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# SCOPE NEWSLETTER

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## Struvite its role in phosphorus recovery and recycling

### SUMMARY REPORT

The conference organised by Cranfield University School of Water Sciences, with support from CEEP, brought together some 70 scientists, water industry experts and other actors interested in struvite recovery from sewage and from animal manures.

The conference showed that today there is a very wide interest in struvite recovery, with scientific research underway in countries across the world: USA, Australia, Japan, Canada, South Africa, UK, Germany, Spain, Switzerland, The Netherlands, Greece, France, Italy, Poland ...

Work underway ranges from detailed investigation of the chemical parameters of struvite precipitation, (e.g. the team at Patras University, Greece), through development of pilot reactors at the laboratory and semi-industrial scale, to operation of full-scale struvite recovery reactors (several in Japan, Thames Water UK at the Slough sewage treatment works, installations treating calf manure and potato factory waste streams in The Netherlands).

Experience of re-use of recovered struvite was also presented, including field trials of struvite as an agricultural fertiliser, use in horticultural products for garden centres, and industrial recycling in the Thermphos International phosphorus furnace in Vlissingen The Netherlands.

#### Questions asked



**John Driver, industrial consultant,** opened the conference by recalling the predictions made at the first international conference on phosphorus recovery and recycling, Warwick University UK, 1998. At the time, the European phosphate industry believed that calcium phosphate

recovery from sewage would be the route to provide industry with a significant proportion of its raw material needs from secondary sources. This has not come about, and today struvite is seen as the feasible route for phosphorus recovery.

The technical feasibility of struvite recovery in both sewage treatment and manure installations is now proven, however, as Mr Driver emphasised, there are now two major obstacles: regulatory and social issues regarding the classification of recovered phosphates as “waste” and perception of re-use in agriculture of products recovered from sewage ; economics in that recovered struvite will not in the foreseeable future be economically competitive with mineral fertilisers because of their low costs.

For struvite recovery and recycling to develop significantly, a political initiative is therefore needed, both to classify recovered struvite as a secondary raw material not a “waste”, and to require the water and animal waste industries to move towards recycling of phosphorus resources. Possible initiatives in this direction are appearing in Germany and Sweden, for example.

### Struvite re-use



**Willem Schipper**, **Thermphos International**, presented operational experience of industrial re-use of recovered K-struvite in the company's industrial thermal phosphorus production process at Vlissingen, The Netherlands. For some years now,

Thermphos is successfully processing calcium phosphates recovered from municipal sewage at the Geestmerambacht waste water treatment plant. Recently, Thermphos has also conducted a trial on the processing of K-struvite (potassium magnesium phosphate) precipitated at a cooperative calf manure treatment installation at Putten The Netherlands.

The factory tested compatibility of K-struvite as a raw material with the existing process, by processing one year of the Putten installations K-struvite production over 4 days (K-struvite was thus 3% of process input phosphate). Magnesium is fully compatible with Thermphos' thermal process and comes out in the slag (in place of the calcium in the usual calcium phosphate rock raw material), but with improved slag characteristics. Potassium was a question mark, as it is not a usual constituent of phosphate rock and, as a "volatile" metal, might be expected to accumulate in the dust-sludge recycle and may need to be bled off. The test showed, however, that at this level of K-struvite use the incorporation potassium posed no problems, and also that no other detectable operating problems occurred.

Thermphos have also been looking into the feasibility of using recovered MAP struvite (magnesium ammonium phosphate) in their process. Although ammonium would be problematic in the phosphorus furnace, it should in fact be driven off during the prior raw material sintering stage, with the resulting ammonia or NO<sub>x</sub> being retained in the plant's gas scrubbing circuits. Full scale testing is planned shortly using struvite which will be

precipitated from a food industry factory waste stream (see ???).

Mr Schipper emphasised that today Thermphos would therefore welcome further supplies of struvite or K-struvite as a secondary raw material.



**Andrew Johnson et al.**, **TERRA / TES Eco Systems / Thames Water**, and a poster by Emma Sharp, Cranfield University, presented experience of re-use of struvite recovered from the Slough municipal waste water

treatment plant operated by Thames Water. A full-scale pilot struvite recovery unit (7m<sup>3</sup>/hour) treats sludge digester centrifuge effluent (after a buffer tank to float off organic particles) from one quarter of the plant's capacity (total capacity 260,000 pe). The struvite production unit has been operating since 2002 (see [\*SCOPE Newsletter n°41\*](#)), testing different operating conditions. The Slough struvite precipitation unit precipitates 80% of inflow soluble phosphate to struvite. Heavy metal levels in the recovered product are low.

Following simple washing and air drying steps (both carried out as manual operations at this scale) the struvite produced is a reasonably clean material with a free moisture content of ~5%.

