Phosphorus Removal from Wastewater and Manure Through Struvite Formation
An Annotated Bibliography

One method of removing phosphorus from manure is through the formation of struvite. Recently, there has been an upsurge in the study of the formation of struvite as a method to remove phosphorus from dairy manure, similar what has been used in some other wastewater processes for a number of years. This bibliography gives an introduction to what struvite is, and reviews some of the literature on struvite formation as a means of phosphorus removal from waste waters and manure, with an emphasis on dairy manure. While not exhaustive, it summarizes some of the research to provide a possible foundation for knowledge and an evaluation of this technique. It uses the abstracts provided with the papers reviewed where available, with slight modifications in some cases. Corrections, additions and questions can be directed to the compiler, as listed at the end of this document.

From Wikipedia, an edited version of its entry on struvite has the following information:

> Struvite is an ammonium magnesium phosphate mineral with formula: ($NH_4MgPO_4 \cdot 6(H_2O)$). Struvite crystallizes in the orthorhombic system as white to yellowish or brownish-white pyramidal crystals or in platey mica-like forms. It is a soft mineral with Mohs hardness of 1.5 to 2 and has a low specific gravity of 1.7. It is sparingly soluble in neutral and alkaline conditions, but readily soluble in acid.
>
> It is sometimes a problem in sewage and waste-water treatment, particularly after anaerobic digesters release ammonium and phosphate from waste material, as it forms a scale on lines and clogs system pipes. Recovery of phosphorus from various waste streams, particularly agricultural manure and municipal wastewater treatment plants, as struvite and recycling those nutrients into agriculture as fertilizer appears promising.
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> Struvite was first described from medieval sewer systems in Hamburg Germany in 1845 and named for geographer and geologist Heinrich Christian Gottfried von Struve (1772-1851). Use as an agricultural fertilizer was first reported in 1857.

This bibliography is divided into the following categories;

Municipal wastewater
Livestock – Dairy
Livestock – Swine
Livestock – General
Process research
Miscellaneous
Conferences

<u>Municipal Wastewater</u>

1. Münch, Elisabeth V., and Barr, Keith, "Controlled Struvite Crystallisation for Removing Phosphorus from Anaerobic Digester Sidestreams", *Water Resources*, 35(1):151-159, 2001

> Enhanced biological phosphorus removal wastewater treatment plants that use anaerobic digesters for sludge treatment have high phosphorus concentrations in the sidestreams from their sludge dewatering equipment. To remove phosphorus from such sidestreams, controlled struvite crystallisation can be used. Struvite (or MAP) is a naturally occurring crystal of magnesium, ammonium and phosphate. We present operational results obtained with a continuously operated pilot-scale MAP reactor. The influent to the MAP reactor was centrate from the centrifuge that dewaters anaerobically digested sludge at the Oxley Creek wastewater treatment plant in Brisbane. We used a 60% magnesium hydroxide slurry to add the required magnesium to the process and to obtain the alkaline pH value required. The pilot-scale MAP process achieved an ortho-P removal ratio of 94% from an average influent ortho-P concentration of 61 mg/l. The reactor was operated at a pH of around 8.5. Insufficient dosing of magnesium reduced the P removal performance. There was no influence of the hydraulic residence time on the process in the range of 1±8 h. The dry MAP product had cadmium, lead and mercury concentrations well below the legal limits for fertilisers in Queensland, Australia and can be reused as a valuable slow-release fertiliser.

2. Yoshino, M., et. al., “Removal and Recovery of Phosphate and Ammonium Struvite from Supernatant in Anaerobic Digestion“, *Water Science and Technology*, 48(1):171-178, 2003

In this study, reaction kinetics and design parameters of struvite production are experimentally investigated by using basic reaction type and a draft-tube type reactors. Struvite production rate, which is a very important parameter in reactor design and efficiency estimation, is formulated in an equation consisting of a rate constant (k_2), and magnesium, phosphate and ammonium concentrations. The value of k_2 is shown to be increased with struvite concentration and mixing intensity in the reactor. The developed equation is applied to the results obtained from the draft-tube type reactor experiments and verified for its applicability. High struvite concentration of 10–25% is maintained in the draft-tube reactor experiments. 92% removal and recovery efficiency with effluent phosphorus concentration of 17 mg/L is achieved under the conditions of 4 minutes reaction time, pH of 8.5 and Mg/P molar ratio of 1.1.

3. Jaffer, Y., et. al. “Potential Phosphorus Recovery by Struvite Formation”, *Water Research*, 36:1834-1842, 2002

A mass balance was conducted at full scale across the whole sewage treatment plant in order to identify a stream to conduct bench-scale struvite crystallisation studies. The most suitable stream was identified as the centrifuge liquors. The average flow of the liquor stream was $393m^3$ d^{-1} and the composition was as follows: 167 mg L^{-1} phosphorus, 44mg L^{-1} magnesium, 615mg L^{-1} ammonium, 56mg L^{-1} calcium and 2580mg L^{-1} of alkalinity. The pH averaged at 7.6 and the stream had a predicted struvite precipitation potential of 140 mg L^{-1}.

Struvite crystallisation occurred quickly during the trials, by raising the pH of the centrifuge liquors to 9.0 and dosing with magnesium. Up to 97% phosphorus removal as struvite was achieved. Struvite formation occurred when the molar ratio of magnesium: phosphorus was at least 1.05 : 1. Below this ratio, phosphorus removals of 72% were observed, but not exclusively as struvite. Annual yields of struvite were calculated to be 42–100 tonnes a year, depending on the dose regime. Revenue from the sale of produced struvite could be between £8400 and £20,000 a year.

