# SCOPE NEWSLETTER

# NUMBER 93

#### **Policies and perspectives**

Phosphorus management

European Sustainable Phosphorus Platform initiative

The European Phosphorus Platform will bring together industry, knowledge centres, regulators and NGOs to work together, share experience and develop an operational value chain in phosphate recycling, efficient phosphorus use and phosphorus stewardship.

#### Phosphates 2013

#### **Phosphate industry outlook**

The CRU "Phosphates" conferences, now annual, bring together phosphate industry actors worldwide to discuss technologies, markets and development perspectives.

#### **Global Phosphorus demand**

Predicting future phosphorus needs for agriculture

Phosphorus that accumulates in soil through use of fertilizers could lead to less future phosphorus needs for food production.

#### Quantification of phosphorus flows (1)

#### **Phosphorus balance for France**

The assessment of P-flows and a P-balance in France show significant net balance (import) of c 263 000 tonnes P/year in 2006. Only around 78 000 tonnes P reached households in food, of which around half was lost to municipal refuse in food wastes.

Quantification of phosphorus flows (2)

Agricultural phosphorus use in 4 French regions

An assessment of phosphorus flows, stocks and balances in agriculture in 4 French regions: one intensive arable, one concentrating livestock, and two mixed farming.

#### Urban phosphorus flows

Fate of phosphorus in food and municipal wastes

Two studies in Sweden look at flows of phosphorus in an urban area and P-recovery from municipal waste incineration fly ash, in the context of Sweden's national phosphorus recycling objective.

# May 2013

#### Life cycle assessment

#### Sewage sludge and P-recovery

Four different options for sewage sludge utilisation with valorisation of phosphorus were assessed for direct and indirect environmental impacts.

#### **P-recycling technologies**

#### Food waste aerobic composting

#### Struvite precipitation and nitrogen loss

Three different phosphate compounds were added to food waste aerobic composters, resulting in significantly different nitrogen losses

#### Zirconium ferrite

# P-recovery by adsorption/desorption and magnetic separation

*P-recovery from sewage using a ferromagnetic adsorbent and magnetic separation was tested using pure solutions and wastewater plant effluent at the laboratory level.* 

Novel P-recovery from wastewaters

Amorphous calcium silicate hydrates (A-CSHs)

A-CHSs showed to be highly effective in removing phosphorus from sewage sludge digestion liquor, enabling P-recovery by settling and direct use of the product.

#### Sewage sludge incineration ash

#### Acid extraction from ashes

Sulphuric and nitric acid were tested for phosphorus extraction from aluminium or iron rich sewage sludge incineration ashes.

#### Conferences

**Symphos** 

RRB-9

Global TraPs

IWA Nutrient Removal and Recovery

Agenda

## Phosphorus management European Sustainable Phosphorus Platform initiative

The European Sustainable Phosphorus Platform initiative came out of the European Sustainable Phosphorus Conference, Brussels, 6-7 March 2013, at which the European Commissioner for the Environment, EU Member States, industry and for scientists called European action for phosphorus stewardship and recycling. Over 150 organisations signed the conference declaration calling for such an initiative, and it is now being taken forward by an open committee involving national nutrient platforms, regulators, knowledge centres and companies and industrial associations in the fertiliser, animal feeds, waste management and phosphorus recycling sectors.

The **European Sustainable Phosphorus Platform** is currently defining an action plan for the coming year including a number of concrete actions to progress phosphorus stewardship and P-recycling, and the objective of establishing the Platform as a permanent structure by 2014.



#### **Action Plan**

The European Sustainable P Platform's action plan for coming months proposes:

- organising technical meetings to exchange information and develop proposals on issues such as regulations impacting phosphorus recycling and re-use, contaminant control and societal implications of recycled phosphorus in the human food chain ...
- advocacy coordinate input to European and national policies and initiatives, for example raw materials and resource efficiency roadmap, bioresources, water, agriculture, chemicals policies
- develop and support national/regional phosphorus value chain actions

Centre Européen d'Etudes des Polyphosphates

- circulate information on economic and employment opportunities of phosphorus management
- catalogue of value-chain industry actors, technology suppliers, companies managing secondary phosphorus resources, producers and users of recovered and recycled phosphates ...
- information exchange with initiatives on phosphorus stewardship in Europe and worldwide, P-recycling newsletter, website, communications
- propose a research agenda for phosphorus management in Europe
- > joint project proposal development

