



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech



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

Michael S. Massey^a, James A. Ippolito^b, Jessica G. Davis^{c,*}, Ron E. Sheffield^d

^a Department of Environmental Earth System Science, Stanford University, Y2E2 Building, 473 Via Ortega, Stanford, CA 94305-4020, USA

^b USDA-ARS Northwest Irrigation and Soils Research Laboratory, 3793 North 3600 East, Kimberly, ID 83341, USA

^c Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO 80523-1170, USA

^d Department of Biological and Agricultural Engineering, Louisiana State University AgCenter, 111 E.B. Doran Building, Baton Rouge, LA 70803-4505, USA

ARTICLE INFO

Article history:

Received 1 July 2008

Received in revised form 28 August 2009

Accepted 28 August 2009

Available online 29 September 2009

Keywords:

Struvite

Dittmarite

Phosphorus

Recovery

Wastewater treatment

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.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Existing rock phosphate (RP) reserves are projected to last approximately another 90 years, making the recovery and re-use of phosphorus (P) necessary for the long-term sustainability of agricultural production (Vaccari, 2009). In addition to agriculture, P is used in products such as detergents, matches, grenades, and flares. As quality RP reserves continue to decline and energy prices rise, P recovery from various outside sources will likely become increasingly economical (Gaterell et al., 2000). Many P recovery efforts have focused on the precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) using “heterogeneous nucleation” crystallization processes, which precipitate phosphates onto seed particles such as sand or Ca/Mg phosphate.

Several studies (Battistoni et al., 2001, 2005; Munch and Barr, 2001; 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,b; 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

* Corresponding author. Tel.: +1 970 491 1913; fax: +1 970 491 0564.

E-mail address: Jessica.Davis@ColoState.edu (J.G. Davis).

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; Massey et al., 2009). 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, 2005; Wu and Bishop, 2004; 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 derived from real wastewater under field conditions.

2. Methods

2.1. 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 ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) crystals removed from mixing paddles and outlet valves of an anaerobic digester at a cheese processing facility; and a heterogeneous product manufactured at dairies in Colorado, using the “conventional” and “new” processes described by Massey (2008), hereafter referred to as “Colorado product”; finely ground Ca phosphate (a mixed material containing carbonate-fluorapatite) and sand material, used to seed the reactor bed, were also examined to evaluate the effects of the treatment process on the bed material.

The Colorado product was made by precipitating magnesium and phosphate in a pilot-scale, cone-shaped fluidized-bed reactor at a flow rate between 410 and 456 L h^{-1} . Given the flow rate, the wastewater hydraulic retention time in the reactor was approximately 4 min. Precipitation was achieved by manipulating the pH of dairy wastewater: with hydrochloric acid and gaseous ammonia in the “conventional” process; and, with acetic acid and potassium hydroxide in the “new” process. This induced struvite supersaturation and precipitation onto a bed of finely ground seed material.

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

Table 1

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)	12.30 (0.2)	4.20 (0.3)	17.9 (0.9)
Struvite (ideal)	12.62 (0.0)	9.91 (0.0)	0.0 (0.0)
Dittmarite (food processing plant)	19.80 (0.1)	12.20 (0.6)	<0.1 (0.0)
Dittmarite (ideal)	19.94 (0.0)	15.65 (0.0)	0.0 (0.0)
Colorado product (dairy wastewater)	7.10 (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)

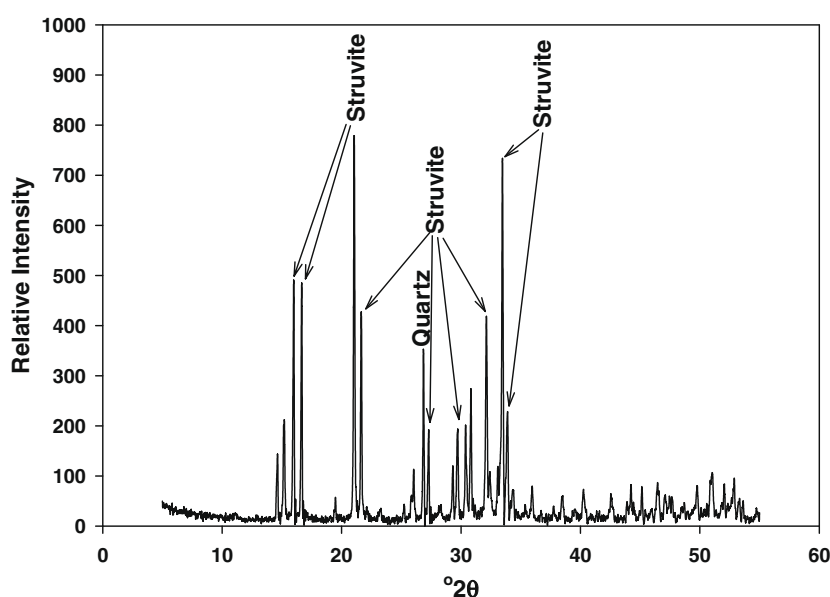


Fig. 1. X-ray diffractogram of struvite crystals (JCPDF #15-0762) recovered from dairy wastewater using a fluidized-bed reactor seeded with ground calcium phosphate. Differences from a pure struvite diffraction pattern are likely attributable to the presence of seed material such as quartz (JCPDF #46-1045).

