
SCOPE NEWSLETTER

NUMBER 91

February 2013

Phosphate resources

European raw materials strategy

Risks and opportunities in phosphate resources for the EU

A report funded by the Dutch Ministry of Infrastructure and the Environment assesses developments in the global phosphate rock market, implications for the EU's phosphate security and possible ways forward to reduce European vulnerability.

USGS Report

Phosphate rock reserves and production

The USGS (US Geological Survey) has published updated estimates of world phosphate rock reserves, showing no significant changes from 2011 estimates, and figures on phosphate rock and fertiliser consumption, showing highest ever world P-rock production in 2011.

Phosphorus resources

Dynamic perspectives and complexity of predictions

Multiple peaks and plateaus of world phosphate production are more likely than a resource crisis, but other factors such as environmental impacts of phosphorus dispersion, geopolitics and changes in agriculture make predictions complex and require a transdisciplinary approach.

Economic and social context

Japan and Switzerland

Case study of P-recycling implementation at six sewage works

An ETH Zurich thesis on the experience of P-recovery and recycling operation in 5 Japan wastewater plants, analyses factors affecting implementation, and considers how these would impact a P-recycling project at a Zurich sewage and sludge treatment plant.

Global TraPs

Reprocessing Industry Cluster Europe (RICE) meeting

Science and industry exchange on the state of development and implementation of P-recycling technologies in Europe, resource and market potential and policies needed to promote P-recycling.

Struvite recovery

P-recovery thesis

Struvite from acid-treated pig manures

This experimental thesis studied parameters influencing struvite precipitation from synthetic solutions and from acid-treated swine manures, using MgO reagent, enabling calibration of a full-scale P-recovery process.

Henan Province, China

Struvite from nylon production wastewater

Natural brucite and phosphoric acid were shown to be effective and economic to remove ammonia from nylon wastewater digester supernatant, by struvite precipitation, prior to biological treatment.

Guangdong

Struvite pyrolysate

Pyrolysis of struvite then reuse, combined with magnesite pyrolysate, enabled nutrient removal from anaerobically digested piggery waste with reduced reagent costs

European conferences

Brussels, 6-7 March 2013

European Sustainable Phosphorus Conference

The aim of the ESPC conference is to raise awareness about the necessity for sustainable phosphorus management, to facilitate the transition towards less phosphorus is used and a sustainable market for recycled phosphorus, and to develop the phosphorus value chain throughout Europe. ESPC is the initiative of over 40 businesses, knowledge institutes, NGO's and governments and of the European Commission (Green Paper on Phosphates, Revision of the Fertilizer Regulation, Raw Materials Initiative). Programme and registration (limited to 250 participants)
<http://www.phosphorusplatform.org/espc2013.html>

Monte Carlo, 25-27 March 2013

Phosphate industry conference

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



European raw materials strategy

Risks and opportunities in phosphate resources for the EU

The Dutch Ministry of Infrastructure and the Environment has political discussions on sustainable phosphorus management should be based on a thorough assessment of the phosphate rock market and trends susceptible to affect it in the future, and so commissioned a report from the Hague Centre for Strategic Studies (HCSS) to inform the EU policy making process on phosphorus, in preparation for the European Sustainable Phosphorus Conference, Brussels, 6-7 March 2013. This 101 page report looks at global phosphate market dynamics, political-economic supply disruption risks, technical hindrance risks, and possible strategies to respond to these risks and enhance EU supply resilience.

The report presents the **current world market for phosphate rock**, makes a distinction between production, exports and reserves which make the position of producing countries on the world market different and assesses different estimations of global phosphate rock reserves, emphasising the considerable uncertainty of data on phosphate rock reserves. For the authors, it is not particularly the depletion of phosphate rock resources we should worry about, but more the **accessibility of supply, and a number of political and market risks** that could result in increasing and volatile prices or disruption of supply because of political unrest.

Supply insecurity

Both China and the USA have largely stopped exporting phosphate, as they are depleting their resources rapidly and see these resources as critical for their economy. India and Brazil are expected to continue to develop strong demand. Thus, although China and the USA are today the world's biggest phosphate rock producers, the world export market is dominated by North Africa (in particular Morocco with 35% of world exports) and the Middle East.

Although other countries have potentially exploitable phosphate rock reserves, it is not clear whether new production (and exports) will **come in time to avoid price shocks or prevent disruptions of supply**.

Overall phosphate consumption is expected to increase over coming years, in particular in Latin America and Oceania, in response to increasing world population, food consumption and biofuel production.

General expectation is thus for an overall upward trend in prices. Price instability, with price peaks, is likely because of price inelasticity both for demand (food related and so non flexible) and for supply (because of the very long delay times and high investment costs of developing new resources).

Increasingly, countries with phosphate rock reserves are moving towards processing locally and exporting fertilisers or other chemicals, reducing the availability of phosphate rock on the world market which could have the effect of **more expensive fertilisers** for the agriculture and food production.

Europe's import dependency

The report notes that Europe is the only region of the world which imports almost all of its phosphate needs and therefore needs to be concerned about supply security. **Europe is already highly dependent on North Africa and the Middle East**, and this is expected to accentuate in the future. Europe is thus very exposed to price pressures, geopolitical pressure from supply countries, and to supply disruption in case of production difficulties in these regions. Such difficulties could result from political or labour unrest, from environmental concerns about phosphate mining (contamination) or from competition for water (needed for phosphate beneficiation, but also for agriculture and cities).