4. Oerther, Daniel B., et. al., *Final Report: Phosphorus Recovery from Sewage*, US EPA, no date (project period through May 30, 2005), no pages, accessed on the Internet on September 26, 2006 at http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7345/report/F. Follow up grant abstract through May 31, 2006 is described at http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7760/report/0

The abstract notes that

> The innovative design that will be pursued in this project links bioprocess engineering for enhanced biological phosphorus removal, phosphorus recovery through chemical precipitation of struvite, and experimentally assessing phosphorus bioavailability from struvite as a slow-release fertilizer.

While the project has been deemed a success by the investigators (for example, the struvite did act as a fertilizer for alfalfa and coleus), only general details are provided in a three page summary on the Internet. A follow up grant was provided for September 2005 to May 2006, but no reports are yet posted on the web page.

<u>Livestock - Dairy</u>

1. Young, Montessa, “Phosphorus Removal from Dairy Wastewater”, December 2, 2003, 23 overhead slides. On the Internet at http://courses.ag.uidaho.edu/bae/bae404/Enhance%20Proj.html, accessed September 11, 2006

After highlighting some reasons to remove phosphorus from dairy wastewater, six processes for its removal from dairy manure are described and compared. These are:

Mechanical or gravity separation: 5%-75% removal
Lime (calcium): in one hour, 39% removal of soluble phosphorus (SP) with low dosage (1.3 g/L), 78% with high dosage (6.6 g/L)
Liquid alum (aluminum): in one hour, 41% removal of SP with low dosage (0.8 g/L), 100% SP removal and 82% total phosphorus removal with high dosage (8.0 g/L)
Iron compounds: in one hour, 42% removal of SP with low dosage (0.8 g/L), 100% SP removal and 74% total phosphorus removal with high dosage (8.0 g/L)
Biological processes: on swine manure, 31% to 91% removal, depending on pH, species of phosphorus and metal ions
Magnesium, struvite precipitation: 90% reduction for soluble phosphorus in swine manure

The presentation then gives results of a test case of a system with struvite precipitation with a fluidized bed crystallizer, showing a diagram and photo of the system and estimating the annual costs of $66,000 for a farm of 5,750 mature cows with young stock. This costs includes an amortization of $26,000 a year for capital costs of $78,000, labor costs of $27,000 a year at $50 an hour, power costs of $7,000 a year, and ammonia and magnesium brine costs of $3,000 each.

2. Sheffield, Ron, E., "Phosphorus Export via Struvite Precipitation, August 31, 2005, 13 overhead slides. Accessed on the Internet at http://www.oardc.ohio-state.edu/ocamm/msr%2005%20presentations.htm on September 11, 2006

This presentations builds on the presentation of Montessa Young, and starts with the same information on the technology and reported separation of phosphorus from swine manure, along with the same diagram and photo of the fluidized-bed crystallization unit. However, it then provides data from tests done at the Si-Ellen farm, that has 4,000 cows that has a flush cleaning system.

Treatment of the manure first goes through a slope screen and then to a gravity basin, followed by 3 storage ponds. The analysis of the wastewater is given as a total phosphorus of 85 mg/L, PO_4 at 25.4 mg/L and a pH of 7.8. The stage at which these data were obtained was not given.

By adjusting the pH and added magnesium, comparisons were made on four levels of removal, as follows:

pH	Mg (ppm)	% PO_4 removed	% total P removed
8.4	60	69.8	18.5
8.8	60	81.4	14.7
8.4	120	46.0	18.3
8.8	120	64.6	26.5

3. Harrison, Joe, **"**Got Too Much Phosphorus? Help Is on its Way!", *WSU State Dairy News*, 15 (2), July 2006. Accessed on the Internet at http://www.puyallup.wsu.edu/dairy/readArticle.asp?intArticleID=180 on September 11, 2006

In 2004, the WSU Livestock Nutrient Management Program and Multiform Harvest Inc. received a grant from the Washington Technology Center to adapt a process that uses a fluidized bed to remove phosphorus from liquid manure as a granular material called struvite. Since the fall of 2004, additional research funds for this project have been received.

As of the spring of 2006, the project is achieving ~ 50% removal of total phosphorus, and 70-80% removal of orthophosphate phosphorus, in the form of struvite from liquid dairy manure stored in a lagoon after removal of large solids. Several advances have allowed the project to achieve the 50% removal rate, including use of a better-suited pump type, acidification to break phosphorus from the calcium that binds it, and a shift toward a deeper, finer bed. The current effort focuses on removal of phosphorus from liquid dairy manure that has been processed through an anaerobic digester.

As part of this project there has been an evaluation of the "fertilizer" value of the struvite to grow triticale, corn silage, and alfalfa. The triticale growth studies were conducted in a green house and compared struvite to commercial fertilizer at an equivalent rate of phosphorus addition. The results indicated that struvite can serve as a good source of phosphorus. During the summer of 2006, the project is growing corn for silage and alfalfa in large plots at the WSU Prosser - Irrigated Agriculture Research and Extension Center.

4. Sheffield, R.; Bowers, K.; and Harrison, J., "Phosphorus Removal on Dairies in the Pacific Northwest: Applying a Cone Shaped Fluidized Bed Phosphorus Crystallizer", *Proceedings, Symposium State of the Science. Animal Manure and Waste Management January 5-7, 2005, San Antonio, Texas,* 6 pages. Accessed on the Internet at http://www.cals.ncsu.edu:8050/waste_mgt/natlcenter/sanantonio/Sheffield.pdf on September 11, 2006. Also, Sheffield, Ron; Bowers, Keith.; and Harrison, Joe, "Phosphorus Removal on Dairies in the Pacific Northwest: Applying a Cone Shaped Fluidized Bed Phosphorus Crystallizer", a 13-overhead presentation accessed on the Internet at http://www.cals.ncsu.edu/waste_mgt/natlcenter/sanantonio/phosphorusremoval.ppt on September 29, 2006

These references include data from the use of the struvite crystallizer on swine manure in work done at North Carolina State University and on two dairy farms in the Northwest – the Si-Ellen 4,000 cow open-lot farm in Idaho and the 600 cow freestall Werkhoven farm in Washington.