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 410–456 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.

2.2. 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).

2.3. 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° min⁻¹. Diffractograms were analyzed using the software package DMSNT (Scintag, Inc.) and the JCPDF library of diffraction patterns (International Centre for Diffraction Data).

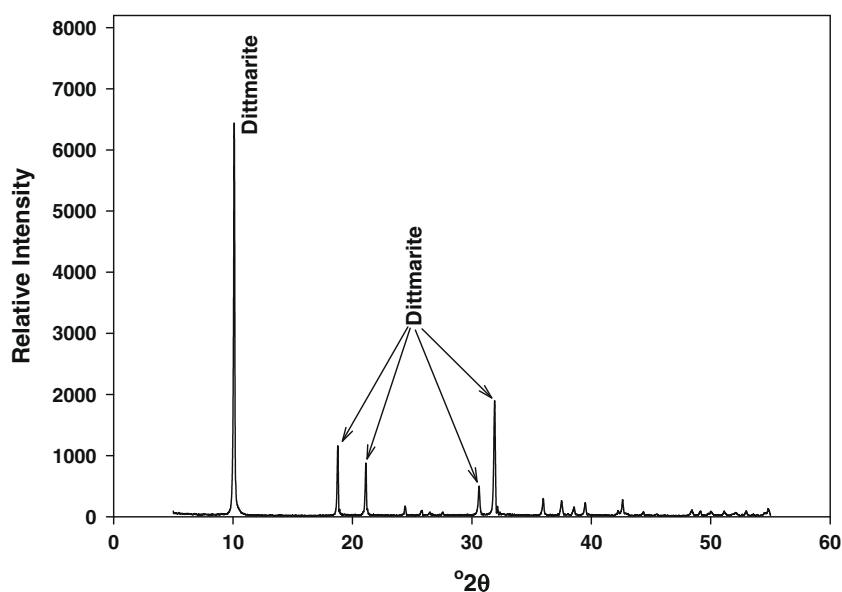


Fig. 2. X-ray diffractogram of dittmarite crystals (JCPDF #20-0663) recovered from a food processing plant during cleaning.

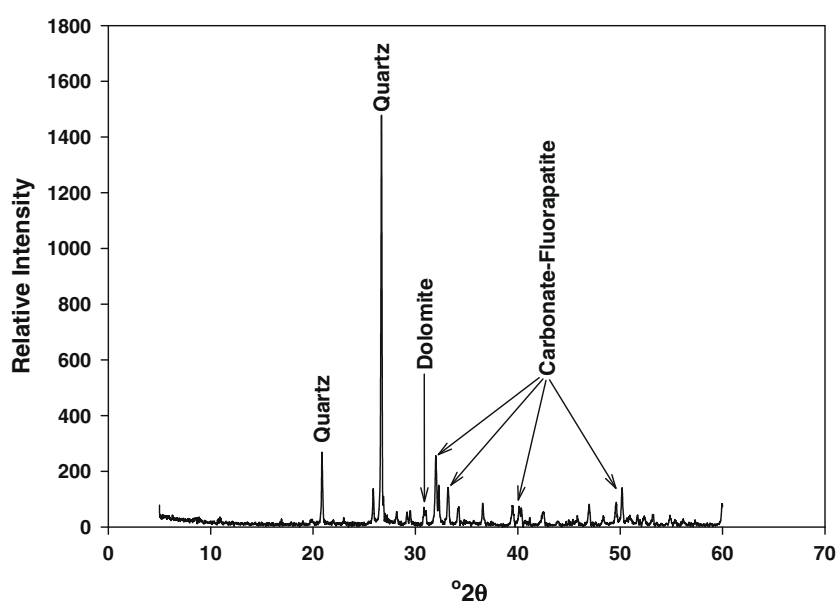


Fig. 3. X-ray diffractogram of Colorado product material using the “new” method. Analysis of diffractogram showed crystalline phases of quartz (sand, JCPDF #46-1045), carbonate fluorapatite (JCPDF #31-0267), and dolomite (JCPDF #36-0426). The conventional method diffractogram was similar, but with a small, unidentified peak at low 2-theta angle.