Europe also needs to be **concerned about grades of phosphate rock supply**, with a risk of lower phosphorus content in exploited reserves resulting in a higher cadmium or uranium content. There is currently discussion in Europe as to whether this poses an environmental or health issue.

Response strategies for Europe

The report suggests a number of strategies which Europe should develop to reduce the risks of geopolitical supply dependency, price peaks and environmental pressures on phosphate mining and uses:

- Improve phosphorus management to reduce losses (and so reduce needs) throughout the phosphorus use chain (in agriculture, food ...)
- Develop phosphate recovery and recycling from waste streams, to substitute part of the imported phosphate need by secondary materials
- Investigate processes for decadmiation of phosphate fertilisers, in cooperation with phosphate rock producing countries

- Develop relations with phosphate rock producing countries on the basis of a mutual gains approach, including partnership in mining and rock processing, to have a more stable and sustainable phosphorus market in the future.

“Risks and opportunities in the global phosphate rock market – robust strategies in times of uncertainty”, The Hague Centre for Strategic Studies, n° 17, 12, 12.

http://www.phosphorusplatform.eu/images/download/HCSS_17_12_12_Phosphate.pdf

USGS Report

Phosphate rock reserves and production figures

The USGS annual publication of estimated world phosphate rock reserves (January 2013) shows no significant changes from 2011 estimates, maintaining the estimate of 67 billion tonnes, which was considerably increased from only 16 billion tonnes January 2010 estimate. This estimated level of world reserves of 67 billion tonnes compares to world mine production estimated at approx. 0.5 billion tonnes.

The USGS figures also indicate that world phosphate rock mining again set a record, at 210 million tonnes, up from 198 million tonnes in 2011, which was at the time the **highest ever figure** for world phosphate rock extraction. This ongoing increase is considered to be the result of global economic recovery and fertiliser demand in China, India and South America.

The increase in estimate of world P-rock reserves from 2010 to 2011 resulted principally from a factor change in the **estimate of Morocco’s reserves**, from 5.7 to 50 billion tonnes (unchanged from 2011 to 2013). Relatively smaller changes from 2011 to 2013 estimates include increases in estimates for reserves in Peru (820 million tonnes), Saudi Arabia (750 million tonnes), Iraq (460 million tonnes) – these were previously covered in the “Other countries” category which has decreased by a total of -230 million tonnes – and Australia (+308 million tonnes). The estimate of China’s reserves is unchanged since 2010 at 3.7 billion tonnes.

The world’s leading phosphate rock mining country in 2011 was China (81 million tonnes), followed by the USA and Morocco (both 28 million tonnes). Morocco is however planning to increase rock production to 50 million tonnes by 2018.

USGS (United States Geologic Survey), minerals information, phosphate rock statistics and information:
http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/

Phosphorus resources

Dynamic perspectives and complexity of predictions

The authors analyse consumption, reserve and resource prediction for phosphorus, taking examples of various other materials as illustrations. The importance of a dynamic perspective and the inadequacies of static methods such as reserve lifetime, Hubbert curve or Herfindahl-Hirschman Index (HHI) applied to phosphorus are demonstrated. They conclude that the recent rapid changes in world phosphate production and consumption result from demand changes, linked to economics and to the considerable stock of phosphate in developed countries’ farm soils, rather than to resource constraints. The environmental impacts of phosphorus losses to surface waters, and the geopolitical consequences of small farmers’ vulnerability to phosphate fertiliser price increases, mean that global action is needed on phosphate resource stewardship, even if there is no short or medium term risk of global P-rock resource shortage.

Unlike many resources (eg. fossil fuels), phosphorus is non substitutable, in that it is necessary for plants and animals, and so for food production. Man has more than tripled global natural P-flows. The concepts of essentiality, criticality and scarcity, reserves, resources and geopotential are presented and discussed.

Phosphorus is critical for world food supply, unlike the other two key elements of fertilisers, nitrogen which can be produced (in plant accessible form) in unlimited supply from the air (with a significant energy consumption cost) and potassium which is needed at similar levels by plants but is with resources c. 20 x more available.

Changes in estimates of phosphorus reserves

Phosphorus reserves are the known amounts of rock which can be exploited under current economic conditions. Resources are the known amounts of rock which are not exploitable under current economic conditions. The geopotential is an estimate of the further, today unknown, resources which are likely to exist. Estimates of phosphorus resources vary widely, and have been modified considerably over the past few years, suggesting either considerable uncertainty or a lack of exploration.

The market share inequality of a company of country is measured using the Herfindahl-Hirschman Index (HHI). The HHI for phosphorus rock production is

around 2000, which is in the middle of the range for metals and other natural resources. The HHI for P rock reserves changed from 2150 to 6000 to 5050 from 2008 – 2010, however, showing considerable instability as different countries published new estimates of reserves. Though the geographic concentration index increased formally, the future world supply became more diverse in the last five years, as not only the documented reserves of Morocco increased by factor ten but the reserves of ‘all other countries’ by factor two.

Phosphate rock currently shows high R/C (Reserve / Consumption) ratios compared to other commodities, resulting in exploration expenditures which are comparatively low. Data quoted indicates that phosphate plus potassium exploration was extremely low (< 0.25 % of total world mineral exploration spending).

Dynamic approach

Data from other minerals shows that R/C can change considerably over periods of less than a decade, because of changes in mining investments or in reserve estimates. Dynamic models are therefore needed to estimate future phosphate production and consumption, taking into account advances in technology and exploration.

