

---

---

---

# SCOPE NEWSLETTER

---

---

NUMBER 82

November 2011 - II

## P-recovery by adsorption

### Tunisia

#### **Plant fibres for phosphate and ammonium removal and recovery**

Marine *Posidonia* plant fibres were tested for removal of phosphorus from laboratory solutions of orthophosphates and other ions. The P-enriched biomass could be used as an agricultural amendment.

### Turkey

#### **Calcined eggshell waste for P-recovery**

Calcined eggshell was tested for adsorption of phosphate from laboratory solutions and for desorption of the phosphate to enable P-recovery.

### Polymeric anion exchanger

#### **Iron loaded resin can recover phosphate**

Three polymeric anion exchangers impregnated with iron oxide nanoparticles were tested for P-removal from laboratory phosphate solutions, followed by P-release regeneration and phosphate precipitation for recovery.

## Optimising struvite recovery

### Reduced nitrogen leaching

#### **Struvite recovery from swine wastewater**

A 12 litre combined aeration (CO<sub>2</sub> stripper) and struvite precipitation reactor was tested with piggery effluent. The recovered struvite was tested in soil columns, showing 3x lower nitrogen leaching than conventional fertilisers, indicating a potential to reduce water table nitrate contamination.

### Feeding bio-P removal

#### **Alkaline fermentation and P-recovery**

Increasing pH in sludge fermentation increases production of fatty acids needed to feed biological P-removal. Recovery of phosphorus and nitrogen as struvite enables further process optimisation.

### P-recovery Germany

#### **Adapting sludge treatment to optimise struvite recovery**

Appropriate management of the sludge thickening process can increase soluble phosphorus release, enabling recovery as struvite of up to 40% of sewage works P inflow.

## P-recovery technologies

### Australia

#### **P-recovery and water recycling**

Water recycling from sewage treatment plants results in membrane and reverse osmosis reject streams where P-recovery via struvite precipitation could be implemented

### Technology update

#### **Review of P-recovery patents**

A recent overview paper presents different technological routes for phosphorus recovery and recycling with a summary of available scientific literature and of 13 US and EU patents.

## Phosphorus in sewage

### Nancy, France

#### **Forms of phosphate in sewers and sewage**

Identification of the different forms of phosphate present in raw sewage suspended solids, biofilms and deposits at different sites in a varied sewerage network.

## Conferences and publications

### Phosphates 2012

#### **Phosphate industry conference**

Major 2-yearly conference for the worldwide phosphate industry (rock production, fertiliser, animal feeds, food, detergents, other industrial uses). El-Jadida, Morocco, 19th - 21st March 2012:

<http://www.crugroup.com/events/phosphates/>

### Science and policy

#### **3<sup>rd</sup> sustainable phosphorus summit**

29<sup>th</sup> February – 2<sup>nd</sup> March 2012, Sydney, Australia

<http://sustainablepsummit.net/>

## P-recovery by adsorption

### Tunisia

#### Plant fibres for phosphate and ammonium removal and recovery

Adsorption of phosphates onto solid materials could provide a relatively inexpensive and simple method for removing phosphates from wastewater. Experimental studies have been published using a variety of minerals (including apatite = calcium phosphates, bauxite, dolomite, gravels, limestone, sands, zeolite, hydrotalcite ...), wastes (bone char, alum sludge, mine sludge, blast furnace slag ...), but also biological materials such as sawdust or orange wastes (SCOPE Newsletter n°76). These papers report laboratory tests with *Posidonia oceanica* fibres collected from nearby beaches in Tunisia, washed, dried, ground and sieved to < 150 µm.

*Posidonia oceanica* is an angiosperm seagrass, endemic to the Mediterranean. It grows in 1m long thickets, forming underwater forests from 40m depth up to the shore, and is the principal Mediterranean ecosystem. **Dead *Posidonia* biomass accumulates in considerable quantities on Mediterranean beaches in the Spring and Summer**, and are often collected to clean beaches and taken to landfill or dumped back to the sea.

#### Orthophosphate adsorption

In the 2011 (A) paper, 100 ml batch adsorption experiments were carried out in pure orthophosphate solutions at 5 – 33 mg/l P-PO<sub>4</sub> (prepared from potassium dihydrogenorthophosphate KH<sub>2</sub>PO<sub>4</sub>). The jars were stirred to maintain the biomass in suspension for 90 minutes. Different pHs were tested (3 – 11, adjusted using HCl or NaOH), biomass doses (1 – 20 g dry mass /l), temperatures (20 – 60°C) and presence of other ions such as chloride (from NaCl) and sulphate (from Na<sub>2</sub>SO<sub>4</sub>).

**Most of the orthophosphate adsorption took place in the first 20 minutes**, with equilibrium being reached at around 40 minutes. Overall phosphorus removal showed to be around 25% at only 1g biomass/litre, increasing to around 75% at 20g biomass/litre.

Chloride ions has little impact on the orthophosphate adsorption, whereas **sulphate ions** had little effect at

150 mg/l but reduced orthophosphate adsorption by nearly 75% at 1500 mg/l. EDS analysis (Energy Dispersive X-ray Spectroscopy) suggests that orthophosphate adsorption results from ion exchange with chloride ions on the vegetable fibre surface. FTIR (Fourier Transform Infrared Spectroscopy) is used to look at molecular bond transformations which might also explain the adsorption mechanism.

**After orthophosphate adsorption, the biomass contains 0.38% phosphorus (P, dry weight)**, with 48% carbon and 36% oxygen. The authors suggest that **it could be used as an agricultural amendment**, providing both fertiliser and compost.

The maximum orthophosphate adsorption capacity was estimated to be approx. 2.4 mgP/g biomass (0.24% P).

#### Continuous flow experiments

In the 2011 (B) paper, continuous flow experiments used a 300 rpm stirred 1.2 litre reactor, with both continuous through flow of the orthophosphate solution and continuous addition of biomass. Different orthophosphate concentrations (3 - 17 mg/l P-PO<sub>4</sub>), biomass dosing rates (2 – 10 g/l), sulphate and chlorine ion addition, and solution through flow rates of 20 and 40 ml/minute were tested.

**Real wastewater from the Soliman city (Tunisia) sewage treatment plant was also tested** (secondary wastewater treatment effluent), with phosphorus concentration of c. 3 mgP/l, ammonium c. 30 mg/l and sulphate c. 450 mg/l.

These experiments suggested that the dosage of *Posidonia* biomass was important for P-removal effectiveness, but that reactor residence time made little difference. As above, **adsorption of orthophosphate was significantly reduced in the presence of sulphate ions**. Probably because of the sulphate concentration, orthophosphate removal was poor with the real wastewater, with a reduction of P concentration from 2.6 to around 2 mg/l after 20 minutes at 5g *Posidonia* fibre / litre, and to around 1.3 – 1.6 mgP/l with 10 g/l *Posidonia*.