2.4. 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 × 10 mm Al stub, and the system was al-

lowed 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,

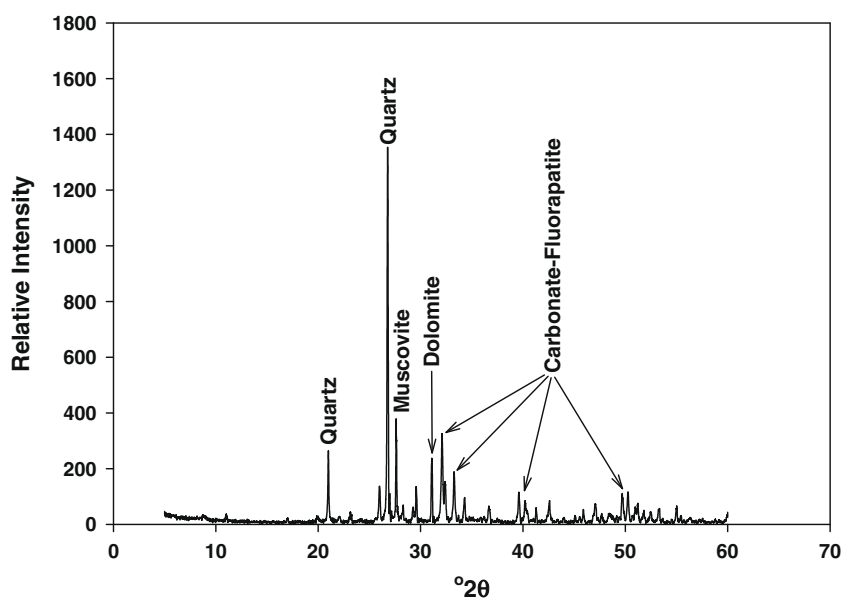


Fig. 4. X-ray diffractogram of reactor seed material used in making Colorado product. Analysis of diffractogram showed crystalline phases of quartz (sand, JCPDF #46-1045), carbonate fluorapatite (JCPDF #31-0267), dolomite (JCPDF #36-0426), calcite, whitlockite, and traces of muscovite (JCPDF #46-1409) and illite.

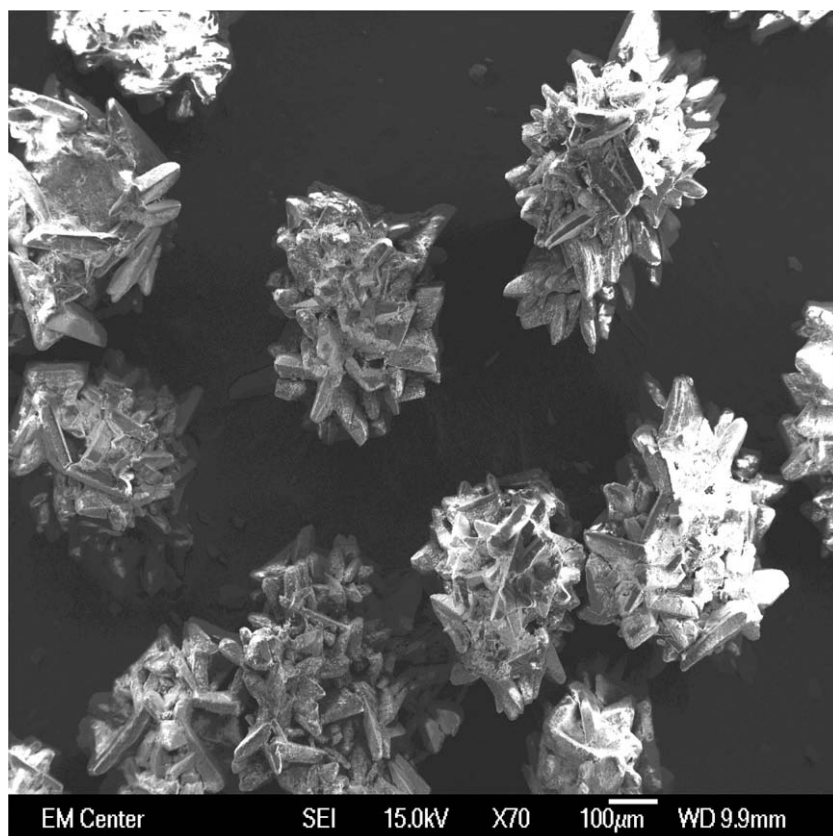


Fig. 5. Scanning electron micrograph of struvite crystals recovered from dairy wastewater by Bowers et al. (2007) using the “conventional” method. The energy dispersive X-ray analysis of the exterior layer of a single particle showed an approximate 1:1 M ratio of Mg:P, with a molar composition of 11.78% P, 12.65% Mg, 0.38% Ca, 70.44% O, 2.18% S, and 1.89% Fe.

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 an 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.

3. Results

3.1. Chemical analysis

Struvite crystals recovered from dairy wastewater contained larger and lesser amounts of Ca and Mg, respectively, than ideal struvite (Table 1). 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 the treatment system.

3.2. 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 ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$; Fig. 1), and the deposit recovered from the food processing facility was an excellent match with dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$; Fig. 2). The “new” Colorado product (Fig. 3) and RP seed material (Fig. 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.