Recently, use of magnesium hydroxide plus pH adjustment has been tested instead of magnesium chloride. This proved more expensive and resulted in smaller struvite crystals and higher levels of organic impurities in the precipitated struvite.

Struvite quality has been improved by avoiding operating during centrifuge start-up phases, when high organics levels are present.

Thames Water have estimated that if biological nutrient removal (BNR) and struvite recovery were installed at just 7 target waste water treatment plants, this would result in around 1,000 tonnes/year of struvite. Current production is however insufficient

for the logistics of agricultural recycling. TERRA are therefore developing its use as a phosphorus source in an organic garden fertiliser, after combination with other ingredients widely used in such fertilisers (rape seed meal, feather meal, kali vinasse), with a struvite content of around 10%. Their business model is to sell the fertiliser, along with other branded products through a network of garden centres to whom TERRA already sells compost products produced from sewage sludge

Growth trials using the struvite-containing organic fertiliser show good results compared to both a commercial inorganic and organic fertilisers.



***Florian van Sothen***, Member of the task force on phosphate recovery within the German Water Association (ATV-DVWK), presented the results of a survey of organic farmers' organisations and of the grain mills' association in Germany, asking their opinions and positions on the idea of use of sewage-recovered struvite in organic farming. Three out of four German organic farmers are members of such organisations. Although organically-grown products currently make up only 3% of the German food market this is seen as a fast growing sector and, importantly, a sector with a high level of public trust.

45% of sewage sludge in Germany is presently used for farmland spreading, but the use of sewage sludge is increasingly not accepted by the public, and it is strictly not allowed on organic farms. Although the survey showed that most organic farmers' organisations had not heard of the potential for the recovery and recycling of phosphate from sewage treatment in the form of struvite, they are, nonetheless, open to the idea of using sewage recovered struvite, with the objective of contributing to closing resource recycling loops. Particular interest was shown by the two largest German organic farmers' organisations (in terms of land surface farmed). The organisations are, however, concerned that acceptance of sewage recovered struvite might turn against them through public

concern about possible contamination of the food chain. Above all, the organisations were concerned to maintain the "organic status" of their members' land and it could be inferred that whilst they are open-minded about the possibilities for the use of recovered struvite, they will first require to be convinced that their organic status can be maintained.

The organic organisations indicated that they do not currently have sufficient knowledge concerning sewage struvite, and would be interested in information concerning: energy balance, levels of heavy metals and other possible sewage contaminants, costs, plant availability of struvite phosphorus and nitrogen.

### Struvite reactor design and operation



***Denis Mangin***, LAGEP - University Lyon 1, France, summarised how interactions between the crystallization reaction and local mixing effects can enable effective reactor design and operation:

- impact of possible localised high concentration effects around reagent injection points (leading to scaling and to production of fines because of high local supersaturation);
- significance of reactor hydrodynamics in influencing the chemical and physical processes of struvite precipitation (including the forms of crystal/aggregate produced);
- poly-nucleation on the surface of fines (or primary agglomeration), occurring probably at the earlier stage of particle formation and leading through growth to star-shaped poly-crystals, appears as a significant mechanism. These structures can readily agglomerate, by meshing and by catching fines, because of their multi-pointed form.

Experiments with a 10 litre stirred reactor and pure chemical solutions were presented, in which sand and recovered struvite pellets being used as seed

material. In both cases, struvite precipitation occurred mainly as fines, and not on the surface of the seed material, so seeding was then abandoned. Unseeded experiments resulted in large particles, mainly poly-crystals, and many fines, but the latter were not lost in the outflow and were retained in the reactor. Further work is needed to confirm that larger particles can be produced with longer run times than the 3-5 day runs in this work, and this is now underway at the University of Valencia (see below).

A full report of this experimental work is available at <http://www.nhm.ac.uk/mineralogy/P-recovery/> (see "[Lagep report](#)").

**Questions** were raised concerning the relatively high concentration of sodium hydroxide solution used to adjust pH: addition of a more dilute reagent might limit local supersaturation at injection points, and thus reduce production of fines.

The stirrer mixed reactor was presented as offering the advantage over fluidised bed reactors or reactors mixed by air bubbles, that the required mixing can be obtained by adjusting the stirrer design and power, independently of through-flow rate required in FBRs to ensure bed fluidity (thus avoiding the need for recycle or return streams to ensure adequate residence times) and independently of aeration (which affects pH and ammonia offgassing). However, the feasibility of stir-mixing aerated columns was questioned.