An estimation of capital and operation costs for using *Posidonia* fibres for P-removal from wastewater is provided.

#### Ammonium adsorption

The 2011 (C) paper presents 100 ml stirred batch experiments to test ammonium adsorption onto the

same *Posidonia* biomass material. Ammonium concentrations of 4 – 40 mgN/l were tested (ammonium chloride solution), at pHs of 3 – 10, in all cases using 3g biomass/l and at room temperature.

The authors conclude that the **Posidonia biomass offers an ammonium adsorption capacity of c. 1.4 mgN/g biomass**. Adsorption is lower at pH 5 or less, but similar in the range pH 6 – 10. It was verified that the *Posidonia* biomass did not release metal ions into the solution (Cr, Fe, Mn, Ni, Zn not detectable with ICP/AES).

SEM (Scanning Electron Micrograph), EDS and FTIR analysis suggest that the principal adsorption mechanisms are ion exchange with magnesium and calcium ions or intraparticle sharing with organic molecules.

A previous 2010 paper (D) showed that **ammonium could also be adsorbed onto sawdust**, with biosorption capacities of up to c. 1 mgN/g sawdust.

A: “*Posidonia oceanica* (L.) fibers as a potential low-cost adsorbent for the removal and recovery of orthophosphate”. *Journal of Hazardous Materials* 191 (2011), pages 333-341. Elsevier: [www.elsevier.com/locate/jhazmat](http://www.elsevier.com/locate/jhazmat)  
M.A. Wahab(i), R. Ben Hassine(ii), S. Jellali(i)

B: Removal of phosphorus from aqueous solution by *Posidonia oceanica* fibers using continuous stirring tank reactor”, *Journal of Hazardous Materials* 189 (2011), pages 577–585. Elsevier: [www.elsevier.com/locate/jhazmat](http://www.elsevier.com/locate/jhazmat)  
M.Wahab(i), R.Hassine(ii), S.Jellali(i)

C: “Biosorption characteristics of ammonium from aqueous solutions onto *Posidonia oceanica* (L.) fibers”, *Desalination* 270 (2011), pages 40–49. Elsevier: [www.elsevier.com/locate/desal](http://www.elsevier.com/locate/desal)  
S. Jellali(i), M. Wahab(i), M. Anane(i), K. Riahi (iii), N. Jedidi(i)

D: “Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modelling”, *Bioresource Technology* 101 (2010), pages 5070–5075, Elsevier : [www.elsevier.com/locate/biortech](http://www.elsevier.com/locate/biortech)  
M.Wahab(i), S.Jellali(i), N.Jedidi(i)

[salah.jallali@certe.rnrt.tn](mailto:salah.jallali@certe.rnrt.tn)      [waheb\\_med@yahoo.fr](mailto:waheb_med@yahoo.fr)

(i) University of Carthage, Water Research and Technologies Center (CERTE), Wastewater Treatment Laboratory, Tunisia

(ii) International Environmental Green Technology (IGET), Tunisia

(iii) University of Jendouba, School of Engineering in Rural Equipment of Medjez El Bab, Laboratory of Chemistry and Water Quality, Tunisia

## Turkey

### Calcined eggshell waste for P-recovery

In this paper, eggshells, collected from the food industry where they are a widely available waste material, then calcined, were tested for adsorption and desorption from pure laboratory solutions and in the presence of other ions. Near 100% removal of soluble phosphate was demonstrated, with little inhibition by other ions. Nearly 40% of the phosphate was desorbed by sodium hydroxide, and was thus available for phosphorus recovery and recycling. The authors note, however, that it would probably be more efficient to use the phosphate containing eggshell directly as a fertiliser or soil conditioner.

Eggshells were collected from bakeries in Eskisehir, Turkey, washed, dried for 24 hours at 100°C, ground and screened to 0.15 – 0.42 mm, then calcined. The specific surface area of the eggshell particles was then measured by BET nitrogen gas sorption and their chemical analysis estimated by EDX (Energy Dispersive X-ray spectrometry). **Phosphate sorption was tested using pure solutions of potassium phosphate in shaken flasks at controlled temperatures**. Different doses of eggshell material of the order of 2 – 10 g/litre were tested with phosphate concentrations of 16 - 65 mg soluble phosphorus (P-PO<sub>4</sub>) per litre and at different initial adjusted pH. Phosphate sorption was calculated by subtracting the initial from the final P concentration after filtration.

### Calcination and eggshell chemistry

Calcination at temperatures of 200 – 1000 °C were tested. Before calcination, most of the eggshell (94%) was calcium carbonate. Calcination began to change the chemical form of the material from around 600°C, resulting in **near complete conversion to calcium oxide (CaO)** for temperatures of 800°C or higher.

**Adsorption was rapid**, and equilibrium was reached in all conditions within one hour. At higher temperatures, phosphate removal decreased slightly. Initial pH made effectively no significant difference to adsorption in the range pH 2 – 10.

### Phosphate sorption from pure solutions

**Phosphorus removal from pure potassium phosphate solution was consistently very efficient, in the range 98.4 – 99.6%** with 2 – 10 mg eggshell per litre of phosphate solution. An adsorption kinetic

equation and adsorption isotherms are calculated and presented.

To test the possible interference of other ions present in real wastewaters, sulphate, nitrate and ammonium ions were added to the potassium phosphate solution tested. **These did not significantly deteriorate the phosphorus removal performance**, which remained well above 99% in these tests.

### Phosphate desorbability and P-recycling

Desorption of the phosphate from the calcined eggshells used for P-removal was tested by adding 0.5 M sodium hydroxide and sodium chloride. Sodium chloride proved to release very little phosphate, whereas **sodium hydroxide released around 38% of the adsorbed phosphate**. Calcium phosphate could then be precipitated from the elution medium.

The authors conclude that eggshells, which are a widely available waste material, after calcination at 800°C, potentially provide a **cheap and very effective material for removing phosphate from wastewaters** through a relatively simple adsorption process. Desorption using sodium hydroxide would be expensive, whereas the calcined eggshell with bound phosphates **could be used directly as an agricultural fertiliser / soil amendment**, as it contains calcium, magnesium and (on the basis of the results of this study) up to 0.75% phosphorus (P).