3.3. 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 (Massey, 2008), Colorado product samples, as well as the other samples, were examined using SEM. The struvite crystals recovered from dairy wastewater had a crystalline, large, and homogeneous nature (Fig. 5). Examination of “conventional”

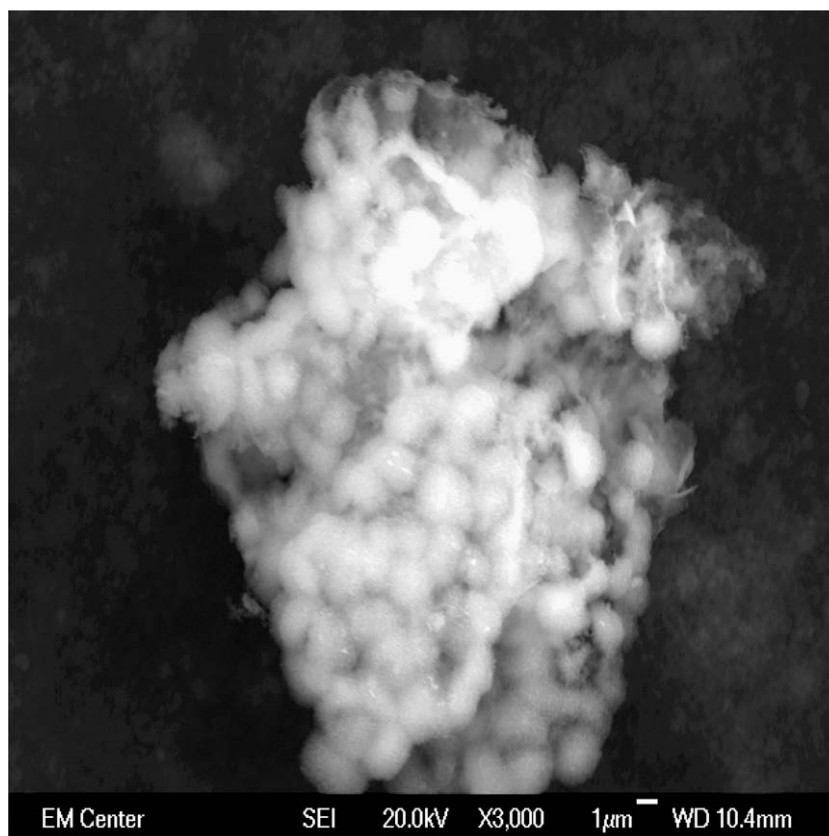


Fig. 6. Scanning electron micrograph of a Colorado product particle produced using the same method as the particle in Fig. 5 (the “conventional” method). The energy dispersive X-ray analysis showed a molar composition of 12.91% P, 9.99% Mg, 5.17% Ca, 66.18% O, 2.02% Si, and small amounts of Fe, K, and Cu. Note the small size and semi-crystalline nature of the particle.

method Colorado product found smaller, less crystalline particles (Fig. 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 (Fig. 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 (Fig. 8).

3.4. 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 (Fig. 9a). No evidence of heterogeneous nucleation (seed material) was found using EDS analysis of the crystalline dittmarite from the food processing plant (Fig. 9b). In Fig. 9c and d, 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 (Fig. 9a); homogeneous nucleation or heterogeneous nucleation on pipe or pump surfaces rather than seed particles (Fig. 9b); or as a crystalline or amorphous precipitates partially covering seed materials (Fig. 9c and d). 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.

4. Discussion

Along with the fine Mg phosphate particles in Figs. 6 and 8, the Mg phosphate precipitates depicted in Fig. 9c and d provide microscopic evidence that helps explain the macroscopic performance of the treatment process. 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 Figs. 5 and 9a.

4.1. Formation of the different materials

The physical and chemical differences between materials can be linked to the conditions of their formation. 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). The crystalline struvite precipitated by heterogeneous nucleation on Ca phosphate seed particles by Bowers et al.

