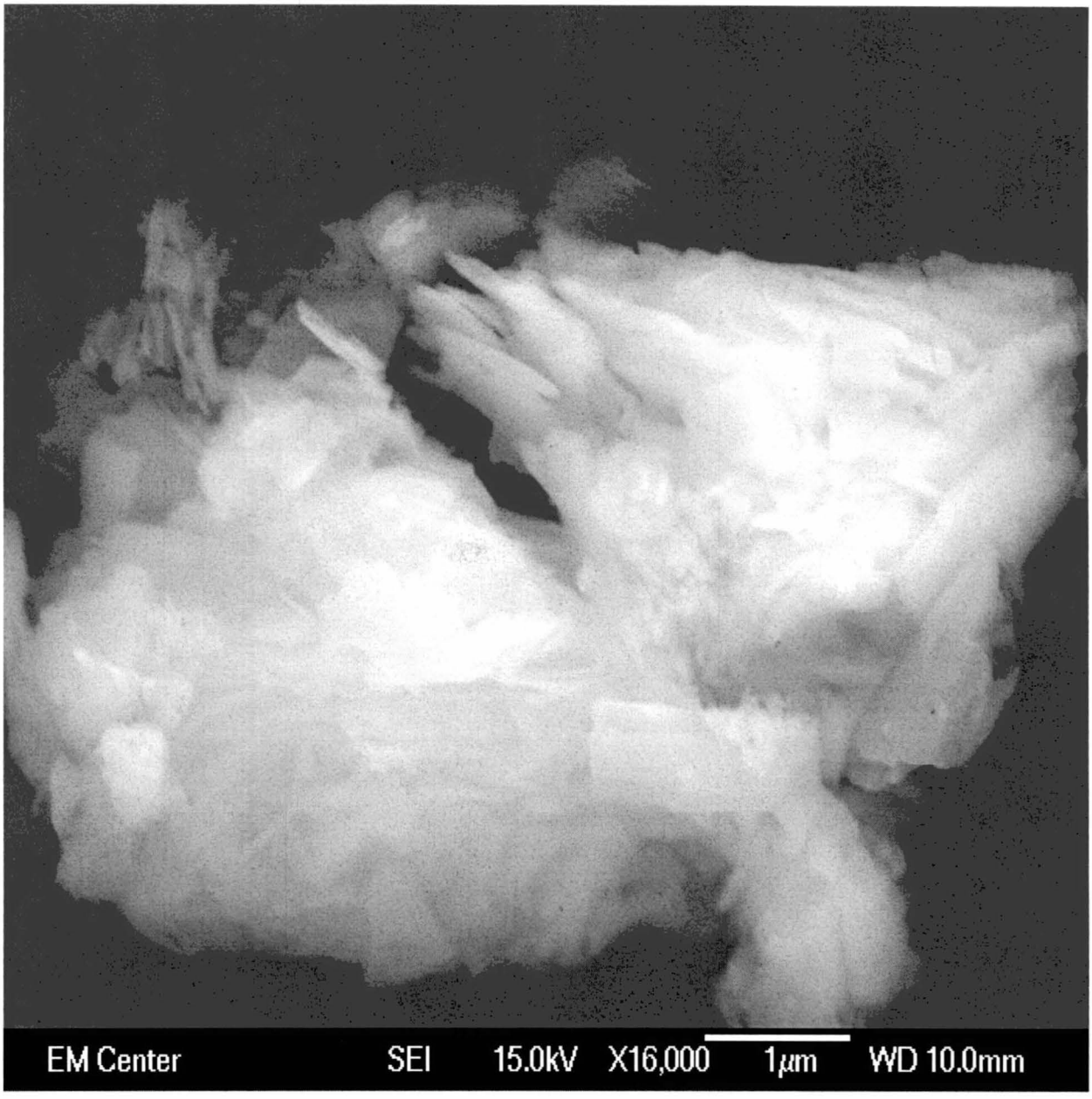

Figure 3.8. Scanning electron micrograph of a small Mg phosphate particle found during examination of the "new method" Colorado product samples. The energy dispersive x-ray analysis showed a molar composition of 16.40% P, 16.40% Mg, 64.86% O, and traces of Fe, Al, Si, and Ca.

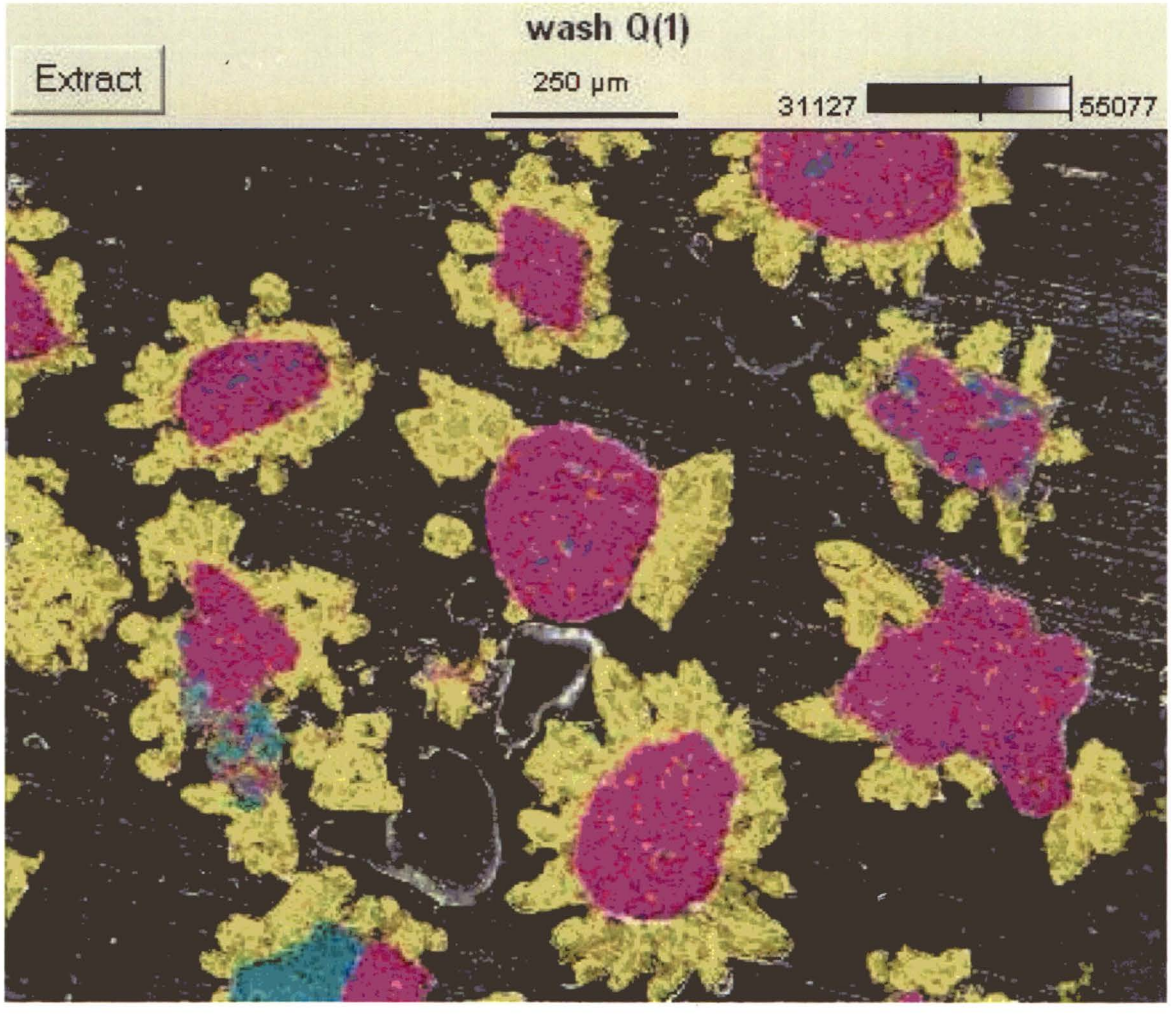

Figure 3.9. Energy dispersive x-ray component analysis of the inside of recovered struvite crystals. Calcium phosphate seed material is shown in magenta (center of particles), and Mg phosphate crystals are shown in yellow (outside edge of particles). Silicon oxides (sand) in the seed material can also be seen in cyan (center of particles, lower left).