*“Adsorption of phosphate from aqueous solutions using calcined waste eggshell”, Chemical Engineering Journal 2011, in print [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)*

T. E. Köse, Dept. Chemical Engineering, Engineering and Architecture Faculty, Eskisehir Osmangazi University, 26480 Meselik-Eskisehir, Turkey, [emnilb@ogu.edu.tr](mailto:emnilb@ogu.edu.tr) and Betül Kivanc, Eti Food Industry and Trade Co., PD. Analytical Lab. Engineer, Eskisehir, Turkey [kivanc@etigida.com.tr](mailto:kivanc@etigida.com.tr)

---

## Polymeric anion exchanger

### Iron loaded resin can recover phosphate

Phosphate removal from wastewaters by adsorption using materials with a regeneration cycle offers the potential to then precipitate the phosphate from a relatively clean, concentrated liquor and so recover it in a form appropriate for industrial recycling or use as a fertiliser. This paper presents laboratory scale studies using synthetic wastewater (pure chemical solutions)

and three different commercially available polymeric anion exchanger resins impregnated with iron oxide nanoparticles. Batch and fixed bed column flow P-removal experiments were carried out, as well as regeneration (release of the removed phosphate) and precipitation of the phosphate from the regeneration solution for P-recovery.

Commercially available polymeric anion exchange resins offer durability and mechanical strength, but not specific affinity for phosphates (affinity also for sulphates which are widely present in wastewaters). However, these materials can be **modified to form PLEs (Polymeric Ligand Exchangers) which are phosphate specific, by loading with certain metals**. Loading with copper enables selectivity for orthophosphate (rather than chloride, sulphate, carbonate or nitrate, Zhao & SenGupta, Water Research 32(5), 1998). This paper tests polymeric anion exchange resins impregnated with **hydrated ferric oxide (FeOOH) nanoparticles**.

Iron impregnation of DOWEX M4195 resin (which is based on Bis-picolylamine) was achieved by mixing with FeCl<sub>3</sub> at pH2, then progressively increasing the pH to 8 by sodium hydroxide addition to form FeOOH precipitate, followed by drying. This resulted in an iron loading of 4-5% by weight. The same Dow resin was also used when first loaded with copper ions to approx. 6%, and then loaded as above with iron FeOOH. Also, the commercially available HAIX resin (which is based on quaternary ammonium impregnated with FeOOH nanoparticles) was tested for a third comparison. The resins had particles sizes in the range 300 – 1200 µm.

### Phosphate adsorption tests

The three different resin combinations were first subjected to batch equilibrium and kinetic tests: 48 hours, agitated beakers, using 0.5 – 1 g of exchanger per litre of 5 – 75 mgP/litre solutions of sodium phosphate. The exchanger was then filtered out, washed, and stirred with c. 20 bed volumes of a regenerant solution of 2.5% sodium chloride and 2.0% sodium hydroxide. Fixed bed up-flow tests were carried out using a 10 mm diameter, 300 mm tall column with an empty bed contact time (EBCT) of 3 minutes. Regenerant was then passed in downflow, before washing the bed and reusing for another run.

### The influence of varying concentrations of sulphate and chloride on the phosphate uptake was assessed.

Sorption isotherms, sorption capacities, kinetic modelling of sorption and sorption mechanisms are evaluated and discussed. The phosphate sorption capacities of the three materials, at around 23 mgP/g suggest that each two molecules of FeOOH bind to one molecule of phosphate.

#### Phosphate recovery

Phosphate was recovered from the regenerant solution, after analysis, by adding either calcium nitrate (to precipitate **calcium phosphate**) or magnesium sulphate plus ammonium chloride (to precipitate **struvite**), followed by settling, filtration, rinsing, drying and analysis (Energy Dispersive X-ray EDX and a Scanning Electron Microscope SEM). This enabled **precipitation of >90% of the phosphate present in the regenerant**. Sodium hydroxide was added to the recovered regenerant, to replace depleted OH<sup>-</sup> ions, which was then used again for regeneration.

The authors conclude that **all three exchangers showed high selectivity towards orthophosphate** compared to other ions and can be readily regenerated, with only a very small phosphate sorption capacity reduction (1.5%) after 10 exhaustion – regeneration cycles. No significant loss of iron or copper from the exchangers was noted in the regenerant.

*“Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer”, Water Research, Vol. 45, Issue 11, May 2011, pages 3318-3330 [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)*

S. Sengupta, Dept. Civil & Environmental Engineering, University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA [ssengupta@umassd.edu](mailto:ssengupta@umassd.edu) and A. Pandit, Dept. Civil & Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

### Optimising struvite recovery

#### Reduced nitrogen leaching

#### Struvite recovery from swine wastewater

The paper (A) presents an innovative struvite reactor design, laboratory scale testing with real swine wastewater, and soil column tests comparing nutrient leaching from soils fertilised with this recovered struvite to soils fertilised using

a conventional fertiliser (Fused Super Phosphate; FSP plus urea). Soil pH changes and phosphate and nitrogen leaching were measured in the soil columns for a period of 35 days after an initial applications of high and low fertilisation doses of recovered struvite (MAP magnesium ammonium phosphate), and doses of FSP+urea calculated to give the same level of phosphorus and nitrogen dosage.

In a second paper (B), the recovered struvite re-dissolved in order to release phosphate and magnesium ions, which are used to improve the ammonium removal ratio in the swine wastewater struvite reactor.

Struvite precipitation was tested in a laboratory scale reactor using **piggery wastewater collected from a local farm**, sieved to 0.5 mm mesh to remove large solids.

#### Struvite precipitation reactor

**The continuous non-stirred 12.3 litre struvite recovery reactor shows an original design**, including an aeration and reaction zone within the main reactor. The aeration – reaction zone is a 2.7 litre volume column, in which the influent wastewater and dosed magnesium chloride moved in downflow past an airstone which enables carbon dioxide stripping, thus increasing pH and facilitating struvite precipitation, as well as mixing the reaction zone. The struvite sinks to the bottom of the sloped main reactor in which the effluent then moves upwards towards an outflow at the top, thus allowing settling of the precipitated struvite. Struvite is recovered at intervals through a spigot at the bottom of the reactor cone.

Hydraulic retention time in the reactor was 4 hours (time calculated for the aeration – reaction zone) and aeration was 0.73 litres of air/minute.

When magnesium was added at a 1:1 ratio to the soluble phosphate in the influent, the reactor achieved **93% soluble phosphorus removal from the swine wastewater**. However, a considerable amount of suspended solids also settled with the precipitated struvite, which would thus have a significant organic content (figure not given), posing problems for drying, storage or distribution as a fertiliser. The reactor also removed 31% of ammonium nitrogen, more than the molar ratio for the phosphorus precipitation,

presumably because of significant **ammonium stripping to the atmosphere with the aeration.**

For the soil leaching tests, the recovered struvite was purified by centrifuging, dissolving in sulphuric acid, and then precipitating as a clean struvite by increasing pH.