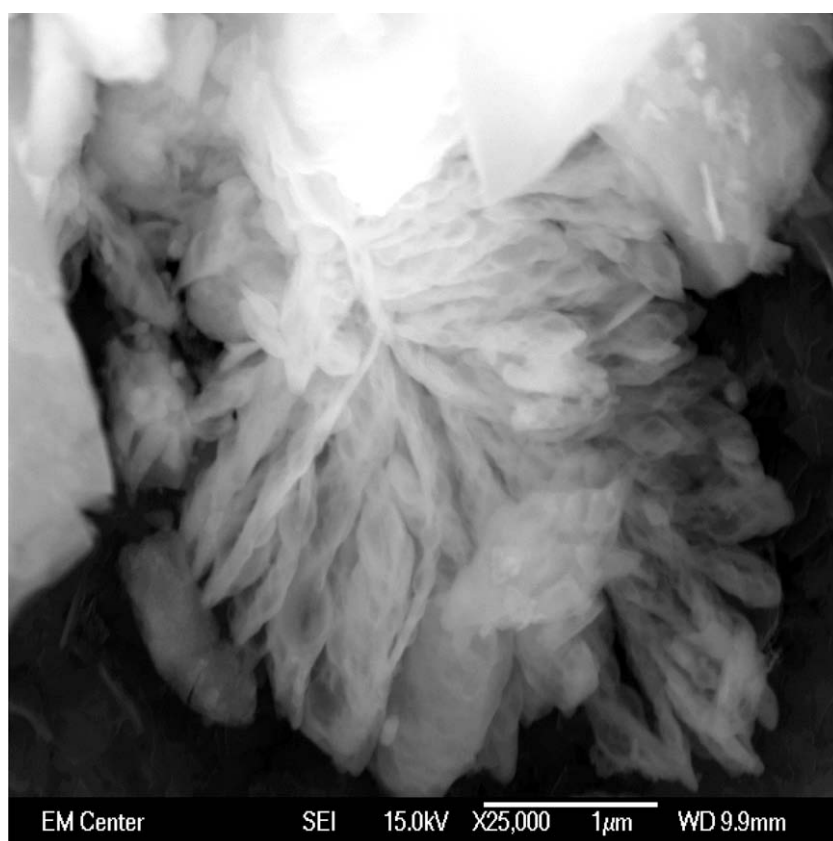


Fig. 7. Scanning electron micrograph of a small region of dittmarite crystals recovered from a food processing facility. This region is notable for its dendritic (“tree-like”) crystalline structure. The energy dispersive X-ray analysis showed a molar composition of 18.55% P, 16.86% Mg, 63.57% O, and 1.02% Fe.

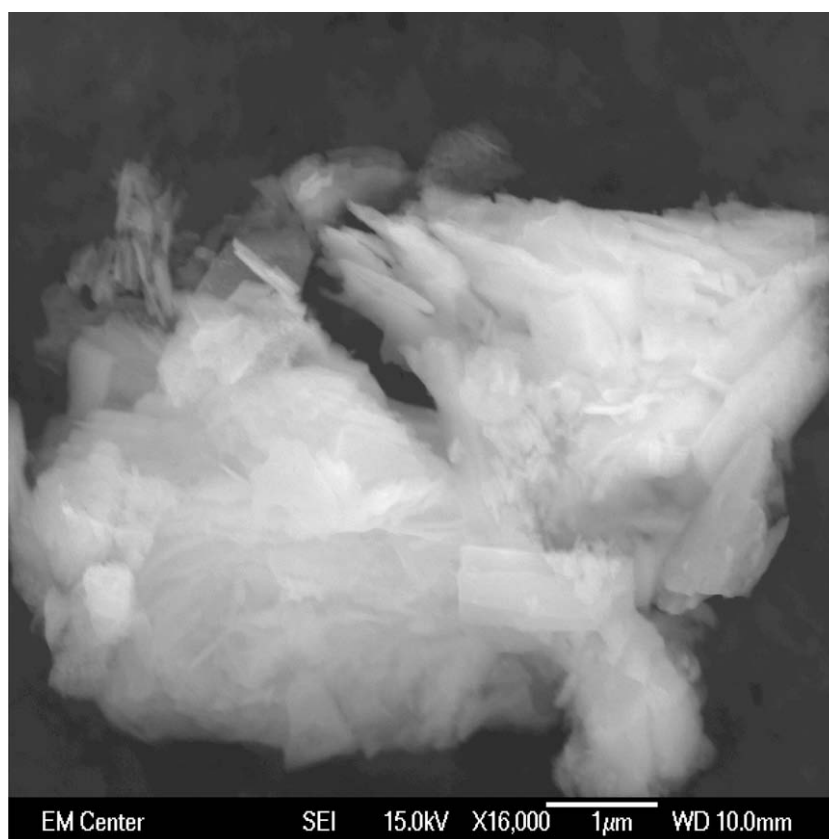


Fig. 8. Scanning electron micrograph of a small Mg phosphate particle found during examination of the “new method” Colorado product samples. The energy dispersive X-ray analysis showed a molar composition of 16.40% P, 16.40% Mg, 64.86% O, and traces of Fe, Al, Si, and Ca.

(2007) was an example of the 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.

The Colorado product particles showed a combination of homogeneous nucleation resulting in the formation of fine particles (Figs. 6 and 8), and seed particles incompletely covered by precipitate (Fig. 9c and d). These Mg phosphates cannot be confirmed as struvite by the methods of this study, but ammonia removal was observed in the water treatment process (Massey, 2008). Additionally, Babic-Ivancic et al. (2006) found that struvite, rather than newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), formed at a higher pH and high ammonium phosphate concentration, such as the concentrations and pH measured by Massey (2008). 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 such as used in the current study (i.e. 4 min), the fine particles could have become larger crystals just as the layer of Mg phosphate precipitate (Fig. 9c and d) could have grown, if conditions were more conducive. Short retention times, excessive mixing velocities in the reactor, and interference from ions and organic ligands might have influenced product formation with these irregular characteristics, as others (Bowers et al., 2007; van der Houwen and Valsami-Jones, 2001) have observed.

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 recov-

ered 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 (Fig. 9c), 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. 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.