#### **Invitation to participate**

Companies, knowledge centres and other concerned organisations are invited to join the European Sustainable Phosphorus Platform, in order to benefit from networking, information sharing and to participate in technical meetings and joint actions.

www.phosphorusplatform.org

# Phosphates 2013 Phosphate industry outlook

"Phosphates 2013" (CRU conference, Monte 26-27<sup>th</sup> Carlo March 2013 http://www.crugroup.com/events/phosphates/) is the first time that this conference has been organised annually rather than every two years. "Phosphates 2012", see SCOPE following Newsletter n° 86), "Phosphates 2013" brought together some 300 delegates and industry experts from across the world, to discuss new supplies of phosphate rock, P-recovery, recycling and use efficiency, phosphate industry integration from Prock to fertiliser and phosphorus chemical production, and perspectives for the agriculture and the fertiliser phosphate and animal feed phosphate markets.





SCOPE Newsletter - nº 93 - May 2013 - Page 2 www.ceep-phosphates.org In addition to plenary presentations on these strategy and perspectives questions, 15 showcase presentations covered **phosphate industry technologies and applications**.

Nick Edwards, CRU, opened the conference, underlining that we are in unpredictable times of change for the phosphate and fertiliser industry, with three key questions: growth of global demand for fertiliser (because of increasing global population and changing diet in developing countries, as well as biofuels), the advent of shale gas radically modifying energy costs and supply geography, and questions around the financing of supply development (new phosphate rock production or processing capacity).

#### New sources of phosphate rock supply

Glenn Gatcliffe, BMO Capital Markets, showed that possible new phosphate rock production projects are currently numerous, with often large, currently unexploited phosphate rock reserves identified in Angola, Australia, Brazil, Canada, China, DRC, Guinea-Bissau, Idaho, Kazakhstan, Mali, Mongolia, Mozambique, Namibia, Peru, New Zealand, Saudi Arabia, South Africa, Tunisia, Ukraine, USA, ... At current phosphate prices and demand, however, few if any of these are likely to be developed, as global supply is already in overcapacity. Public markets financing for phosphate mining investments is difficult to obtain, especially for projects with large capital expenditures and with research analysts not expecting rock prices to increase in the long term.

Specific phosphate mining developments and projects were presented by Allen Picket, Aguia Resources (Brazil), Roderick Smith, Cominco Resources (Congo) and Andy Jung, Stonegate Agricom (Idaho USA, Peru).

**Thomas Schantze, Jacobs Engineering**, summarised the challenges of delivering major investment projects in phosphate extraction and processing.

Yahya Al-Yami, Ma'aden Phosphate, presented a paper about Ma'aden Phosphate growing to support a balanced market. He gave an introduction to the Ma'aden company, provided a summary on key phosphate markets (size and growth rate) and touched upon phosphate developments within Saudi Arabia. Ma'aden currently operate the Ma'aden Phosphate Company (MPC) which produces 1.3 million tonnes P/year of phosphate fertilisers (DAP/MAP). In addition to MPC, in 2017 Ma'aden will deliver a new project called Wa'ad Al Shammal located in northern Saudi Arabia. This project will add 0.7 million tonnes P/year to Ma'aden's capacity, with product breakdown of 80% to DAP/MAP, 13% downstream and 7% NP/NPK.

# Efficiency, recovery and recycling

Paul Speight, European Commission DG Environment, presented the EU perspective on phosphorus resources. Phosphorus is a case study for the need for resource efficiency, as Europe has very little phosphorus resources, and only 2-3% of phosphorus applied in agricultural fertilisers and feeds finally reaches consumed human food. For example, 30% of food produced in the EU ends up as waste instead of being eaten. This inefficiency results in pollution (eutrophication) as phosphorus is lost to surface waters, and also in a long-term and irreversible problem of soil contamination by cadmium from mineral fertilisers.

