

Sustainable phosphorus

Berlin, 3rd-4th March 2015 2nd European Sustainable Phosphorus Platform

(ESPC2)

Preparation for ESPC2 has started, themes are proposed and proposals are welcome.

Science update

Phosphorus bio-mineral chemistry

Changes in understanding of *P* mineralisation in biological and geobiological systems

Phosphorus recycling

Regulatory REACH and recycled nutrient products

Stakeholder positions on REACH legislation application to anaerobic biogas digestate and to biochar

Phosph-OR

2nd France Phosphorus Seminar

The second French seminar on phosphorus recycling was held at IRSTEA, Rennes, 23rd January 2014

WERF research challenge report Nutrient recovery: state of the knowledge

Water Environment Research Foundation summarises current development, perspectives and information gaps, and proposes research projects to address these.

Appropriate technology

Using waste snail shells for phosphorus recycling

Snail shell removes *P* from synthetic wastewater producing a *P*-rich biogenic fertiliser material

Berlin, Amsterdam, Ghent, Antwerp Phosphorus Circular Economy in cities

Initiatives for phosphorus recycling in the local economy

Struvite precipitation

Manure digestate

Bittern and bone meal for struvite recovery

Desalination bittern and bone-meal tested as reagents for struvite precipitation from cattle manure digestate

Poland

Effects of different ions on struvite crystallization

8 further publications assess effects of nitrate

P-recovery

Review of struvite precipitation and reuse

A paper in the Arabian Journal of Chemistry summarises struvite precipitation and fertiliser effectiveness

Pharmaceutical wastewater Struvite recovery from 7-ACA acid production wastewater

Lab-scale tests of struvite precipitation from a medical antibiotic production process wastewater.

Reactor design

Lab trials of struvite precipitation reactor design

Continuous fluidized bed struvite reactor tested in two different designs for 133 day using pure solutions

Berliner Wasserbetriebe From sewage to a CO2-positive fertiliser product

3 years of full-scale P-recovery from sewage sludge digestate, producing a quality, ecological fertiliser.

Partnership opportunities

US & Canada: proposed phosphorus "partnership"

R&D projects and opportunities

Agenda: dates 2013-2014

The partners of the European Sustainable Phosphorus Platform



European Sustainable Phosphorus Platform SCOPE Newsletter newsletter @phosphorusplatform.org | www.phosphorusplatform.eu c/o European Partners for the Environment, av. Tervuren 216, B-1150 Brussels, Belgium The ping life flow smoothly

United

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Sustainable phosphorus policy

Berlin, 3rd-4th March 2015 2nd European Sustainable Phosphorus Platform (ESPC2)

A first preparation meeting to organise **the 2nd European Sustainable Phosphorus Conference** (**ESPC2, 3rd-4th March 2015**) took place in Berlin on 21st January. See SCOPE Newsletter n°92 for summary of the 1st ESPC conference).

It is proposed to structure the conference around several wide themes, covering the full range of phosphorus sustainability issues, with in each case a high-level decision-maker speaker, an overview of today's situation and tomorrow's challenges, and a presentation of business and stakeholder action success stories. For each theme, this will then be followed by breakout table working groups or parallel sessions.

In particular, the Conference will widen the current phosphorus sustainability initiative to the challenges of southern and eastern Europe, including the Baltic, Black Sea and Mediterranean areas.

Contributions invited

The themes proposed, open to input and comment, are:

- Phosphorus losses and environmental impacts (soil erosion, freshwater and marine eutrophication, biodiversity)
- From farm to plate: P efficiency in agriculture and food processing, food safety and phosphorus in the diet
- Food security and international phosphorus supply, including mutual-gains approaches with phosphorus producing countries
- **Reuse of phosphorus and P-recycling** from waste waters and from waste streams
- Addressing the 'Phosphorus Challenge': assessing progress made on the objectives fixed at the first ESPC conference

The conference will welcome posters, presentations and stands showing actions, initiatives, products and services or scientific work, and proposals are already welcome.

Contact: Christian Kabbe, German Phosphorus Platform christian.kabbe@kompetenz-wasser.de

Conference website on www.phosphorusplatform.eu coming soon.



Science update Phosphorus bio-mineral chemistry

This paper provides a detailed review of current science of biological and geo-biological processes of phosphate mineralisation. It suggests that a better understanding of relationships between cellular polyphosphate accumulation and metabolism and mineral (calcium) phosphate precipitation may enable progress both in medical sciences (tissue calcification and bone formation), in understanding the geological history of phosphate and phosphorite deposits, and in other applications involving phosphate-mineralizing micro-organisms.

A paradox of biology and geology is that phosphate concentrations in the environment and within organisms are too low for spontaneous precipitation of phosphorite mineral phosphates, yet minerals accumulate in the environment and within organisms. Throughout evolution, from microbes through shellfish to humans, phosphate minerals precipitate; sometimes precipitation is a controlled process for structural purposes (e.g. bones and teeth).

Polyphosphate biochemistry

Accumulation of **cellular polyphosphates** is known both in micro-organisms (providing the metabolic basis for enhanced biological phosphorus removal EBRP processes applied in wastewater treatment over recent decades) and in larger organisms (e.g. in liver cells). This mechanism of polyphosphate formation by mitochondria enables organisms both to store and to concentrate calcium and phosphorus.

Polyphosphates have contradictory properties. They are negatively charged polyanions, with a high affinity for calcium and other ions, with which they produce an amorphous, non-crystalline, bio-available calciumphosphorus complex. Polyphosphates, like pyrophosphates, are known to be strong inhibitors of calcium phosphate mineral formation. But on the other hand, if broken down (hydrolysed) they release soluble phosphate, which (if within an environment with slow diffusion, such as sediments, organic matter or within body tissues) can result in calcium precipitation. phosphate Specific phosphatase enzymes can separate soluble phosphate ions from polyphosphates, and therefore also create conditions for phosphate mineral precipitation.

Phosphate rock deposit mechanisms

Geological phosphorite refers to sedimentary phosphate rock deposits, principally apatite (calcium phosphate), sometimes with carbonate and/or with high fluorosilicate concentrations. Many theories have been put forward to explain their formation on ocean floors, including both mineral precipitation and biomineralisation processes. The wide variation in such deposits has generated **different explanations**, including: inorganic precipitation, biological formation by plankton, residual skeletons of micro-organisms sinking to the ocean floor, and organisms living on the ocean floor.

Inorganic phosphate precipitation in nature may result simply from mixing of nutrient-rich water (e.g. run-off from a guano deposit) with calcium rich water (e.g. limestone run-off), upwelling of phosphate-rich waters, or sediments exposed to periodic anaerobic conditions. However, recent research demonstrated that marine sulphate-reducing bacteria on the ocean floor induce phosphorite deposit formation by accumulating polyphosphates (the same biological mechanism as used in EBPR phosphorus-removal processes in sewage works) in oxic conditions, then cleaving and releasing soluble phosphate (from polyphosphate) in anoxic conditions to generate energy. This process can generate local high soluble phosphate concentrations resulting in phosphate precipitation within the bacterial mats.

Induction of calcium phosphate (**dental calculus**) precipitation has been observed in the human mouth, and may be caused by oral bacteria that contain polyphosphates. This demonstrates another biological phosphate mineral formation process in the external organism environment.

Cellular phosphate metabolism for mineralization

Certain **marine brachiopods** have shown to be able to accumulate and concentrate phosphorus, producing amorphous calcium and phosphorus-containing granules that eventually form biological apatite mineral in their shells.

The mechanisms whereby **osteoblasts** generate bone calcium phosphate minerals are also discussed, with evidence suggesting that this proceeds by initial release of amorphous calcium and phosphoruscontaining granules which are a precursor of biological



apatite formation in bone. These granules may be composed of calcium and polyphosphate, but sample preparation conditions are also likely to hydrolyse polyphosphate, therefore chemical identification within mineralized tissues such as bone is difficult.

The authors conclude that apatite biomineralisation processes remains an intricate and still unsolved mystery. Phosphate biomineralisation external to and within organisms requires the generation of local supersaturation concentrations of calcium and phosphate. Phosphate biomineralization within organisms also requires a high level of biochemical control on the rate, amount, and location of apatite However, it does seem likely that the minerals. generation of high phosphate mineral supersaturation involves the biological concentration of inorganic phosphate from the environment as polyphosphate by mitochondria, its storage within the cell as polyphosphates, and then the release of local high concentrations of soluble calcium and phosphate by biochemical breakdown of the polyphosphate. This understanding can also be applied to metabolic phosphate processes in organisms, and possibly to developing biologically induced phosphate precipitation processes in wastewater treatment (see Manas et al. SCOPE 90)

"A review of phosphate mineral nucleation in biology and geobiology", Calcif. Tissue. Int. 2013, http://dx.doi.org/10.1007/s00223-013-9784-9

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Phosphorus recycling

Regulatory **REACH and recycled nutrient products**

European stakeholder associations EBA and Fachverband Biogas, with the support of German consulting company BiPRO, have written to the EU Commission requesting confirmation that anaerobic biogas digestate is exempted from **REACH registration**.