The total phosphorus in all three manure streams was similar (83 to 93 ppm), while orthophosphate phosphorus concentration averages varied from 27 ppm at the Idaho farm to 39 ppm at the Washington farm to 42 ppm with the swine manure. Significant differences where found with magnesium (Mg) concentrations, at 60 ppm with the swine manure and 155-241 ppm with the dairy farms, and total ammoniacal nitrogen (TAN), which was 178 ppm in the swine manure and 332-662 ppm at the dairy farms.

Tests were done by adding either ammonia water or anhydrous ammonia to achieve different pH values and with either acidified magnesium oxide, magnesium sulfate or magnesium chloride at four different levels (0, 30, 60 and 120 ppm).

The removal efficiencies for both total phosphorus (TP) and PO_4 were substantially lower for the dairy manure than for the swine removal as shown in the following table. Also, there was a much greater variance in manure composition and phosphorus removal efficiencies with the dairy manure than with the swine manure.

Parameter	NCSU (swine)	Idaho Dairy	Washington Dairy
TP removal (%)	66	19 (0 to 55)	6 (-41 to 63)
PO_4 removal (%)	80	56 (-59 to 89)	4 (-55 to 38)

It is believed that with the dairy manure, part of the phosphorus was already tied up as struvite, given the high values of TAN and Mg. It was thought that perhaps these were in very small particle sizes that could not be trapped by the crystallizer. One way to test this hypothesis is to acidify the untreated manure, which would dissolve struvite and this is proposed as further research.

Next steps include using a portable struvite crystallizer to test various wastewaters, test of a full-scale crystallizer for more than 10 million gallons a year, working for certification of the resulting struvite as an organic products, testing crop response to the struvite, and testing anaerobic digestion as apart of the struvite crystallization formation process.

5. Bowers, K., Harrison, J. and Sheffield, R. "Application and Evaluation of a Cone-Shaped Fluidized-Bed Phosphorus Crystallizer in Dairy Wastewater" *2005 Animal Waste Management Symposium, October 5-7, 2005, Research Triangle Park, NC*. Accessed on the Internet on September 27, 2006 at http://www.cals.ncsu.edu/waste_mgt/05wastesymposium/PDFS/Bowers.pdf. Also available from the compiler of this bibliography.

Tests were performed of a system to form struvite from dairy manures at two farms in Idaho and Washington, using a system developed at North Carolina State University for swine manure. Both farms use a flush system for handling manure.

The device consists of a cone-shaped device in which ammonia and magnesium are added to the manure stream to encourage the formation and settling of struvite. Modifications were made to the device for the insertion of the additives at the two farms, and the results are summarized in the following table.

Average raw wastewater content and TP removal for five sets of tests. (Excludes periods of zero pH adjustment.)

Parameter	Bowers and Westerman, 2003 (swine)	Idaho Dairy	Washington Dairy, Part 1*	Washington Dairy, Part 2* (no acid)	Washington Dairy, Part 2* (with acid)
TP (ppm)	88	93	83	91	103
OP (ppm)	42	27	39	41	47
Mg (ppm)	60	155	241	No data	322
TAN (ppm as N)	178	332	662	No data	1101
pH	7.7	7.5	7.8	7.8	7.8
TP removal (%)[1]	66	14	3	0	15

*****Adjusted for dilution by water in Mg and trona solutions.

The researched concluded that "the cone-shaped fluidized-bed crystallizer removed phosphorus from wastewater at the two northwest dairies where it was tested. However, removal fell short of that previously reported for the system in swine wastewater in North Carolina. The lower degree of removal may be explained by the fact that the dairy wastewater contained higher amounts of Mg and TAN, indicating that much of the struvite may already be precipitated in fine suspended form, unavailable for capture by the fluidized bed. The TP removal increased when wastewater was acidified prior to treatment, consistent with the theory, but still only reached 32% at most. Further experiments should concentrate on the question of whether the phosphorus is being held in other form of phosphorus, such as calcium phosphates, and thus interfering with the ability of the crystallizer system to remove it. "

6. Bowers, Keith, E. "Apparatus and Method For Removing Phosphorus from Waste Lagoon Effluent ", United States Patent Application 2006000078*,* January 5, 2006, 66 pages. Accessed on the Internet at http://cxp.paterra.com/uspregrant20060000782.html on September 29, 2006

The patent abstract is as follows:

> An apparatus and method for removing phosphorus from a wastewater effluent stream from a hog waste lagoon. The wastewater effluent is introduced to the bottom of an inverted cone-shaped continuous crystallizer including a fluidized bed of struvite therein. An effective amount of ammonia is introduced to the wastewater effluent at the bottom of the crystallizer to elevate the pH of wastewater effluent a predetermined amount. An effective amount of magnesium is also introduced to the wastewater effluent at the bottom of the crystallizer. The composition adjusted wastewater effluent is then continuously passed upwardly through the fluidized bed of struvite to reduce the total phosphorus content of the wastewater effluent a predetermined amount of up to about 80% or more. The treated wastewater effluent stream is removed from the top of the crystallizer, and struvite crystals that grow large enough to sink from the bottom of the crystallizer are periodically removed from a collection chamber there beneath.