The European Commission considers that Europe needs to improve agricultural efficiency of



agricultural efficiency of phosphorus application, in particular by improving soil quality and organic content to reduce soil erosion. for example by crop rotations. Phosphorus recycling must be developed, including manure processing and reuse, recovery and recycling of phosphorus from wastewaters, P-recycling from animal byproducts, reduction and composting of food and green wastes.

The European Commission has already engaged a number of **actions to improve phosphorus management**, including:

- Update (underway) of the **Fertiliser Regulation**, to include organic amendments (manures, compost ...) and to set cadmium limits
- EU **raw materials initiative**, where phosphorus will be considered
- Implementation of the **Nitrates Directive**
- Use of **agricultural policy** to try to combat soil erosion, and to encourage efficiency in fertiliser use
- Water legislation: at present P-removal from sewage is required, but not P-recycling
- **Biowaste** (via the Landfill Directive) and sewage sludge management legislation
- Sustainable food initiative
- **R&D** support

The European Commission also expects to publish soon a **'green paper' or a consultation document in some other form**, for stakeholder discussion, and proposing a range of possible further actions





SCOPE Newsletter - nº 93 - May 2013 - Page 3 www.ceep-phosphates.org specifically targeting phosphorus stewardship, and is supporting the European Phosphorus Platform, currently being launched (see SCOPE Newsletter n° 92 and *www.phosphorusplatform.org*)

John Wing, John Wing PE and Chaker Chtara, Groupe Chimique Tunisien, presented potential technologies for recovering other values during phosphate rock processing and purification, including uranium, rare metals and fluorine, and for recovering higher levels of phosphorus and so reducing residual phosphate in phosphogypsum. Phosphogypsum is the calcium sulphate generated during phosphoric acid production by the sulphuric acid process, which is the principal processing route worldwide. They also presented routes for reuse of the phosphogypsum. These two issues are closely linked, as the removal of the uranium, heavy metals and other contaminants from phosphogypsum may condition the acceptability by regulators of its reuse in applications such as the cement industry, plasterboard manufacture, road foundations ...

**Steve Wirtel, Ostara**, presented the company's Pearl® crystallisation process, for recovery of phosphates from liquid waste streams as struvite (magnesium ammonium phosphate) granules, a slow-release, environmentally-responsible phosphate fertiliser, which the company markets as Crystal Green®.

**Struvite recovery in municipal wastewater treatment plants is an agent for change** in the phosphorus cycle, closing the local phosphorus loop, and contributing to municipal sustainability strategies. Struvite recovery integrates into biological phosphorus removal, improving pollution control, and sewage biosolids methanisation energy recovery.

Mr. Wirtel explained that Crystal Green is not water soluble, which prevents loss of phosphate from soil to surface waters after application, and also means that the phosphate is not taken up and bound by iron, aluminium or other ions in soil. The nutrients in struvite (N, P, Mg) become available only when plants actually need them, because the plant roots then locally release acid which solubilises the struvite. With soluble fertilisers on the other hand, only 25% of applied phosphorus is generally taken up by the crop in the season of application, the remainder is either lost from soil or becomes unavailable to plants.

Ostara is also developing industrial applications for the Pearl process, including a process to recover phosphate from phosphogypsum storage pond waters. The proposed process involves a fluorine and silica removal stage, followed by struvite precipitation, then membrane water clarification, resulting in a highly pure discharge or reuse quality water. The recovered struvite contains very low levels of heavy metals or other contaminants.

Debbie Hellums, IFDC, presented fertiliser challenges for tomorrow's agriculture. World demand for fertiliser has increased over the last half century, and is expected to continue to increase because phosphate fertilisers are essential for food production. Drivers for increasing fertiliser use will include population increase, urbanisation and changes in diet (more animal protein in the emerging economies), and possibly biofuels production. Decreasing water availability for agriculture and decreasing arable land will require intensified production per unit of water and land area, but should reduce phosphate fertiliser demand over time as phosphate inputs provide annual and residual benefits. The residual phosphates supply slowly available phosphates over the long term and can reduce the rate of annual application required. One major question remains as to how the impact of climate change will influence cropping patterns and associated fertilizer demand.