The European Sustainable Phosphorus Platform has also written to the EU Commission supporting this position, and requesting that digestates be exempted from REACH

Stakeholders in the biochar sector on the other hand recognise that the product is subject to REACH and propose to develop strict and recognised quality requirements for acceptance of biochar under Endof-Waste criteria, REACH registration and under revision of the EU Fertiliser Regulation.

Digestate is the fully-fermented, mostly liquid endproduct of anaerobic digestion of organic materials (manures, sewage biosolids, food wastes, crop residues, food industry by-products, green waste, etc.), generated during operation of biogas plants (anaerobic digesters).

The biogas associations EBA (European Biogas Association) and Fachverband Biogas (German Biogas Association) represent an industry with a total of around 13 800 anaerobic digesters, producing some 81 500 GWh of electricity from biogas per year (equivalent to the electricity needs of 13.5 million households).

Position paper

The EBA - Fachverband Biogas - BiPRO 17-page document submitted to the EU Commission explains why they consider that anaerobic biogas digestate is e exempted from the obligations of European Chemical legislation 1907/2006 REACH (Registration, Evaluation and Assessment of Chemicals).

Explaining digestates

The document outlines the natural biochemical processes which take place within anaerobic



digestion: hydrolysis breaking down polymers to fatty acids, sugars, amino acids; acidogenisis, breaking these down to short-chain fatty acids, alcohols, lactic acid, producing carbon dioxide and hydrogen; acetogenisis, further breakdown producing acetic acid, carbon dioxide and hydrogen; methanogenisis, producing methane and carbon dioxide.

Digestates generally have excellent fertiliser properties, because nutrients present in the digested biomass are concentrated in the digestate: phosphorus, potassium, most of the organic nitrogen, microelements. Analysis data from 1 800 digestate samples are presented, showing typical organic matter, nutrient and trace metal contents.

The document explains that digestate is therefore comparable to "compost" (which is specifically exempted from REACH), which is produced from the same biomass substrates, but with an aerobic process. Indeed, proposed EU End-of-Waste criteria are currently being elaborated covering both composts and digestates.

Why digestates should be exempt from REACH

REACH explicitly exempts "compost and biogas" (Annex V, entry 12) but does not refer to digestates. The stakeholders consider that digestate should also be exempted from REACH, as comparable to compost and biogas: produced from the same substrates, comparable natural decomposition process carried out by bacteria.

This position is already clearly taken by some member states, e.g. UK Competent Authority leaflet 14, Nov. 2012 http://www.hse.gov.uk/reach/resources/waste.pdf This is conform to ECHA (European Chemical Agency) Guidance which suggests that, under some circumstances, certain biosolids which "have undergone digestion or decomposition" are exempted from REACH.

The European Sustainable Phosphorus Platform written to the European Commission has supporting the position that digestate should generally be exempted from REACH, so long as it is produced by natural fermentation processes (artificially developed in a digester), including if the digestate goes through End-of-Waste status to become a product recognised under revision of the EU Fertiliser Regulations.

On the other hand, **if the digestate is further processed to extract chemicals or specific products** (e.g. ammonium recovery, phosphate recovery, ...) then the recovered products should be subject to REACH requirements, with application of Art. 2(7)d "recovered substances" (only one registration required = not for every producer, each producer subject to specific minimal product information requirements only = sameness, eSDS).

The European Sustainable Phosphorus Platform therefore supports the EBA – Fachverband Biogas – BIPRO request to the EU Commission for a written clarification that digestates are exempted from **REACH** by comparison to composts, and the launch of a process to clarify if and when certain processed digestates or substances recovered from digestates may become subject to REACH and the conditions under which Art. 2(7)d is applicable.

Biochar under REACH



Biochar is produced from biomass by pyrolysis treatment (reductive thermal conditions) at 450° C - 550° C (plant biomass) or 550° C - 650° C (animal byproducts), producing both syngas (an

energy product mixture of hydrogen and carbon monoxide) and a carbon-based byproduct comparable to charcoal, rich in the nutrients originally present in the biomass: phosphorus, potassium, trace metals, but little nitrogen as this is lost in the heat treatment.

There are two types of biochar: that **based on plant materials and forestry by-products**, which is a high carbon content soil-improver with low nutrient content, and that **based on food-grade animal bone** (**ABC = animal bone biochar**) which contains high levels of phosphorus (c. 10% P). Both types of biochar offer soil-improvement characteristics, including water and nutrient retention capacity.

Like other ashes and heat treatment products, biochar is subject to REACH if or when it is not considered a waste. Under REACH, both types of biochar are considered UVCB (that is: "substances of unknown or variable composition, complex reaction products or biological material").

REFERTIL

The REFERTIL project (FP7 contract no.: 289785), led by Terra Humana Ltd – Edward Someus, is **developing quality criteria for biochar**, including



definitions of acceptable biomass substrates, processing criteria, carbon and nutrient content specifications, organic and inorganic contaminant levels, plant nutrient availability / agronomic efficiency and material quality criteria (particle size, dry matter, pH ...). The proposed quality criteria for biochar also include safety testing such as phytotoxicity, germination inhibition, which would be coherent with chemical testing requirements for REACH regulation. These proposed criteria are currently open public consultation to on http://www.refertil.info.

The objective of the REFERTIL project is that these criteria should be used both in EU End-of-Waste Criteria and coherently in revision of the EU Fertiliser Directive EC 2003/2003 (authorisation of biochar as a soil amendment and/or organic fertiliser), and also in Member State regulations. REFERTIL also proposes to develop an advisory network to inform and accompany users of biochar products in the field.

EBA – Fachverband Biogas – BiPro position paper "Digestate and REACH" http://european-biogas.eu/wpcontent/uploads/files/2013/11/2013-11-28-Position-paperdigestate-and-REACH-EN-final.pdf

EBA (European Biogas Association): http://european-biogas.eu/

Fachverband Biogas www.biogas.org

BiPRO www.bipro.de

REFERTIL: http://www.refertil.info/

Phosph-OR 2nd France Phosphorus Seminar

The second French Seminar on Phosphorus was organised by the agriculture technology research centre IRSTEA in Rennes on 23rd January 2014, bringing together 50 researchers and stakeholders from national ministries, farmers' organisations, water companies and local authorities.



For summary of the first French Phosphorus Seminar see SCOPE Newsletter n°83 (Toulouse, 2011).

Marie-Line Daumer, IRSTEA, presented conclusions of the seminar. The Phosph-OR project has shown the feasibility of recovery of struvite from swine manures, and further work is underway to look for processes to solubilise the P in the solid fraction (to make it available for struvite recovery) without using through formic acid, if possible biological acidification. The accumulation of inorganic phosphate in a granular sludge process shows potential to combine sludge volume reductions with production of a recovered phosphate product, and work is underway to look at drying of the granules to produce a stable, ready to handle and store, fertiliser product.

Homologation of digestate as a fertiliser

There are at present important **regulatory issues to be resolved**. There is a need to enable struvite producers to obtain rapidly approval of their product as a "Fertiliser" in France (as is already the case in other countries), pending Europe-wide homologation through revision of the EU Fertiliser Regulation. Significant discussions are underway regarding homologation of digestates as fertilisers/soil amendments in France.

One company (Geotexia) has obtained a positive opinion, recommending homologation, from the French agency for food and work safety (ANSES) for one digestate product (Fertixia-NKS, digestate from methanisation of manure and food industry byproducts). This opinion assesses the characterisation of the product and the production process (membrane reverse osmosis), toxicity and ecotoxicity, residues and consumer safety, fertiliser value (N, K, S, but not P). The formal homologation decision following this opinion not published. See is vet https://www.anses.fr/sites/default/files/documents/FER TIXIANK FSIM 2013-0856 Ans.pdf

At present homologations in France require a new dossier application for each production site, whereas it needs to become possible to cover in one dossier all products made by the same process from similar waste streams (subject to demonstrating that product properties are comparable), to respond to the decentralised structure of nutrient recovery industries (many relatively small production sites at different digesters, sewage works or food processing installations).

Alain Mollier, INRA Bordeaux, presented work assessing phosphorus flows at the national and



regional levels in France (see in SCOPE Newsletter 93). **He emphasised France's dependency on imported fertilisers, but also on imported phosphorus in animal feed and human foodstuffs** (around 50% of P imports in mineral fertilisers). The agri-food system shows low phosphorus efficiency of around 10% (P in human food / total P applied to land in fertilisers, biosolids, manures).