### Soil nutrient leaching

The soil leaching tests were carried out using 55 cm high, 8 cm diameter columns containing 5 cm sand, 15 cm subsurface and 15 cm top soil, soaked before starting the experiments. The fertiliser doses were placed 2-3 cm below the soil surface. **Leachate was collected weekly, for five weeks**, from a valve at the bottom of each column, and replaced with the same volume of water at pH 6.5 added to the soil surface. Soil pH was also measured weekly, by extracting a sample of soil from each column.

Five sets of columns (each with 3 replicates) were tested: control (no fertiliser), struvite at 30 kgP/ha (normal) and at 40 kgP/ha (high), FSP+urea at the same P and N doses.

The results show similar levels of phosphorus leaching for struvite and FSP+urea at the high fertiliser dose, but lower P leaching with struvite at the lower dosage. **Nitrogen leaching was c. 3x lower with struvite than with FSP+urea at both high and normal fertiliser doses.**

Soil pH showed a greater increase with FSP+urea in the first week of the experiment, but by the third week the pH was higher with the struvite fertilisation. By the 5<sup>th</sup> week, the pH with the struvite fertilisation remained somewhat higher than the initial soil pH (6.3 – 6.4 compared to 6.1 – 6.2) whereas the pH with the FSP+urea had fallen back to its initial level.

**The authors conclude that struvite can be successfully recovered from swine wastewater using the presented reactor design, and that struvite showed significantly lower nitrogen soil leaching than when SFP+urea fertilisers were applied.** Struvite thus appears as very positive for use in acidic soils, as an effective and environmentally friendly fertiliser.

### Electrolytic re-dissolving struvite for ammonium removal

In paper (B), the recovered struvite from the swine wastewater, using the struvite precipitation reactor

above, is purified (as above), then re-dissolved using a 4 litre experimental electrolytic reactor. It was demonstrated that an electrolyte of 0.06% sodium chloride solution and a voltage of 7V DC for 1 ½ hours were optimal, enabling much of the struvite to be dissolved to soluble magnesium and phosphate, but with **no residual ammonium in solution.** The ammonium is probably converted to nitrogen gas by HOCl / OCl<sup>-</sup> oxidants formed by electrolysis of the NaCl electrolyte.

The resulting phosphate and magnesium solution was then recycled to the struvite reactor. The addition of dissolved struvite (phosphate and magnesium) to the swine wastewater struvite precipitation reactor, compared to a control where magnesium chloride was dosed at 0.5M ratio to the influent phosphate, **significantly improved both ammonium and phosphate removal.** For the ammonium removal, this is to be expected because the ammonium : phosphate ratio in the swine wastewater is much higher than the 1:1 ratio of struvite.

The improved phosphate removal is more surprising, because the magnesium : phosphate ratio is not significantly improved by dosing dissolved struvite. The effect may be because of higher ionic concentrations of magnesium and phosphate improving struvite precipitation, improved ratios compared to ammonium or seeding by small particles of undissolved struvite.

The authors conclude that the **recycling of electrolytically re-dissolved struvite can provide a practical method for significantly improving the efficiency of struvite precipitation** from wastewater, at a cost around 3x lower than purchasing magnesium and phosphate chemicals.

A: “Recovery of struvite from animal wastewater and its nutrient leaching loss in soil”, *Journal of Hazardous Materials*, vol. 186, Issues 2-3, February 2011, pages 2026–2030 <http://www.journals.elsevier.com/journal-of-hazardous-materials/>

M. Rahman, Y-H.Liu, C-S. Ra, Laboratory of Livestock Environment, College of Animal Life Science, Kangwon National University, Chunchon 200-701, South Korea [changsix@kangwon.ac.kr](mailto:changsix@kangwon.ac.kr) and J-H.Kwagb, National Institute of Animal Science, RDA, Suwon 441-350, South Korea

B: “Recycle of electrolytically dissolved struvite as an alternative to enhance phosphate and nitrogen recovery from swine wastewater”, *Journal of Hazardous Materials*, vol.195, November 2011, pages 175-181 [www.elsevier.com/wps/locate/jhazmat](http://www.elsevier.com/wps/locate/jhazmat)

Y-H. Liu, Sanjay Kumar, J-D. Kim, C-S. Ra, Dept. Animal Life System, Kangwon National University, Hyoja 2, 192-1, Chunchon 200-701, South Korea and J-H. Kwag, J-H. Kim, National Institute of Animal Science, RDA, Suwon 441-350, South Korea

## Feeding bio-P removal

### Alkaline fermentation and P-recovery

Adequate supply of readily available organic carbon, in particular short chain fatty acids (SCFA, also termed volatile fatty acids VFA), is essential for effective biological phosphorus removal in sewage works. One cost effective way to produce these is by anaerobic digestion (fermentation) of excess sewage sludge and/or other organic wastes (e.g. food wastes). This series of papers looks at how production of SCFAs can be optimised by adjusting the pH of the fermentation process, and how such production of SCFAs can be combined with phosphorus and nitrogen recovery (as struvite), thus further optimising the sewage works P-removal.

The 2006, 2007 and 2009 papers report experimental work using wastewater and sludge from a biological nutrient removal municipal waste water treatment plant (BNR wwtp) in Shanghai, China. The 2011 paper reports a pilot installation operated at an A<sup>2</sup>/O process BNR wwtp in Jiangsu Province, China.

#### 2006 paper: increasing SCFA production at pH 10

The 2006 paper presents **20 day batch fermentation experiments** using nine 1.5 litre vessels, stirred at room temperature, operating on excess sludge from the wwtp secondary sedimentation tank after settling at 4°C for 24 hours. The fermentation vessels were operated with pH controlled (by sodium hydroxide or hydrochloric acid addition) at 4, 5, 6, 7, 8, 9, 10 and 11, plus one vessel where pH was not adjusted. Further fermentation experiments were carried out using bovine serum albumin (protein) and glucose (carbohydrate), both inoculated with sludge, to **establish whether short chain fatty acid (SCFA) production was related to protein or carbohydrate** at the different pHs, and with sterilised sludge to **establish whether SCFA production was resulting from chemical hydrolysis or biological processes**. The sludge itself contained 61% protein and 11%

carbohydrate. SCFAs and methane concentrations were analysed by gas chromatography.

The initial SCFA level in the sludge was c. 1.5 mg SCFA COD/gVSS. After 4 days SCFAs had increased in all vessels, but with the greatest increase at pH 10 (to 130 gCOD), whereas pHs 4, 6 and 7 only increased to around 30 – 35 gCOD. After 8 days, the comparison between the different pHs remained similar, reaching 250 gCOD at pH 10. After 8 days, SCFAs did not further increase except at pH11, where they continued to increase up to 262 gCOD on day 20.

**The authors conclude that SCFA production can be reliably increased by maintaining pH 10.** Although similar results can be achieved at pH 11, this takes much longer.