Hubbert curves

Another approach to prediction is to fit Hubbert Curves to past data to model future mineral production. This uses a production increase - peak - decrease model developed with other resources. The authors argue that this is not applicable to phosphates because phosphorus is a demand market. Given reserves of more than 70 Gt and an annual demand of about 0.2 Gt, there is no reason to postulate a Peak Phosphorus (relating to resource shortage) in coming decades.

The authors suggest that recent changes in levels of phosphate rock production and consumption are related to temporary factors such as world economic development and food production, phosphate mining investment and exploration, and to changes in consumption of phosphate fertilisers in developed countries where past use has created large soil reserves of phosphate enabling farmers to now reduce P-fertiliser use.

Future increases in costs for phosphate rock extraction, as more easily accessible resources are used up, or resulting from deterioration in ore grade (P-content, contaminant levels) may be balanced by technology improvements in mining and beneficiation.

On the other hand, poor smallholder farmers in developing countries are extremely vulnerable to increases in phosphate prices, so that phosphate rock price increases may cause critical situations, including for food security.

Phosphate resource global stewardship

New technologies, population developments, changes in lifestyle, geopolitics and other factors may cause rapid changes in phosphate rock demand, and so price. Future resource management needs to avoid bottlenecks in supply, and so price instability and potentially critical situations. In the long term, phosphorus recycling must be developed, both to reduce consumption of the non-renewable phosphate rock resource and to reduce environmental impacts of phosphorus dissipation.

Such global resource stewardship requires more reliable models on resources, production and demand, and transdisciplinary processes involving scientists, experts, and stakeholders and practitioners involved in the different areas of phosphate resource exploration, production, use, management and environmental fate.

“Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus?”, *Global Environmental Change*, 23, pages 11-27, 2013
www.elsevier.com/locate/gloenvcha

R.W. Scholz, Fraunhofer ISC, Project Group Materials Recycling and Resource Strategies IWKS, Brentanostrasse 2, 63755 Alzenau, Germany, and F-W. Wellmer, Neue Sachlichkeit 32, 30655 Hannover, Germany Scholz@env.ethz.ch

Economic and social context

Japan and Switzerland

Case study of P-recycling implementation at 6 sewage works

In both Japan and Switzerland, no sewage sludge is spread on fields and all goes to incineration. Japan is the most advanced country in the world as regards P-recycling implementation, and this thesis looks at 3 municipal sewage works and 2 industrial process water treatment works where P-recovery has been in operation for some years. Conclusions are drawn concerning socio-technical mechanisms which have either facilitated or hindered implementation. These conclusions were then compared to the situation at a municipal sewage and sewage sludge treatment plant in Zurich, Switzerland, where a P-recovery project was being planned.

The thesis presents phosphorus flow assessments for Switzerland and Japan, public policies relevant to inciting phosphorus recycling in the two countries, and an overview of how P-recovery can fit into waste management flows. The case study analysis was based on the water/sewage processing processes presented in the form of material flow analyses, as well as a method to assess the social structure around the wastewater plants. Through structured interviews with WWTP operators and/or engineers at the 6 plants, the **system picture was developed**. Additionally, interviews were held with a number of research and regulatory experts in the two countries.

The thesis produces **Agent-Structure diagrams** describing the agents, interactions and goals within the system. This is based on the Structural Agent Analysis (SAA) methodology as developed by Binder 2007 and the Human-Environment Systems framework (Scholz & Binder 2003; Scholz 2011). Analysis of synergies and conflicts between the different actors' stated goals then enabled identification of sociotechnical and regulatory factors influencing P-recovery and P-recycling implementation.

P-recycling operating experience in Japan

The five wastewater treatment plants studied in Japan are as follows:

Municipal sewage works:

- **Senboku**, northern Honshu (30 000 pe): P-recovery from wastewater (municipal sewer wastewater, plus more concentrated wastewater coming from partial digestion of collected blackwater from the Kakunodate municipality), operating P-recycling since 2009 by calcium phosphate precipitation (HAP)
- **Fukuoka**, northern Kyushu (household sewage only, western WWTP n°4, 147 000 m³/year): P-recovery from sludge liquor (bio-P sludge methanisation liquor, from filter press), operating P-recycling by struvite precipitation since 1999
- **Gifu**, southern Honshu: P-recovery from sewage sludge incineration ash from 4 WWTPs serving c 400 000 population, operating P-recycling since 2010 using sodium hydroxide solution at pH 11 to release P from ash, followed by solid-liquid separation then reaction with calcium hydroxide to form calcium phosphates.

Industrial wastewater treatment plants

(P-recovery from process water):

- **Japan Synthetic Alcohol Co (JSAC)**, near Tokyo (168 000 m³/y wastewater): operating P-recycling since 1998 by calcium phosphate precipitation
- **Kyowa Hakko Bio Company (KHBC)**, Hofu, southern Honshu: operating P-recycling since 2007 by calcium phosphate precipitation

Value of recovered phosphorus

The 3 public (municipal) plants openly disclosed the selling price of their recovered phosphate and were **not strongly concerned about the economic profitability of the P-recycling operation**. The recovered phosphates were sold as below. The 2 industrial plants have high P-recovery levels, because of the relatively pure process waters being treated, but have to date been **selling the recovered phosphate at a low price** (objective to avoid landfill costs, rather than to obtain value from the recovered P).