Phosphorus inefficiency

Newly developed data shows low recycling levels: 75% of P in food industry wastes are recycled (from a total of 28 ktP/y) but only 43% of P in sewage (of 63 ktP/y) and 46% of P in solid municipal waste (mainly organic materials, 44 ktP/y). Of the 63 ktP/y in sewage, 17 are lost to sewage sludge incineration and 19 are lost to surface waters (sewage not collected or phosphorus not removed before discharge).

Total annual P losses from agriculture to surface waters are estimated at 58 ktP/y (43 in soil erosion, 15 in runoff).

Phosphorus recovery processes

Anne-Cécile Santellani, IRSTEA Rennes, presented the development of and pilot tests of a process to recover phosphorus as struvite from swine manure after biological treatment (see SCOPE Newsletter n° 91, n° 83 and n° 60). The process involves first acidification of the (treated) manure to release P from solid to soluble fraction (at present formic acid is used for this), dosing of a polymer to improve solid/liquid separation, draining, struvite precipitation by MgO dosing, then separation of the struvite using a 100µm filter. A pilot plant, treating 1 m3/day, is being tested on a pig farm at Pledran, Brittany, France.

Mathieu Spérandio, LISBP Toulouse, presented further results of pilot-scale experiments with batch biological nutrient removal reactors operated in cheese production wastewaters to generate granular sludge, rather than flocs (see SCOPE Newsletters n° 89 and 90). This enables to reduce sludge volumes and improve the sludge index (accelerating sludge control settling). Specific of the anoxic/anaerobic/aerobic cycles in the reactor (pH, dissolved oxygen, redox) results in production of sludge where bacteria group into granules, and also accumulate calcium phosphate (hydroxylapatite) in the granule. Granules of size 1-3 mm diameter with up to 97 % inorganic calcium phosphate were produced.

Béatrice Biscans, LGC Toulouse and Hélène Auduc, INSA Toulouse, presented results obtained in synthetic media showing that the preparation of the MgO suspension was one of the main parameters to control magnesium availability and struvite crystallisation in the above process developed for swine manure. A modelling approach of pH increase by aeration was presented and will help to understand mechanisms involved in phosphate precipitation in both processes developed in the Phosph'Or project.

Christophe Mêlé, Veolia, presented **the new company's STRUVIA**TM **struvite recovery process currently nearing completion of a one-year test at Brussels North (Veolia-Aquiris)** sewage treatment works (2.5 - 25 m³/day pilot reactor) in the scope of the P-REX European project.

This builds on Veolia group's experience of phosphorus recovery operation: **Phostrip®** process operated at 3 sites in Japan (Urabandai municipal sewage works – hydroxylapatite, Hakusya distillery – struvite, Kyoto distillery – struvite), **Nishihara process** (Kitakyushu City – Hiagari sewage works, pilot – struvite using seawaters as a magnesium source, see SCOPE Newsletter n° 39 and n° 36).

STRUVIATM struvite recovery

The STRUVIATM reactor is a stirred reactor (30 - 300 rpm) with a stirred mixing zone (with Mg injection and if necessary caustic soda injection) and a lamella settling zone above this in which the precipitated struvite settles. There is no separated settler nor external struvite recirculation, so **minimising energy use and installation footprint**. A high struvite concentration is maintained into the mixing zone to promote the crystals growth.

In Brussels, it is being tested on different streams: liquor from anaerobic sludge digestion or from the **Wet Air Oxidation** (**ATHOS**TM **process**), other mixes of sludge treatment liquors, and also on an industrial F&B effluent.

Different sources of magnesium have been tested, in particular magnesium chloride solution (byproduct potash mines) and also magnesium oxide (byproduct magnesiamines) injected as a suspension. The objectives of the pilot study have been met with a soluble phosphate removal higher than 80% and a struvite capture higher than 80%.



Tests are underway to integrate the produced struvite into Veolia's organo-mineral fertiliser products.

Christian Morel, INRA Bordeaux, presented results of **tests of fertiliser value of the recovered phosphate products** indicated above: struvite recovered from pig manures, IRSTEA Rennes, and hydroxylapatite (HAP) containing granules recovered from cheese production wastewater, LISBP Toulouse. These were compared to a control (no P applied), commercial triple super phosphate (TSP), pure chemical grade struvite and pure chemical grade hydroxyapatite (HAP). The plant results were obtained from a pot trial using mixed grasses grown in a soil of pH 6.5.

Changes in P solubility and mobility were obtained after 28 d of soil incubation mixed with the different treatments in soils with different pH (4 – 8). The **test method used radioactive marked** ³²P to assess plant availability and uptake of phosphorus, and also phosphorus mobility in soils. Plant results indicated that both of the two recovered products offered fertiliser value equivalent to TSP and pure struvite in soil of pH 6.5. This is as expected from many previous literature data for recovered P products containing struvite. The good plant availability of the recovered HAP granules is considered to be explained by the presence in the granules of amorphous calcium phosphate which is more soluble in water than HAP.

Struvite plant availability at soil pH 8

The incubation results with different soils also suggest that the recovered struvite (but not the recovered HAP granules) offers the same phosphorus availability as TSP and pure struvite at pH=8.

Sylvaine Berger, Solagro, presented an economic assessment and Arnaud Hélias, LBE, a Life Cycle Assessment of the IRSTEA Rennes and LISBP Toulouse phosphorus recover processes above. This shows that the formic acid used for solubilising the phosphorus in the solid fraction of the swine manure renders this process very costly, whereas the granular sludge/HAP process applied to cheese production wastewater (where the phosphorus is already mostly soluble) is potentially profitable. The LCA shows the environmental benefits due to the "avoided fertiliser production" (fertiliser value of the recovered products), both phosphorus and nitrogen.

Phosph'OR onclusions and perspectives

Discussion with participants **confirmed interest for phosphorus and nitrogen recovery processes** of Brittany farmers' organisations, who face an important regional manure nutrient excess and increasingly restrictions on land application, as **France is finally forced, by European Commission legal actions, to implement European water protection legislation**. Interest was also expressed by regulators/water agencies, to enable transport away from Brittany of nutrients to other regions where they are needed in a form where sale will cover transport and partly contribute to mitigate manure treatment costs.

Participants underlined that the context for phosphorus recovery from manure is expected to evolve significantly with accelerating implementation of anaerobic digestion processes for manures.

Phosph-OR project: http://phosph-or2014.irstea.fr/

WERF research challenge report Nutrient recovery: state of the knowledge

The recovery of useful products from wastewater and biosolids, including energy (from organic content by methanisation or other routes, heatpumps) and nutrients, is identified by WERF (Water Environment Research Foundation) subscribers as a key driver for new wastewater processes and technologies, and to help transition wastewater treatment facilities to become resource recovery factories or utilities of the future.



The WERF Resource Recovery challenge aims to identify key recoverable resources and markets for these, and to **define and document effective recovery technologies**.

This builds on **WERF's recent report on resource** and energy recovery from biosolids which includes an overview of nutrient recovery potential, existing processes today and R&D needs.



Nutrient recovery is an emerging area within this overall objective of **producing value from wastewater**, alongside possible recovery of other chemicals or materials (e.g. algae for biofuels, animal feed or fermentation feedstocks, biopolymers such as polyhydoxyalkonoates PHA, lipids or biodiesel, trace metals, etc.).

Making values from wastewaters

WERF notes that **nutrient recovery is unlikely to generate significant revenue for wastewater treatment operators**, but may help offset operating costs for meeting more stringent nutrient discharge requirements. It is also noted that economically viable recovery may require modification of wastewater stream management to generate streams with better recovery potential, by source-separation, combination with other waste streams (e.g. industrial or agricultural) or solid / liquid treatment.

The health and environmental safety of recovery from wastewater needs to be taken into account, in dialogue with public health officials and concerned NGOs.

In particular, recovery processes should aim to integrate systems which improve biosolids quality (reduce contaminant levels, balance nutrients) in order to ensure ongoing use of carbon, beneficial organic matter, and other values in biosolids, either by agricultural use or through processing.

US wastewater treatment plants (WWTPs) currently generate more than 7 million tonnes (dry weight) of biosolids per year and face strong pressure to avoid landfilling. At the same time, cropland available for agricultural use of biosolids is being reduced by urban encroachment: 40 million hectares of farmland was lost over the decade 1997-2007.

Economic value

The theoretical economic potential for recovery of different elements present in municipal wastewater is summarised, suggesting for a large sewage works:

- > 4,000 US\$/year for silver
- ➢ 300 \$ for cadmium
- 75 \$ for nitrogen
- > 10 \$ for phosphorus.

WERF notes that the **markets for some recovered materials may be highly variable**, and that long term prices for phosphorus and nitrogen will be driven by natural gas prices.

The drivers for nutrient recovery will however not be the economic value of the recovered nutrients, but other factors such as biosolids disposal, synergy with nutrient removal requirements.