The SCFAs produced at pH 10 showed straight and branched molecules with 2 – 5 carbons, with acetic acid being the most prevalent molecule.

The studies with proteins and carbohydrates showed that these both generated more SCFAs at pH 10, which corresponded to experiments showing that **proteins and carbohydrates in the sludge itself were more soluble at pH 10 and 11**. The studies with sterilised sludge showed very much lower SCFA production, demonstrating that the biological fermentation process was the main cause.

#### 2007 paper: soluble phosphorus and ammonia

The 2007 paper reports the same experimental set-up. In this case, **concentrations of soluble phosphorus (PO<sub>4</sub>) and ammonia (NH<sub>4</sub>) in the fermentation mixed liquors were assessed**. These concentrations increased at all the tested fermentation pHs, from initial values of around 50 mg P-PO<sub>4</sub>/l and 10 mg N-NH<sub>4</sub>/l. The increases were highest in the low pH (4 or 5) fermentation vessels, but even at pH 10, soluble phosphorus and ammonia both reached around 150 mg/l. At lower pHs, the release of ammonia was much higher (in mg/l) than of soluble phosphorus, so that **relatively low ammonia release at higher pH** was surprising. The authors suggest that it may be because the higher pH prevents the function of protease and peptidase enzymes.

The authors also note that at pH 10 and 11, there is **no methane production**. This is conform to literature reports, that high and low pH prevent methane production.

The optimised SFCA production is therefore an “alternative” to methane production for energy, but the release of soluble phosphorus and ammonia means that the return of the liquor to the biological nutrient removal process (to provide SCFA) will also add to the base nutrient load and thus deteriorate operating efficiency.

### 2009A paper: P-recovery

**Struvite precipitation from the alkaline fermentation liquors** (produced at pH 10 as indicated above) was tested as a route for removing the soluble phosphorus and nitrogen. Because the molar concentration of ammonium nitrogen was significantly higher than that of soluble phosphorus, potassium phosphate was dosed, in addition to magnesium chloride and pH adjustment (using sodium hydroxide or hydrochloric acid). 500 ml batch precipitation experiments tested different pH, Mg/N and P/N molar ratios.

After the struvite precipitation, the treated fermentation liquor was then added, at different dosing rates, to **four pilot batch reactor biological nutrient removal plants** (4 litre working volume). Central composite design or response surface methodology (CCD RSM) modelling was used to optimise the process model.

### Struvite recovery and improved nutrient removal

The predicted and experimental optimal removal rates through **struvite precipitation** were 73 and 76% for ammonia nitrogen and 82 and 83% for soluble phosphorus.

The addition of the fermentation liquid to the nutrient removal pilots did not significantly modify nitrification, whereas **considerable increases in removal of soluble phosphorus (from 44 to 76%), total nitrogen removal (from 63 to 71%) and COD removal (from 84 to 91%) were observed**. Above a ratio of 1/35, addition of further fermentation liquid did not result in further improvements. In some cases, the pilot plant effluent COD increased with fermentation liquor addition, because of the COD load added (as humic acid) with the liquor.

The authors conclude that alkaline fermentation of sludge to produce fatty acids, followed by phosphorus recovery as struvite (to avoid soluble phosphorus load in the fermentation liquor), is **an effective way of improving biological nutrient removal operation**.

In the 2009B paper, the authors investigated the possibility of **precipitating struvite from fermented waste active sludge before sludge liquid separation**, and the positive effects of this on the following sludge liquid filtration system. Conditions for ammonium and phosphorus recovery as struvite were investigated and optimised using Response Surface Methodology (RSM), a combination of modelling optimisation and experimental testing of parameter conditions identified by the modelling CCD central composite design). Different parameters tested included pH, magnesium addition, phosphate addition, struvite powder addition, cationic polyacrylamide polymer (PAM) dosing.

**The sludge dewatering properties were improved considerably when struvite had been precipitated** in the fermented waste activated sludge. The simple addition of powdered struvite also improved the sludge dewatering.

In the 2011 paper, the authors show that **calcium hydroxide (instead of sodium hydroxide) can be used to increase the pH and provide alkaline fermentation conditions**. Again, soluble phosphorus can be removed from the fermentation liquor by magnesium (or iron) addition. The use of calcium hydroxide however resulted in better wwtp sludge dewatering, lower chemical costs and better liquid/solid separation in the fermentation liquor.

2006: “Improved Bioproduction of Short-Chain Fatty Acids (SCFAs) from Excess Sludge under Alkaline Conditions”, *Environ. Sci. Technol.* 2006, 40, pages 2025-2029

<http://pubs.acs.org/journal/esthag>

H. Yuan, T. Chen, H. Zhang, S. Jiang, Q. Zhou, G. Gu, State Key Laboratory of Pollution Control and Resources Reuse, School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China  
[yg2chen@yahoo.com](mailto:yg2chen@yahoo.com)

2007: “Hydrolysis and acidification of waste activated sludge at different pHs”, *Water Research* 41 (2007), pages 683 – 689 [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)

Y. Chen, S. Jiang, H. Yuan, Q. Zhou, G. Gu, as above

2009A: “Recovery of nitrogen and phosphorus from alkaline fermentation liquid of waste activated sludge and application of the fermentation liquid to promote biological municipal wastewater treatment”, *Water Research*, 43 (2009), pages 2969-2976

J. Tong, Y. Chen, as above.

2009B: “Simultaneous nitrogen and phosphorus recovery from sludge-fermentation liquid mixture and application of the fermentation liquid to enhance municipal wastewater



biological nutrient removal”, *Environmental Science and Technology*, 2009, 43, pages 6164-6170.

C. Zhang, Y. Chen, as above

2011: “Pilot-Scale Waste Activated Sludge Alkaline Fermentation, Fermentation Liquid Separation, and Application of Fermentation Liquid To Improve Biological Nutrient Removal”, *Environmental Science and Technology* 2011, 45, pages 1834–1839

X. Li, H. Chen, L. Hu, L. Yu, Y. Chen, G. Gu, as above.

More publications related to this topic are available.

[1] Xiaoyu Zhu, Yinguang Chen. Reduction of  $N_2O$  and  $NO$  generation in anaerobic-low DO biological wastewater treatment process by using sludge alkaline fermentation liquid. *Environmental Science and Technology*, 2011, 45, 2137–2143.

[2] Peng Zhang, Yinguang Chen, Qi Zhou, Xiong Zheng, Xiaoyu Zhu, Yuxiao Zhao. Understanding short-chain fatty acids accumulation enhanced in waste activated sludge alkaline fermentation: kinetics and microbiology. *Environmental Science and Technology*, 2010, 44: 9343-9348.

[3] Zhouying Ji, Yinguang Chen. Using sludge fermentation liquid to improve wastewater short-cut nitrification-denitrification and denitrifying phosphorus removal via nitrite. *Environmental Science and Technology*, 2010, 44, 8957-8963.