There are opportunities to improve phosphate fertiliser use efficiency. Only 15-20% of fertiliser phosphate is taken up during the season of application by the crop. In temperate agriculture, most of the remainder may be surface adsorbed to soil particles and so be slowly available to crops over following years, but in highly weathered soils of the tropics, applied phosphates may be strongly bound to iron and aluminium present in the soil. Only after the soil's "thirst" for phosphate is satisfied (often requiring initially high levels of phosphate fertilizers) will the plant have access to the phosphate it requires. For these important tropical agricultural soils to be productive, initial phosphate application must occupy all the soil binding sites, so that subsequent fertiliser applications can be largely available for crops.

IFDC is working on development of **slow-release phosphate fertilisers** to address these issues, and on biological systems to improve crop phosphate usage. For example, some crops (ie. canola) have acidic root rhizosphere characteristics that enable extraction of plant available phosphate from the soil or from phosphate rock. Identification of these traits and transfer to other crops could significantly increase phosphate use efficiency in the short term.

**Juan von Gernet, CRU**, presented 2-3 year perspectives for the world fertiliser market. Demand is expected to continue to increase in Brazil (new agricultural land, soy and sugarcane crops with high P and K requirements), in the USA (with high crop prices) and in China. India poses questions, as large stocks of fertiliser have been accumulated and demand may decrease further if fertiliser subsidies are reduced





SCOPE Newsletter - nº 93 - May 2013 - Page 4 www.ceep-phosphates.org in 2013 - 2014. The tendency towards specifically adapted fertilisers is expected to accelerate, with a greater emphasis being placed on more balanced nutrient application, as well as the agronomic need for secondary and micro nutrients. However, prices of phosphate fertilisers will be kept in check, as new production plants come online.

#### Human food and animal feed perspectives

Heike Hinze-Gharres, CRU, presented expected developments in agricultural markets for the next 3-5 years, based on the CRU Nutrient Demand Model using analysis of 180 countries and 11 different crops. There is a need to replenish world food reserves after consecutive years of demand outstripping production. In addition, crop demand is expected to increase due to growing population and changing dietary patterns which will see increased demand for input-intensive meat and fried foods particularly in developing countries. This will further raise the demand for feed crops like corn and oilseeds. More of these crops will need to be grown in the future with the required additional crop area likely to be in Brazil, India, Africa and the former Soviet Union countries. Increased fertilizer applications will be necessary to boost production, with productivity and intensity gains varying from country to country. However, weather extremes caused by climate change, supply response and long-term land availability may impact fertilizer demand growth in the short term. Overall, phosphate consumption in fertilisers is expected to increase +2.5% per year to 2017.



**Increasing world cultivated cropland area** (in particular in Brazil, India, Africa and former Soviet Union countries) and **biofuel production** will contribute to increasing fertiliser demand, whereas weather extremes caused by climate change, supply response and long-term land availability may reduce demand. Overall, phosphate consumption in fertilisers is expected to increase +2.5% per year to 2017.

**Ugo Pica-Ciamarra, FAO**, presented perspectives for animal food markets. At present, developed countries consume 81 kg meat per capita per year compared to 6 kg in developing countries, 247 litres milk compared to 62 litres, and 14 kg of eggs compared to 8 kg. FAO estimates increases of + 111% (more than doubling) of total meat, milk and egg consumption by 2050, with the increase almost entirely in developing countries.

However, the relation between increases in the consumption of animal-sourced foods and the demand for phosphate animal feeds are not linear will depend on many factors, including whether the increase in meat consumption is largely in poultry (2kg of feed (dry matter) to produce 1 kg meat, compared to 6 to 10 kg for beef), whether production is by small farmers or larger-scale, intensive animal production units. Factors which might influence developments include the issue greenhouse gas emissions from of cattle, environmental and welfare questions relating to intensive animal production, and concerns about animal health and human-transmittable diseases.

#### **Phosphate industry perspectives**

Steve Markey, CRU, presented the expected impacts of shale gas exploitation on the markets for the ammonium phosphate raw materials, anhydrous ammonia and sulphur. Many regions have large potential shale gas reserves including China, Argentina, USA, Mexico, Australia, parts of Europe ... However, the USA offers the best opportunities for fracking extraction because of availability of water resources, waste water treatment capacity and infrastructure. Ammonia production is thus expected to increased and become more economic, but most production will be downstream integrated to fertiliser production, so that merchant market availability of ammonia will remain limited. With regards to sulphur, shale gas is "sweet", containing low levels of sulphur; and so, it will not directly impact availability of recovered sulphur.