Literature and knowledge review

An overview of existing knowledge is presented, including a list of relevant publications and information sources. **Technologies cited include** struvite recovery, SaNiPhos (struvite plus ammonium sulphate production), source separation of urine, specific crops grown using wastewater (crops for animal feed protein or biofuel production, or to feed anaerobic digestion methane production, small grain crops, algae for oil extraction for biofuels, duckweed lemna harvesting ...), biosolids-enhanced granular inorganic fertilisers (e.g. Unity Envirotech or VitAG), production of synfuel and/or biochar from biosolids, etc.

A table of 30 technologies is presented, indicating the state of development and information available for each one: Sludge to Biogas: Bioterminator, Cambi, BioThelys, MicroSludge, Ultrasonic, Ozonation, Pulse Electric, Sludge-to-Syngas: Kopf, Thermylis HTFB. Sludge-to-Oil: EBARA, EnerSludge, SlurryCarb, STORS, Sludge-to-Liquid: Aqua Reci, Aqua Citrox, Athos, P from sludge: KREPO, Seabornet, Aqua-Reci, Kemicond, P from Ash: BioCon, SEPHOS, P from Side-stream: Crystalactor, Phostrip, Ostara, Nitrogen Recovery: ARP, Building Material: ALWA, Slag, Brick, GlassPack

Challenge

The WERF challenge aims at research and demonstration – dissemination, integrated into a **holistic resource recovery from wastewater approach**, addressing the following points:

- 1. **New Innovative Ways to Beneficially Use Biosolids**: provide needed sustainable long-term and costeffective management practices, cost savings
- 2. New Innovative Nutrient Recovery and Use Methods: provide cost savings (with (a) lower cost nutrient removal methods, (b) struvite control, (c) reduced biosolids produced), potential Revenue Stream, Green attributes
- 3. New Innovative Metals Recovery and Use Methods: provide potential revenue stream, regulatory benefits – such as cleaner biosolids and effluent



4. Innovative Methods to Recover and Use Other Useful Materials (such as thermoplastics from biophosphate polymers, or methanol and ammonia from digester gas, etc.): provide potential revenue stream, reuse/recovery of phosphorus or some other pollutant, Green attributes

Objectives are to identify, define, quantify:

- Existing and potential **new markets** in terms of quantities, product types and quality, costs, and market types and distances for a range of products (biopolymers and others) and commodities (e.g. fertilizers, increased methane from intensified anaerobic digestion)
- **Commodities that can be produced** in wastewater treatment plants and those that would have to be transported away for third parties to produce.
- Potential **strategic alliances** with other industries to produce commodities
- **Quality requirements** of the new markets so that quality specifications for the commodities from wastewater are acceptable.
- Typical **existing wastewater treatment processes** and technologies that can be "tweaked" to produce the commodities that meet market requirements (regulatory and others).
- **Cost analysis of new technologies** that would be required to produce commodities that meet specifications
- Design plan to establish a **pilot plant demonstration facility** for the production of an agreed commodity. This includes the identification and engagement of a suitable industrial partner.
- **Funding opportunities** for continuing R&D.

First project underway – phosphorus recovery

The first project (NTRY1R12) funded under the WERF Resource Recovery challenge focuses on **nutrient recovery, specifically phosphorus**. In this project, the research team is seeking to:

- 1. Characterize factors influencing the **adoption** of extractive resource recovery systems,
- 2. Provide **guidance on the implementation** of extractive resource recovery technologies at Water Resource Reclamation Facility,
- 3. Experimentally **evaluate** innovative extractive nutrient recovery technologies with an emphasis on P recovery

To date, the project has generated a state of the science review of extractive nutrient recovery

technologies. A complementary electronic interactive technology matrix has also been developed.

As part of this review, the researchers have identified that extractive nutrient recovery can best be facilitated using a three-step framework in which nutrients are: 1) accumulated to high concentrations using biological or chemical means, 2) Released to a small liquid flow with low organic matter and solids content and then, 3) Extracted and Recovered as chemical nutrient product(s).

A concurrent assessment by this project of the market value of nutrient products commonly recovered from extractive nutrient recovery indicates that P containing chemical nutrient products that can be used for agricultural purposes tend to have a higher resale value than products that comprise strictly of N and that these values are highly dependent on regional demand.

The team is currently assembling case study data for North American utilities that have evaluated, are in the process of being implemented, or are operating extractive nutrient recovery technologies. The team is also developing a Tool for Evaluating Resource RecoverY (TERRY), which will enable users to estimate capital and operational costs as well as payback periods associated with implementing struvite crystallization technology, identified by the team as the most mature extractive nutrient recovery technology. Research into innovative approaches for maximizing struvite production as well as electrochemical strategies for facilitating nitrogen, phosphorus and potassium recovery are also being pursued by the team.

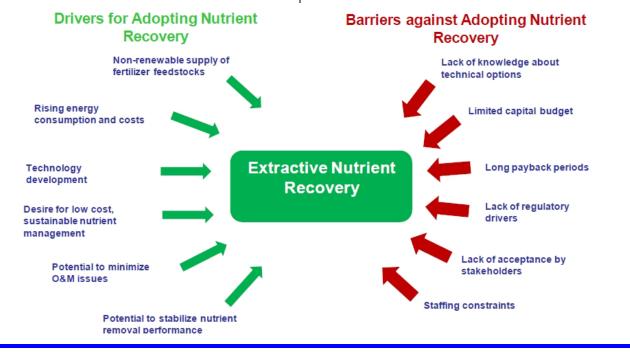
Energy and resource recovery from biosolids.

The 2013 report "Enabling the future: advancing resource recovery from biosolids" (88 pages) presents an overview of potential and issues relating to energy and resource recovery from biosolids, including regulatory, policy and funding framework. technologies, research and implementation needs, based on information from surveys concerning biosolids practice, biosolids quality, regulation and biogas production.

The report notes that a number of US States are implementing policies to remove barriers to resource recovery and that "zero waste initiatives" in cities or regions (maximising diversion away from landfill) incite towards resource and energy recovery from biosolids. Examples cited are Massachusetts policies intended to facilitate co-digestion and California policies in favour of composting.

A 10-page section of this report addresses nutrient recovery. Nutrient removal represents 30 - 80% of electricity consumption in waste water treatment plants, so that efficient nutrient recovery can offer significant potential.

Barriers and drivers for nutrient recovery are identified as below, from Latimer et al. 2012:



European Sustainable Phosphorus Platform SCOPE Newsletter newsletter@phosphorusplatform.org | www.phosphorusplatform.eu c/o European Partners for the Environment, av. Tervuren 216, B-1150 Brussels, Belgium February 2014 n° 101 page 10

The report assesses processes for nutrient recovery from wastewaters based on the principles indicated above of: (1) accumulation of nutrients to high concentrations (2) release to a low-volume liquid flow with high nutrient and low organic and solid content (3) extraction and recovery of nutrient as a chemical nutrient product.

Concentration routes identified include using microalgae or cyanobacteria, adsorption or ion exchange, enhanced biological phosphorus removal or chemical processes.

Nutrient release options include chemical extraction, thermochemical processing, enhanced phosphorus release from WAS (waste activated sludge) and anaerobic digestion. Chemical nutrient product extraction processes include struvite or calcium phosphate precipitation, liquid gas stripping of ammonia and electrodialysis.

This section concludes that no single technology is appropriate for nutrient recovery for all scenarios and that robust data is therefore needed to define the optimum operating space for different options. Further research is needed into a number of currently 'embryonic' and innovative technologies and there is a strong need for full-scale operating data on different processes, in order to assess the costs as related to nitrogen and phosphorus treatment, regarding both removal of the nutrients and recovery.

The report also looks at organics and energy recovery, other resource opportunities (e.g. enhanced fertiliser production, bio-plastics, methanol replacement).

WERF is also progressing work in this area in with collaboration WEF (Water Environment Federation) through a LIFT programme (Leaders Innovation Forum for Technology). This has to date selected five technology areas for evaluation: short-cut nitrogen removal (e.g., deammonification); phosphorus recovery; biosolids to energy; energy from wastewater; and digestion enhancements.

WERF (Water Environment Research Foundation), "Nutrient recovery state of the knowledge", December 2010 and September 2011:

http://www.werf.org/CMDownload.aspx?ContentKey=1b99f4aa-7a01-433d-8c6b-8e8092316484&ContentItemKey=ded28586-7552-45a1-8a40-376e22288c50

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WERF (Water Environment Research Foundation), WEF (Water Environment Federation) and National Biosolids Partnership "Enabling the future: advancing resource recovery from biosolids", 88 pages, 2013, L. Moss, J. Donovan, S. Carr, CDM Smith Inc., L. Stone, C. Polo, Black & Veatch, W. . Khunjar, R. Latimer, Hazen and Sawyer, S. Jeyanayagam, CH2M HILL, N. Beecher, North East Biosolids and Residuals Association, L. McFadden, Water Environment Federation

Latimer 2012: "Towards a renewable future: assessing resource recovery as a viable treatment alternative" WERF, R. Latimer, W. Khunjar, S. Jeyanayagam, C. Mehta, D. Batstone, R. Alexander.