7. Sherman Hansen, Alice, "Technology Tackles Phosphorus Problem", *Capital Press*, October 10, 2004. Accessed on the Internet at http://www.bluefish.org/tackphos.htm on September 27, 2006

Ron Sheffield of the University of Idaho and Joe Harrison of Washington State University-Buckley have been testing a cone-shaped device to remove phosphorus from dairy manure through the formation of struvite. It is estimated that this system can remove from 60-85% of the dissolved phosphorus. They have teamed up with Keith Bowers of the Seattle firm Multiform Harvest Inc, who developed the device as a graduate student for use with hog farms. The system is said to need very little power – a one horsepower pump can handle 1 million gallons a year.

8. Schuiling, R. D. and Andrade, A, "Recovery of Struvite from Calf Manure", *Environmental Technology*, vol. 20, pp 765-768, 1999

During an archaeological excavation of a site in the heart of Amsterdam, large struvite crystals were found dating from the 13th century in a latrine. Using a principal of duplicating nature, it was decided to test the struvite process for the removal of phosphorus from organic waste streams. It was found that it worked for calf and chicken manure (if made into a slurry), but did not work as well with unprocessed pig manure. Laboratory and pilot-scale experiments were tested with denitrified calf manure, and dephosphatization occurred within 2-3 hours in the lab and within 30 minutes in the pilot-scale plant.

Based on these results, one of the calf manure treatment plants at Putten, The Netherlands, was fitted with a full-scale dephosphatization unit in October 1997, with operation begun in March of the next year. Struvite formation began in April, and the phosphorus level in the effluent was kept below 30 mg/liter.

9. Massey, Michael, and Davis, Jessica, "Phosphorus Recovery in Colorado Agriculture", *Colorado Water*, April/may 2007, pages 16- 19. Accessed on the Internet on June 22, 2007 at http://cwrri.colostate.edu/pubs/newsletter/2007/April%20May2007.pdf

Using the cone-shaped fluidized-bed reactor developed in part by Dr. Ron Sheffield of the University of Idaho, tests were done of struvite removal at two dairy farms in northern Colorado. Wastewater was pumped from anaerobic lagoons into a holding tank, where the pH was adjusted to 5.2 using hydrochloric acid in one set of tests (the conventional approach) and acetic acid as a new method. The liquid was then pumped at a rate of about 2 gallons per minute to the reactor, where the pH was rapidly increased to a value of 7.5-8.3 using NH_3 in the conventional approach and potassium hydroxide in the new approach. This rapid change in pH caused the precipitation of phosphates onto the seed material in the reactor. While the article does not present actual results, the recovery rate was said to be the same in both the conventional and new approaches, but relatively low and in a amorphous form, rather than the crystalline form expected.

An email note was sent to the authors about the actual removal data and the following results were obtained.

Mean Results for Conventional and a New Struvite Removal Process
(Conventional n=5; New n=30)

	Conventional			New		
	Input (ppm)	Output (ppm)	Removal	Input (ppm)	Output (ppm)	Removal
ortho-P (as P)	25.5	4.77	81%	60.3	31.3	48%
total P (as P)	94.9	81.0	14%	78.4	67.2	14%

Livestock - Swine

1. Laridi, R, Auclair, J-C, Benmoussa, H., "Laboratory and Pilot-scale Phosphate and Ammonium Removal by Controlled Struvite Precipitation Following Coagulation and Flocculation of Swine Wastewater", *Environmental Technology*, 26(5):525-536, May 2005 (abstract only reviewed)

To reduce the suspended solids load to a trickling filter, raw swine effluent was pre-treated with ferric chloride and a cationically-charged coagulant. This resulted in struvite formation downstream and struvite precipitation studies were carried out as a function of pH in both laboratory and pilot scale studies.

It was found that the optimal pH was 8.5 with a retention time of 30 minutes with removal of phosphate and ammonium at 98% and 17% respectively in lab tests and 99% and 15% in pilot-scale tests of both batch and continuously operated reactors.

2. Burns, R. T., et. al., “Optimization of Phosphorus Precipitation from Swine Manure Slurries to Enhance Recovery”, *Water Science and Technology*, 48(1):139-146, 2003

Laboratory experiments were conducted using magnesium chloride ($MgCl_2 \cdot 6H_2O$, 64% solution) to force the precipitation of phosphorus and reduce the concentration of soluble phosphorus (PO_4^{3-}) in two swine wastes. One of the swine wastes tested contained a high concentration of PO_4^{3-} (initially ~ 1,000 mg/L), and the other swine waste tested contained a low concentration of PO_4^{3-} (initially ~230 mg/L). The precipitation reactions were performed to determine the required reaction time, pH, magnesium addition rate and seed material for future precipitate recovery work. For the high and low concentration waste, a 10 minute reaction time at a pH of 8.6 was sufficient to remove 98 and 96% of the PO_4^{3-} from solution. A molar ratio of Mg^{2+}:PO_4^{3-} of 1.6:1 was determined to be effective for PO_4^{3-} removal from both the low and high strength wastes. At a molar ratio of 1.6:1, the PO^{3-} in the high concentration waste was reduced from 590 to 12 mg/L. In the low concentration waste, the PO_4^{3-} concentration was reduced from 157 to 15 mg/L. Seeding the reaction did not significantly enhance the recovery process.

Livestock – General

1. Burns, Robert T. and Moody, Lara B., “Phosphorus Recovery from Animal Manures using Optimized Struvite Precipitation” reprint from *Proceedings of Coagulants and Flocculants: Global Market and Technical Opportunities for Water Treatment Chemicals*, Chicago, IL, May 22-24, 2002, 7 pages

This paper reviews the status of work done to remove phosphorus from animal manures through struvite formation, citing just over 20 references. The paper notes that phosphorus recovery has been in use in Europe and Japan for municipal waste water treatment, but that farm-scale operations have not been developed. Most of the work reviewed deals with swine manure.