In all cases, the plants in Japan had some difficulties finding markets for their recovered phosphates, and in all cases solutions only recently have contracts been established with fertiliser manufacturers or wholesalers who blend the recovered phosphates (calcium phosphate, struvite) into more complete NPK fertilisers. The prices obtained for the recovered phosphates in these contracts are not adequate to cover the P-recovery operation costs.

The P-recovery operated at these Japan municipal works thus appears to be economically justified through cost savings such as reduced landfill disposal costs or nuisance struvite deposit avoidance, or possibly not economically viable. The industry plants are operating the P-recovery processes principally because this is a cost-effective way of achieving P-discharge consents and reducing landfill costs for their operations.

Recovered P sales prices:

- ✓ Senboku: 27 000 JY/t calcium phosphate, for fertiliser use
- ✓ Fukuoka: 21 000 JY/t struvite, sold to a fertiliser wholesaler for blending
- ✓ Gifu: 40 000 JY/t calcium phosphate, if sold direct to farmers in 20 kg bags, or 30 000 JY/t, if sold to fertiliser wholesalers.

Positive and negative mechanisms

The thesis identifies four each of principal negative and positive **socio-technical mechanisms**:

➤ Negative mechanisms

- **Subsidy lock-in**: once a P-recovery technology has been installed with public subsidies, it is not possible for the operator to abandon or modify it, even if it is inefficient or uneconomic
- **Powerless actions**: the Japan WWTPs are not decision makers, and technology is decided by other organisations
- **Market position**: transaction costs to sell the recovered P as fertiliser are very high (the market is not accessible to small, local producers) and the WWTPs took considerable time to find a market, and ended by selling each to a single buyer (so losing their capacity to negotiate price)
- **Differing timelines**: Japan government P-recycling objectives are long-term, subsidies to P-recycling implementation in WWTP are short-term, but delay WWTP construction because they oblige innovative design and technology, and then lock-in over 15-20 years (see above)

➤ Positive mechanisms

- **Environmental awareness**: WWTP operators wish to go beyond regulation and contribute to resource stewardship
- **Controlled market**: it seems likely that P-recovery implementation would not have developed in Japan without the centralised regulatory decisions to both authorise the recovered product use as fertiliser and to subsidise P-recycling technology
- **Public-private cooperation**: partnership between the public WWTP operators and private P-recycling technology providers and private fertiliser companies/wholesalers
- **Farmer interest**: farmers' reluctance to change to a new and 'unknown' fertiliser has been mitigated by the Japan national agricultural authority's involvement and validation of recovered phosphates. Farmers could benefit from the price stability offered by a locally produced fertiliser, and in contributing to local recycling

The authors conclude that of these mechanisms applicable in Japan, only some also apply in Zurich. In particular, **the economics of P-recycling may be largely driven by other cost savings, such as reducing landfill costs.**

The **establishment of a market for the recovered phosphate, as a fertiliser**, is a key question in Switzerland, as in Japan, because of the structure of the fertiliser market (two distributors only) and the difficulties and costs of establishing a regional market for a locally produced fertiliser.

"Closing the phosphorus nutrient cycle by recovery from waste water: the social and technical factors of implementation in Japan and Switzerland", ETH (Eidgenössische Technische Hochschule) Zurich, Master Thesis 05/12, 21st August 2012, D. Wemyss. To obtain a copy of the thesis, contact Scholz@env.ethz.ch

Other papers referenced above:

Binder, C. R. (2007). From material flow analysis to material flow management Part II: The role of structural agent analysis. Journal of Cleaner Production, 15(17), 1605-1617.

Scholz, R. W. (2011). Environmental literacy in science and society: From knowledge to decisions. Cambridge: Cambridge University Press.

Scholz, R. W., & Binder, C. R. (2004). Principles of human-environment systems (HES) research. In C. Pahl-Wostl, S. Schmidt, A. E. Rizzoli & A. J. Jakeman (Eds.), Complexity and integrated resources management transactions of the 2nd biennial meeting of the international environmental modelling and software society (Vol. 2, pp. 791-796). Osnabrück: Zentrum für Umweltkommunikation (ZUK).

Global TraPs

Reprocessing Industry Cluster Europe (RICE) meeting

The Global TraPs (Global Transdisciplinary Processes for Sustainable Phosphorus Management, 2010-2015) is now in its operational phase, with stakeholder groups working on the specific questions defined by the workshop held in March 2012 (SCOPE Newsletter n° 86). The Global TraPs Reprocessing Industry Cluster Europe (RICE) met at the merging Fraunhofer Institute Resources Strategies and Material Recycling (IWKS), Alzenau, Germany, 8th February 2013, brought together companies interested in P-recycling, scientists and independent experts to discuss resource and market potential and policies needed to promote P-recycling.

Roland Scholz (Global TraPs www.globaltraps.ch) reminded participants that the Global TraPs follows a transdisciplinary approach, a process designed to **integrate perspectives from participants who represent diverse parts of society**, to allow for discussion and learning in a non-politicized and non-competitive arena, and with the overall objective of identifying options for more sustainable use of phosphorus. Transdisciplinarity involves joint leadership of research and case studies by scientists and concerned actors from society (industry, users, NGOs ...).

Christian Kabbe (P-Rex www.p-rex.eu, see SCOPE Newsletter n°88) presented the **streams of recyclable phosphorus in sewage and animal manures in Europe**. He estimates that P in sewage in Germany (c. 75 000 tonnes P/year) corresponds to over 60% of imported phosphates (in mineral rock, fertilisers, chemicals), P in meat and bone meal (ash) c. 9% and P in animal manures c. 200% (much of this manure phosphorus is already reused on farmland, but not always efficiently).