**Hideyuki Ishikawa et al., Ebara Corporation Japan**, presented the ongoing investigation of a double reactor struvite precipitation unit (inflow inflow 0.56-0.95 m<sup>3</sup>/hour m<sup>3</sup>/hour) operating on anaerobic digester sludge centrate. The main reactor tank is a fluidised bed precipitation

reactor, the second smaller tank is used to grow seeds washed out of the fluidised bed reactor up to 0.3mm diameter, for use as seeds in the main reactor (see summary in [SCOPE Newsletter n°49](#), page 4).

Phosphate recovery from inflow liquor was >90%, resulting in struvite with a P-content of 12.5% and very low heavy metals in particles of 0.4mm diameter.

### Integration into sewage treatment



**Bernd Heinzmann, Berlin Wasserbetriebe** (Berlin Water), presented pilot tests of integrating a struvite recovery process into a very large biological nutrient removal waste water treatment plant. The plant has been suffering major nuisance struvite deposits in anaerobic digester outflow pipes and installations.

Test installations have been designed to avoid struvite precipitation upstream of the recovery unit and to reduce organic contamination of the struvite. Mixing in the anaerobic digester followed by pumping out under pressure to avoid degassing. Struvite is then precipitated in an aeration chamber with magnesium chloride dosing. An English translation of the presentation of this work made at the German Federal Environment Agency (UBA) phosphorus recycling seminar 6-7 February 2003, Berlin is available at <http://www.nhm.ac.uk/mineralogy/P-recovery/> (see "[Case study: Berlin Wasserbetriebe](#)"), summarised in [SCOPE Newsletter n° 54](#).

The liquor is then passed through a hydrocyclone, before going into the sludge centrifuge, in order to separate struvite particles >0.05mm diameter from the less dense organic particles. Using a double cyclone, up to 50% of the waste water treatment plant inflow phosphorus could be recovered as struvite particles. The system proved operational under testing, and the recovered struvite showed nutrient values, heavy metal and organic contents compatible with limits for fertilisers.

Berlin Water is now looking at a better integration of the process into the plant scheme by combining a

struvite precipitation unit, operating on the sludge stream between the first and second stages of sludge digestion, and magnesium addition directly into the second stage digester with hydrocyclone separation of struvite particles in a recycle stream in this second stage of sludge digestion.



**Raffaella Boccadoro**,  
**Marche Polytechnic University Ancona, et al.** presented ongoing development and testing of the full-scale pilot phosphate precipitation unit operating at Treviso waste water treatment plant, Italy (in conjunction

with Venice University and Verona University). A full report of work at this installation up to 2003 is presented at <http://www.nhm.ac.uk/mineralogy/P-recovery/> (see “[Phosphorus recovery trials at Treviso](#)”) and summarised in [SCOPE Newsletter n°49](#), page 7 and previous work in [SCOPE Newsletter n°44](#), page 8. The phosphate precipitation installation, operating on the plant’s sewage sludge centrate liquor line is now effectively producing struvite with low organic content (<2% dry weight), low calcite content, nitrogen content >4% and phosphate >12%, thus conforming to requirements for fertilisers in Italy.

The plant has experienced some scaling problems with phosphate precipitation occurring in piping instead of in the reactor tank. This is being addressed by reducing the struvite super-saturation : aeration is often not necessary to achieve precipitation in the reactor tank (sufficient pH increase through CO<sub>2</sub> off-gassing occurs by mixing only), the addition of magnesium is not necessary.

The plant has also experienced problems of organics in the reactor, resulting in foaming and operating problems, including carry over of fines out of the reactor. This is being addressed by installation of a decanter tank installed between the sludge digester dewatering and the phosphate recovery plant.

**Aurora Seco**, **University of Valencia, Spain**,



presented experimental work integrating the Lyon reactor (above) into a complete pilot scale (40 l/h) BNR sewage treatment plant fed with real sewage. The struvite reactor is installed downstream of the sewage stream thickener, anaerobic digester and dewaterer. Its capacity is

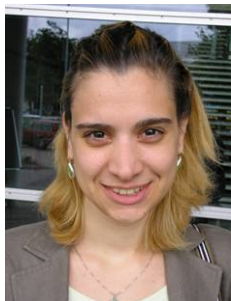
however too large for continuous operation on this sidestream, so a smaller reactor will probably be developed.

Results of 13 runs of 5-12 days using the struvite reactor under different operating conditions were presented. The reactor usually achieved stability after 4 days. Soluble phosphorus removal efficiency was shown to be pH dependent in the range 8.5-8.9, but phosphorus recovery efficiency was variable,, probably because of some loss of fines in the outflow leaving the top of the reactor.

Accurate control of pH was shown to be very important in reactor operation. Installation of a “fuzzy logic” computer pH control system helped to achieve stable operating conditions. 60-90% of reactor inflow phosphates were then reliably recovered as readily dried struvite particles.