4.2. Practical implications of material characteristics

The most common use usually suggested for recovered struvite is as an agricultural fertilizer, although stream rehabilitation is also a possible end use (Sterling et al., 2000). 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

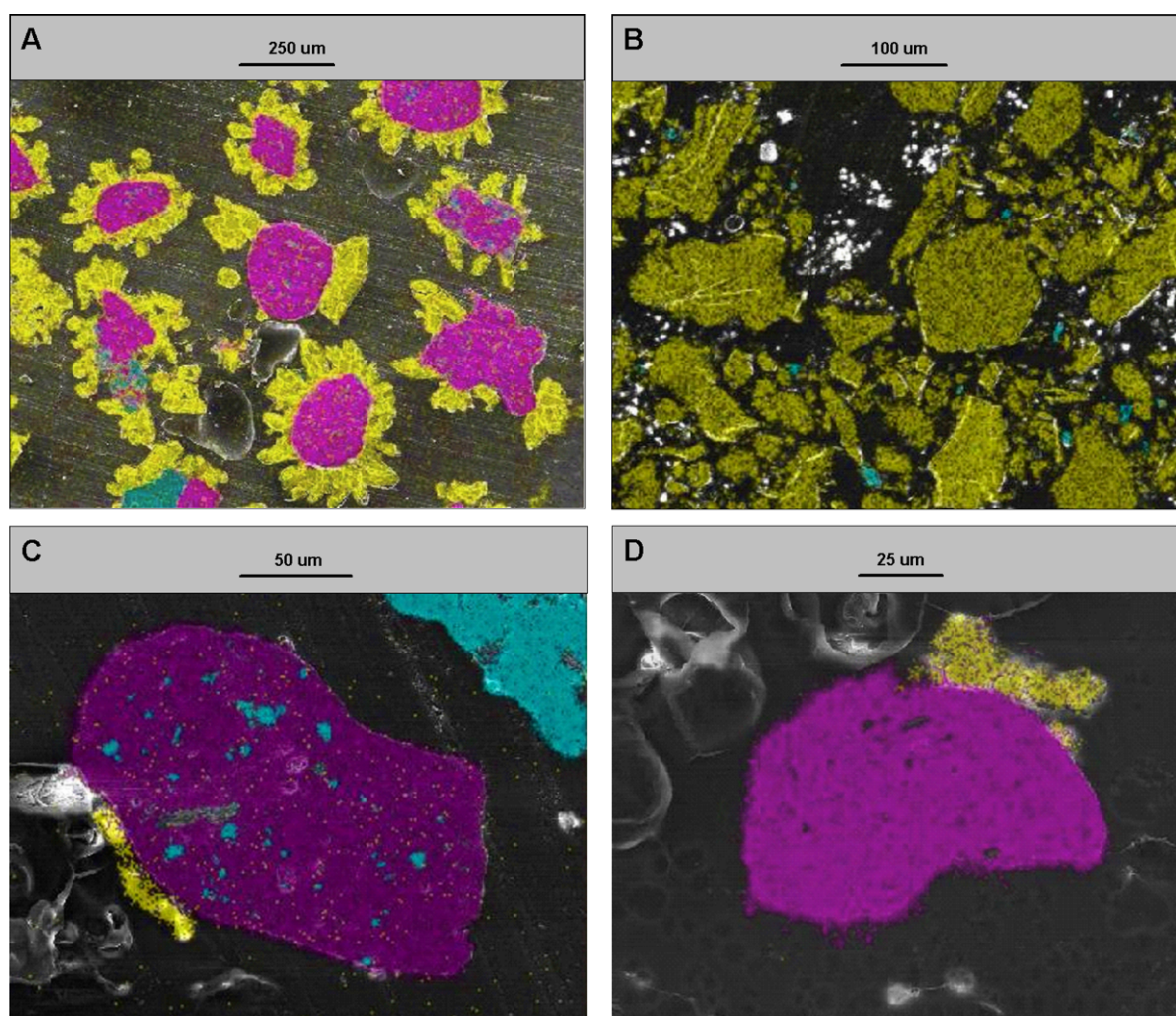


Fig. 9. Energy dispersive X-ray component analysis of the interior of recovered struvite crystals. Calcium phosphate seed material is shown in magenta, Mg phosphate crystals are shown in yellow, and silicon oxides (sand) are shown in cyan. (A) Recovered struvite, (B) recovered dittmarite, (C) “new” method particles demonstrating preferential precipitation of Mg phosphate layer on Ca phosphate seed, (D) detail of “new” method particle showing Mg phosphate precipitate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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. 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 variations may limit some recovered P materials' potential for use as a fertilizer.

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 engineered process exists for its recovery, limiting the practical viability of dittmarite crystals as 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 Fig. 9a, may 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; Bauer et al. (2007) found recovered amorphous Ca phosphate to be an effective fertilizer in a greenhouse study. Similarly, 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.

5. Conclusions

Most P recovery research, to date, has focused on the wastewater treatment phase of P recovery and re-use, with findings showing that products may or may not be chemically or physically desirable as a potential 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.

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 precipitating onto 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.