Appropriate technology Using waste snail shells for phosphorus recycling

A range of previous publications have shown that shells of various seafood (mussels, crab, oyster) are effective for P-removal from wastewater after calcination at 700°C+, see SCOPE Newsletters n° 89 and 84. In these papers, shells of the African land snail Achatina achatina were simply ground and dried then tested for phosphate removal from synthetic wastewaters (pure chemical solutions), including testing in the presence of other ions (sodium, chloride, carbonate, sulphate, nitrate) and of organics (humic acid).

Up to 99% P-removal was achieved in the pure solutions, dropping to around 70% in presence of high levels of organics. The phosphorus-enriched shell product could contain up to c. 220 mg/g phosphorus (P) dry weight.

Shells of African land snails, like most mollusc shells, include three layers: inner hypocastrum, mainly calcium carbonage as Aragonite; ostracum, mainly prism-shaped calcium carbonate; outer periostracum, mainly the organic proteid conchin.

Biogenic secondary material

The snail flesh is a special culinary delicacy in Nigeria and also used for medicinal purpose. For these papers, the snails were boiled and the mollusc body removed. The shells were then washed and dried (90°C, 4 hours), then mechanically ground and sieved to 180 µm mesh. It is expected that the drying does not modify the chemical nature of the shells and could be skipped, but in the experimental work it was carried out to enable exact dry weights of materials to be known.

This differs from previous work with various seafood shells in which calcination of the shells showed to be necessary (at 700°C or higher) to achieve effective phosphate removal.

Phosphorus removal from synthetic wastewater was tested, at different phosphate concentrations, different pH, different ionic strength (concentrations of potentially interfering ions:, chloride, carbonate, sulphate, nitrate) and in the presence of organics (concentrations of humic acid). These solutions were prepared using pure chemicals: potassium dihydrogen phosphate, humic acid, sodium chloride, potassium carbonate, potassium sulphate, potassium nitrate. pH was adjusted using (HCl) or NaOH.

99% P-removal

In the pure potassium phosphate dihydrogen solution, up to 99% phosphate removal was achieved by adding 2g of snail shell per litre solution (10 - 300 mgP/l) after stirring for 4 hours followed by centrifuging to separate solids and liquids. P-removal was not significantly affected by pH from pH4 to pH12. Competing ions and humic acid both had negative impacts on the phosphate removal, which dropped, for example, to around 70% at 500 mg/l humic acid. On the other hand, the snail shells also adsorbed the humic acid, removing up to 20% of humic acid from solution. This confirms the need to test the effectiveness of the snail shells for P-removal in real wastewaters.

Kinetic modelling showed that reversible first order and pseudo first order kinetic models gave poor descriptions of the phosphate removal process, and a pseudo second order kinetic model gave the best description. The Freundlich model gave a better description of the process isotherm than Lagmuir or Temkin models.

Good sorption capacity

The monolayer sorption capacity of the snail shell was calculated to be 222 mgP/g shell, higher than that of other sorbants in literature (see paper I): natural palygorskite, layered double hydroxides, akageneite, iron or aluminium coated quartz sands, calcite, calcinated metal hydroxide sludge, date palm fibres, steel slag, treated coal fly ash, zeolite synthesised from fly ash, aluminium oxide hydroxide.

The phosphate (and organic acid) containing snail shell, after the sorption process, can contain up to c. 6%P (22% phosphate, dry weight). It is a sludge



which can be simply allowed to dry in the open air then used as an agricultural soil amendment/fertiliser, bringing both calcium and phosphorus to soils.

In further papers, (in II) calcium chloride solution was prepared from the snail shells (by reacting with hydrochloric acid) and this was tested for phosphate removal from pure chemical solutions, and (in III) a combination of a natural kaolinitic clay (from Ozanogog) and the snail shells.

I: "Low-cost biogenic waste for phosphate capture from aqueous system", Chemical Engineering Journal 209, p 170-179, 2012 http://dx.doi.org/10.1016/j.cej.2012.07.125

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II: "Appraisal of gastropod shell as calcium ion source for phosphate removal and recovery in calcium phosphate minerals crystallization procedure", Chemical Engineering Research and Design, 91(5) pages 810-818, May 2013 http://dx.doi.org/10.1016/j.cherd.2012.09.017

N. Oladoja, I. Ololadea, A. Adesina, R. Adelagun – as above. Y. Sanic, Dept. Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

III: "Intercalation of gastropod shell derived calcium oxide in clay and application in phosphate removal from aqua medium", Ind. Eng. Chem. Res. 2012, 51, pages 14637-14645, http://pubs.acs.org/doi/abs/10.1021/ie301520v

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Berlin, Amsterdam, Ghent, Antwerp Phosphorus Circular Economy in cities

At Berlin Green week, the cities of Berlin, Amsterdam, Ghent and Antwerp presented their actions towards developing an urban Circular Economy for secondary phosphorus. This followsthe Memorandum signed between up the Netherlands, Flanders and German nutrient (see **SCOPE** Newsletter 99). platforms Participants participated in round tables to discuss different approaches.

Ministry Maarten Camps, Netherlands of Economic Affairs, opened the seminar, emphasising the drivers for phosphorus sustainability. Phosphorus is a strategic resource for the Netherlands because it is non-replaceable for food production with concerns about supply security and because of the necessity to manage its impact in the environment.

Dr Helge Wendenburg, German federal Ministry of Environment, indicated that at present around 50% of phosphorus in municipal is recycled to agriculture through farmland application of biosolids, but that it is planned to ban this and oblige incineration of sewage biosolids. P-recovery processes from ash will then **be necessary** if the phosphorus is not be lost.

Christian Kabbe, Berlin Competence Centre for Water, indicated that phosphorus in sewage and other biosolids in the Berlin urban area is over 3 000 tonnes P/year, which if recovered could provide around ³/₄ of the mineral fertiliser need of the surrounding Brandenburg region. At present, Berlin Wasserbetriebe are recovering phosphorus as struvite at Wassmannsdorf sewage treatment plant (see in this Newsletter).

Zonneldt. **Sustainabiliy** Edgar Advisor to Amsterdam City Council, presented actions the city's initiatives for phosphorus recycling:

> Struvite recovery from sewage sludge digestion liquor at the WATERNET West installation, treating sludge from several sewage works. Production of c. 3 tonnes of struvite per day (c. 200 tonnes P/year) started in Autumn 2013, at an installation developed by PCS AirPrex. The produced struvite is used in fertiliser formulation at the ICL Fertilisers factory nearby



- > The city is supporting the use of secondary phosphates from a range of sources at the ICL Fertilisers factory which has fixed an objective to use 25 000 tonnes P/year of recovered phosphates.
- ▶ With Heineken, the city is working to develop phosphorus recovery from urine at the Heineken Music Festival event. Specific waterless toilets, to replace standard "porta-loos" used at events, will enable separate urine collection. The urine will be transferred to WATRENET for phosphate recovery by struvite precipitation. The objective is to then 'Close the Loop' by using the struvite to replace mineral fertilisers used on grassland producing grain for Heineken breweries. Amsterdam's objective is to extend P-recovery to all events and festivals, by conditioning event permit delivery to separative urine collection and development of a centralised infrastructure to store the urine and recover struvite.

Wouter Demuynck, Vanhaerens Development, presented a generic model for phosphorus recycling in new buildings, where separative toilets and struvite P-recovery can be foreseen. He explained the interest of specific investment funding tools and service supply companies for such projects, to enable residents and stakeholders to contribute to funding and to share the reduced operating cost benefits. It can be put into practice in projects in Antwerp or Ghent (like e.g. the Old Docks projects, a large scale residential city project).

Participants then exchanged ideas in small groups around four themes: education for phosphorus sustainability, P-recovery at events, P-recycling from waste waters, innovative sanitation in building projects.

See: "Opportunities for a circular economy in the Netherlands", T. Bastein, E. Roelofs, E. Rietveld,, A. Hoogendoorn, TNO 2013 R10864 http://www.government.nl/documents-andpublications/reports/2013/10/04/opportunities-for-a-circulareconomy-in-the-netherlands.html

Struvite unit under construction at Amsterdam-West sewage works. 1/10/2013: http://www.dutchwatersector.com/newsevents/news/7635-europe-s-largest-phosphate-recoveryinstallation-under-construction-at-wwtp-amsterdam-thenetherlands.html

"Struvite recovery from digested sludge at WWTP West", B. Bergmans, Feb. 2011, see SCOPE Newsletter n° 89



Struvite precipitation

Manure digestate Bittern and bone meal reagents for struvite recovery

Lab-scale struvite precipitation experiments were carried out to assess ammonium removal from digestate from (1) anaerobic digestion of cattle manure (with some other food production wastes) and (2) landfill leachate, using waste products desalination bittern and bone meal as magnesium and phosphorus sources.