[4] Leiyu Feng, Yinguang Chen, Xiong Zheng. Enhancement of waste activated sludge protein conversion and volatile fatty acids accumulation during waste activated sludge anaerobic fermentation by carbohydrate substrate addition: The effect of pH. *Environmental Science and Technology*, 2009, 43, 4373-4380.

[5] Peng Zhang, Yinguang Chen, Qi Zhou. Waste activated sludge hydrolysis and short-chain fatty acids accumulation under mesophilic and thermophilic conditions: effect of pH. *Water Research*, 2009, 43: 3735-3742.

## P-recovery

### Adapting sludge treatment to optimise struvite recovery

RWTH Aachen University, Germany, Institute of Environmental Engineering (ISA) has investigated several different routes for recovering phosphates for recycling from sewage. This paper shows experimental results using struvite precipitation from sludge thickening liquor (Phosphorus Recovery at ISA = PRISA process). Experiments were carried out at the laboratory scale (5 litres) and in a pilot scale waste water treatment plant (350 l/h) fed with municipal wastewater and

operating enhanced biological phosphorus removal (EBPR).

The sludge treatment line consisted of a pre-thickener, an anaerobic digester, a post-thickener and a filter press. These were held in an equalising tank, fed through a cloth filter to remove solids, and then struvite precipitated by adding magnesium oxide and caustic soda (NaOH) for pH adjustment.

### Modulating sludge processing

Initial experiments showed that simple variations in hydraulic residence time and periodic stirring in the pre-thickener could **increase soluble phosphorus** concentration in the supernatant from around 10 to around 60 mg P- $PO_4$ /l.

Eleven pilot scale runs were carried out to **optimise the dissolution of phosphate, using different mixing times and hydraulic residence times**, occasionally using a mixture of excess sludge and pre-treated waste water. Optimal results were obtained with a relatively long hydraulic residence time (3 days not 1 day), and relatively little stirring (once a day only). This resulted in **dissolution of up to 25% of the sludge total phosphorus in the pre-thickener**. In operation adding 10% of waste water (probably this provides readily available organic carbon) could induce an even higher phosphate release from the sludge.

This supernatant was then mixed post-thickener supernatant and process water from the filter press (which together contained a further c. 15% of the sludge phosphorus), and then fed to the struvite precipitation process.

### Struvite precipitation

Using a magnesium to phosphorus ratio of 1.5 and a pH >9.0 **more than 90% of dissolved phosphorus was precipitated as struvite**. The liquor after struvite precipitation is recycled back to the water treatment plant, with the advantage that phosphorus has been mostly removed and additionally the nitrogen content is reduced.

**The precipitated struvite was tested as a fertiliser**, showing fertilising effect comparable to commercial fertilisers. As expected the heavy metal content of the struvite is quite low.

The authors conclude that this PRISA struvite precipitation process, from Enhanced Biological P Removal sewage works sludge treatment liquors, can

enable **recovery of around 40% of sewage works inflow phosphorus as struvite**, which can be used as an agricultural fertiliser.

“A Feasible Approach of Integrating Phosphate Recovery as Struvite at Waste Water Treatment Plants”, in: LeBlanc, R. J., Laughton, P. J., Tyagi, R. (Ed.): IWA-Conference Proceedings “Moving Forward” 24.-27. June 2007, available at : [http://www.cepis-ops-oms.org/bvsaar/cdlodos/pdf/afeasibleapproach551.pdf](http://www.cepis.ops-oms.org/bvsaar/cdlodos/pdf/afeasibleapproach551.pdf)

D. Montag and J. Pinnekamp, Institute of Environmental Engineering, RWTH Aachen University, D-52056 Aachen, Germany. [montag@isa.rwth-aachen.de](mailto:montag@isa.rwth-aachen.de)

## P-recovery technologies

### Australia

#### P-recovery and water recycling

It is expected that 30% of Australia’s water supply will come from recycled water from sewage treatment by 2030. This is generally achieved by “adding on” microfiltration and reverse osmosis membranes to the discharge of existing waste water treatment plants (wwtps). This paper compares the efficiency of such process configurations with more integrated designs including anaerobic digestion, looking particularly at the phosphorus recovery potential and the net energy consumption.

The authors underline that water conservation is a key route to securing water supplies, and that **reducing water consumption will increase influent nutrient concentrations** in sewage treatment plants, thus decreasing effluent quality and increasing phosphate concentrations in water recycling reject streams.

#### Four different scenarios are compared:

- 1) Conventional wwtp with microfiltration and reverse osmosis (RO) membranes applied to the treated water (“**add on**” configuration). Struvite precipitation is then applied to the RO brine stream. In scenario 1, the conventional wwtp uses an aerobic secondary treatment.
- 2) As above, but with biological nutrient removal (anoxic – aerobic modified Ludzack-Ettinger = MLE) operated in the conventional wwtp.
- 3) After primary treatment (settling), the sewage goes directly to nanofiltration membranes (“**integrated**” configuration). From these, the reject goes to

anaerobic digestion, and then the supernatant to struvite precipitation, whilst the purified water goes to reverse osmosis.

- 4) Similar to scenario 3, but in this case the anaerobic digester treats all the discharge from the primary treatment, upstream of the nanofiltration membranes. The struvite precipitation is fed by the nanofiltration reject stream.

The assessment of the different scenarios is based on literature values for the functioning of the different types of membrane, for struvite precipitation and for anaerobic digestion. The question of **loss of methane dissolved in digester supernatant** is raised as this may cause real energy production to differ from expected values.

### Integrated systems

In the two integrated system scenarios (3 and 4), **nutrient concentrations in the brine streams were significantly higher** than for the conventional plus add-on scenarios (59-62 mgP/l compared to 24-44 mgP/l), because phosphorus was not being transferred to the secondary sludge. The lowest potential for P-recovery is in scenario 2, because of the phosphorus removal in the secondary treatment (editor’s note: though this could be improved if the secondary BNR sludge were digested or separated and the supernatant used for struvite precipitation).

In all scenarios, the P concentration in the brines is lower than is often found in BNR sludge supernatant, and the overall rate of P-recovery is also lower (compared to sewage plant inflow phosphorus).

### Energy consumption

The estimated energy consumption of the membrane filtration plus reverse osmosis is considerably greater than that of the conventional primary and secondary treatment (14 -17 000 kWh/d compared to 5 – 9 000 kWh/d). The energy production from methane in the anaerobic digester is 3 – 4 000 kWh/d. The **energy consumption of the struvite precipitation process is relatively very low** (100 kWh/d).

Overall, the “**add on**” scenarios have **higher net energy consumption than the two “integrated” scenarios**, because of the energy consumption in the conventional treatment plant and the absence of methane production.