Significant precipitation of phosphorus and magnesium are however being encountered in the pilot installation’s digester. Further work will address this question and look at the integration of the struvite precipitation reactor into the whole pilot installation, including aspects such as CO<sub>2</sub> degassing in the centrate dewaterer and magnesium recycle from the struvite reactor to the sewage treatment installation inflow.

### Struvite chemistry and modelling



**Aikaterini Kofina and Petros Koutsoukos, University of Patras, Greece**, presented ongoing systematic pH-controlled experiments which are feeding an increasingly detailed data bank concerning struvite precipitation parameters in multi-ion solutions representative of waste water.

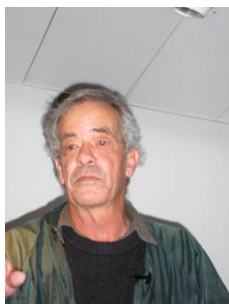
Phosphate, magnesium, ammonium ions are maintained at 1:1:1 ratios to test super-saturation; sodium, chloride, nitrate, carbonate and glucose are included ; pH s of 8.5 and 9.5 were investigated.

Current work is investigating the effects of concentrations of other non-competing ions on struvite precipitation: sodium and sulphate were shown to have a threshold inhibition effect, retarding precipitation.

At pH 8.5, struvite crystals were formed as long prisms, whereas at pH 9.5 rhomboid shapes were found. The specific surface area of the crystals was rather high (150 m<sup>2</sup>/g) suggesting that they may be porous. Further work is needed to look at this question.

When left at room temperature the struvite, initially formed as a hexahydrate (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) evolved to a monohydrate (MgNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O), with the well formed crystals changing into a complex platelet structure.

See summary of several recent papers on struvite chemistry by this team in [SCOPE Newsletter n°55](#), page 3.



**Dick Loewenthal et al., University of Cape Town, South Africa**, presented the ongoing development of a chemical kinetic model for struvite precipitation in waste

water liquors. Models are important tools for process control. In the case of struvite, the modelling is complex because of the interference of various different possible magnesium and calcium mineral precipitations (ion competition and simultaneous precipitation). The model presented is based on kinetics (rates of reaction) rather than on static equilibrium data, consistent with the situation in continuously operated waste water treatment installations which are effectively permanently in a non-equilibrium state.

The three phase (aqueous / gas / solid) mixed weak acid/base kinetic model for struvite precipitation has been under development for some years (see [paper](#) presented at the Second International Conference on Phosphorus Recovery and Recycling and [also](#) in Environmental Technology, volume 22, number 11, 2001). The model now takes into account ion pairing kinetics, and includes H<sup>+</sup> as a specific parameter (rather than treating pH as a consequence of other conditions). It was tested on results from struvite precipitation experiments carried out by K. Suzuki (see paper above at this conference) in swine wastewater and [Van Rensburg](#) (Cape Town University) in anaerobic sewage sludge digester liquor. The model predicted measured data accurately, except for calcium concentration changes in the swine wastewater.



**Isik Kabdasli, Istanbul Technical University, et al.** presented studies of struvite precipitation induction time (key chemical kinetics factor) in synthetic waste waters containing relatively low ammonium concentrations (35mg/l, that is 2.45 mMolar 1:1:1 concentrations of magnesium, phosphate, ammonium) and other ions typically found in waste liquors (calcium, sodium, chloride, sulphate, carbonate). pH was in the range 8.5 – 9.2. UV-visible absorbance measurement by spectrophotometer proved a reliable tool for detecting precipitation and thus measuring induction time.

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## SCOPE NEWSLETTER

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Sodium and sulphate both showed significant retarding effects on precipitation (increase in induction time). Carbonate showed no significant effect. Calcium concentrations had varying effects depending on pH.



**Kristell Le Corre, Cranfield University, Great Britain, *et al.*** also presented results of studies of struvite precipitation induction time measured by absorbance, particle size and crystal form. In this case, magnesium : phosphate : ammonium ratios were fixed at 1:2:2 and magnesium concentrations ranged from 1.2 – 3.5 mMolar. pH was adjusted to 9.0. The effects of calcium and carbonate ions on struvite precipitation were investigated with Mg : Ca : CO<sub>3</sub> ratios of 2:1:1, 1:1:1 and 1:2:2 being tested.

Calcium and carbonate addition was shown to retard precipitation (increase induction time) but also to increase light absorbance (this may be due to precipitation of small calcium carbonate particles = calcite). Calcium and carbonate addition resulted in smaller average precipitated particle size after just three minutes reaction, and after 20 minutes: a larger average size for high calcium and carbonate concentrations (2x Mg molar) and a smaller average size for low calcium and carbonate concentrations (0.5x Mg molar), both when compared to the 1:1:1 magnesium : calcium : carbonate ratios.