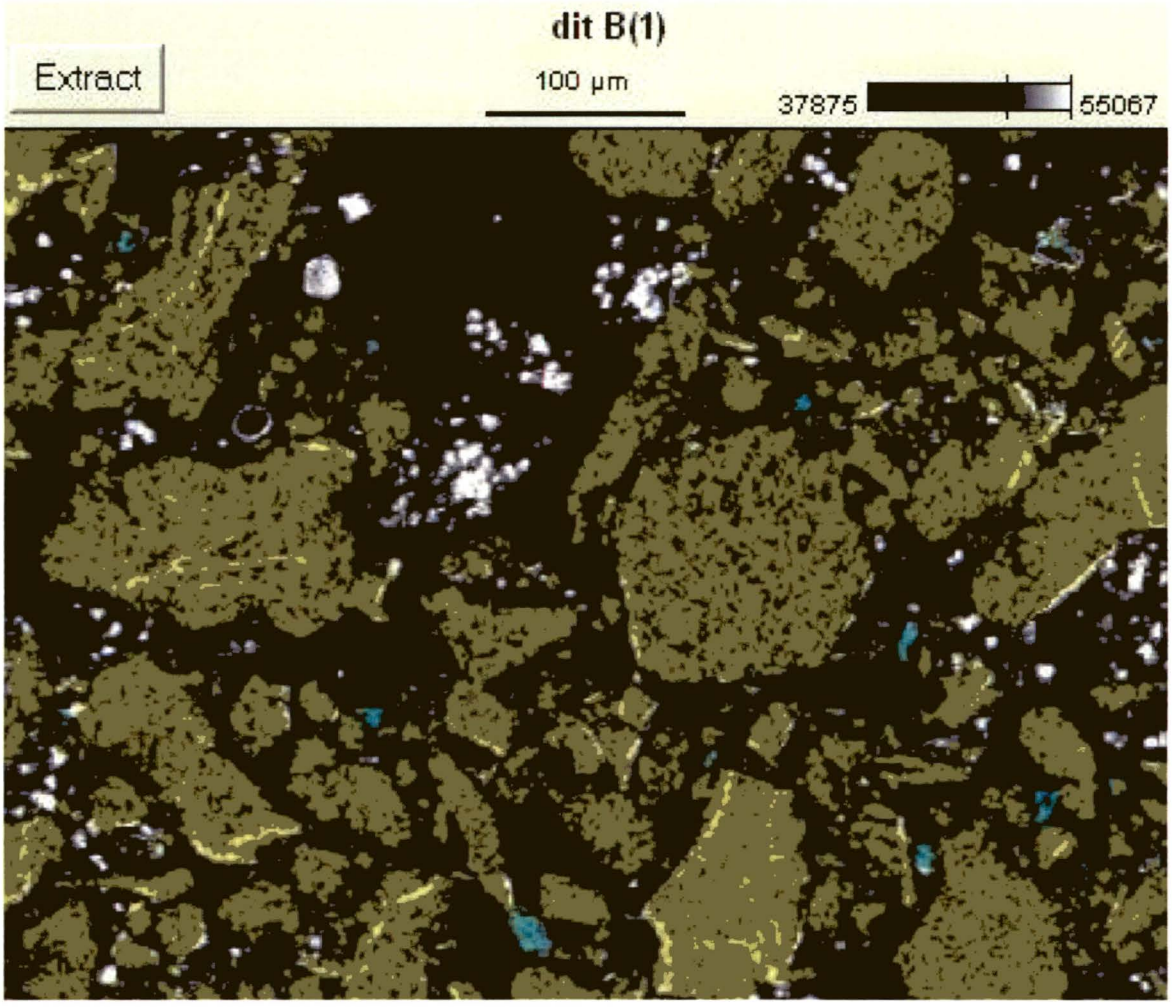

Figure 3.10. Energy dispersive x-ray component analysis of the inside of recovered dittmarite crystals. Only Mg phosphate (yellow) and Si oxide particles (cyan) were observed, with no evidence of seed particles for the Mg phosphates.