**Dmitry Magazanik, MCC Eurochem**, presented the phosphate industry in Russia. The country's mineral fertiliser consumption fell by a factor of 4x in the 1990's, and has not yet recovered. 80% of national phosphate fertiliser production is exported. The Russian phosphate industry is increasingly integrated, with over 75% of phosphate fertiliser production by vertically integrated companies.

**Isaac Zhao, CRU**, presented the phosphate industry in China. Over ten years, China has invested heavily in fertiliser production, passing from an exporter of phosphate rock to being an exporter of ammonium phosphate fertilisers, with a current significant overcapacity of fertiliser production which is placed on the export market subject to tariff and custom controls. P-rock is not in short supply in China, but prices are increasing and quality deteriorating. China also has overcapacity of animal feed phosphate production, despite slowly growing national demand.





SCOPE Newsletter - nº 93 - May 2013 - Page 5 www.ceep-phosphates.org China produces elemental phosphorus by the thermal process, but only in the rainy season when hydroelectric energy is available. New wet-route phosphoric acid purification plants are now competing with the thermal process acid.

Nandurdikar, Paradeep Phosphates, Sharad presented the situation in India, where 65% of the population depends on farming for its livelihood, with an average landholding of 1.3 ha. Phosphate and nitrogen fertilisers both benefit from significant government subsidies to encourage use by farmers and so increase agricultural production. Phosphate use has increased by around 40% since 2005 and is expect to increase by as much again or more in the coming 5 years. The subsidy system shows however a range of problems, including leading to over-use of urea nitrogen fertilisers in some areas, problems because of delays in subsidy payments, and instability because of frequent changes in policy. Many soils are deficient in microelements such as zinc, sulphur, boron ...



John Malinowski, JR Simplot Company, presented the phosphate market outlook in the USA. Economic pressure and phosphate costs have led over the last 15 years to significant reductions in animal feed phosphate use (animal diet P content). The fertiliser market has seen a considerable move towards N-P-S fertilisers, providing nutrients targeted to crop and soil needs. Technologies are being developed to improve phosphate fertiliser efficiency, including polymers, humic acids and biological systems, for example to protect the applied fertiliser from being 'lost' to crops by fixation to soil iron, aluminium, magnesium or calcium ions. Increased pressure on nutrient stewardship is expected from regulators, consumers, restaurants and supermarkets.

John Hany, Purina Animal Nutrition, presented developments in animal feed phosphate demand in the USA and observations regarding significant changes affecting the USA Livestock Industry. Significant factors affecting the demand for supplemental animal feed phosphates in the USA is the major change is the availability of DDGS (distillers grains), a byproduct of bioethanol production,. The DDGS have become a major component of feed mixes and as a result of going through the fermentation process involved in biofuel production contribute significant digestible phosphates for the livestock. As DDGS is added to the diets, the result is a lower need for animal feed phosphate supplements. Other major factors that have resulted in lower supplemental feed phosphate demand in the USA is the growth in the use of phytase and the increased focus on diet management. The use of DDGS, however, also can result in increased phosphorus contents of manures, posing pollution abatement challenges and offering opportunities for Precovery and recycling.

A very significant change over the last 30 years in the USA related to the production of meat, milk and eggs is the significant **gain in production efficiency**. Meat production efficiency has risen considerably for beef, hogs and poultry while at the same time the efficiency of milk production has also risen substantially. We are simply able to produce more with less. The numbers of cattle in the USA have fallen -27%, whereas hogs (+50%) and poultry (+98%) have risen.

Alberto Persona, CRU, presented on the global market for animal feed phosphates, which is gaining relevance in international trade. The key cost advantage will be the vertical integration with phosphate rock supply. This is generating a migration of capacity further from end-markets, pushing towards higher volumes exchanged internationally. Some growth in demand, with increased livestock and aquaculture production, may be balanced by the use of phytase, and prices are liable to be stable as global production capacity is in excess.