This concurs with the results of Kabdasli above, that calcium ions have variable effects on struvite precipitation, and suggests that further work is needed on this interaction.



**Jan Suschka *et al.*, University of Bielsko-Biala, Poland,** presented results of struvite precipitation experiments in anaerobic sewage sludge digester liquors, concentrating on the fate of ammonia. He suggested that the form of struvite crystals produced may

depend on levels of free ammonia present, this being affected by air stripping and by pH, as well as initial ammonium ion concentration. The use of magnesium oxide as a reagent for struvite precipitation is liable to result in the presence of free ammonia, because its poor solubility reads to molar overdosing and thus to pH increases. He suggests that high levels of free ammonia could result in struvite crystals forming as long needles, and lower levels lead to rhomboid crystals.

Suschka also suggested that, because magnesium oxide is a cheap by-product in Poland (prices comparable to calcium hydroxide = lime), its addition along with phosphorus addition to cause struvite precipitation could be a viable solution for ammonium removal from sludge liquors. This would avoid the return of ammonium to the sewage works head, thus improving biological nutrient removal. Phosphorus could be provided either from internal sewage works liquors and/or by addition of phosphoric acid or superphosphate fertilisers.

A full report of experiments up to 2003 is available at <http://www.nhm.ac.uk/mineralogy/P-recovery/> (see "Suschka" in the bibliography)



**Bruce Jefferson *et al.*, Cranfield University, Great Britain,** presented studies of struvite scaling rates and propensities of different materials: stainless steel, PTFE poly tetra fluoro ethylene (Teflon), PMMA poly methylmethacrylate, both smooth and after modification via surface abrasion using silicon carbide papers. Results using coupons of the materials attached to struvite precipitation stirrers showed that most scaling occurred on stainless steel, and least on PMMA, with scaling being accentuated when materials were modified. Work up to 2002 is summarised in [SCOPE Newsletter n°50](#), page 7.

Work is currently underway to try to compare scaling results with data concerning surface properties observable via Atomic Force Microscopy

(AFM). To date, this suggests that scaling is not correlated to “roughness” (as measured using this apparatus) but is correlated to surface adhesion forces. At present, work is ongoing to try to modify the AFM point (stylus) by growing struvite onto it, in order to then measure the struvite – struvite adhesive surface force.

### Struvite recovery from manures



***Kazuyoshi Suzuki et al.***, National Institute of Livestock and Grassland Science Japan, presented operation of different configurations of a pilot struvite recovery installation in pig manure wastewater. Pig manure is generally treated differently in Europe, where animal faeces, urine and wash water are mixed,

whereas in Japan, faeces go to a separate treatment line. He estimates that around 13%, 24% and 17% of initial phosphorus, magnesium and calcium are found in the liquid fraction of the swine wastewater.

Nuisance phosphate deposit problems occur in swine wastewater treatment plants. The potential for struvite recovery from swine wastewaters is estimated at 10,000 tonnes P/year.

Dr Suzuki presented a 4m<sup>3</sup>/day stirred, aerated reactor for struvite precipitation and recovery from swine wastewaters. pH increase results from the aeration. Magnesium is added as magnesium chloride, and vegetable oil is added to avoid foaming caused by organics.

This reactor has been operated continuously for 2 years. The solids recovered were 2.0- 25% struvite with significant organic content, and had to go to composting before agricultural re-use.

Relatively pure (95%) struvite deposits were observed on the air injection tubes and reactor walls. A 34 day test showed better struvite precipitation onto coarse and metal surfaces, than onto smooth plastics. It was therefore decided to try to improve

struvite recovery by facilitating struvite precipitation onto a 1 mm steel wire mesh, submerged in the reactor.

After 30 days of submersion in the reactor, one kilogramme of struvite was easily recovered by scraping from the wire mesh. This product was >99% pure struvite after simple washing. However, more than ¾ of the struvite precipitating in the reactor was still accumulating in the base of the reactor, with high organic content.

The installation achieved 70% removal of phosphate from inflow water without magnesium addition, and 90% with magnesium addition.

Running costs were estimated at 2,000 US\$/year for energy consumption and 1,000-3,000 US\$ for magnesium dosing, for a 1,000 fattening pig farm. Experiments with a demonstration installation are ongoing.

See summary of 2002 published paper in [\*SCOPE Newsletter n°50\*](#), page 6



***Rachid Laridi et al.***, INRS (University of Québec, Canada) and CRIQ presented experiments into struvite precipitation from swine wastewater, following the occurrence of nuisance struvite deposits downstream of iron and coagulant addition to

reduce suspended solids loads to a trickling filter. The reason for these nuisance deposits (despite the reduction in soluble phosphorus resulting from the iron addition) is thought to be the +78% increase in soluble magnesium during this treatment. The release of magnesium occurs following coagulant addition, due possibly to ionic exchange with Fe or compression of the diffusive layer at the solid/solution interface.