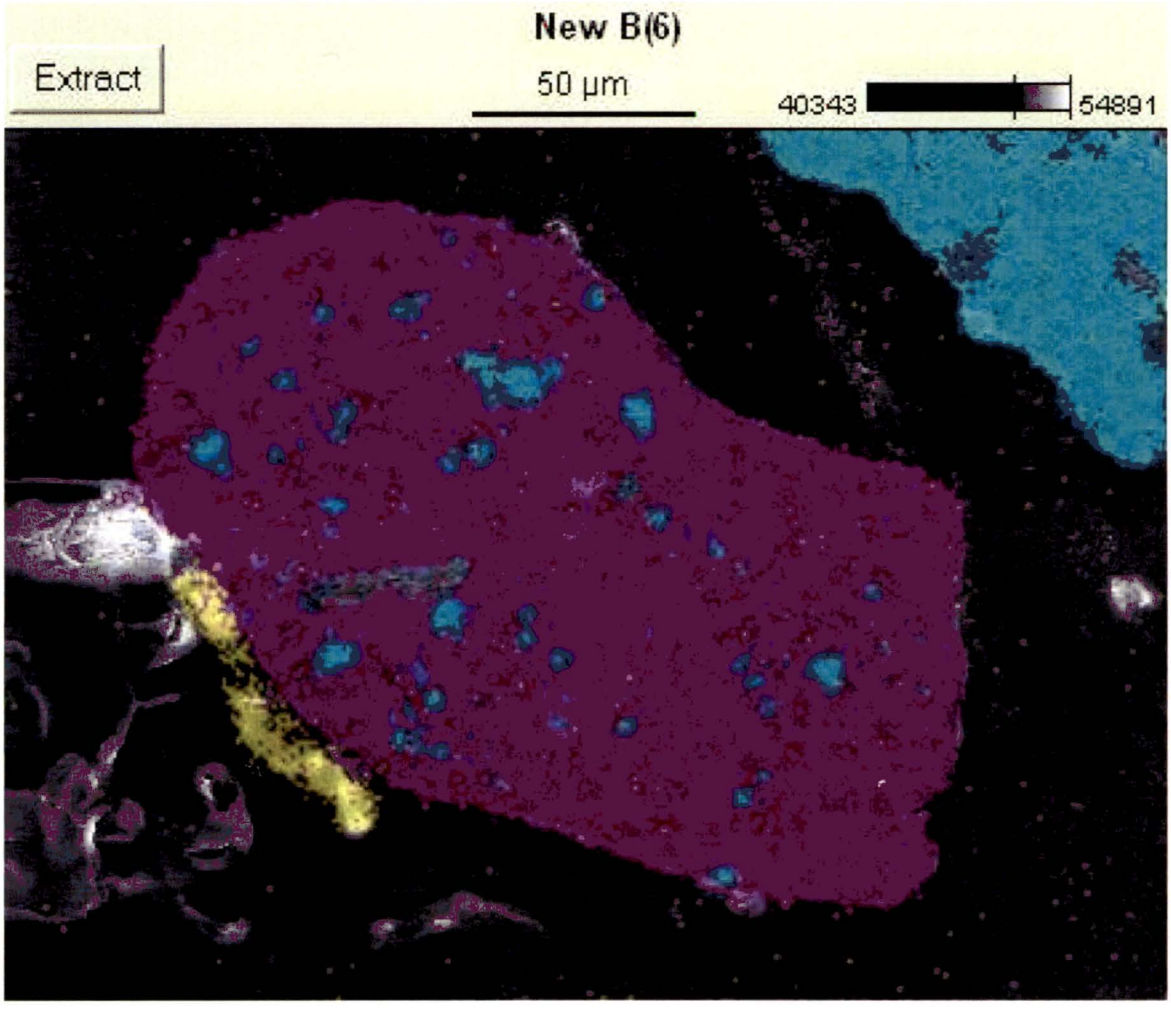

Figure 3.11. Energy dispersive x-ray component analysis of Colorado product particles. The Ca phosphate seed crystal (magenta) had a Mg phosphate surface layer precipitate (yellow). No Mg phosphate layer was observed on the Si particle in the upper right (cyan), or on other Si particles.

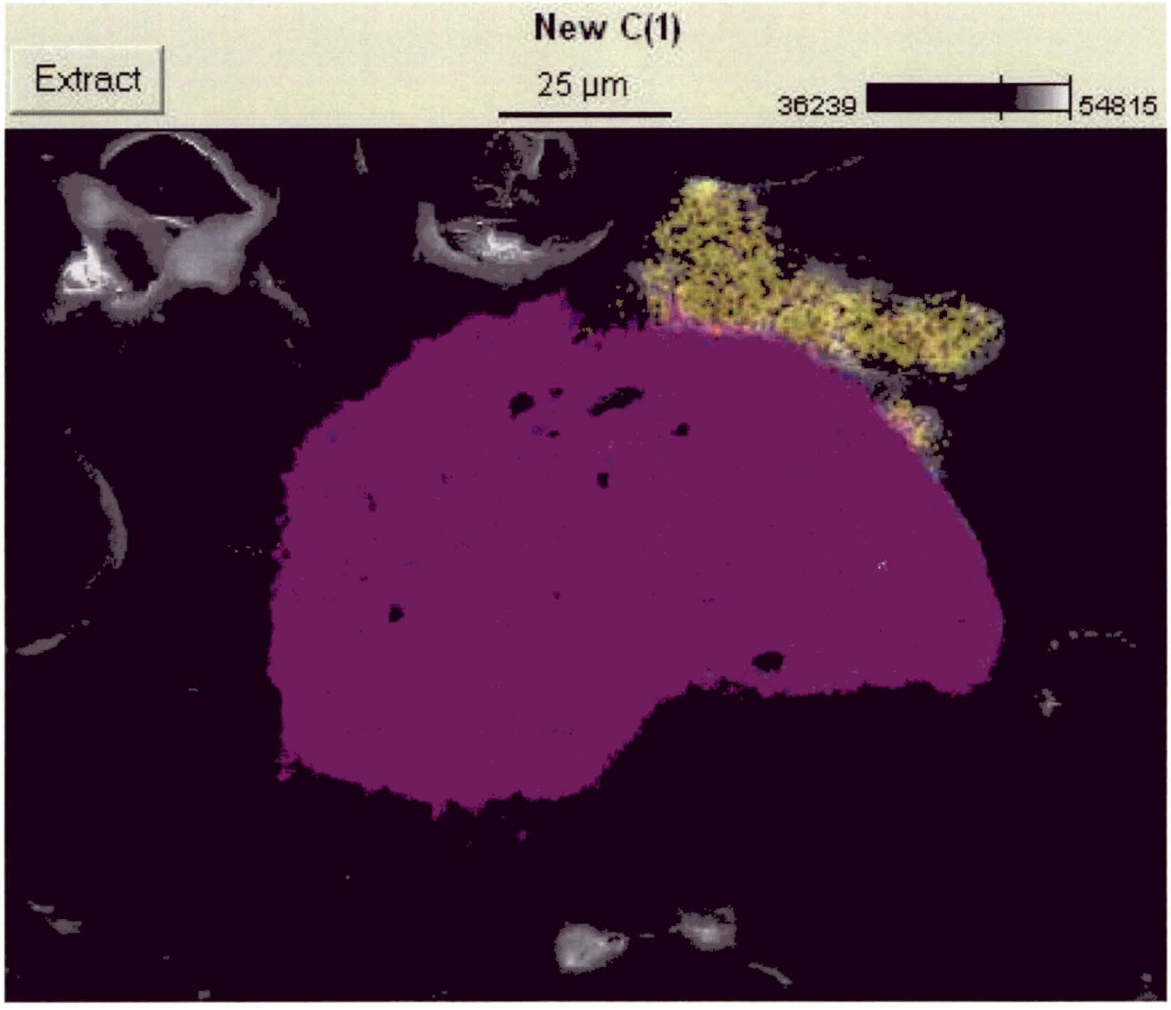

Figure 3.12. Energy dispersive x-ray component analysis of another Colorado product particle. The Ca phosphate seed crystal (magenta) had a Mg phosphate surface precipitate that may have been crystalline in nature (yellow).

Chapter 4: The effectiveness of recovered magnesium phosphates as fertilizers in acidic and slightly alkaline soil conditions

Abstract

Magnesium phosphates such as struvite ($MgNH_4PO_4 \bullet 6H_2O$) can be recovered from municipal, industrial and agricultural wastewaters. However, minimal research has been conducted on the beneficial reuse of these recovered products; conducted research has focused on low pH soils. This study determined whether recovered struvite and dittmarite ($MgNH_4PO_4 \bullet H_2O$) were effective P fertilizers in alkaline soils. In addition to commercially available triple superphosphate (TSP) and certified organic RP, recovered struvite, dittmarite, and a heterogeneous recovered phosphate were evaluated in a laboratory dissolution study and as fertilizers for spring wheat (*Triticum aestivum L.*) in a greenhouse study. Struvite and dittmarite were much more soluble than RP, but less soluble than TSP. Laboratory dissolution kinetics were fast, with most materials nearing equilibrium within 24 hours. At a soil pH of 6.5, both dittmarite and struvite increased the average plant P concentration over the control. Struvite and dittmarite performance was similar to TSP. There were no significant differences in plant dry matter (DM) production or total P uptake at pH 6.5. In the limed soil (pH 7.6), many treatments had plant P concentrations significantly lower than the control, but most fertilizers increased DM production over the control; all fertilizers generally performed similarly to one

another. These findings support previous work showing recovered Mg phosphates to be effective in acidic soils, and provide evidence that they are also effective in alkaline soils. Recovered Mg phosphates could become a useful alternative for P fertilization in arid and semi-arid environments.

Introduction

Enrichment of surface waters with phosphorus (P) from municipal wastewater treatment discharge or agricultural runoff is an important water quality concern that can lead to eutrophication (Carpenter et al., 1998). The recovery of P by crystallization from municipal and agricultural wastewater has the potential to reduce eutrophication while creating relatively pure, useful byproducts. While it is unclear exactly how long existing rock phosphate (RP) reserves will last, P is a limited resource and its re-use is necessary for the long-term sustainability of agricultural and industrial production (Driver et al., 1999). Recovery efforts have focused on wastewater treatment plants (WWTPs), where spontaneous struvite precipitation can be destructive to facility operations (de-Bashan and Bashan, 2004). There exist several full-scale, working examples of WWTPs using crystallization processes for P removal. Depending on the process, the product recovered is either calcium (Ca) phosphate (apatite) or magnesium (Mg) phosphate (struvite, dittmarite, or newberryite) (Driver et al., 1999; de-Bashan and Bashan, 2004). At least one plant sells recovered struvite ($MgNH_4PO_4 \bullet 6H_2O$) as a slow-release component of a commercial fertilizer mix (Ueno and Fujii, 2001).