Acknowledgements

The authors would like to thank the United States Natural Resources Conservation Service, Farm Pilot Project Coordination, Inc., and Applied Chemical Magnesias Corp. for financial support. Thanks also to Dr. Keith E. Bowers of Multifarm Harvest, Inc. for providing recovered struvite crystals. Additionally, we are grateful to Dr. Wendy Harrison at the Colorado School of Mines and Dr. Sandeep Kohli at Colorado State University for their assistance with XRD analysis. Finally, thanks to Dr. Patrick McCurdy at Colorado State University for his patience and assistance with SEM–EDS analysis.

References

- Babic-Ivancic, V., Contrec, J., Kralj, D., Brecevic, L., 2002. Precipitation diagrams of struvite and dissolution kinetics of different struvite morphologies. *Croat. Chem. Acta* 75, 89–106.
- Babic-Ivancic, V., Kontrec, J., Brecevic, L., Kralj, D., 2006. Kinetics of struvite to newberyite transformation in the precipitation system $\text{MgCl}_2\text{--NH}_4\text{H}_2\text{PO}_4\text{--NaOH--H}_2\text{O}$. *Water Res.* 40, 3447–3455.
- Battistoni, P., De Angelis, A., Pavan, P., Prisciandaro, M., Cecchi, F., 2001. Phosphorus removal from a real anaerobic supernatant by struvite crystallization. *Water Res.* 35, 2167–2178.
- Battistoni, P., Boccadoro, R., Fatone, F., Pavan, P., 2005. Auto-nucleation and crystal growth of struvite in a demonstrative fluidized bed reactor (FBR). *Environ. Technol.* 26, 975–982.
- Bauer, P.J., Szogi, A.A., Vanotti, M.B., 2007. Agronomic effectiveness of calcium phosphate recovered from liquid swine manure. *Agron. J.* 99, 1352–1356.
- Bhuiyan, M.I.H., Mavinic, D.S., Koch, F.A., 2008. Thermal decomposition of struvite and its phase transition. *Chemosphere* 70, 1347–1356.
- Bowers, K.E., Westerman, P.W., 2005a. Design of cone-shaped fluidized bed struvite crystallizers for phosphorus removal from wastewater. *Trans. ASAE* 48, 1217–1226.
- Bowers, K.E., Westerman, P.W., 2005b. Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. *Trans. ASAE* 48, 1227–1234.
- Bowers, K.E., Zhang, T., Harrison, J.H., 2007. Phosphorus removal by struvite crystallization in various livestock wastewaters. In: *Proceedings of International Symposium on Air Quality and Waste Management for Agriculture*. American Society of Agricultural and Biological Engineers Meeting Paper No. 701P0907cd. St. Joseph, Mich., ASABE.
- Bridger, G.L., Salutsky, M.L., Starostka, R.W., 1962. Metal ammonium phosphates as fertilizers. *J. Agric. Food Chem.* 10, 181–188.
- Buchanan, J.R., Mote, C.R., Robinson, R.B., 1994. Struvite control by chemical treatment. *Trans. ASAE* 37, 1301–1308.
- de-Bashan, L.E., Bashan, Y., 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer. *Water Res.* 38, 4222–4246.
- Doyle, J.D., Philip, R., Churchley, J., Parsons, S.A., 2000. Analysis of struvite precipitation in real and synthetic liquors. *Trans. Inst. Chem. Eng.* 78, 480–488.
- Doyle, J.D., Parsons, S.A., 2002. Struvite formation, control, and recovery. *Water Res.* 36, 3925–3940.
- Driver, J., Lijmbach, D., Steen, I., 1999. Why recover phosphorus for recycling, and how? *Environ. Technol.* 20, 651–662.
- Gaterell, M.R., Gay, R., Wilson, R., Gochin, R.J., Lester, J.N., 2000. An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environ. Technol.* 21, 1067–1084.
- Goto, I., 1998. *Gesuidou shisetsu yori kaishuu shita rin no riyou gijutsu* (Application of phosphorus recovered from sewage treatment facilities). *Kankyou Gijutsu* 27, 418–422 (in Japanese).
- Greaves, J., Hobbs, P., Chadwick, D., Haygarth, P., 1999. Prospects for the recovery of phosphorus from animal manures: a review. *Environ. Technol.* 20, 697–708.
- Huang, H., Mavinic, D.S., Lo, K.V., Koch, F.A., 2006. Production and basic morphology of struvite crystals from a pilot-scale crystallization process. *Environ. Technol.* 27, 233–245.
- Isaac, R.A., 1990. Metals in plants – atomic absorption spectrophotometric method. Method 975.03. In: Helrich, Kenneth (Ed.), *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th ed. AOAC, Inc., Arlington, VA.
- Johnston, A.E., Richards, I.R., 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. *Soil Use Manage.* 19, 45–49.