He identified as **hotspots for potential P-recovery from sewage**: sludge incineration ash, sludge liquors after dewatering, sludge after anaerobic digestion, and agricultural use of dewatered sewage sludge.

P-recovery case studies

P-Rex and Outotec (Ludwig Hermann www.outotec.com) summarised a number of operational P-recycling projects identified in Europe:

Struvite recovery in sewage works:

- Ostara Pearl, Slough (Thames Water, UK)
- PCS AirPrex: Berliner Wasserbetriebe Wassmannsdorf (D), MG-Neuwerk Niersverband (D), BB-Steinhof (D), Wieden-Echten (NL)
- Gifhorn ASG (D)
- Rephos Remondis, Altentreptow (D)
- Lysogest PCS, SE Lingen (D)

Calcium phosphate in sewage works:

- Geestmerambacht DHV Crystallactor (no longer operating)
- Fix-Phos, Hildesheim SEHi (D) (in sludge)

From incineration ash:

- Mephrec SUN Ignitec, Nürnberg (D)
- Chicken litter incinerators (UK, NL) – 120 000 tonnes/year ash sold as fertiliser

Struvite from food industry:

- NuReSys Biostru, dairy and potato processing liquors (NL)

Pilot plants and projects – in sewage works:

- Stuttgart process, Offenburg (D)
- Budenheim process, Mainz
- P-Roc, Neuburg (D)
- Phostrip Veolia Aquiris, Brussels North
- LeachPhos BSH, MSWI Bern (CH)
- Loser Chemie, Tangermünde (D)

Pilot plants and projects – from incineration ash

- Susan Outotec Reterra, Königs Wusterhausen, Berlin - Hamburg (D), sludge ash
- SNB/HVC, Moerdijk – Dordrecht, sludge ash
- Recophos - processing sludge ash to elemental phosphorus (Leoben, Austria)
- ERZ/AWEL, Zürich Werdhölzli (CH)
- Leningrad Oblast, chicken litter ash project

Obstacles to implementation

Participants identified a number of **regulatory and policy obstacles to P-recycling implementation**, explaining why some of the projects above are not being launched.

For recovered struvite, there are clear **legal requirements regarding the recycled-P product** (for use as a fertiliser) including the obligation of REACH registration. However, market and user needs are less clear.

For P-recovery from ashes, policy or regulation is needed to ensure mono-incineration (incineration of sewage sludges not with other wastes), in order to give a consistent P-content of ash.

Policy measure proposals

Other policy measures proposed by participants included, for example:

- **legal requirement** to recover and recycle phosphorus where feasible
- integration of P-recycling requirements into **BAT** documents
- **incentives** by reduced wastewater fees or increased disposal taxes
- requirement to blend recovered P into mineral **fertilisers** (enabling lower cadmium content)
- **banning of co-incineration** of sewage sludge unless with prior P-recovery
- **separation and storage of sludge ashes** which could potentially be used as a P-resource in the future
- **harmonisation** of legislation across Europe for fertilisers and soil protection legislation
- **definition of “end of waste status”** for recovered P products

Global TraPs (Global Transdisciplinary Processes for Sustainable Phosphorus Management) project www.globaltraps.ch

P-recovery thesis

Struvite precipitation from acid-treated pig manures

Auréli Capdevielle's chemistry thesis (University of Rennes - IRSTEA, France) is part of a wider project on P-recovery from manures and food wastes (Phosph'Or <https://phosphor.cemagref.fr/>). The thesis studies physico-chemical parameters influencing struvite precipitation in synthetic solutions and in biologically treated pig manure, pretreated by acidification (to render the P soluble) and differing degrees of filtration. Parameters studied experimentally and modelled included: crystallisation and dissolution processes for struvite, calcium phosphates and other minerals, impacts of pH, stirring energy, effects of organics present in real manure (particular, colloidal, dissolved).

The objective was to **develop parameters for precipitating struvite from pig manure**, after biological treatment (denitrification), then acidified with 99% formic acid to make the get the phosphate in solid fraction of the manure into soluble form, then treated with a high molecular weight cationic polymer and sieved at 250 µm.

The **prior acidification of the manure** also means that carbonate is eliminated, thus preventing interference with phosphate precipitation and also reducing pH buffering.

Initial 5 hour stirred **beaker tests** were carried out using differing magnesium : phosphate ratios, various pH (adjusted using NaOH) and different magnesium reagents (magnesium oxide MgO slurry and magnesium chloride MgCl₂). These showed that MgO slurry was an effective reagent, and this was adopted for the remainder of the experimental work.

Particle analysis

Automatic photographs and image analysis software were used to assess particle size and shape. However, the large number of particles present (MgO, precipitates) resulted in superposition of particles and prevented the software operating. This was resolved by **developing a specific method** for diluting (using the supernatant of the sample to prevent particles being redissolved or be modified).

Magnesium oxide slurry

Magnesium oxide (MgO) has the advantage that it is **available at low cost as an industrial by-product**

from the animal food industry, that it can be safely handled by farmers, and that it increases pH so avoiding dosing with sodium hydroxide (caustic soda NaOH) which is not appropriate for handling by farmers.

The MgO was probably **particularly effective for this acidified manure**, because the low pH increased solubility of the MgO (and so magnesium availability) and because the acidification reduced the pH buffering of the manure.