Mr Laridi reported 1 litre beaker scoping experiments, then testing of different stirred reactors of 15, 120 and 450 litre capacity using raw swine



wastewater after ferric chloride addition and settling. No magnesium addition was required but pH adjustment was necessary. An optimal pH of 8.5 and a hydraulic residence time of 30 minutes enabled 84-98% phosphorus removal (and 15% ammonia removal) to be achieved in the smaller reactors, but not in the 450 litre reactor, probably because of inadequate mixing (under-sized stirrer).

Further work is currently underway to better understand the magnesium release mechanism and to optimise ferric chloride addition to combine magnesium release, effective settling of organics and a limited immobilisation of soluble phosphorus.



***Ipek Celen et al., University of Tennessee, USA***, presented experimental work on struvite precipitation in liquor collected from a pig farm manure holding lagoon. The liquor was dosed with sodium hydroxide only (NaOH) and with NaOH plus magnesium chloride in 1 litre beakers. Results were compared with the MINTEQ software model.

A pH increase to 8.5 (no magnesium addition) resulted in a 55% removal of soluble phosphorus as both struvite and calcium phosphates (monetite  $\text{CaHPO}_4$  and brushite  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), whereas magnesium addition plus pH adjustment enabled 98% phosphorus removal as struvite only (in this case, no reduction in soluble calcium). The experimental results corresponded well with the MINTEQ model predictions for both phosphorus removal efficiencies and for the precipitation product, after the addition of struvite to the model data base.

### Other processes



***Alex Weidener, Stuttgart University Germany, et al.*** presented a proposed process for extraction of soluble phosphorus from sewage sludges using acid, followed by struvite precipitation. Acid addition to the sludges to pH 2 proved more effective than alkali (pH13). To enable struvite recovery by pH increase after sludge acidification, however, iron and calcium ions must be neutralised to avoid their precipitation with phosphates. Sodium citrate proved effective in neutralising calcium and sodium sulphate in neutralising iron.

Participants suggested that this process appeared however as excessively complex and potentially costly (reagents for acidification, pH increase, ion neutralisation ...) except in specific circumstances. It was noted that Thermphos can recycle the phosphorus from sewage sludge incineration ash in their furnace in Vlissingen, The Netherlands, provided that sludges produced at sewage works using iron-based chemical P-removal are separated prior to incineration (bio-P and aluminium P-removal sludge ashes are compatible with the process, but not high iron levels).



***Demet Antakyali et al., Stuttgart University Germany***, discussed the potential interest of struvite recovery for ammonium removal from sewage works sludge digester liquors and presented experimental struvite precipitation results.

Like Suschka (above), she emphasised the influence of high ammonium concentrations in sludge digester dewatering liquors returned to the head of sewage works operating biological nutrient removal (BNR). Sludges are often spread on farmland, and there is an increasing demand for mobile sludge dewatering

units to facilitate sludge management and transport. In this case, levels of ammonium from the sludge dewatering unit (treating relatively large quantities of sludge compared to sewage works capacity, over a short time) could have a major impact on works nitrogen removal when the dewatering liquor is returned to the works inflow – indeed, certain German regional statistics showing that BNR plants achieve in reality only 60-70% nitrogen removal. To improve this performance, the sludge liquor should be treated before being supplied to the WASTE WATER TREATMENT PLANTS.

Struvite precipitation, achieved by magnesium and phosphate addition and pH adjustment if necessary, could provide an efficient route to remove ammonium from these return liquors, with compact installations (short reaction and settling time) compatible with mobile units.

Laboratory tests using digested sludge dewatering liquors from three BNR sewage works (ammonium > 1,000 mg/l) showed 80% nitrogen removal from liquors at pH 8.5 after 30-40 minutes. Magnesium oxide (MgO), although poorly soluble (thus requiring longer reaction times and above 1:1 molar dosing) was the most cost-effective solution. Effectiveness was improved if MgO was dosed before phosphate addition. Calcium concentrations did not have significant effects at the magnesium and ammonium concentrations studied, because in this case the amount of calcium in sludge liquor coming from municipal sewage works is generally not very high.

With magnesium chloride (rapid struvite precipitation), very pointed crystals formed. With MgO, the crystals did not show sharp corners.

The study concluded that struvite precipitation provided a good solution. One company contacted in Germany indicated that they would buy struvite for 100€/tonne.



**Matthias Hartmann**, Bauhaus-University Weimar, Germany, presented work concerning the precipitation of struvite and hydroxyapatite (HAP) from urine. Precipitation can occur spontaneously in urinals (blocking piping) and in storage of urine samples (up to 50% of initial phosphates).