Recently, on-site P removal from agricultural wastewater has become a focal point of research. Greaves et al. (1999) noted that P is typically more concentrated in manures than in sewage, making manure an ideal target for P recovery. The authors also

noted that while land application is the preferable method of manure P re-use, application of manure to meet crop nitrogen (N) needs results in the over-application of P. Phosphorus recovery through crystallization could be used to correct this imbalance, and could also reduce a farm's land base requirement. Ideally, a crystalline product for agricultural re-use would have a high P concentration and could be easily dried, handled, marketed, and transported at a fraction of the cost of manure or compost.

A number of wastewater P removal technologies exist, such as that outlined in Bowers and Westerman (2005a, 2005b), which utilizes a cone-shaped fluidized bed crystallizer. However, very few studies have evaluated the use of the recovered products. Many recovery processes focus on Mg phosphates such as struvite, but few applications for recovered struvite have been tested. The chemical composition of struvite makes it impractical for use as a raw material in the modern P industry (Driver et al., 1999; Schipper et al., 2001). Bridger et al. (1962) noted the effectiveness of struvite and dittmarite as fertilizer for turf, on ornamentals and flowers, in forests and orchards, and even on field crops. More recently, Johnston and Richards (2003) compared a variety of recovered phosphate fertilizers in a greenhouse setting, and found recovered struvite to be an effective fertilizer for ryegrass on soils with pH 6.6 and 7.1. Recovered struvite from a Hong Kong landfill leachate was found to be as effective as commercial fertilizer for vegetables grown on a nutrient-poor soil with pH 6.2 (Li and Zhao, 2003). Goto (1998) found recovered struvite granules to be an effective fertilizer for winter greens in a soil with pH 5.8 that had been amended with lime to an unspecified pH level. Bauer et al. (2007) examined the usefulness of recovered Ca phosphates in a greenhouse setting, on soil with a pH of 4.9, amended with lime to pH 6.5. The amorphous Ca phosphates were

fairly soluble, with a large amount of plant available P, and were nearly as effective as triple superphosphate (TSP).

Rothbaum and Rohde (1976) suggested that struvite dissolution might be increased by an aerobic microbiological mineralization mechanism, though this finding has not subsequently been investigated. Mackay and Syers (1986) found that high Ca concentration in the soil solution inhibited the dissolution of Ca phosphate rock. Increased P availability through biotic or abiotic factors might make recovered Mg phosphate a useful alternative P fertilizer that is not as inhibited by high Ca concentrations typically found in calcareous soils.

Phosphorus fertilization in calcareous soils can be challenging. This is especially true for certified organic growers, who cannot use conventionally manufactured fertilizers such as TSP. With the exception of manure and compost, other certified organic P fertilizers such as rock phosphate (RP) and bone meal are not effective in calcareous soils (Elliott et al., 2007; Chien and Menon, 1995) Bolland et al. (1986) even found RP to be ineffective at mildly acidic (pH ~6) soil pH. Phosphorus recovery and re-use from livestock waste could help alleviate P loading in areas with large numbers of livestock while providing producers with a valuable resource and potential source of additional revenue. The use of recovered Mg phosphates could improve the sustainability of livestock operations, and conventional and organic crop production in semi-arid to arid areas containing calcareous soils.

Documented studies could not be identified which specifically addressed the effectiveness of recovered Mg phosphates in alkaline or calcareous soils, even though Lindsay (1979) noted that Mg phosphates such as struvite might be more useful than Ca

phosphates as fertilizers in such conditions. In this study, laboratory and greenhouse trials were conducted to determine the effectiveness of dittmarite ($MgNH_4PO_4 \bullet H_2O$), struvite, and a heterogeneous recovered phosphate material under acidic and basic soil conditions.

Materials and Methods

Laboratory Dissolution Study

In order to assess the dissolution kinetics and equilibrium characteristics of different fertilizers and recovered phosphates at environmentally relevant pH levels, a laboratory-scale dissolution study was conducted. Three pH levels, 5.9, 7.0, and 8.0, were selected as most relevant to the soil environment. The pH 5.9 buffer consisted of 0.05 M potassium hydrogen phthalate adjusted to the target pH with sodium hydroxide. The pH 7.0 and 8.0 buffers consisted of 0.05 M tris(hydroxymethyl)aminomethane adjusted to the target pH with hydrochloric acid. All chemicals were obtained from Thermo Fisher Scientific, Inc. (Pittsburgh, PA).

In addition to commercially available TSP and certified organic RP fertilizers, three recovered phosphates were tested. These include crystalline dittmarite from an Idaho food processing plant pump, crystalline struvite manufactured at a dairy in northwestern Washington, and a mixed product from a phosphorus recovery process at a Colorado dairy, hereafter referred to as "Colorado product". The Colorado product consisted mainly of ground apatite seed crystals, recovered magnesium phosphate, and sand grains from the bottom of the dairy manure storage lagoon. Fertilizers were analyzed for total P, Mg, Ca, and K at Ward Laboratories, Inc. in Kearney, NE (Table 4.1) using the methods outlined in Padmore (1990) and Isaac (1990).

For each fertilizer, the total P equivalent of approximately 0.10 g of TSP was placed into plastic 50 mL centrifuge tubes. Approximately the same amount of P (0.021 g, as P) was put into each tube. Then, 40 mL of buffer solution was added, and each set of tubes was placed on a reciprocating shaker at 120 rpm for time increments of 1, 4, 7, 14, 35, 75, and 105 days. The total length of time approximated that of a growing season. The experiment was set up in a 5×3 factorial design (5 treatments, 3 pH levels), with 3 replicates (blocks) for each time-step. Following shaking, solutions were filtered through a 0.45 μm syringe filter (Millipore, Inc.) and analyzed colorimetrically using an optimized ascorbic acid method (Rodriguez et al., 1994), or, in some cases, via inductively coupled plasma atomic emission spectrometry (Thermo Jarrell Ash IRIS Advantage, high resolution, dual view).

Dissolved P means and standard deviations were calculated in Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA, USA).

Greenhouse Fertilizer Trial

A slightly acidic soil (pH 6.5; 0-15 cm depth) with a moderate amount of available P (31 mg kg^{-1} Mehlich-3 P) was collected from a rangeland in northern Colorado. The soil was classified as fine-loamy over sandy or sandy-skeletal, mixed, mesic Aridic Argiustoll, 0-3% slopes. The Altvan series consists of deep, well drained soils that formed in mixed alluvial deposits (NRCS, 1980). Half of this soil was limed from an original pH of 6.5 to pH 7.6 using pure calcium carbonate ($CaCO_3$, Thermo Fisher Scientific, Inc.). The limed soil was moistened and dried several times to ensure $CaCO_3$ dissolution and pH adjustment. Soils were sieved through a 12.5 mm mesh frame prior to potting in order to remove pebbles. The untreated and limed soils were analyzed

for pH, NO_3-N, P, K, organic matter, and soluble salts at Servi-Tech Inc. in Dodge City, KS (Table 4.2).