However, the MgO is only **slowly soluble**, necessitating its introduction as a stirred slurry. Also, the industrial byproduct showed varying solubility characteristics between batches.

One consequence of using MgO, is that pH was not adjusted, other than the increase resulting from the MgO addition, and also that the reaction availability of the magnesium (dissolved) could only be estimated. This made the process chemistry modelling more complex.

Beaker test plan

A set of 48 beaker experiments (**modified Box-Behnken plan**), all stirred for 24 hours, was then carried out using magnesium oxide slurry as the magnesium dosing reagent. Five different factors were assessed: N:P ratios 1-3, agitation 10 – 90 rpm, initial Mg:Ca ratio 0.6 – 1.7 and the part of the MgO which was not initially dissolved.

Results showed that higher temperatures or increased stirring speed improve P-precipitation, by making the magnesium from the **MgO more available and soluble**. Ammonium loss could however be significant at higher temperatures in this open, stirred beaker set-up, so reducing struvite precipitation.

At 15°C, the optimal conditions tested were agitation 60 rpm, N:P ratio 3, initial Mg:Ca ratio 1.7 (resulting from a free Mg concentration of 500 mg/L, and corresponding to a pH of approx.. 6.7). With these optimal conditions, >95% of phosphate was precipitated as struvite and >85% of the particles were >100µm.

The authors concluded that P precipitation as struvite (rather than as calcium phosphates) is **principally influenced by the concentration of MgO added and by N:P ratio** and that struvite particle size is improved by lower MgO addition rates (this also reduces ammonia volatilisation).

These results are published in J. Hazardous Materials (2012), details below.

Crystallisation kinetics

6 further beaker experiments were carried out using the optimal conditions identified above, with morphological analysis of the struvite crystals over time throughout the 24 hour experiments. Analysis showed that **struvite crystal growth** is limited by the transport of ions in solution for a N:P ratio of 3, and by rate of integration into the crystal at N:P ratio of 1. Some 70% of struvite precipitation was taking place in the first 30 minutes.

Calcium phosphate precipitation showed to be more complex. Initially, amorphous calcium phosphate (ACP) was formed, but this redissolved progressively as struvite precipitation reduced the soluble P concentration, thus enabling further struvite formation. This redissolution of ACP was optimal at agitation 60 rpm and is improved by a high initial Mg:Ca ratio.

Phosphate precipitation was accelerated at higher pH, with an optimum at pH 8-9, but **more large struvite particles were formed at pH 7.** Optimisation achieved 85% of struvite crystals > 100 µm, but after 10 hours crystal size began to decrease as larger crystals were broken by the stirring.

The MgO addition resulted in two distinct pH increases, a rapid increase (<5 mins) from pH 4.5 to pH 6-7, followed by a plateau, then a further increase to pH 8-10 between 30 – 90 mins.

Real manure and impact of organics

In a final set of tests, real acidified manure was used (1) as is, (2) after removal of particles by centrifuging at 10 000 rpm for 20 minutes and (3) after further removal of colloids by filtration at 0.45 µm leaving only dissolved organic matter (DOM) (total 3 tests, each duplicated). In all cases, MgO was added (as a 10g/100ml slurry) to a Mg:Ca ratio of 2, with 60 rpm stirring for 24 hours at 15°C.

Results showed that the **presence of dissolved organics** slowed down the pH increase and modify brushite formation (calcium phosphate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The colloid particles slowed down the precipitation and dissolution kinetics, increased the size of struvite crystals produced, but inhibited crystal agglomeration. The presence of organic particles did not significantly modify precipitation.

The authors suggest that **these effects result from various mechanisms**: higher fluid viscosity than in synthetic solutions slowing ion diffusion reducing crystallisation kinetics, ions trapped by charged particles not being available to precipitate, interference with fast or slow growing sites of crystals (modifying

crystal shape), inhibition of MgO dissolving so that magnesium is less available, pH buffering effect.

In the real manures, 90% phosphate precipitation was achieved after 24 hours at a pH of only 6.8. 60% of the precipitated phosphate was struvite, and 80% of the precipitant was in particles > 100 µm.

The results of this work have been used to parameter a lab-scale **continuous agitated struvite reactor** running on the acidified pig manure.

Further work is now underway to scale up to a process adapted to on-farm implementation. However, for this, a treatment other than acidification using formic acid is being looked for, because of the high cost and Life Cycle Analysis of formic acid. Partial (acidifying) anaerobic digestion is one possibility being examined.

“Influence des paramètres physico-chimiques et des caractéristiques de la matière organique sur les cinétiques de formation de struvite: application au recyclage du phosphore des lisiers de porcs” (Influence of physic-chemical parameters and of the characteristics of organic matter on struvite crystallisation kinetics: application to pig manure phosphorus recycling), Thèse University of Rennes 1, France, A. Capdevielle, 2012, partly in French with main articles in English included. Publication online pending.