*CRU's "Phosphates 2014" conference will take place in March 2014, see http://www.crugroup.com/events/phosphates/* 

### Global Phosphorus demand Predicting future phosphorus needs for agriculture

A two-pool soil phosphorus (P) model, at the continent level, has been developed for agricultural phosphorus inputs from fertilisers and manure, crop phosphorus uptake, and so global phosphorus requirements for crop production in Taking into account residual 2050. soil phosphorus, accumulated from historical application of fertilisers, results in estimates of 21 million tonnes P in 2050 (compared to 18 million tonnes P today), that is around 2x less than previously published estimates.



SCOPE Newsletter - nº 93 - May 2013 - Page 6 www.ceep-phosphates.org



The DPPS model developed in this paper considers two soil pools of phosphorus, both fed by fertiliser and manure application: a stable pool and a labile pool. Exchanges between the two are possible, and the labile pool can be removed mostly by crop uptake.

#### Grasslands

A large proportion of the phosphorus recycled to cropland in manures originates in grasslands, resulting in **a P transfer from grasslands to croplands**. This is particularly important in developing countries. Given the increasing demand for grass (dairy and meat production), phosphorus fertiliser will be needed to maintain grassland productivity.

#### Legacy soil phosphorus

Agricultural phosphorus application rates (fertiliser plus manure) have varied considerably over the past c. 50 years (1965 – 2007), for example peaking at 34 kg P/ha in Europe in the 1980's falling back to 17 kg P/ha in 2007. In Oceania, rates have fluctuated but are today back at levels comparable to the 1960's. Rates in North America have remained relatively stable around 9 - 12 kg P/ha. Rates in Latin America and Asia have risen considerably from 4 to 21 and 6 to 28 kg P/ha respectively.

**Soil phosphorus accumulation** results in hysteresis of fertiliser demand, and differing rates of crop phosphorus uptake for the same fertiliser P application rate over time.

Phosphorus demand in 2050 is estimated from Millennium Ecosystem Assessment predictions of target crop production. Including residual soil phosphorus in the estimate of fertiliser application needed to meet this crop demand results in a **reduction of P inputs compared to previous published studies**.

The model shows that **the legacy accumulation of phosphorus in soil reduces global estimates of total P fertilizer required** to meet coming food security challenges. This reduction in estimated phosphorus fertiliser consumption has important consequences for considerations of global mineral phosphate (P-rock) reserves, because fertiliser production accounts for over 80% of phosphate rock use.

"Residual soil phosphorus as the missing piece in the global phosphorus crisis puzzle", PNAS (Proceeding of the National Academy of Sciences USA), in print March 2012 http://www.pnas.org/content/early/2012/03/15/1113675109

S. Sattaria (a), A. Bouwman (b,c), K. Giller (a), and M. van Ittersum (a). a = Plant Production Systems Group, WageningenUniversity, 6700 AK Wageningen; <math>b = PBL EnvironmentalAssessment Agency, 3720 AH, Bilthoven; c = Dept. Earth Sciences–Geochemistry, Faculty of Geosciences, Utrecht University, 3508 TA, Utrecht - The Netherlands

# **Quantification of phosphorus flows (1) Phosphorus balance for France**

Phosphorus flows and balances were evaluated for France for 1990 – 2006 using a conceptual model with 25 internal and 8 external P-flows, quantified using substance flow analysis principles. If mineral fertilisers are considered to concern agriculture (not industrial), then the agricultural sector is much the largest user of phosphorus in France. Net soil phosphorus balance (difference between annual P input and output in crops) was however reduced from 18 to 4 kgP/ha/y over the 16 year period studied.

France has a typical developed country diet, and intense agriculture, with a human population of around 60 million and a farm animal population of 320 million.

# Agricultural phosphorus use

French agriculture received a net inflow of 533 000 tP/y, and agricultural soils received 778 000 tP/y including internal flows of manures and crop residues during the period 2002-2006. **40% of total P application in agriculture was from manures, 37% from mineral fertilisers,** 14% from crop residues and 9% from municipal wastewater biosolids application. Only 564 000 tP/y was removed from agricultural soils in crops.