The same fertilizers used in the laboratory dissolution study were used in the greenhouse study. In addition to a control group which received no fertilizer, fertilizers were applied at two rates, 0.05 g and 0.1 g P_2O_5 pot^{-1}, equivalent to 45 and 90 kg P_2O_5 ha^{-1}. The low rate was based on the agronomic P rate for spring-seeded small grains in a broadcast application outlined in Mortvedt et al. (1996), modified for the use of the Mehlich-3 soil P test. Soil test P levels for Olsen-P recommendations were doubled to account for the use of Mehlich-3 extractant. Note, however, that these rates were determined using total P_2O_5, rather than citric acid soluble or "available" P_2O_5. As a result, the same amount of total P (0.05 g or 0.1 g P_2O_5) was applied to each pot receiving a given rate. Fertilizer treatments were mixed thoroughly with 2.5 kg of soil, placed in 3.8 liter pots (the experimental unit used in statistical analyses), and then organized in the greenhouse as a randomized complete block design with four replicates.

Pots were watered from the bottom with tap water approximately every other day, depending on sunlight and greenhouse temperature, in order to maintain the soil near field capacity. Hard red spring wheat (*Triticum aestivum L.* "Zeke") was planted at a rate of 15 seeds per pot, and after germination excess plants were thinned to eight plants per pot. Above ground plant samples were collected, at one-month intervals, by cutting plants approximately 10 cm above the soil surface. A quantity of 30 mL of dilute N solution (0.027 M NH_4NO_3) was applied after the first cutting and approximately every two weeks thereafter to eliminate the possibility of N limitation on P uptake. No N was applied before the first cutting to avoid the possibility of "burning" the seedlings. For the

second and third cuttings, reproductive and vegetative growth were harvested and weighed separately. All cuttings were washed in de-ionized water, dried at 70°C, ground, and sent to Ward Laboratories, Inc. for total P analysis.

Statistical analysis was performed using SAS version 9.1 (SAS Institute, Inc., Cary, NC, USA) proc glm. Block and treatment were modeled as fixed effects, with DM, P content, or P uptake as the response variable. Comparisons were made only between treatment means with the same soil pH. Multiple comparisons were made using Fisher's F-protected LSD at a significance level of α=0.10.

Results and Discussion

Laboratory Dissolution Study

Dissolution kinetics were generally fast, with all treatments reaching approximate equilibrium within 7 to 14 days at all pH levels (Figures 4.1-4.3). Two distinct groups of treatments were observed, those with high P availability (TSP, struvite, dittmarite) and those with low P availability (RP, Colorado product). As expected, commercial TSP was the most soluble (~60-95%), and solubility decreased with increasing pH. Recovered struvite and dittmarite were essentially equivalent in terms of dissolution (~15-40%), which was expected because in solution, dittmarite rehydrates to struvite prior to dissolution (Bridger et al., 1962; Bhuiyan et al., 2008). Struvite and dittmarite were less soluble than TSP, though more soluble than either RP or the Colorado product at all pH conditions. As with TSP, struvite and dittmarite solubility decreased with increasing pH. The RP and Colorado product P solubility remained less than 1% across the range of pH studied.

Highly soluble P fertilizers can release P too quickly, while P fertilizers with low solubility release little P to the environment. In both cases plant P deficiencies could easily occur later or throughout the growing season, respectively. Goto (1998) noted, however, that the moderate solubility of struvite makes it an attractive fertilizer in soils with high P fixation, such as soils rich in aluminum or $CaCO_3$. In high P fixing soils, struvite's "slow release" characteristics might actually provide more P to plants over the course of the growing season than an immediately soluble P fertilizer such as TSP.

Low pH Soil

At low soil pH (6.5), there was no significant difference from the control in total dry matter (DM) production or in DM production at any single harvest, or in total P uptake over the course of the experiment (data not shown). Several of the fertilizer treatments, however, did result in increased P concentration in vegetative and seed material at low soil pH (Table 4.3). At certain cutting times, plants receiving dittmarite, Colorado product, TSP, and RP showed significant increases in P concentration as compared to the control. This was especially true at the higher P application rate. Overall, plants receiving struvite, dittmarite, and TSP showed increases in P concentration as compared to the control (Table 4.3). In addition to outperforming the control in P concentration, dittmarite increased plant P concentration over that of the RP and the Colorado product treatments ($p < 0.05$). At the high application rate, TSP also significantly increased P concentration over the high and low RP treatments ($p < 0.01$) and the high and low Colorado product treatments ($p < 0.05$).

Three factors potentially influencing the observations in the low pH soil were the soil P content, soil P availability, and soil organic matter content. At a soil pH of 6.5, P

availability is typically optimal for many plants. The optimal pH, coupled with this soil's moderate level of available P (Table 4.2), may have led to conditions sufficient for substantial DM production in the un-fertilized pots. Another possibility is that of P release to plants through the mineralization of organic matter over the course of the experiment. The greenhouse in which the experiment was conducted was considered to be abnormally warm, so the temperature coupled with the irrigation of the pots could have created ideal conditions for microbiological mineralization of organic matter. Lack of significant differences in plant P content in the last cutting suggests increased P availability, supporting this conclusion.

Although the addition of fertilizer did not increase DM production at low pH in this experiment, some of the fertilizers did increase plant P concentration both early in the experiment and overall. While RP and the Colorado product had an early effect, the overall average was not significantly different from the control mean P concentration of 0.34%. Struvite and TSP significantly increased plant P concentration at the high application rate, to 0.36% ($p=0.047$) and 0.37% ($p < 0.01$), respectively. Dittmarite increased overall average plant P concentration at both the high and low rates of application to 0.37% ($p < 0.01$). These findings support previous work (Goto, 1998; Johnston and Richards, 2003; Li and Zhao, 2003) that found recovered Mg phosphates to be effective fertilizers in slightly acidic soils.

High pH soil

All fertilizers except RP and struvite at the low rate increased overall DM production over the control at high soil pH (Table 4.4). The RP increased DM production at the high application rate ($p=0.0805$). That RP was less effective than other

fertilizers at high soil pH was not a new finding. Mackay and Syers (1986) found that high Ca concentrations inhibit RP dissolution. Chien and Menon (1995) noted that high pH and high Ca concentration, in addition to other factors, limited the effectiveness of RP in soil. The Mg phosphate fertilizer treatments all showed increased DM production, supporting the contention that recovered Mg phosphates can indeed be used as fertilizers on alkaline soils. Field trials and further tests across a wide range of alkaline soil pH and $CaCO_3$ content will help to determine the agronomic effectiveness of these fertilizers under alkaline soil conditions.

One matter of concern regarding the interpretation of plant P concentrations for the limed soil is the high average P concentration for the control, and relatively lower P concentrations in the fertilized plants (Table 4.5). This could be attributed to a "dilution" effect from increased DM production. Also perplexing is the increased soil test P in the limed soil (Table 4.1). These results seem counterintuitive, given the common perception that high pH and the presence of $CaCO_3$ will inhibit P availability to plants, and the application of fertilizer to increase yields and plant P content. Indeed, liming of the soil was selected as a method of controlling overall P availability across both pH values used in this experiment, since the total P content of the soil does not change with the addition of $CaCO_3$. The addition of large amounts of free Ca may unexpectedly have had the opposite effect on P availability, possibly by rendering P bound as iron or aluminum phosphates more soluble. Consequently, comparisons between performance in the low pH and high pH soils are not possible. Liming may be an unsuitable choice to manipulate soil pH for similar P fertilizer experiments in the future. However, liming of

soil for greenhouse studies is common practice, as seen in the studies by Goto (1998) and Bauer et al. (2007), so caution is warranted.