Laboratory precipitation experiments with addition of magnesium oxide, magnesium hydroxide, magnesium chloride, calcium hydroxide and calcium chloride were presented. Both magnesium chloride and magnesium hydroxide resulted in >90% phosphate precipitation after 30 minutes at 2x molar ratio (to phosphorus), whereas magnesium oxide or calcium addition resulted in slower and/or less effective phosphorus removal. Magnesium oxide addition resulted in a phosphate product with <12% P content, which may be too low for use as a fertiliser. Magnesium chloride was rejected as leading to undesirable increases in effluent salinity.

Magnesium hydroxide at 2x molar ratio was thus identified as the optimal solution for phosphorus recovery.

### Poster presentations

**Phil Schneider** *et al.*, James Cook University, Townsville, Queensland, Australia: pilot scale tests of a 40 litre capacity, seeded fluidised bed reactor, for recovery of struvite from piggery wastes, including dynamic modelling using PHREEQC and gPROMS.

**David Montag**, RWTH Aachen University, Germany: the PRISA process, involving struvite precipitation within sludge treatment (combination of different process water streams) in biological nutrient removal sewage treatment systems, using a high-efficiency struvite crystallising reactor. Field trials of plant availability of nutrients in the recovered struvite, used as a fertiliser, are currently underway, and analysis of heavy metals and organic

chemical contaminants are also being carried out to ensure compatibility with agricultural use.

Jozef Hoffmann, Wrocław University of Technology, Poland, *et al.* presented results from a 1 litre laboratory agitated struvite precipitation reactor tested for phosphorus removal from industrial and fertiliser factory waste streams, by magnesium and ammonium addition. Near 100% P-removal is achieved by 1.3x molar addition of magnesium and ammonium at pH9.

David Philo, Kralingseveer Waste Water Treatment Plant, The Netherlands: this waste water treatment plant, which treats around half of Rotterdam's sewage with biological nutrient removal, has, since 2001, been experiencing considerable nuisance struvite deposits in the outflow pipes and pumps from the plant's two 5,000 m<sup>3</sup> sludge digesters. The problems started occurring when the plant moved from chemical P-removal (pre-precipitation) to entirely biological nutrient removal. Chemical analysis of the deposits showed them to be struvite. Examination of the digester inner walls showed that the struvite precipitation is taking place downstream of and not within the digesters. Increased dosing to the digesters of iron chloride (already being added to reduce H<sub>2</sub>S production) led to some "softening" of the struvite deposits but did not resolve the problems. Tests were carried out into controlled struvite precipitation as a solution to these problems, but the process problems encountered led to this route being abandoned, and a polymer provided by Cytec Industries is now used to effectively prevent struvite deposits.

John Hammond et al., Warwick HRI, Great Britain, presented ongoing field trials of commercially manufactured chemical struvite (Budite 370, Budenheim), comparing potato growth with conventional triple super-phosphate fertiliser (TSP). Leaf, stem and potato tuber development will be sampled, as well as tissue mineral content. Results will be available Autumn 2004.

Hipolito Garcia et al., University of Cantabria, Spain: studies of ammonium removal from the anaerobically treated (UASB reactor) liquid fraction

of dairy manure (ammonium concentration 900-1,200 mg/l), by addition of magnesium chloride and potassium phosphate. Over 2 months operation, with a pH at average 8.3 and 1:1:1 magnesium and phosphate addition (to molar ammonium concentration), >80% ammonium removal was achieved. At pH9.8 and Mg:N:P ratio of 1.2:1:1.4, then 92% ammonium removal was achieved. The resulting precipitate was 3%N, 9%K<sub>2</sub>O, 25% P<sub>2</sub>O<sub>5</sub>, compatible with use as an NPK fertiliser under European regulations.

Julita Kowalczyk and Mieczyslaw Szustakowski, University of Zielona Gora, Poland: samples of swine manure, after sedimentation, were boiled, then struvite precipitation was tested by addition of magnesium chloride and ammonium chloride, and pH adjustment using concentrated ammonium solution. Phosphorus removal from this substrate was >90% at pH9. Tests at pH11 showed no effect of ammonium acetate, as a trial soluble organic compound.

Raffaele Molinari et al., University of Calabria, Italy: a laboratory installation tested five 15 cm<sup>2</sup> ultrafiltration membranes followed by struvite precipitation, using pure chemical solutions, to model possible application to remove phosphate and ammonium from sewage works liquors such as biological nutrient removal outflow. A magnesium:phosphorus molar ratio of 1.3:1 and a pH of 9.5 achieved rapid struvite precipitation (96% phosphorus removal in 15 minutes). A flowsheet of an integrated membrane process where reverse osmosis could be used to concentrate the sewage liquor prior struvite precipitation is proposed.