In paper (1), struvite was precipitated from digestate from the thickener of the outflow of an anaerobic digester operating a 20-day solid retention time and treating mainly cattle manure, but also some food production wastes (e.g. maize, silage, olive oil waste). The digestate had over 1.5 g total nitrogen / litre (of which 2/3 as ammonium), around 0.5 g total P/l, 0.15 m magnesium/l and around 0.6 g calcium/l.

In paper (2), leachate samples from a municipal solid waste landfill site (in methanogenic phase) near Vibo Valentia, Southern Italy, were first treated by hydrogen peroxide addition to promote oxidation of organics. Oxidation was carried out after by adding hydrogen peroxide after adjusting to different pH values, then stirring for 3 hours at defined temperatures. The pH was adjusted using the acidic phosphate and magnesium solutions produced as below, or sulphuric acid if necessary.

Struvite precipitation experiments were carried out in 0.5 litre laboratory flasks, batchwise, at room temperature, stirred at 300 rpm. Parameters tested included aeration or not (CO₂ stripping), different pH. incremental or instantaneous adjustment of PH, reaction time, different ratios of P and N to ammonium nitrogen. Each experiment was repeated four times. Samples of precipitate were filtered at 0.45µm, washed, dried at low temperature (40°C) and analysed by SEM (scanning electron microscopy).

Using by-products as Mg and P sources

Seawater bittern, resulting from a desalination process, was used as the magnesium source. The bittern was supplied as a dried powder, and was dissolved in water resulting in a brine with magnesium concentration of around 70 gMg/l. The bittern also contained chloride (approx 3x the Mg concentration,



weight for weight), sodium (c 1/4 of Mg), potassium (c 1/50th) and calcium (c 1/100th).

Bone meal was dissolved in 3 molar sulphuric acid, so producing phosphoric acid and a solid calcium sulphate waste (gypsum, which was discarded). This resulted in a solution with c. 80 gP-PO₄/l and only 0.12gCa/l (whereas the bone meal contained nearly 2x more calcium than phosphorus, weight for weight).

P and N recovery efficiency

In (1), using digestate, aeration proved not effective to induce struvite precipitation, probably because the pH of the treated liquor, after addition of the phosphoric acid as above, was too low: only 45% nitrogen and 28% phosphorus recovery were achieved.

Chemical pH adjustment was therefore tested using NaOH (caustic soda). Optimal results were achieved when the P and Mg were added before pH adjustment. A pH of 9 showed to be sufficient to achieve maximal P and N recovery.

Optimal conditions showed to be pH=9, molar ratio of P:Mg:N of 1.3:1.3:1 and a reaction time of 15 minutes. Under these conditions 91% abatement of ammonium-N, 99% abatement of soluble P and 99% abatement of magnesium were achieved.

SEM analysis of the precipitate showed mainly orthorhombic crystals, typical of struvite, with size 10 – 40 um.

A calculation of chemical reagent and raw material costs, for struvite recovery from the digestate, compared those used above (bone meal powder, bittern power, NaOH for pH adjustment and sulphuric acid to dissolve the bone meal) to chemicals for struvite precipitation for ammonium removal (phosphoric acid P source, magnesium chloride, NaOH), suggesting a lower cost for the use of the by-products above compared to chemical reagents (5.4 compared to 10.2 ∉m³ manure liquor).

Landfill leachate oxidation

In (2), the landfill leachate used had a high carbon content of c. 12 gCOD/l, of which only around 26% was even slowly biodegradable. It contained around 2.6g N-NH₄/l ammonia but negligible phosphorus or magnesium. Its initial pH was around 7.8. Optimal oxidation conditions were shown to be pH 5.5, $0.75 gH_2O_2/gCOD$ and ambient temperature,



reducing phytotoxicity of the leachate by -90% and COD by -50%. Also, the remaining COD was rendered 50% biodegradable, meaning that it could be then biologically treated.

The struvite precipitation step, using the seawater bittern and bone meal derived magnesium and achieved 90% ammonia (N-NH₄) phosphorus, removal.

Chemical costs for the combined oxidation ammonia removal/struvite recovery process were estimated to be 15-16 €per m³ leachate. The authors estimate that the chemical costs for the oxidation step are comparable to other landfill leachate treatment processes in literature, and for the ammonia removal are significantly lower.

(1) "Recovery of ammonia in digestates of calf manure through a struvite precipitation process using unconventional reagents", Environmental Technology 2013 http://dx.doi.org/10.1080/09593330.2013.853088

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(2) "A new integrated treatment for the reduction of organic and nitrogen loads in methanogenic landfill leachates", Process Safety and Environmental Protection 91, pages 311-320, 2013 age: www.elsevier.com/locate/ps

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Poland

Effects of different ions on struvite continuous-reaction crystallization

Impacts of different foreign ions (nitrate(V), copper, fluoride, fluosilicate, aluminium(III), sulphate(VI), combinations of various ions) on continuous struvite reaction crystallization process were predicted.

The ANN (artificial neural network) models was compared with statistical analysis of results from experiments involving 0.6 litre continuous stirred reactor (DT MSMPR crystallizer) and-laboratoryprepared solutions, as well as from 1.2 litre continuous gas-liquid jet-pump crystallizers (two modes of internal circulation), using injection of compressed air and industrial wastewater from phosphate mineral fertiliser factory (summarised in SCOPE Newsletter n° 94)

Nitrate(V) showed to impact continuous struvite reaction crystallization process effects very little, with higher nitrate(V) concentrations resulting in slightly smaller average struvite crystal size.

Copper, fluoride, fluosilicate, aluminium(III) ions showed to slightly inhibit struvite nucleation, providing thus small increase in average struvite crystal size.

Sulphate(VI) tended to reduce struvite crystal size, which could be partly compensated by lowering pH or increasing mean residence time of suspension in a crystallizer.

In all cases, the experimental results matched well to predictions made by the ANN (artificial neural network) models developed by the authors.

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Effect of nitrate(V) ions on CSD of struvite produced in a continuous DT MSMPR crystallizer – neural network model of reaction crystallization process, K. Piotrowski, N. Hutnik, A. Matynia, Proceedings of 18th International Symposium on Industrial Crystallization ISIC18, published by Associazione Italiana di Ingegneria Chimica, 2011, 43-44

Influence of Cu²⁺ ions on CSD of struvite produced in continuous reaction crystallization process -neural network approach, K. Piotrowski, A. Matynia, N. Hutnik, Proceedings of 38th International Conference of Slovak Society of Chemical Engineering, Publishing House of Slovak University of Technology, Ed. J. Markoš, Bratislava, 2011, 757–763, CD-ROM No 036

Model neuronowy wpływu jonów fluorkowych i fluorokrzemianowych na skład ziarnowy struwitu wytwarzanego w sposób ciągły na drodze krystalizacji z reakcją chemiczną w krystalizatorze DT MSMPR, K. Piotrowski, N. Hutnik, A. Matynia, Inż. Ap. Chem., 50(5), 2011, 88-89

Continuous reaction crystallization of struvite in presence of Al³⁺ ions – neural network model, K. Piotrowski, N. Hutnik, A. Matynia, Proceedings of 39th International Conference of Slovak Society of Chemical Engineering, Publishing House of Slovak University of Technology, Ed. J. Markoš, Bratislava, 2012, 734–741, CD-ROM No 074

Effect of sulphate(VI) ions on CSD of struvite – neural network model of continuous reaction crystallization process in a DT MSMPR crystallizer, K. Piotrowski, N. Hutnik, A. Matynia, Procedia Engineering, 42, 2012, 521 - 531

Influence of impurities composition on struvite continuous reaction crystallization process – neural network model, K. Piotrowski, N. Hutnik, J. Piotrowski, A. Matynia, Proceedings of 40th International Conference of Slovak Society of Chemical



Engineering, Publishing House of Slovak University of Technology, Ed. J. Markoš, Bratislava, 2013, 126–134, CD-ROM No 026

Phosphorus recycling as struvite in a continuous gas-liquid jet pump crystallizer – neural network model, K. Piotrowski, A. Matynia, N. Hutnik, Proceedings of 40th International Conference of Slovak Society of Chemical Engineering, Publishing House of Slovak University of Technology, Ed. J. Markoš, Bratislava, 2013, 117-125, CD-ROM No 025

Gas-liquid jet pump crystallizer in phosphorus recycling technology – neural network model, K. Piotrowski, A. Matynia, N. Hutnik, Procedia Environmental Sciences, 18, 2013, 756 - 765

P-recovery

Review of struvite precipitation and reuse

The review of struvite science in the Arabian Journal of Chemistry summarises publications concerning precipitation parameters, struvite crystal nucleation and growth and fertiliser value of struvite.