Many of the fertilized pots had lower plant P concentration than the control at high pH (Table 4.5). The decreased plant P concentrations were the result of a "dilution effect" resulting from greater DM production in the fertilized pots, so total P uptake provides a more complete picture of the effectiveness of the P fertilizers in this case. Although the treatment effect for total P uptake (DM × P concentration) was not statistically significant ($p=0.144$), the high level of significance of individual pairwise comparisons is important to note (Table 4.6). These pairwise comparisons show a trend of increased total P uptake for all of the treatments except RP and low rate struvite as compared to the control. There were no significant differences among the non-control treatments, demonstrating that struvite, dittmarite, and even the heterogeneous Colorado product performed similarly to commercial TSP in high pH, high Ca soil conditions. Given the ineffective nature of RP in these particular environments, recovered Mg phosphates might provide certified organic producers with a viable alternative for P fertilization on calcareous soils.

Conclusion

The recovery and beneficial re-use of phosphate has the potential to help protect water quality, improve the sustainability and efficient cycling of P (a limited resource), and provide sources of revenue and materials for producers and consumers of phosphate. Several recovery technologies have focused on the crystallization of Mg phosphates such as struvite and dittmarite, which cannot be recycled as a raw material for the current phosphate industry but have potential as fertilizer. Several studies have documented the

effectiveness of Mg phosphates in acidic soils, but no known body of work examining recovered Mg phosphate usefulness under alkaline soil conditions exists. This study found evidence that recovered Mg phosphates may be useful across a broad range of soil pH conditions. Recovered Mg phosphates increased wheat P concentration in slightly acidic soil conditions, and increased plant DM production in alkaline soil conditions. A trend showing that Mg phosphates and TSP increase total P uptake was also evident under alkaline conditions, though it was not statistically significant. No such trend in total P uptake was observed for the fertilizers under acidic soil conditions. These results indicate that recovery of Mg phosphates could be an effective source of P fertilizer in areas with both acidic and alkaline soils.

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Tables

Table 4.1. Bulk fertilizer chemical characteristics. Standard deviations listed in parentheses (n=3). Percentages were determined after a total digest of fertilizer samples. Struvite differs from pure struvite due to Ca phosphate seed crystals, and Colorado product is very heterogeneous in nature due to the presence of sand from treatment. Pure Mg phosphate composition from Bridger et al. (1962).

fertilizer	P_2O_5	Mg	Ca	K_2O
	---------- % ----------			
struvite	28.2 (0.4)	4.2 (0.3)	17.9 (0.9)	0.3 (0.0)
dittmarite	45.4 (0.3)	12.2 (0.6)	0.30 (0.02)	< 0.1
Colorado product	16.2 (0.6)	0.41 (0.01)	18.3 (1.0)	0.5 (0.1)
TSP	48.1 (0.3)	0.61 (0.03)	13.7 (0.7)	0.2 (0.0)
RP	21.7 (0.1)	0.10 (0.01)	25.4 (0.6)	0.2 (0.0)

Table 4.2. Soil characteristics of the untreated and limed soils used in the greenhouse trials (n=2). Soil pH and salinity were determined by measurement in a 1:1 soil:water slurry, NO_3-N was determined by Cd reduction, P was measured by Mehlich-3, and K was measured with the ammonium acetate method. The increase in soil NO_3-N was likely due to organic matter mineralization during liming.

soil	pH	NO_3-N	P	K	O.M.	soluble salts
		----------	mg kg^{-1}	----------	%	dS m^{-1}
			----			
un-limed	6.5	5	31	257	2.4	0.16
limed	7.6	23	44	316	2.4	0.42

Table 4.3. Average percent P concentrations for wheat grown on the low pH (6.5) soil. Values presented are the weighted average of plant and seed P concentration, based on the relative amounts of plant and seed material. An asterisk indicates a P concentration that is significantly different from the control ($p < 0.10$). The last row shows overall p-values of each comparison for the treatment effect from the type III analysis of variance table.

Fertilizer treatment	P rate as P_2O_5	time 1 P, plant	time 2 P, plant	time 2 P, seed	time 2 P, average	time 3 P, plant	time 3 P, seed	time 3 P, average	P overall average
	kg ha^{-1}	%							
struvite	45	0.362	0.335	0.340	0.337	0.280	0.420	0.373	0.356
	90	0.385	**0.338***	0.340	0.338	**0.305***	0.405	0.369	**0.360***
dittmarite	45	**0.398***	**0.360***	0.350	**0.357***	0.278	0.422	0.370	**0.371***
	90	**0.403***	**0.375***	0.372	**0.373***	0.238	0.412	0.350	**0.368***
Colorado product	45	0.380	0.295	0.328	0.307	0.265	0.400	0.357	0.341
	90	**0.390***	0.310	0.368	0.339	0.232	0.378	0.320*	0.347
TSP	45	**0.392***	0.322	0.338	0.328	0.298	0.400	0.363	0.354
	90	**0.412***	**0.352***	0.342	0.349	**0.315***	0.402	0.373	**0.373***
RP	45	0.375	0.302	0.328	0.312	0.290	0.392	0.358	0.342
	90	0.350	**0.340***	0.410*	**0.352***	0.238	0.388	0.334	0.332
control	0	0.368	0.309	0.342	0.322	0.261	0.400	0.351	0.341
treatment effect p-value		**0.002**	**0.002**	0.532	**0.032**	**0.048**	0.323	0.176	**0.033**

Table 4.4. Average DM production (in grams per pot) for wheat grown on the high pH (7.6) soil. An asterisk indicates DM production that is significantly different from the control ($p < 0.10$). The last row shows overall p-values of each comparison for the treatment effect from the type III analysis of variance table.

Fertilizer treatment	rate	time 1 DM, plant	time 2 DM, plant	time 2 DM, seed	time 2 DM, total	time 3 DM, plant	time 3 DM, seed	time 3, DM total	DM overall total
	kg ha^{-1}	g pot^{-1}							
struvite	45	1.99	2.18	**1.48***	3.66*	1.12	1.96	3.08	8.73
	90	1.98	2.18	**1.52***	3.70*	**1.49***	**2.52***	**4.01***	**9.69***
dittmarite	45	2.10	2.05	**1.43***	3.54	**1.30***	**2.66***	**3.96***	**9.59***
	90	2.05	2.16	1.48	3.43	**1.42***	**2.62***	**4.04***	**9.52***
Colorado product	45	2.00	2.41*	1.40	3.81*	**1.49***	**2.60***	**4.09***	**9.90***
	90	1.99	2.42*	1.32	3.74*	**1.72***	**2.99***	**4.71***	**10.44***
TSP	45	2.28*	2.03	1.24	3.27	**1.34***	**2.52***	**3.85***	**9.40***
	90	1.90	2.51*	**1.43***	3.94*	**1.52***	**2.86***	**4.38***	**10.23***
RP	45	1.82	2.33*	1.20	3.53	1.08	2.05	3.13	8.48
	90	2.03	2.21	1.32	3.53	1.23	2.22	3.45	**9.02***
control	0	1.85	1.83	1.14	2.97	0.94	1.63	2.57	7.39
treatment effect p-value		0.700	0.271	**0.036**	0.303	**0.011**	**0.048**	**0.024**	**0.063**

Table 4.5. Average P concentrations (in percent) for wheat grown on the high pH (7.6) soil. "Average" refers to the weighted average of plant and seed P concentration, based on the relative amounts of plant and seed material. An asterisk indicates a P concentration that is significantly different from the control ($p < 0.10$). The last row shows overall p-values of each comparison for the treatment effect from the type III analysis of variance table.