Process Research

1. CEEP (Centre Européen d’Etudes des Polyphosphates), “Phosphate Recovery by Struvite Precipitation in a Stirred Reactor”, 66 pages, June 22, 2002

The conventional phosphate removal technique applied for the wastewater treatment is based on phosphate fixation in activated sludge. The processes unfortunately generate huge amounts of a water-rich sludge which has to be disposed off at continuous increasing costs.

An alternative would be to intercept a significant proportion of phosphorus by phosphates precipitation in wastewaters. Phosphorus could then be recycled into industrial processes instead as simply being transferred to sewage sludges as a residual. This would also reduce the quantities of sludge generated. It exists other techniques, for example, the KEPRO process (phosphate – as well as 3 other products – removal from sludge, based on thermal hydrolysis with sulphuric acid), or the REM NUT process (P, NH_4 and K removal through selective ion exchange followed by struvite precipitation in proper conditions).

This work focuses on phosphate removal by precipitation. Numerous studies have been reported in literature on this subject. The reactors tested are mainly fluidised bed reactors (FBR) and the phosphate is mainly recovered as calcium phosphate or struvite (MAP, Magnesium Ammonium Phosphate, principally). Our choice turned to the struvite precipitation. Owing to the need of having a simple and flexible technology, a new reactor was designed. This reactor is composed of a mixing zone in which precipitation takes place and a settling zone to keep the solid particles inside of the reactor. Thus, the reactor is operated in continuous mode with the liquid phase and batchwise with the solid particles. This operating mode is needed by the low phosphate concentration level in wastewater. FBR are also operated with this mode but the reactor developed in this current study is much more easy to operate. It should also accept more easily variations in wastewater works parameter.

After a description of the theory on crystallization and precipitation, a brief description of the calcium phosphate and struvite chemistry will be presented. Then, the different processes developed in literature for P-recovery are described.

The last parts deal with the study of the feasibility of the new reactor. Phosphate is recovered as struvite (Magnesium Ammonium Phosphate or MAP) which is precipitated by sodium hydroxide and magnesium chloride addition. The pH studied vary from 8 to 9.2 and the molar ratios Mg/P go from 0.9 to 1.5. Two different seed materials (sand and struvite pellets supplied by Unitika) are tested. The seeded experiments are finally compared with unseeded precipitations.

2. Shimamura, K., et. al., " Development of a High-Efficiency Phosphorus Recovery Method Using a Fluidized-Bed Crystallized Phosphorus Removal System", *Water Science and Technology*, 48(1):163-170, 2003

In the reactor of the fluidized-bed crystallized phosphorus removal system, seed crystals (of MAP) are fluidized previously and new MAP crystals are produced on the seed crystal surfaces. Conventionally, the reactor consisted of one reaction tank only, but this practice had the problem that as the crystallization progresses, the seed crystal grows excessively and as a result, the effective reaction surface areas are decreased and the fluidization effect is degraded, causing the recovery ratio to be decreased. Recently, the authors have devised a two-tank type reactor by adding a sub reaction tank to the reactor (now the main reaction tank) so that the MAP particle size in the main reaction tank may be kept constant making the recovery ratio stable. They conducted a demonstration test with a pilot experimental system of the 2-tank type reactor. For raw water T-P 111 to 507 mg/L, the main reaction tank treated water T-P 14.0 to 79.5 mg/L and phosphorus recovery ratios 84 to 92% were obtained. Because the mean MAP particle size in the main reaction tank could be kept constant, the phosphorus recovery ratio could always be above 80%, realizing stable treatment.

3. Adnan, A. Mavinic, D. S., and Koch, F. A., "Pilot-scale Study of Phosphorus Recovery Through Struvite Crystallization – Examining the Process Feasibility", *Journal of Environmental Engineering and Science*, 2(5):315-323, September 2003

The suitability of a new pilot-scale reactor to recover phosphorus through struvite crystallization was examined. Based on the similar principles previously tested in bench-scale reactors and scaled up to overcome operating problems, the pilot-scale crystallizer achieved rates of ortho-P removal rates as high as 90% for low (~50-70 Mg/L P), and medium (~70-100mg/L P) synthetic wastewaters. To achieve these removal rates, a pH of 8.3 was required. A new concept of crystal retention time was found to be one of the main factors in controlling mean crystal size.

4. Adnan, Ali, et. al., "Preliminary Investigation into Factors Affecting Controlled Struvite Crystallization at the Bench Scale", *Journal of Environmental Engineering Science*, 3:195-202, 2004

A preliminary investigation of factors affecting controlled struvite crystallization was conducted in bench-scale studies using a new crystallization reactor design in 21 different experiments. The pH value is an important operating parameter, and low temperatures appears to favor struvite formation. Reactor seeding was not found to be a factor of any particular importance, since, once struvite crystallization reactions were underway, the reactor appeared to be "self-seeding".

<u>Miscellaneous</u>

1. Weigang Yi, et. al., "The Effects of Magnesium and Ammonium Additions on Phosphate Recovery from Greenhouse Wastewater", *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes*, 40(2):363-374, March 2005 (abstract only reviewed)

Phosphorus recovery from greenhouse wastewater, using precipitation-crystallization, was conducted under three levels of calcium concentration, 304 mg/L (7.6 mmol/L), 384 mg/L (9.6 mmol/L), and 480 mg/L (12 mmol/L), and also with additions of ammonium and magnesium into the wastewater. Jar test results confirmed high phosphate removal, with more than 90% of the removal achieved with a pH as low as 7.7. Under the low calcium concentration, ammonium addition affected the chemical reactions at pH lower than 8.0, where struvite was produced; when the pH was raised to 8.8, other calcium compounds dominated the precipitation. Under the medium calcium concentration, ammonium and magnesium addition helped struvite precipitation in the low pH range. Hydroxylapatite (HAP) was the main product.