The paper provides a wide bibliography of publications concerning struvite recovery and use as a fertiliser:

- Struvite **crystal forms and parameters** affecting the crystal form (rhomboid, rod-like)
- Struvite hexahydrate **decomposition to dittmarite** (monohydrate)
- Struvite crystal nucleation and growth parameters (pH, molar ratios, zeta potential)
- Formation of **amorphous phosphate** at higher pH and possible XRD confusion with struvite
- Precipitation operating modes
- Fertiliser value of struvite, for different crops and different soil types

The authors suggest that struvite offers environmental advantages over certain mineral nitrogen fertilisers because of lower soil ammonium-N or N₂O emissions and lower nitrogen leaching to groundwaters.

The authors estimate that 55% of phosphorus reaching sewage works could be recovered as struvite, that is 0.6 million tonnes of phosphorus (P) per year if 50% of the world's population were connected to sewage works operating struvite recovery.

"Production of slow release crystal fertilizer from wastewaters through struvite crystallization - A review", Arabian Journal of Chemistry, 2013 http://dx.doi.org/10.1016/j.arabjc.2013.10.007

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Pharmaceutical wastewater Struvite recovery from 7-ACA acid production wastewater

7-aminocephalosporanic Acid (7-ACA) is a key intermediate for production of important antibiotic cephalosporins such cephalaglycin, as cephalothin. An enzyme mediated process for synthesis of 7-ACA. developed as an environmentally friendly production process, results in a wastewater high in ammonium and chemical oxygen demand. Struvite precipitation from this wastewater was tested by dosing magnesium and phosphate and adjusting pH, in 1litre stirred jar batch reaction experiments, using different chemical reagents and reaction conditions.

7-ACA (antibiotic precursor) production The wastewater had a pH of around 12, COD (chemical oxygen demand) 1100 mg/l, ammonia 1100 mgN- NH_{4}/l and phosphorus 36 mg P-PO₄/l. Struvite precipitation was tested in a 1 litre, stirred jar.

Ammonium removal

The main objective of the struvite precipitation was to reduce ammonium levels in the wastewater, but it was also intended to not increase phosphate levels, as both nutrients are not desirable in discharge.

Parameters tested included different combinations of chemicals for magnesium and phosphate dosing (phosphoric acid, Na₃PO₄, NaH₂PO₄, magnesium oxide, magnesium chloride, magnesium sulphate), Mg:PO₄:NH₄ ratios, pH (range 7 - 11), mixing time (5 – 60 minutes).

Results showed that ammonia could be effectively without significantly removed. increasing wastewater phosphate concentrations, at an optimum pH of 9, and with a Mg:PO₄:NH₄ ratio of 1:1:1. Magnesium chloride with 85% phosphoric acid was the most effective combination of chemical reagents for ammonium removal, and also gave the lowest residual wastewater phosphate concentration. Ammonium removal of 60 - 70% was achieved.

Optimal reaction time (stirred) was 20 minutes, with residual phosphate increasing with longer reaction times. The authors note that this may be due to breaking of struvite crystals during longer stirring.



COD removal was 16 – 18%, so it can be deduced that the precipitated struvite contained some organic contaminants. The precipitated struvite was examined with XRD and SEM.

The authors conclude that, at the laboratory scale, struvite precipitation offers good potential for removing a significant part (60-70%) of the ammonium for this pharmaceutical industry biological wastewater, without increasing phosphate loading. Further work is required to assess the quality of the recovered struvite (organic and other contaminants) and to develop a continuous process producing recoverable struvite (pellets or significant size particles).

"Struvite precipitation for ammonia nitrogen removal in 7aminocephalosporanic acid wastewater", Molecules 17, pages 2126-2139, 2012 www.mdpi.com/journal/molecules (open access).

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Struvite reactor design Lab trials of precipitation reactor design

An approx. 9.5 litre total capacity fluidized bed reactor was tested for struvite precipitation from pure chemical solutions for 133 day runs of continuous operation. The reactor had a total height of 1095 mm, with three sections: a narrow bottom section (diameter 60 mm), a medium width middle section, and a wider top section (d =170 mm), plus an external recycle tank.

The reactor was operated in two different designs, the first with flat surfaces between each section and at the reactor base, the second with conical 45° joins between the different sections and at the reactor base.

The reactors were tested using different hydraulic residence times (1 - 10 hours), pH (pH 7.5 - 10), phosphorus concentrations (low = 12.5 mgP/l, high = 120 mgP/l) and molar ratios of magnesium:phosphorus, nitrogen:phosphorus and calcium:magnesium. The reactor influent was prepared using pure chemical reagents: magnesium chloride, potassium phosphate, ammonium chloride and calcium chloride. pH was adjusted using sodium hydroxide.

Reactor mixing was ensured by the upflow of the influent (from the feed and flow recycling tanks), without stirring or aeration.

Optimal struvite precipitation parameters

Optimal operating parameters showed to be hydraulic residence time = 2 hours, pH9, Mg/P = 1.25, N/P = 7.5. At these parameters, 93% phosphate precipitation was achieved at low P concentration and 98% at high P concentration. At hydraulic residence times or pH higher than these values, reactor performance continued to increase, but only very slightly.

Phosphate precipitation efficiencies (at these optimal operating parameters), calculated from the reactor inflow and outflow soluble phosphate concentrations, were slightly higher in the 'conical' (with cone) reactor than in the flat surface reactor (without cone): 93 and 98% with cone (for low and high P influent) and 78 and 81% without cone.

Phosphorus removal efficiencies (under the same conditions), calculated from the reactor inflow and outflow total phosphorus concentrations, considered to give an estimate of phosphorus recovery performance, were more significantly different, at 75 and 92 % with cone and 47 and 65% without cone.

The authors conclude that the conical design significantly improves struvite recoverv performance, probably because of reduced losses of fine crystals in the reactor outflow.

Calcium interference

The authors note that the presence of **calcium** (at Ca:Mg ratios above 1) in the reactor influent causes the precipitated struvite to be amorphous, rather than the structured orthorhombic crystals precipitated in pure reagents without calcium.

Nitrogen removal efficiencies in the reactor were much more variable than phosphorus removal, possibly because of ammonia stripping (loss to air).

Membrane bioreactor nitrogen removal

In further work, reported in a second paper, the 9.5 litre lab-scale conical fluidized bed struvite reactor above was combined with membrane bioreactors (MBR), operating on the struvite reactor treated



outflow, to ensure also ammonium nitrogen removal. Synthetic wastewater was used for the experiments.

Two identical MBRs were operated downstream of the struvite reactor, each with a working volume of 8.4 litres. They were inoculated with mixed anoxic and aerobic sludges from the Quyang sewage treatment plant. The system was operated for over 7 months, testing different pH and hydraulic residence times in the struvite reactor, and different intermittent aeration cycles and sludge residence times in the MBRs.

The combination of struvite reactor and MBR was considered by the authors to largely resolve the contradiction current in MBRs that phosphorus removal requires anaerobic – aerobic cycles whereas nitrogen removal requires aerobic – anoxic cycles. Up to 93% phosphorus removal, 99% ammoniumnitrogen removal and 99% COD-carbon removal were achieved with the combined struvite reactor + MBR (membrane bioreactor) system.

The authors note that the optimal operating pH for the struvite reactor (pH9) and optimal intermittent aeration cycle (on/off 15/45 mins) in the MBR resulted in minimized membrane fouling, possibly because of lower concentrations of extracellular carbohydrate and improved biodegradation at these (EPS) conditions.

"Enhanced struvite recovery from wastewater using a novel coneinserted fluidized bed reactor", J. Environmental Sciences 2013 http://www.jesc.ac.cn/jesc_en/ch/reader/view_abstract.aspx?flag=2 &file_no=201305150000006&journal_id=jesc_cn

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Berliner Wasserbetriebe From sewage to a CO₂-positive fertiliser product

After a number of years of process development, Berliner Wasserbetriebe started full-scale phosphorus recovery from sewage sludge anaerobic digester liquor in 2009, at the company's Wassmannsdorf sewage treatment plant (see SCOPE Newsletter n°97). The struvite recovery reactor treats the complete digestate outflow from the 4 anaerobic digesters, which treat the plant's sewage sludge (1.2 million population connected).

Wassmannsdorf sewage works uses biological nutrient removal to achieve 0.5 mgP/l phosphorus discharge consents, sometimes with low levels of iron dosing if needed to enhance P-removal.



Struvite precipitation from the sludge digester liquor, upstream of dewatering (centrifuges) was developed in order to avoid major incrustation problems occurring in the dewatering process and in piping. The struvite precipitation also improves sludge dewatering (reducing the need for flocculants) and the return of phosphorus to the sewage works inflow in the dewatering liquor (so improving biological nutrient removal performance). These effects are estimated to result in c. 300 000 Euros/year cost savings.



CO₂- positive

BWB also estimates that the recovered struvite fertiliser has a 890 kg CO₂/kg net positive carbon balance, by improving sludge dewatering, and so reducing the energy consumption needed in the dewatering and then sludge incineration processes, after taking into account the carbon balance of the energy and chemicals (magnesium) needed for the struvite production compared to that of rock-phosphate based mineral fertiliser.