If the total energy consumption of the plant is compared to the estimated production of struvite to

deduce an energy/kg phosphorus recovered (260 – 1200 kWh/kgP depending on the scenarios), this is considerably higher than estimated energy costs of recovering struvite from source separated urine by evaporation (100 – 240 kWh/kgP) or by reverse osmosis (5 – 12 kWh/kgP). However, the comparison is not necessarily meaningful, in that **the sewage plant scenarios considered also provide water treatment and water recycling in addition to P recovery**. Notwithstanding this, the prospect of P recovery from waste should not be dismissed on comparison of expended energy of P recovery (kWh/kgP). The infrastructure of waste collection and treatment is a valuable asset that ensures public health by providing communal sanitation and can **provide the platform for both water and nutrient recovery as a means to making urban centres more sustainable**.

If domestic water consumption is reduced, the nutrient concentrations in the plant inflow will increase, and the energy per kgP recovered will decrease.

The authors note that overall costs will also include chemicals for struvite recovery (magnesium, pH adjustment), membrane cleaning and membrane replacement.

*“Phosphorus recovery from centralised municipal Water Recycling Plants”, 2011, Chemical Engineering Research and Design (Elsevier)*

<http://www.sciencedirect.com/science/journal/02638762>

Z. Bradford-Hartke, G. Leslie, School of Chemical Engineering, Chemical Sciences Building (F10), The University of New South Wales, Sydney 2052, Australia and P. Lant, School of Chemical Engineering, University of Queensland, St Lucia 4067, Australia [g.leslie@unsw.edu.au](mailto:g.leslie@unsw.edu.au)

## Technology update

### Review of P-recovery patents

This paper provides an overview of technologies for recovery of nitrogen and phosphorus from wastewaters such as sewage, sewage sludge supernatant, animal manures and industrial wastewaters. Scientific literature summarised, but more unusually, particular emphasis is placed on patent applications.

Recovery of phosphate for recycling as struvite (magnesium ammonium phosphate) is presented as a route which is already operational in Japan, producing a marketed fertiliser.

#### Struvite recovery

**Four patents relating to struvite precipitation** are summarised, including cone fluidised bed reactor, (Bowers, 2006-7005072), concentrating the soluble phosphate and magnesium salts using a membrane (Barak, 2007-7182872), combining phosphorus recovery as struvite with nitrogen recovery as ammonia gas (Haggerty, 2006-7135116) and processes to extract soluble phosphorus from sewage sludge then precipitate struvite (Stendahl, 1998-5720882).

Other recent patents, not summarised in this article, relating to struvite recovery include

- Baur (2010-0170875) where **volatile fatty acids** are fed to (sludge) microorganisms to result in phosphate and magnesium release and separately in an anaerobic digester to release ammonia. The two supernatants are then combined so that struvite is precipitated.
- Chung (2009-0308807), **struvite precipitation from anaerobic digester supernatant by carbon dioxide stripping** in a tower where the supernatant free-falls between several shelves, so exposing to air
- Kang (2010-0255562), **struvite crystallisation following thermal hydrolysis of sludge** to release phosphate and magnesium
- Koch (2009-7622047), a **fluidised bed reactor for struvite precipitation**, consisting of four different zones of stepwise increasing diameter (wider higher up the column)
- Ringelberg (2004-6776816), **struvite precipitation from (presumably liquid or filtered) animal manure** is achieved by mixing with a magnesium source and an enzyme to accelerate breakdown of urea to produce ammonia which can combine with P and Mg to produce struvite.

#### Calcium phosphate recovery

The author indicates that **calcium phosphate precipitation** may be an attractive route for P-recovery in waste streams with high phosphorus levels but low concentrations of ammonia, because lime is a cheaper reagent for addition (calcium source) than magnesium sources for struvite precipitation. The recovered calcium phosphate can then be used as a fertiliser or in fertiliser manufacture.

- Fukushima (1995, EU patent 1000904), release of phosphate from **biological nutrient removal sewage sludge**, followed by calcium

phosphate precipitation by calcium dosing and pH adjustment and calcium silicate hydrate seeding

- Malcom (1996-5562829), precipitation of calcium phosphate from **milkhouse wastewater**
- Kikuyama (1996-6666973), **precipitation of tricalcium phosphate and calcium fluoride** from industrial wastewater containing fluorophosphates

### Other phosphate precipitation routes

Three other patents (Hughes 2005-6923917, Goel 2004-6706185, Vanotti 2005-6893567), are presented which **precipitate various metal phosphates from municipal, agricultural or industrial wastewaters**. However, it is not clear how the metal phosphate precipitated can then be usefully recycled.

### Nitrogen recovery

Two patents are summarised which propose methods for removing nitrogen compounds from liquors and which can then enable **nitrogen recovery as struvite**.

- Sunyer (2000, EU patent 1041058), for treatment of **swine manure**, involving sterilisation and mixing at 70°C to convert nitrogen to ammonia, followed by struvite precipitation. Struvite separation is assisted by flocculant addition, and the remaining liquid goes to biological treatment.
- Hallberg (1992-5126049), a **biological process for removing nitrites from polluted waters**. The nitrogen is transformed to ammonia, and so can be recovered by struvite precipitation.

Burke (2006-7153427) uses heated air to **strip ammonia from anaerobic digester supernatant**. Nitrogen is then recovered from the air flow by conversion to nitrate and biomass in a biofilter.

*“Nitrogen and phosphorus recovery from wastewater and the supernate of dewatered sludge”, Recent Patents on Food, Nutrition and Agriculture, 200 – 1, pages 236-242.*

D-B Wang, X-M. Li, Y. Ding, T-J. Zeng, G-M. Zeng, College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China  
[wwyy44339745@yahoo.com.cn](mailto:wwyy44339745@yahoo.com.cn)

US patents online <http://worldwide.espacenet.com/>

EU patents online <http://www.uspto.gov/>

## Phosphorus in sewage

### Nancy, France

#### Forms of phosphate in sewers and sewage

It is now recognised that sewers do not simply drain sewage, but also function as a large scale biological and physicochemical reactor, effectively acting (positively or negatively) as part of the overall waste water treatment system. Reactions taking place can include methane emission, hydrogen sulphide production, modification of organic matter, and changes in minerals. Phosphates are mainly present in raw sewage as orthophosphates, and these are known to react with surfaces and other ions to form a variety of minerals. This paper studies the phosphate minerals at 15 different sites in the Nancy greater urban community sewerage network, North East France.