<u>Conferences</u>

1. *Second International Conference on the Recovery of Phosphorus from Sewage and Animal Wastes,* Golden Tulip Leuwenhorst Conference Centre Hotel, Noordwijkerhout, The Netherlands, 12 & 13 March 2001. Program on the Internet at http://www.nhm.ac.uk/research-curation/projects/phosphate-recovery/finalprog3.doc

This was a very extensive conference; the program follows, with links to many of the presentations. Several of the links were tested on October 31, 2006 and worked for the compiler of this bibliography.

Recovery from sewage: where and why?

A broad view: phosphorus recovery is today included in UK Environment Agency policy – why ?
Nina Sweet, Bob Robinson, Simon Leaf, UK Environment Agency

Implications of within-wwtp P-recovery for biosolids management: biosolids volumes, P:N ratio and recycling (agronomic, LCA and economic implications) – an European perspective
Tim Evans, CIWEM (Chartered Institution of Water and Environment Management)

Technical and economic feasibility of recovery: case studies

Boundary conditions for recovered phosphates to be useable for industrial recycling at Vlissingen
Willem Schipper, Thermphos International, The Netherlands
Assessing the potential of full-scale P-recovery by struvite formation
Yasmin Jaffer, Pete Pearce, Thames Water UK

Phosphorus recovery in wastewater treatment plants
Bernd Heinzmann, Berlin Wasser Betriebe, Germany

Implications for the quantity, quality and disposal of sewage sludge; regulatory issues,

Implications of P-recovery for sludge production and management
Nicolas Jeanmaire, Office International de l'Eau, France
Sludge production related to P-removal
Etienne Paul, INSA Toulouse, France
Swedish policy on phosphorus recovery
Bjorn Wallgren, Swedish Environmental Protection Agency, Sweden

Struvite deposit issues and implications of P-recovery for EBNR operation optimisation and bio-P sludge handling

Sewage treatment and methods for phosphate recovery in BCFS process
Marc van Loosdrecht, Delft Technical University,
and Frank Brandse, Waterboard Reest en Wieden, The Netherlands
Refixation of phosphates released during bio-P sludge handling as struvite or aluminium phosphate
Norbert Jardin, Rurhverband Planungsabteilung, Essen, Germany
Struvite deposit problems, causes, avoidance, implications for P-recovery
Simon Parsons, Cranfield University UK

Possibilities for recovering P from sludges (including iron containing) and from ash

Effects of wastewater treatment technology on P-recovery from sludge and ash
Bengt Hultman, Swedish Royal Institute of Technology, Sweden
Recovery of phosphorus from sewage
Bram Klapwijk, Wageningen Agricultural University, The Netherlands
Phosphate availability for beneficial use in biosolids products
Fiona Hogan, WS Atkins, United Kingdom
Phosphate recovery from iron phosphate sludges
Jan Suschka, Lodz Technical University Bielska Biala, Poland

Calcium phosphate precipitation chemistry and reactor design

The influence of organic ligands on calcium phosphate precipitation
Jacqueline van der Houwen, Natural History Museum London
Precipitation of calcite in the presence of inorganic phosphates
Lorraine Plant, Alan House, Centre for Ecology and Hydrology UK, joint calcium phosphate chemistry research with Reading University

Current knowledge of calcium phosphate chemistry and in particular solid surface – water interface interactions
Petros Koutsoukos, Patras University Greece
Development of artificial seed crystal for crystallisation of calcium phosphate
Katsumi Moriyama, Kyushu Kyoritsu University, Kitakyushu, Japan
The effects of pH and Ca/P ratios on the precipitation of calcium phosphates
Yonghui Song, Hermann Hahn, University of Karlsruhe, Germany

Struvite precipitation chemistry and reactor design

Struvite characterisation and control
Kurt Ohlinger, California State University, Sacramento, USA
Kinetic model of struvite precipitation from sewage liquors
Mark Wentzel, Cape Town University, South Africa
Problems of dissolution and crystallisation of struvite
Dalibor Matysek, Ostrova Technical University, Czech Republic,
Recovery of ammonia as struvite from anaerobic digester effluents
Ipek Çelen, Gebze Institute of Technology, Turkey
Conditions influencing the precipitation of struvite
Ian Stratful, Imperial College London, UK
Demonstration of the “Struvite 3.1” computer model of struvite precipitation as applicable to P-recovery.
Mark Wentzel, Cape Town University, South Africa
Experimental investigation of effective and economic pathways to recover phosphates from return active sludge
Alice Crook, Anglian Water, UK
Pilot plant tested in a dozen sewage works and farms for recovering phosphates from wastewaters and liquid manures by struvite precipitation
Rainer Schulze-Rettmer, consultant chemist, Aachen, Germany
In-situ reduction of soluble phosphorus in liquid swine waste slurries
Robert Burns et al., University of Tennessee, USA
Removal of phosphates and ammonia from waste water resulting from the production of carmin red dye from cochineals
Gara Villalba Mendez et al., Dept. Chemical Engineering, University of Barcelona
Phosphate recovery following biological aerobic treatment of pig slurry
Marie-Line Daumer, CEMAGREF, Rennes, France
Recovery of phosphorus from waste activated sludge using selective adsorbents
Tomotake Takai et al., Takeda Chemical Industries and Tsukishima Kikai Co., Ltd., Japan
P-recovery research resources at IMAG/Wageningen Agricultural University, Holland
Dick Starmans, Wageningen Agricultural University
Phosphorus accumulation on dairy, poultry and swine farms: can struvite recovery help?
Robert Mikkelsen, N. Nelson, D. Tarkelson, North Carolina State University, USA
A novel approach to the production of wastewater sludges for phosphate recovery
Paul Devine, Queen’s University Belfast, Northern Ireland
Fundamental chemistry and control of struvite precipitation
James Doyle, Cranfield University, UK
Recovery of phosphorus from pig slurry
Julian Greaves, Institute of Grassland and Environmental Research, UKWhat is the fertiliser value of recovered phosphates?
Plant availability of sewage-recovered iron phosphates - results of pot trials
Elisabeth Kvarnström, Lulea University of Technology, Sweden