The full-scale struvite reactor operating at Wassmannsdorf, is a cone-based vertical cylindrical tank, height c 10m, with a volume of 800 m³ and **now** produces around 2 tonnes of struvite per day. The inflow liquor to the reactor is the outflow digestate from the anaerobic sludge digesters, without any filtration or settling. Aeration only (3 000 m³/hour air in a specific high-dispersion, small bubbles system) ensures that the liquor pH is raised to c pH 7.8. Magnesium chloride is dosed and partial recirculation of reactor liquor ensures upflow in the reactor. The reactor is patented by BWB, and commercialisation of is licensed to PCS the process (AirPrex http://www.pcs-consult.de/html)

The washing system etc are in an enclosed building to protect from frost risks. The reactor itself (top part, above this building) is open air and does not risk freezing because the digestate flows out of the digesters at c37°C, their mesophilic operating temperature.

Ammonia loss to the atmosphere from the reactor has not been measured because ammonia is lost anyway in the sludge dewatering centrifuges downstream of the reactor. Also, ammonia remaining in the centrifuge liquor is an operating issue for the works, as it is returned to the inflow and interferes with the biological nutrient removal process. Ammonia recovery processes to produce a recycled nitrogen fertiliser are currently being considered.

Struvite: Berliner Pflanze

The struvite crystals, on reaching appropriate size, settle to the base of the reactor, and are extracted in batches by automatic opening of a nozzle at the reactor base. The struvite is then washed in water (using a process based on a sand-washer, which effectively removes the soluble impurities and low-density particles). This removes most of the small organic particles which may settle with the struvite.

The current one-phase wash process gives a product of >80% purity struvite (<10% organic content plus < 10% inorganic impurities such as sand) which is stable, and can be stored in simple covered containers. Because the organics are inert (fully digested in the anaerobic digesters), this is considered completely acceptable by local farmers. A second stage wash process is currently being considered to produce a < 1%organics product for other higher added-value markets.

Some relatively dense organic particles present in the digestate can be found in the recovered struvite, along with some sand and grit particles, because these are not removed by the washing process.

The recovered struvite is today sold to a number of local farmers as an added-value, recycled fertiliser, offering valuable agronomic properties including slow release of nutrients, no risk of root or plant burning.

The recovered struvite has been tested for particle size, and is not a respirable powder. The remaining humidity present ensures also that it is non-dusting and the crystal form means that it does not bunch or stick, so it is convenient to handle.

The struvite precipitation process operating on the sludge digester outflow stream recovers c. 15 – 20% of the total sewage works inflow phosphorus. Most of the remaining phosphorus passes through the struvite reactor as organic/particulate phosphorus (over 95% of the soluble orthophosphate is removed to struvite in the struvite reactor) and so goes to the sludge dewatering centrifuges and then to (dewatered) sludge incineration. Around 3% only of the total sewage works inflow phosphorus leaves the works in discharge (treated water).

Berliner Pflanze www.bwb.de and http://www.bwb.de/content/language1/html/6946.php





Nutrient Platforms

Europe: www.phosphorusplatform.org Netherlands: www.nutrientplatform.org Flanders (Belgium): http://www.vlakwa.be/nutrientenplatform/ Germany: www.deutsche-phosphor-plattform.de North America project: j.elser@asu.edu

New Meat Atlas

Heinrich Böll Foundation, Berlin and Friends of the Earth, Brussels publish the new Meat Atlas 2014, giving 68 pages of facts and figures about global meat production and consumption and the related societal, economic and ecologic impacts and developments.

http://www.boell.de/en/2014/01/07/meat-atlas

Partnership opportunities

US & Canada Phosphorus research network and proposed phosphorus partnership

North America Sustainable **Phosphorus** "Partnership" project j.elser@asu.edu

P-RCN (Sustainable Phosphorus Research US Coordination Network) j.elser@asu.edu

P-RCN student network: rimjhim.aggarwal@asu.edu

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The SCOPE Newsletter summarises news and publications concerning sustainable phosphorus management, with the aim of furthering debate and knowledge, and does not represent an official position of the European Sustainable Phosphorus Platform nor of its members. To SUBSCRIBE www.phosphorusplatform.eu

ESPP workshop R&D projects and opportunities

Some 40 representatives of companies and knowledge institutes met at the workshop organised by the European Sustainable Phosphorus Platform on 7th February 2014 (with support from Fertilisers Europe, WssTP and Friesland) to exchange information on R&D sustainable projects addressing phosphorus management.

Projects presented and currently open to new partners include:

- > Cities and regions Covenant for a Circular **Economy**, including a focus on phosphorus
- > Evaluation of **plant availability of "legacy" P** in agricultural soils
- > Long-term **field evaluation** of new phosphorus fertiliser products
- **COST network** proposal on P stewardship strategies
- > Manure as a Resource: demonstration plants and economic evaluation
- **Biorefine Cluster**: sustainable biomass use for energy, materials.
- > P-recovery technology dissemination and implementation
- > Socio-economic assessment of technologies, barriers, opportunities
- > Market development for recovered P products
- > Horizon 2020 EIP water resource recovery Action Group proposal ARREAU

Please send information about other projects and info@phosphorusplatform.eu proposals to for communication in this Newsletter

This workshop was followed by the launch meeting of the WssTP (European Technology Innovation Platform) "resource recovery" Working Group, established to provide input and support to define EU R&D policy content, and in particular to provide input to the Horizon 2016-2017 Water 'challenge 5' calls.

For further information about any of these projects: contact info@phosphorusplatform.eu

Agenda 2013 - 2014

- 20-21 February, Dublin, Anaerobic Digestion Europe 2014 www.adeurope2014.eu
- 23-25 March, Paris: Phosphates 2014 (CRU) The annual phosphate industry conference www.phosphatesconference.com



- ♦ 24-26 March, Sofia, Bulgaria: EWPC11 European Workshop on Phosphorus Chemistry http://ewpc11-bg.org/index.php
- ✤ 1-4 April, Amsterdam: International Fertiliser Association Global Technical Symposium www.fertiliser.org
- ✤ 1 May 31 Oct. Expo2015 Feeding the planet, energy for life, Milano http://en.expo2015.org/
- ★ 6 May, 16h-18h, Munich, Germany: phosphorus recycling conference at IFAT (world trade fair for water, waste and raw materials management) www.ifat.de
- ✤ 4-6 June, Valladolid, Spain: 10th International **Renewable Resources and Biorefineries** (RBB) (5th June: Nutrient & Energy cycling sessions) www.rrbconference.com



- 19 June, Leeds, England, Future options for food waste http://www.aquaenviro.co.uk/view-product/Future-Options-for-Food-Waste
- ✤ 23 June, Brussels, Biochar safety, economy, legal harmonisation (REFERTIL) biochar@3ragrocarbon.com
- 26-28 June, Gödöllö Hungary, ORBIT 2014 **Organic Resources and Biological Treatment** http://orbit2014.com
- ✤ 29 June 3 July, Dublin: 20th International **Conference on Phosphorus Chemistry** www.icpc2014.ie



- ♦ 8-9 July, Rennes, Brittany, France, EU Commission/regions at work for the bio-economy Converting bio-wastes to fertilisers
- ✤ 13-17 July, Harbin, China: **IWA Science Summit on Urban Water** http://www.iwahq.org/28f/events/iwa-events/2014/urban-water.html
- ✤ 26-29 August 2014, Montpellier, France: 5th Phosphorus in Soils and Plants symposium http://psp5-2014.cirad.fr/
- ✤ 1 3 Sept., Montpellier, France 4th world Sustainable Phosphorus Summit http://SPS2014.cirad.fr



- ✤ 27 Sept. 1 Oct., New Orleans WEFTEC2014 (Water Environment Federation) www.weftec.org
- ✤ 20-24 Oct., Rio de Janiero CIEC World Fertiliser Congress www.16wfc.com
- 26-30 Oct, Kathmandu, Nepal **IWA: Global Challenges for Sustainable** Wastewater Treatment and Resource Recovery http://iwa2014nepal.org
- ✤ 3-5 Nov 2014, Long Beach, California ASA, CSSA, SSSA (US & Canada soil and agronomy) meetings, Water Food, Energy, Innovation for a Sustainable World www.acsmeetings.org
- ★ 3rd-4th March 2015, Berlin: 2nd European **Sustainable Phosphorus Conference** www.phosphorusplatform.org



- ✤ 23-25 March 2015, Florida: Phosphates 2015 (CRU)
- ✤ 29 March 3 April 2015, Australia. **Beneficiation of phosphates VII** http://www.engconf.org/conferences/environmentaltechnology/beneficiation-of-phosphates-vii/
- May 2015, Morocco: SYMPHOS www.symphos.com