The Nancy area sewerage network has 950 km of pipes, of which 250 km can be entered (diameter of at least 1.2 m). The city is surrounded by hills, and the gradient in parts of the pipe system can reach 5%. The city centre sewers generally combine rainwater and wastewater, whereas peripheral areas have more separate collection systems. Upstream sites generally have only domestic wastewater, whereas downstream sites also have hospital or industrial discharges. **Three different sections of the sewerage system were studied, with 5 sampling sites in each section** ranging from upstream to downstream. Eight sampling campaigns took place from 2004 – 2006, always in dry weather.

### Sediments, biofilms and suspended particles

At each site, samples of sediments from the pipe were collected (type A coarse granular), of biofilm (where possible) and of sewage (from which suspended particles were extracted by filtration at 0.22µm. The principal chemical and physicochemical characteristics of the sewage were also measured for each sample.

An initial extraction procedure was used to identify general types of phosphate present: **loosely sorbed P** (labile), **inorganic P association with aluminium**, inorganic P bonded to **carbonates**, inorganic P associated with **iron**, and P bonded to **organic matter**. The different extracts were centrifuged, rinsed (with pure water and with salt solution), centrifuged, freeze

dried then examined using TEM-EDXS (Transmission Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy) to identify specific phosphate minerals. A total of 1340 individual particles were thus examined.

### Phosphorus in sewage

Labile and organic bound P account for a significant proportion of the phosphorus in the sewage suspended matter (around one third) but near zero in pipe sediments and biofilm.

Concentrations of soluble total phosphorus in the sewage samples varied considerably, from 1.3 to 13.4 mgP-soluble/l, depending on time of day, groundwater infiltration and whether the sewage was only wastewater (separative) or mixed with rainwater. In most samples, this soluble phosphorus was mainly orthophosphate. **Around 20% of the total phosphorus in the sewage samples was in particulate form**, giving a concentration of P in the suspended solids of 0.043 – 1.36 %P. Based on average household daily water use for France, these values correspond to a total P loading of 1.38 gP/person/day, which is lower than literature values, possibly because of groundwater infiltration in the Nancy sewerage network.

Phosphorus content of the pipe sediments was in the range 0.009 – 0.075 %P, with the higher concentrations occurring in the smaller particles (<50 µm).

### Phosphate mineral phases

Around 40% of the 1340 particles analysed were described as phosphate mineral phases. Many showed **amorphous minerals, not giving a workable electron diffraction pattern**. Comparison between measured Calcium/Phosphorus ratios and EDX spectra enabled probable identification of hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , octacalcium phosphate  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6$ , whitlockite  $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$ , brushite  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , crandallite  $\text{CaAl}_3(\text{PO}_4)_2$ , Mg-brushite species  $\text{Ca}_{0.8}\text{Mg}_{0.2}\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , carapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{CO}_3)_2$ .

Various **aluminium containing mineral phases** were also tentatively identified: bearthite  $(\text{Ca}_2\text{Al}(\text{PO}_4)_2(\text{OH}))$ , foggite  $(\text{CaAl}(\text{PO}_4)(\text{OH}_2 \cdot \text{H}_2\text{O}))$ , gatumbaite  $(\text{CaAl}_2(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O})$  and crandallite  $(\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O})$ .

**Iron containing mineral phases were rarely found**, with single occurrences of strengite  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , anapaite  $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , probably melonjosephite  $\text{CaFe}(\text{II})\text{Fe}(\text{III})(\text{PO}_4)_2(\text{OH})$  and iron phosphide  $\text{Fe}_3\text{P}$ , the latter probably from eroded iron piping. Vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , which is commonly found in freshwater sediments and sludges from sewage works using iron chemical dosing, was not identified.

### Changes along the sewerage network

The composition of phosphate minerals evolves along the sewerage network, with a higher calcium/phosphorus ratio upstream (around 1.3) and higher levels of hydroxyapatite, octacalcium phosphate, whitlockite and brushite, than downstream (0.8). Aluminium calcium phosphate species are more abundant downstream. These changes are coherent with **evolution over time from metastable to more stable phosphate species**, and also with generally lower pH in the sewerage network downstream. Also, groundwater infiltrations along the sewerage network dilute the phosphorus concentration and tend to dissolve less stable phosphate mineral phases. Hydroxyapatite levels in biofilms and sediments are higher than in sewage suspended matter, also suggesting that the mineral phases change over time.

The authors conclude that such understanding of the forms of phosphates in sewage, and their evolution along the sewage transport network, is **important for management of biological phosphorus removal in sewage works and in predicting the impact of phosphorus discharges to the environment** in the case of storm overflows.

*“Phosphate dynamics in an urban sewer: A case study of Nancy, France”, Water Research n°43, pages 1088-1100, 2009 [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)*

*J. Houhou, B. Lartiges, G. Frappier, A. Temgoua, Nancy University, LEM-ENSG/INPL-CNRS, Pôle de l'Eau, 15 Avenue du Charmois, BP 40 54501 Vandoeuvre Cedex, France. A. Hofmann, Lille University-Géosystèmes, 8157 UMR-CNRS, Cité Scientifique, 59655 Villeneuve d'Ascq, France. J. Ghanbaja, Nancy University, Service Commun de Microscopie, BP 239 54 500 Vandoeuvre Cedex, France. [bruno.lartiges@ensg.inpl-nancy.fr](mailto:bruno.lartiges@ensg.inpl-nancy.fr)*

Conferences and reports

**Phosphates 2012**

**Phosphate industry conference**

The 2-yearly conference for the worldwide phosphate industry (rock production, fertiliser, animal feeds, food, detergents, other industrial uses) will take place in El-Jadida, Morocco, 19th - 21st March 2012:

- Phosphate rock production and project developments
- Global fertilizer outlook with a focus on key country demand projections and requirements
- Developments in optimizing / streamlining and maximizing the phosphate resource
- Survey of changing industrial phosphate demand, update of regulations and substitutes
- Outlook of future feed phosphate demand and focus on regional growth

The event also offers **site visits to the Jorf Lasfar Chemical Facility and to the Khourlbga Mine Facility.**



<http://www.crugroup.com/events/phosphates/>

**Phosphorus stewardship conference**

**3<sup>rd</sup> sustainable phosphorus summit**

The 3<sup>rd</sup> Summit (29<sup>th</sup> February – 2<sup>nd</sup> March 2012, Sydney, Australia) will bring together key international science, policy and industry stakeholders from different parts of the food production and consumption chain concerned about the role of phosphorus availability and accessibility in global food security, about protecting the environment, and about supporting rural and urban livelihoods.

Themes include:

- Sustainable food systems
- Global phosphate rock production and reserves
- Phosphorus use efficiency in mining, agriculture, food processing
- Phosphorus recovery and reuse
- Phosphorus pollution and waste
- Sustainable phosphorus strategies and global governance



29<sup>th</sup> February – 2<sup>nd</sup> March 2012, Sydney, Australia  
<http://sustainablepsummit.net/>