Brief presentations of P-recovery reactor operating experiences, questions, discussion

Struvite crystallisation in sludge dewatering supernatant using air-stripping : the new full-scale plant at Treviso sewage works, Italy.
Paolo Battistoni et al., Ancona University, Italy
3 years operating experience selling recovered struvite from full-scale plants
Yasanori Ueno, Unitika Ltd., Japan
Full scale calcium phosphate recovery plant operation at Geestmerambacht, in Holland
Simon Gaastra, Waterboard Uitwaterende Sluizen in Hollands Noorderkwartier,

The Netherlands
P-recovery by the crystallisation process: experience and developments
Pieter Piekema, DHV Water BV, The Netherlands
Struvite recovery from wastewater having low phosphate concentration
Fumio Mishina, Japan Institute of Wastewater Engineering Technology, and Satoru Ishiduka, Kurita Water Industries, Japan
Full scale plant recovering iron phosphate from sewage at Helsingborg, Sweden
Ingmar Karlsson, Kemira Kemi Kemwater, Sweden
Pilot plant using seawater as a magnesium source for struvite precipitation
Yoshiharu Nawamura, Nishihara Corporation Ltd, Japan

Economic feasibility of phosphate recovery from sewage

Economic/ environmental costs assessment of phosphate recycling possibilities at Thermphos' plant, Vlissingen, The Netherlands
Berend Potjer, CE (Solutions for environment, economy and technology), Delft, The Netherlands
Logistical and life cycle analysis feasibility of P-recovery
Mark Scrimshaw, Imperial College, London, United Kingdom
Logistic and economic feasibility perspectives for P-recovery from sewage in Holland
Ferdinand Kiestra, Haskoning Ingenieurs- en Architectenbureau, The Netherlands
Making a business from struvite crystallisation for wastewater treatment
Elisabeth von Münch, Brisbane Water, Australia

P-recovery from animal wastes, food factory wastes and other streams

P-recovery in a poultry litter power plant
Hans de Haan, Stichting DEP, The Netherlands
Mobile plant for animal wastes (membrane separation - struvite precipitation)
Kai Höhn, Frauhofer Gesellschaft ICT, Berghausen, Germany
Struvite precipitation from industrial and landfill waste streams
Olcay Tünay, Istanbul Technical University, Turkey
Overview of initiatives in Europe to develop phosphate recovery from separative urine streams
Jac Wilsenach, Delft Technical University, The Netherlands
Pilot studies into phosphate and nitrogen recovery and recycling from human urine
Zsófia Bán, Göteborg University, Sweden
Treatment of pig manures
Julian Greaves, Institute of Grassland and Environmental Research, United Kingdom
Characterisation of waste solutions to determine optimised P-recovery
Kelvin Webb, King's Lynn Borough Council Environmental Health Dept., UK,
Phosphate recovery via precipitation from anaerobically treated manure waste waters
Sergey Kalyuzhnyi, Moscow State University
Anaerobic digestion of phosphorus rich liquors
Andrew Wheatley, Loughborough University, United Kingdom
Biologically driven phosphate precipitation in bio-P sludges
Elaine Dick, Paul Devine, Queen's University Belfast/Questor Centre, Northern Ireland
Integrated bio-P/reversible phosphate adsorption process
Tom Arnot, Saravanan Subramanian, Bath University, United Kingdom
Ultimate removal and recovery of phosphate with a new class of polymeric sorbents
Arup SenGupta, Lehigh University Bethlehem, Pennsylvania, USA
REM-NUT ion exchange plus struvite precipitation process
Lorenzo Liberti, Bari Polytechnic University, Italy

2. *International Conference on Struvite: Its Role in Phosphorus Recovery and Reuse*, 17-18 June 2004, Cranfield University, UK, web page http://www.cranfield.ac.uk/sas/water/struvite/programme.doc. A 13 page summary of the conference can be found in the CEEP SCOPE Newsletter, issue 57, July 2004, on the web at http://www.ceep-phosphates.org/Newsletter/shwNewsList.asp?NID=3&HID=4

The program for this two day conference is divided into six sections, with the sections and the presentations given as follows:

Session 1: Beneficial reuse of struvite

Potassium struvite as an alternative feedstock for elemental phosphorus production
W. Schipper (Thermphos Int., Holland)

Struvite potential as an ingredient in horticultural fertiliser.
A. Johnson (Thames Water, UK)

Fertilisers made out of recovered phosphorus and their acceptance in Germany with special regard to the organised organic farmers
F. Van Sothern (German Water Association ATV-DVWK, Germany)

Session 2: Practical Issues associated with P recovery

Phosphorus Recycling in Treatment Plants with Biological Phosphorus Removal.
B. Heinzmann (Berlin Wasserbetriebe, Germany)

Auto-nucleation and crystal growth of struvite in a demonstration fluidized bed reactor.
R. Boccadoro (Ancona Polytechnic University, Italy)