Emma Sharp, Cranfield University with Thames Water, Great Britain: over one year's experience of operation of a full-scale struvite precipitation and recovery reactor at Slough Sewage Treatment Works, England. The reactor treats 7m<sup>3</sup>/hour inflow of digester centrate liquor (see [SCOPE Newsletter n°41](#)). Magnesium hydroxide or magnesium chloride addition, and pH adjustment, are used to precipitate struvite at pH8. Magnesium hydroxide has proven more expensive than magnesium chloride, and results in smaller particles of struvite with a higher

organic content. The precipitated struvite has shown to have relatively low heavy metal content, compatible with re-use as a fertiliser. Re-use routes are currently being developed as an organic horticultural fertiliser ingredient for garden centres (see above).

### Discussions and conclusions

The conference concluded that there is now a considerable wealth of knowledge concerning struvite precipitation chemistry, reactor design, and operation. Pilot and full scale reactors, as well as laboratory work, show that struvite precipitation can provide a reliable route for removing phosphorus from animal manure or sewage treatment liquors, in particular from dewatering liquors after digestion of biological nutrient removal sludges.

Addition of magnesium up to slightly higher than 1:1 molar ratios (to phosphorus) and operating pH in the range 8 – 8.5 generally result in reliable >80% or >90% precipitation of phosphates, mainly or exclusively as struvite, in a recoverable form which may be easily washed and dried (for example by manual hosing then simply standing to dry) for use as a recovered mineral fertiliser.

This struvite, including when precipitated from sewage works liquors, shows low contaminant levels, and phosphate contents compatible with use as a fertiliser. Further tests of the fertiliser value of struvite are underway, but its value as a fertiliser now seems to be generally accepted.

Magnesium oxide provides a usually cheaper magnesium source than magnesium chloride, but participants reported problems of magnesium oxide mixing, experienced in a number of the laboratory and pilot studies, leading to low efficiency or slow reaction times with this reagent. Conference participants with industrial experience however indicated that such problems can be resolved in full-scale reactors using available technologies for high-shear mixing to generate slurries, as used for other poorly soluble reagents in the chemical industry.

Struvite precipitation also appeared as a viable solution for ammonium removal from sludge dewatering liquors or animal manures, by addition of both magnesium and phosphate, in specific circumstances where ammonium removal is necessary, e.g. to avoid return of ammonium to the head of biological nitrogen removal systems.

Struvite recovery and reuse is thus already operational in a small number of pilot or full scale facilities, and a significant amount of research is ongoing into chemical and reactor parameters, which will facilitate optimisation of process operation.

### Key issues

**Key issues to move forward towards a more widespread uptake of phosphorus recycling through struvite recovery appeared as the following:**

- \* **better understanding of the integration** of struvite recovery (in particular from digester dewatering liquors) into the operation of biological nutrient removal of sewage and of manure treatment processes: nuisance deposit avoidance, BNR performance and reliability improvement by eliminating soluble nutrient returns to works inflows.
- \* consequent **clarification of the economics** of struvite recovery as an element of overall waste water treatment plant process economics
- \* **communication of this information**, and of developing technical knowledge and demonstration experience of struvite recovery, to the water industry and the animal waste treatment industry – as it is these actors who will implement struvite recovery at the industrial level
- \* communication of information regarding the potential for resource recycling of struvite recovery and re-use to regulators and others who will influence the definition of national or European objectives of nutrient recycling

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## SCOPE NEWSLETTER

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\* **dialogue with farmers and their organisations** concerning the potential interest of recovered struvite as an ecological nutrient source

\* **coordination of the varied and rich ongoing research and development initiatives** to ensure ongoing exchange of information, data and experience, in order to optimise the research effort underway and to provide information input to the above targets

### The Scope Newsletter

*The SCOPE Newsletter is produced by the Centre Européen d'Etudes des Polyphosphates, the phosphate industry's research association and a sector group of CEFIC (the European Chemical Industry Council).*

*The SCOPE Newsletter seeks to promote the sustainable use of phosphates through recovery and recycling and a better understanding of the role of phosphates in the environment.*

*The SCOPE Newsletter is open to input from its readers and we welcome all comments or information. Contributions from readers are invited on all subjects concerning phosphates, detergents, sewage treatment and the environment. You are invited to submit scientific papers for review.*

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avenue E. Van Nieuwenhuyse 4, bte 2, B1160, Bruxelles - Belgium.

Tel: (32) 2 6767211 Fax: (32) 2 67673 01 E-Mail: [cja@cefic.be](mailto:cja@cefic.be) [www.ceep-phosphates.org](http://www.ceep-phosphates.org)

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