Fertilizer treatment	rate	time 1 P, plant	time 2 P, plant	time 2 P, seed	time 2 P, average	time 3 P, plant	time 3 P, seed	time 3 P, average	P overall average
	kg ha^{-1}	%							
struvite	45	0.410	**0.345***	0.365	**0.353***	0.370	0.415	0.398	**0.384***
	90	0.418*	**0.320***	0.358*	**0.336***	0.362	0.395	**0.382***	**0.369***
dittmarite	45	0.410	**0.353***	0.355*	**0.354***	0.405	0.412	0.410	0.389
	90	0.415	0.360	0.372	0.365	0.368	0.432	0.409	0.393
Colorado product	45	0.390	**0.343***	0.362	**0.350***	0.305*	0.402	**0.367***	**0.365***
	90	0.398	**0.328***	0.355*	**0.337***	0.345	0.392*	**0.375***	**0.366***
TSP	45	0.400	**0.340***	0.350*	**0.344***	0.365	0.408	0.393	**0.374***
	90	0.398	**0.338***	0.352*	**0.343***	0.380	0.395*	0.389	**0.372***
RP	45	0.410	**0.348***	0.358*	**0.350***	0.425	0.422	0.376	0.387
	90	0.390	**0.340***	0.358*	**0.346***	0.335*	0.402	**0.363***	**0.369***
control	0	0.395	0.386	0.389	0.388	0.409	0.426	0.422	0.401
treatment effect p-value		0.420	**0.042**	0.402	**0.055**	0.270	0.287	0.166	**0.007**

Table 4.6. Total P uptake (in grams) for wheat grown on the high pH (7.6) soil. Total P uptake was determined using the total DM production and the overall weighted average P concentration. Standard deviations are listed in parentheses, and an asterisk indicates total P uptake that is significantly different from the control ($p < 0.10$). P-values shown in the table are for a two-sided comparison with the control.

Fertilizer treatment	rate	total P uptake	p-value
	kg ha^{-1}	g	
struvite	45	0.033 (0.004)	0.2103
	90	0.036 (0.005)*	**0.0525**
dittmarite	45	0.037 (0.004)*	**0.0166**
	90	0.037 (0.005)*	**0.0157**
Colorado product	45	0.036 (0.006)*	**0.0396**
	90	0.038 (0.004)*	**0.0084**
TSP	45	0.035 (0.006)*	**0.0654**
	90	0.038 (0.001)*	**0.0100**
RP	45	0.032 (0.01)	0.3468
	90	0.033 (0.005)	0.2524
control	0	0.029 (0.007)	N/A

Figures

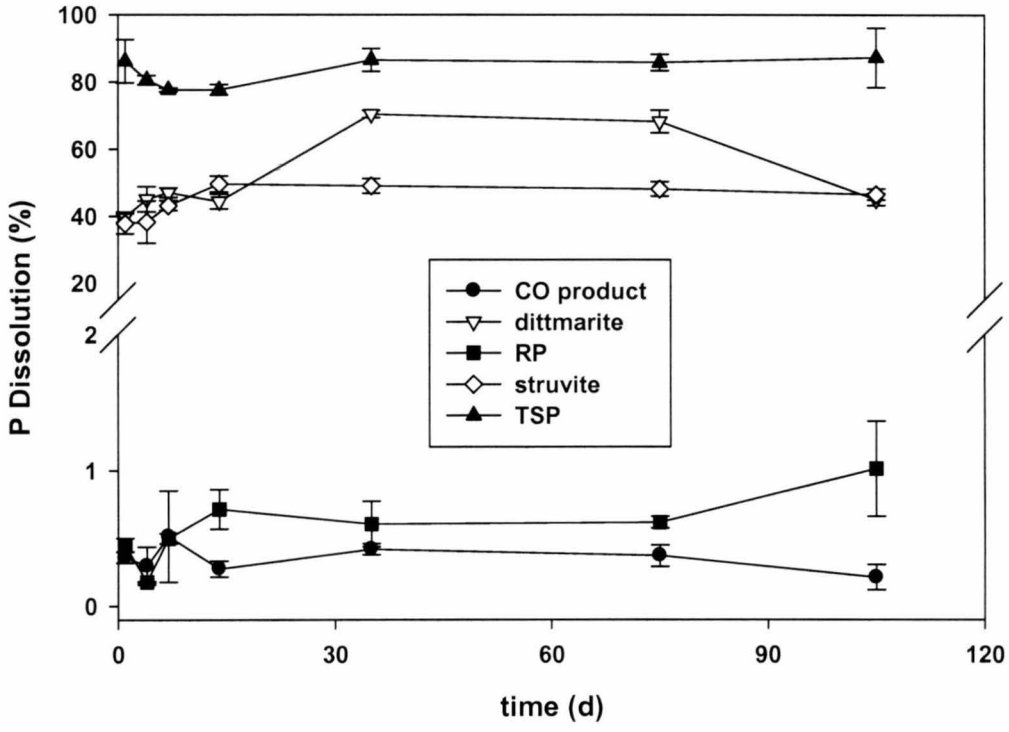

Figure 4.1. Mean values (n=3) of the percent P dissolution for five fertilizer treatments at pH 5.9. Due to the great disparity between fertilizers with high and low dissolution, the percent dissolution is presented on a split y-axis.

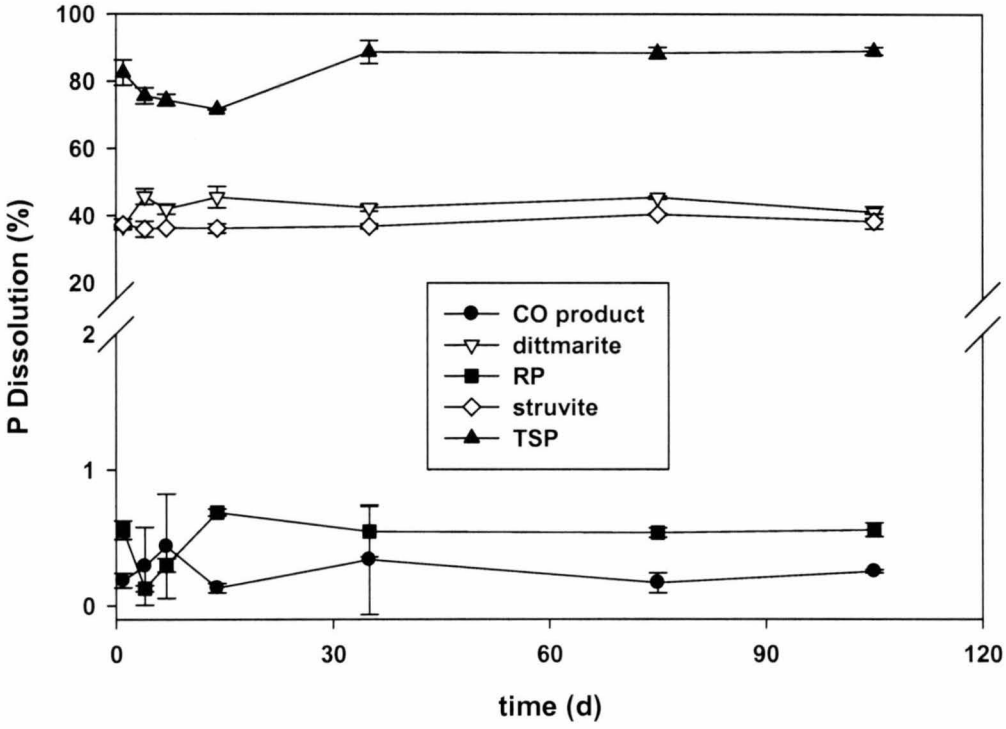

Figure 4.2. Mean values (n=3) of the percent P dissolution for five fertilizer treatments at pH 7.0. Due to the great disparity between fertilizers with high and low dissolution, the percent dissolution is presented on a split y-axis.