“Optimization of struvite precipitation in synthetic biologically treated swine wastewater – Determination of the optimal process parameters”

<http://www.sciencedirect.com/science/article/pii/S0304389412011569>

A. Capdevielle*, F. Béline, M-L. Daumer, IRSTEA/Cemagref, 17 avenue de Cucillé, CS 64427, 35044 Rennes Cedex, France. E. Šýkorová, ICT Prague, Department Technology of water, Technická 5, Prague 6, 166 28, Czech Republic. B. Biscans, Université de Toulouse, Laboratoire de Génie Chimique, UMR 5503 CNRS/INP/UPS, Site de Labège, BP 84234, Campus INP-ENSLACET, 4 allée Emile Monso, 31030 Toulouse cedex 4, France. * Also: Université européenne de Bretagne (UEB), 5 Boulevard Laënnec, 35000 Rennes, France.
aurelie.capdevielle@gmail.com

Henan Province, China

Struvite precipitation from nylon production wastewater

Nylon production wastewater, after anaerobic digestion, contains significant levels of dissolved ammonia. Struvite precipitation was tested to reduce this ammonia, prior to biological treatment in a sequencing batch reactor. Different reagents were tested for addition of magnesium (magnesium sulphate, natural brucite) and phosphorus (disodium phosphate, phosphoric acid). The struvite precipitation reached up to 88% ammonia removal at Mg:N:P ratio of

3.5:1:1.05 and pH8. The brucite and phosphoric acid enabled a reagent cost reduction of over 40%.

The **nylon-66 salt production wastewater**, after anaerobic digestion, had average pH of around 8, COD of approx. 1100 mg/l, total nitrogen of c. 780 mgN/l (of which ammonia 550 mgNH₃-N/l). Phosphorus and magnesium were both negligible (< 1 mg/l).

Natural brucite for the experiments was purchased from a flame retardant supply company, with particle size < 0.05 mm. It consisted principally of magnesium dihydrate Mg(OH)₂.

The biological treatment of the liquor, after struvite precipitation, was carried out using a 2 litre SBR (sequencing batch reactor), seeded with activated sludge and with a carbon source to feed denitrification. The SBR was operated with 8 hour cycles (anaerobic, aerated, anoxic, settling), after which around one third of the liquor was replaced.

Struvite precipitation tests

250 ml of liquor in (20 – 25°C) temperature-controlled 500 ml beakers with airtight lids, stirred at 300 rpm, were used for struvite precipitation experiments. pH was adjusted by NaOH addition. Stirring was for 20 minutes with magnesium sulphate reagent (soluble) and 90 minutes with brucite (because of its low solubility).

Magnesium sulphate and disodium phosphate reagents were tested at pH 8.5 with Mg:ammonia-N:P ratios of 0.9:1:1 to 1.3:1:1. Brucite and phosphoric acid were tested again at pH 8.5 with ratios 2.5:1:1 to 4.5:1:1. Magnesium sulphate and phosphoric acid were tested at pHs from 7 – 9 and at a ratio of 1.5:1:1 to 1.3:1:1

The experiments using brucite and phosphoric acid identified an optimal dosing ratio of Mg:ammonia-N:P ratios of 3.5:1:1.05 at which 88% of ammonia-N was removed from the liquor. This removal rate could be increased with a higher phosphorus dosing, but this resulted in increased residual phosphate in the liquor which would deteriorate the downstream biological treatment efficiency.

The **reagent cost** for brucite and phosphoric acid for this ammonia removal was estimated at c. 3.6 US\$/m³ of wastewater, over 40% cheaper than using magnesium sulphate and disodium phosphate despite the higher doses required for the less soluble brucite. The impact on sodium hydroxide cost (for pH adjustment) is not specified, but this may be higher with the phosphoric acid reagent.

The authors conclude that the use of brucite and phosphoric acid as reagents enable **significant cost savings**, and that this configuration of struvite precipitation and biological SBR treatment enable respect of the China effluent discharge regulations.

The potential for reuse of the struvite is not assessed: this would require verification that it does not contain problematic impurities, because the nylon wastewater contains a number of contaminants including hexamethylene diamine, benzene, copper, zinc ...

"Treatment of anaerobic digester effluents of nylon wastewater through chemical precipitation and a sequencing batch reactor process", Journal of Environmental Management, vol. 101, n° 30 pages 68-74, June 2012

<http://www.sciencedirect.com/science/article/pii/S030147971200062X>

H. Huang, Q. Song, W. Wang, S. Wu, J. Dai, Center for Environmental Engineering Design, Chinese Academy of Environmental Sciences, Beijing 100012, China
huanghaiming52hu@163.com

Guangdong

Struvite pyrolysate

High potassium and calcium concentrations in the anaerobic digestate from a Guangdong province pig farm, China, interfered with nutrient removal by struvite precipitation. Magnesite pyrolysate (magnesite mineral calcined at 700°C for 1 ½ hours) showed to be effective for nutrient removal at Mg:N:P ratios of 2.5:1:1. In order to reduce reagent costs, precipitated struvite was also pyrolysed at 110°C for 3 hours with sodium hydroxide (1:1 ratio), to generate MgNaPO₄ (ammonia driven off to the atmosphere), which was reused as a struvite precipitation reagent. Because the NO₄-nitrogen concentration in the piggery wastewater was over 6x higher than the phosphate concentration, this enabled to additional ammonia removal without adding phosphate.

The **piggery waste anaerobic digester supernatant**, after solid-liquid separation, contained approx. 990 mg/l N-NO₃, 180 mg/l total phosphorus, 800 mg/l potassium, 140 mg/l calcium and only 7 mg/l magnesium (pH 7.8).

Stirred jar batch tests were first carried out to assess the effects of potassium and calcium concentration on struvite precipitation from synthetic waste water (pure chemical solutions). K and Ca to phosphate ratios of 0 – 0.75 were tested with 15 minutes stirring and 10 minutes precipitation time, at pH 9.