Phosphorous in swine wastewater and its recovery as struvite in Japan.
K. Suzuki (National Institute of Livestock and Grassland Science, Japan)

Development of a high-efficiency phosphorus recovery method using a 2-tank type fluidized-bed MAP reactor
H. Ishikawa (Ebara Corporation, Japan)

Pilot-scale phosphate and ammonium removal by controlled struvite precipitation from pre-treated swine waste water
R. Laridi (Université du Quebec, Canada)

Struvite crystallization reaction in a semi-continuous stirred reactor
D. Mangin (LAGEP, Université de Lyon I, France)

Phosphate recovery as struvite: factors influencing the crystallization
A. Seco (Universidad de Valencia, Spain)

Session 4: Struvite Chemistry & Crystallisation

Three phase mixed weak acid/base chemistry kinetic modelling of multiple mineral precipitation problems.
D. Lowenthal (University of Cape Town, South Africa)

Nucleation and growth of struvite from synthetic wastewater.
A. Kofina (University of Patras, Greece)

Effect of major ions on struvite crystallization.
I. Kabdalsi (Istanbul Technical University, Turkey)

Impact of calcium on struvite crystal size, shape and purity
K. Le Corre (Cranfield University, UK)

Session 5: Struvite Chemistry & Crystallisation

Free ammonia mechanism
J. Sushcka (Technical University of Bielsko-Biala, Poland)

Phosphorous precipitation as struvite from swine wastewater
I. Celen (University of Tennessee, USA)

Recovery of phosphorus from sewage sludge as MAP
A. Weidelener (Stuttgart University, Germany)

Struvite precipitation from municipal sewage sludge liquor focusing on the development of a mobile unit
D. Antakyali (Stuttgart University, Germany)

Session 6: Alternative wastes.

Struvite precipitation as a method of industrial wastewater treatment.
J. Gluzinska (Poland)

Recovery of phosphorus from separated human urine by the addition of soluble calcium and magnesium compounds
M. Hartmann (Bauhaus University Weimar, Germany)

Phosphorous and nitrogen removal from waters and recovery as struvite by using hybrid and integrated membrane operations
R. Molinari (University of Calabria, Italy)

Use of surface diagnostics for struvite scale analysis.
B. Jefferson (Cranfield University, UK)

3. 75. Darmstädter Seminar -Abwassertechnik- "Rückgewinnung von Phosphor aus Abwasser und Klärschlamm - Konzepte, Verfahren, Entwicklungen [75th Darmstadt Seminar – Wastewater Techniques – Phosphorus Recovery from Wastewater and Sewage Sludge – Concepts, Processes, Developments], 12-13 December 2005. Three page summary available in the CEEP SCOPE Newsletter, issue 64, at http://www.ceep-phosphates.org/Files/Newsletter/Scope%20Newsletter%2064.pdf

This was a two day seminar, which was attended by about 120 people. The seminar started with an introduction and a summary of legal, technical, and financial means to promote the recovery of phosphorus from wastewater and sludge. As part of this presentatio, the objectives of phosphorus recycling were given as to reduce the ependency on imports, to extend the availability of the limited resource phosphorus and to reduce the environmental impacts of the phosphate industry.

Other talks looked at the phosphorus content in wastewater – with a focus on municipal wastewater – the needs for phosphorus in agriculture, and a variety of technologies, including:

- the P-RoC process (P-Recovery from wastewater by crystallisation of calcium phosphate)

- the Crystalactor process: in a fluid-bed type of crystalliser (pellet reactor), phosphate is removed and recovered from the wastewater as calcium phosphate, by the use of sand as seed material.

- phosphate recovery (as MAP) in sewage treatment plants using EBPR (enhanced biological phosphate removal).

- chemical oxidative sewage sludge treatment on the dewatering potential and the release of phosphorus (Kemicond process).

- wet oxidation and nanofiltration, using the Bayer LOPROX system (Low Pressure Wet Oxidation).

- the SEPHOS process (Sequential Precipitation of Phosphorus). This technique enables a near 100 % release of phosphorus from ashes

- the Seaborne Technology. The process included an acidic treatment of sewage sludge with a separation of heavy metals and a phosphorus recovery as MAP.

- phosphorus recovery by treating sewage sludge, sewage sludge ash and meat-and-bone meal in the iron baths of the steel industry.

The complete proceedings are available in German for *at* 35 €.

4. *Rückgewinnung von Phosphor aus Abwasser und Klärschlamm [Recovery of Phosphorus from Wastewater and Sludge]*, 24 April 2006, Umweltbundesamtes in Dessau, Germany. Program and papers on the Internet at http://www.isa.rwth-aachen.de/index.php?option=com_remository&Itemid=99&func=select&id=51

This was an afternoon meeting, with the following five presentations, all available in an overhead format on the Internet:

Phosphor – Ressourcen und Verbrauch
[Phosphorus – Resources and Consumption]
Prof. Dr.- Ing. J. Pinnekamp

Potentiale und Verfahren zur Phosphorrückgewinnung bei der Kommunal Abwasserbehandlung
[Potential and Processes for Phosphorus Recovery at Community Wastewater Management]
Dipl. – Ing. H. Herbst

Forschungsergebnisse MAPAK (Teil 1)
[Research Results Magnesium Ammonium Phosphate from Wastewater and Sludge (Part 1)]
Dipl. – Ing. K. Gethke

Forschungsergebnisse MAPAK (Teil 2)
[Research Results MAPAK (Part 2)]
Dipl. – Ing. D. Montag

Fazit – Ausblick – Umsetzung
[Results – Outlook – Transposition]
Prof. Dr.- Ing. J. Pinnekamp

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