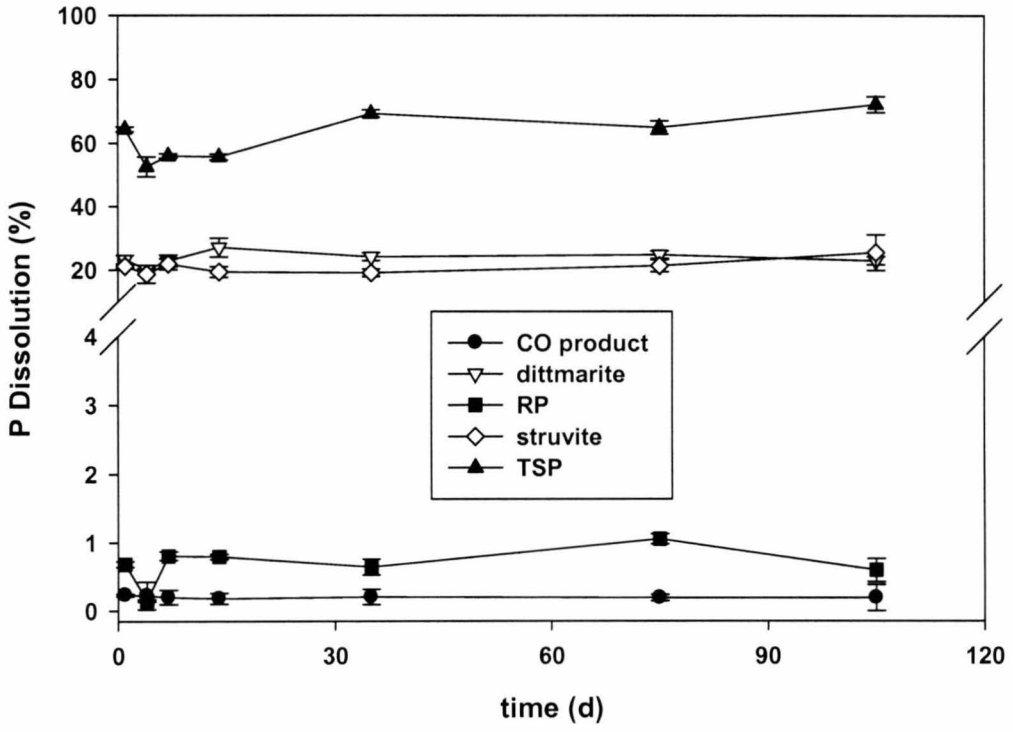

Figure 4.3. Mean values (n=3) of the percent P dissolution for five fertilizer treatments at pH 8.0. Due to the great disparity between fertilizers with high and low dissolution, the percent dissolution is presented on a split y-axis.

Chapter 5: Conclusion and Future Directions of Research

This study has demonstrated that phosphorus (P) recovery on dairy farms through struvite ($MgNH_4PO_4 \bullet 6H_2O$) precipitation in a fluidized bed reactor is potentially a feasible alternative for correcting local nutrient surpluses. Furthermore, it may be possible to develop a treatment process to recover a soil amendment that is in accordance with both the spirit of sustainable nutrient cycling and the specifics of certified organic production guidelines. If it were not effective in a variety of soil conditions, however, the soil amendment would not be as useful as current P fertilizers. To that end, this study also provided evidence that waste stream recovered struvite and dittmarite ($MgNH_4PO_4 \bullet H_2O$) crystals could be effective fertilizers in both acidic and alkaline soil conditions. The finding that recovered magnesium (Mg) phosphates could be effective in acidic soil conditions supports previous studies, while the findings regarding their performance in alkaline conditions are new. In light of these results, recovered Mg phosphates such as struvite and dittmarite show promise as fertilizers for conventional and perhaps certified organic food production.

There are a number of areas, however, that this study has identified as requiring further research. These areas include process optimization and improvements in removal efficiency, improvements in and understanding of product characteristics, further evaluation of the agronomic effectiveness of recovered products, and the development of other uses for recovered products.

Process optimization and removal efficiency improvements

The observed total phosphorus (TP) removal efficiencies of 14% and 9% for the conventional and new treatment methods, respectively, were lower than expected. Furthermore, orthophosphate (OP) levels in the new method effluent remained relatively high, suggesting that more of the OP in solution could have been removed with improved process performance. As suggested in chapter 2, this improved performance could be achieved with increases in hydraulic retention time (HRT), decreases in flow rate and upflow velocity of the wastewater in the reactor, or chemical treatment to reduce interference and achieve optimal physical and chemical conditions for high removal rates.

Further optimization could be performed prior to manure collection, and in the manure waste storage and treatment system itself. Factors such as animal diets could be manipulated to produce conditions optimal for (or less inhibitory of) struvite recovery. For example, reducing excreted calcium (Ca) could improve chemical conditions for struvite recovery by reducing the effect of Ca interference. The waste storage and treatment system could be altered for improved removal of solids and consequently better physical conditions inside the fluidized bed reactor.

Improvements in and understanding of product characteristics

A uniform, consistent product is important for the re-use of recovered phosphates. This is true for practical reasons, since usage guidelines could not reasonably be developed for complex, highly variable products. It is also true for economic reasons, since the ideal recovered product would have to be marketed and distributed widely in order to economically achieve improvements in P cycling and water quality.

However, the current understanding of the effects of macroscopic process parameters on microscopic product characteristics is still limited. The existing understanding of microscopic product characteristics on macroscopic performance in beneficial re-use is even more limited. Both of these areas require further investigation in order to improve our understanding of P recovery and re-use to the level currently enjoyed by more conventional P sources such as rock phosphate (RP) and other commercial P fertilizers.

Further evaluation of the agronomic effectiveness of recovered products

Struvite and other recovered phosphates have been examined as fertilizers mostly in greenhouse situations and with soils of low to neutral pH. While previous work, and the work described herein, is useful in determining the effectiveness of recovered P as a fertilizer, the challenges of P fertilization in alkaline and calcareous soils underscore the need for further examination of the performance of recovered P across a variety of high pH soils with different textures and free calcium carbonate contents. Field trials, rather than greenhouse trials, of real recovered products will also be crucial for establishing a place for recovered P products among commonly accepted and widely used P fertilizers. Ideally, further research would establish guidelines for the field application of real recovered products in a variety of soil conditions.

Development of other uses for recovered magnesium phosphate products

Currently, the only major use for recovered struvite is as a fertilizer. Other recovered P products such as calcium phosphates have the potential for re-use in the current P manufacturing industry, but Mg phosphates such as struvite and dittmarite have limited re-use potential at this time. However, other avenues for the beneficial re-use of

recovered Mg phosphates could be developed, which would only increase the environmental and economic attractiveness of struvite recovery from dairy and other livestock wastes. Perhaps the greatest potential gain lies in integrating struvite into the current P industry, so that struvite could become a P feedstock in its own right. The integration of struvite into the P industry faces substantial hurdles, though, which include collection and transport of materials from distributed sources, in addition to chemical and technical issues.

Final thoughts

Phosphorus recovery and re-use is an important aspect of the continued viability of human society, especially in light of the expectation for phosphorus shortages in the not-so-distant future. Substantial improvements in P recycling are possible using technologies such as the ones described herein, and these improvements come with other benefits like improved water quality through decreased eutrophication of surface waters. Improved P recycling cannot be realized, however, without further research that builds on the work presented here.

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