- Le Corre, K.S., 2006. Understanding Struvite Crystallisation and Recovery. Ph.D. Dissertation. Cranfield University, Cranfield, UK.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2005. Impact of calcium on struvite crystal size, shape, and purity. *J. Cryst. Growth* 283, 514–522.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2007. Impact of reactor operation on success of struvite precipitation from synthetic liquors. *Environ. Technol.* 28, 1245–1256.
- Li, X.Z., Zhao, Q.L., 2003. Recovery of ammonium–nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecol. Eng.* 20, 171–181.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. John Wiley and Sons, New York.
- Massey, M.S., 2008. Dairy Farm Phosphorus Recovery and Re-use to Reduce Water Quality Risk and Improve Phosphorus Cycling in Agriculture. M.S. Thesis. Colorado State University, Fort Collins, CO.
- Massey, M., Davis, J., Ippolito, J., Sheffield, R., 2009. Effectiveness of recovered magnesium phosphates as fertilizers in neutral and slightly alkaline soils. *Agron. J.* 101, 323–329.
- Munch, E.V., Barr, K., 2001. Controlled struvite crystallisation for removing phosphorus from anaerobic digester side streams. *Water Res.* 35, 151–159.
- Padmore, J.M., 1990. Phosphorus in animal feed – photometric method, method no. 965.17. In: Helrich, Kenneth (Ed.), *Official Methods of Analysis of the Association of Official Analytical Chemists*, 15th ed. AOAC, Inc., Arlington, VA.
- Quintana, M., Colmenarejo, M.F., Barrera, J., Garcia, G., Garcia, E., Bustos, A., 2004. Use of a byproduct of magnesium oxide production to precipitate phosphorus and nitrogen as struvite from wastewater treatment liquors. *J. Agric. Food Chem.* 52, 294–299.
- Randall, C.W., 2003. Potential societal and economic impacts of wastewater nutrient removal and recycling. *Water Sci. Technol.* 48, 11–17.
- Rothbaum, H.P., Rohde, A.G., 1976. Long-term leaching of nutrients from magnesium ammonium phosphate at various temperatures. *New Zealand J. Exp. Agric.* 4, 405–413.
- Sarkar, A.K., 1991. Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems. *J. Mater. Sci.* 26, 2514–2518.
- Schipper, W.J., Klapwijk, A., Potjer, B., Rulkens, W.H., Temmink, B.G., Kiestra, F.D.G., Lijmbach, A.C.M., 2001. Phosphate recycling in the phosphorus industry. *Environ. Technol.* 22, 1337–1345.
- Schuiling, R.D., Andrade, A., 1999. Recovery of struvite from calf manure. *Environ. Technol.* 20, 765–768.
- Shu, L., Schneider, P., Jegatheesan, V., Johnson, J., 2006. An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresour. Technol.* 97, 2211–2216.
- Stratful, I., Scrimshaw, M.D., Lester, J.N., 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Res.* 35, 4191–4199.
- Sterling, M.S., Ashley, K.I., Bautista, A.B., 2000. Slow-release fertilizer for rehabilitating oligotrophic streams: a physical characterization. *Water Qual. Res. J. Can.* 35, 73–94.
- Ueno, Y., Fujii, M., 2001. Three years experience of operating and selling recovered struvite from full-scale plant. *Environ. Technol.* 22, 1373–1381.
- Vaccari, D.A., 2009. Phosphorus famine: the threat to our food supply. *Sci. Am.* Available at: <<http://www.scientificamerican.com/article.cfm?id=phosphorus-a-looming-crisis>> (Verified August 2009).
- Valsami-Jones, E., 2001. Mineralogical controls on phosphorus recovery from wastewaters. *Mineral. Mag.* 65, 611–620.
- van der Houwen, J.A.M., Valsami-Jones, E., 2001. The application of calcium phosphate precipitation chemistry to phosphorus recovery: the influence of organic ligands. *Environ. Technol.* 22, 1325–1335.
- van Dijk, J.C., Braakensiek, H., 1984. Phosphate removal by crystallization in a fluidized bed. *Water Sci. Technol.* 17, 133–142.
- Wang, J., Burken, J.G., Zhang, X., Surampalli, R., 2005. Engineered struvite precipitation: impacts of component-ion molar ratios and pH. *J. Environ. Eng.* 131, 1433–1440.
- Wang, J., Burken, J.G., Zhang, X., 2006. Effect of seeding materials and mixing strength on struvite precipitation. *Water Environ. Res.* 78, 125–132.
- Webb, K.M., Ho, G.E., 1992. Struvite ($\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$) solubility and its application to a piggery effluent problem. *Water Sci. Technol.* 26, 2229–2232.
- Wu, Q., Bishop, P.L., 2004. Enhancing struvite crystallization from anaerobic supernatant. *J. Environ. Eng. Sci.* 3, 21–29.
- Yi, W., Lo, K.V., 2003. Phosphate recovery from greenhouse wastewater. *J. Environ. Sci. Health B* 38, 501–509.
- Zeng, L., Li, X., 2006. Nutrient removal from anaerobically digested cattle manure by struvite precipitation. *J. Environ. Eng. Sci.* 5, 285–294.