Effects of potassium and calcium

Removal of both phosphate and ammonia showed to be **significantly affected by potassium concentrations** (both being reduced by 15 – 20% at potassium ratio 0.75:1). Calcium reduced phosphate removal to near zero for a calcium ratio of only 0.15:1 and reduced ammonia removal by around 2/3 at a calcium ratio of 0.75:1.

Magnesite and struvite pyrolysates

Magnesite mineral, a relatively cheap material, was purchased from Xinxing Magnesium Powder Plant (Liaoning Province, China). After calcination at 700°C for 90 minutes, it became principally MgO with a magnesium content of 53%. This was tested for struvite precipitation in both pure chemical solutions and in real piggery digester wastewater at magnesium:ammonia ratios of 1.5 – 3.5, in jar tests under the same conditions as above. **Phosphoric acid was added** to increase the phosphorus:ammonia ratio in the wastewater up to 1:1, and this certainly improved the solubility of the magnesite pyrolysate.

A magnesium:NH₄ ratio of 2.5:1 and a reaction time of 6 hours showed to be optimal for **magnesite pyrolysate** use for struvite precipitation, enabling an ammonia removal rate of over 80% at pH 8 – 8.5

Struvite pyrolysate was produced by precipitating struvite from real piggery digester wastewater as above, filtering, washing, then decomposing at pyrogenation temperature of 110°C for 3 hours with sodium hydroxide at an NaOH:NH₄ ratio of 1:1. The struvite pyrolysate was then used as magnesium and phosphate dosing additive for struvite precipitation from piggery digester wastewater (with the objective of ammonia removal), then again pyrolysed, for 5 re-cycles.

Ammonia removal was almost the same for the first two pyrolysis cycles (at around 80%, that is similar to using magnesite pyrolysate), slightly lower for the third, then falling to around 70% ammonia removal for the 5th cycle. The authors suggest that this may be due to accumulation of inactive Mg₃(PO₄)₂ and Mg₂P₂O₇ or accumulation of potassium or calcium or other ions.

Economic evaluation

The costs of using magnesite pyrolysate and recycling struvite pyrolysate (including energy costs) were compared to costs for ammonia removal by struvite precipitation using pure chemicals as reagents (magnesium chloride and sodium phosphate), showing an **approximately 50% cost saving** from around US\$10 to US\$5 per m³ of wastewater treated.

“Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology”, *Bioresource Technology*, n° 102, pages 2523–2528, 2011
www.elsevier.com/locate/biortech

H. Huang, C. Xu*, W. Zhang, *Center for Environmental Engineering Design, Chinese Academy of Environmental Sciences, Beijing, 100012, China.* * and: *Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, 305-8572, Japan.* huanghaiming52hu@163.com

Brussels, 6-7 March 2013

European Sustainable Phosphorus Conference



Participate
Collaborate
Innovate

Programme and registration:

<http://www.phosphorusplatform.org/esp2013.html>

Capacity limited to 250 participants.

Pre-registration obligatory.

The Square, 2 rue Ravensteinstraat, Brussels,
6th March 9h-19h and 7th March 9h -15h30

Conference objectives:

- Create a clear and coherent **legislative framework** for eco-innovation, a sustainable European market for secondary phosphorus and more efficient phosphorus use.
- **Raise awareness** about the necessity for more sustainable phosphorus management.
- Develop the “**European Phosphorus Platform**” connecting different nutrient waste flows and market possibilities.

Monte Carlo, 25-27 March 2013

Phosphates 2013

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



The CRU Phosphates conferences are the only global meeting for the worldwide phosphate industry (rock production, fertiliser, animal feeds, food, detergents, other industrial uses).

These conferences bring together over 500 delegates from tens of countries worldwide, including senior industry executives and organisations that define phosphate supply and demand. Phosphates 2013 will provide a macro view of historical and current markets, supply, demand and prices to better understand the context for future trends.

Beijing, 18-20 June 2013

Global TraPs world conference



TRANSDISCIPLINARY PROCESSES FOR SUSTAINABLE PHOSPHORUS MANAGEMENT

www.globaltraps.ch

The Global Transdisciplinary Processes for Sustainable Phosphorus Management (Global TraPs) project is studying phosphorus use, management and sustainability from a supply chain perspective involving academia, industry, governments, NGOs and other concerned parties.

The conference theme is “**Learning from Case Studies – Exploring Policy Options.**” with the objective of assessing specific areas for policy intervention to ensure sustainable phosphorus use in the future.

The conference will be co-hosted by China Agricultural University, Ministry of Agriculture, Chinese Ministry of Education, Phosphorus Fertilizer Industry of China, National Science Foundation of China, IFDC, Fraunhofer Institute and other Institutes and will coincide with the **5th International UNEP Global Platform Nutrient Management Symposium**

Vancouver, 28-31 July 2013

International Nutrient Removal and Recovery Conference

<http://www.wef.org/nutrients/>

Combined WEF and IWA-NRR conference: **Nutrient removal and recovery 2013 – trends in resource recovery and use.**

- nutrient recovery processes
- nutrient recovery from source-separated urine and agricultural effluents
- nutrient management of biosolids

Conference organised by WEF (Water Environment Federation), IWA (International Water Association), WERF (Water Environment Research Foundation) and British Columbia Water & Waste Association.



International
Water Association



CEEP

Centre Européen d'Etudes des Polyphosphates

SCOPE Newsletter - n° 91 - February 2013 - Page 12

www.ceep-phosphates.org