213 000 tP/y phosphorus in animal feeds came from crops as fodder, of which 59% from grazing permanent grassland, 21% from temporary (cultivated) pasture, 15% from fodder maize. 177 000 tP/y in animal feeds came from concentrate feed, and among them 113000 tP/y as imported mineral phosphorus feed additives and oil cakes.

Inorganic phosphorus fertiliser use in France fell drastically over the 16 year period studied, from c 600 000 ktP/y (20 kgP/ha/y) to around 250 000 ktP/y (8 kgP/ha/y), resulting in a reduction of annual net soil P accumulation from 18 to 4 kgP/ha/y.

#### **Phosphorus inefficiency**

**Only around 119 000 tP/y reached households**, of which (at the time of the study data) with around two thirds in food products, and one third in detergents (the proportion in detergents would be much lower today) and 6% in other products (eg. pet foods). Around half the phosphorus in food products reaching households ended up in municipal refuse (over 40 000 tP/y).



SCOPE Newsletter - nº 93 - May 2013 - Page 7 www.ceep-phosphates.org



The authors estimate that 37 000 tP/y were actually consumed in food by the French population (1.7 gP/person/day).

#### Sewage phosphorus recovery

The **total phosphorus in municipal wastewaters** in France was estimated at 86 000 tP/y, of which around 45% came from human diet. The remainder is from detergents, small industries, kitchen wastes, urban runoff, etc.

For the years 2002 - 2006, 59% of sewage works biosolids were applied to land (eg. after composting), with 41% going to landfill with or without incineration. Thus only 24 000 tP/y were recycled from sewage back to farmland.

A total of 138 000 tP/y was estimated to be **lost to the environment**, of which around one third to surface waters from sewage works, one third to surface waters from agricultural run-off and soil erosion, and one third to landfill (sewage biosolids, municipal refuse).

#### Points for sustainable phosphorus management

The authors identify as potential areas for improvement in phosphorus management:

- reduction of food waste: around half the P in food reaching households is lost, and up to 80% of this loss is avoidable
- soil P efficiency increased considerably over the study period, with reduced mineral fertiliser inputs yet maintained or even increased crop productivity. Continuing this trend will be a challenge because although some French agricultural soils still have high phosphorus stocks, the soil P balances have already been considerably reduced.
- **P-losses to water bodies** need to continue to be reduced by improving sewage collection and treatment (nutrient removal and recycling) and by reducing agricultural soil erosion

"Conceptual design and quantification of phosphorus flows and balances at the country scale: The case of France", Global Biogeochemical Cycles, vol. 26 GB2008, 2012 http://dx.doi.org/10.1029/2011GB004102

K. Senthilkumar, T. Nesme, A. Mollier, S. Pellerin, UMR 1220 TCEM, INRA- Bordeaux Sciences Agro, CS 20032, 33882, Villenave d'Ornon, France senthilkumar.kalimuthu@gmail.com

# **Quantification of phosphorus flows (2)** Agricultural phosphorus use in 4 French regions

The authors of the national phosphorus balance study for France (see above) have also published an assessment of P in agriculture for France's 21 regions.

The study particularly looked at four regions:

- Centre: 65% farmland under monoculture of cereal, oilseed and leguminous plants (beans, pulses ...)
- Brittany (North West France): 57% of land under livestock production and 2.1 livestock unities/ha (compared to 0.3 – 0.6 for the other 3 regions)
- Lorraine (East France) and Aquitaine (South West): mixed farming regions

The methodology was similar to the above study of France, but only looked at farm animals, crops and soils, and their different inputs and outputs, assessing a total of 13 different flows. The period covered was the same 1990-2006.

#### **Soil budgets**

Data for French region's soil phosphorus stock and budget over this period showed **considerable differences between regions, and considerable variations over time**.

All of France's 21 regions showed positive soil P budgets from 1990 to 2000 (**net accumulation of phosphorus in the soil**), but some regions showed negative P budgets after that (including Centre), whereas other regions continued to show highly positive P budgets (including Brittany, Aquitaine). Soil P budgets showed significant short-term variations, for example the 2003 drought resulted in increases in soil P budgets because crop phosphorus uptake was reduced.

The overall trend over the 1990-2006 period for all regions was however towards lower P budgets, with the national average declining from 17.5 to 4.4 kgP/ha/year over the 16 years. This decrease in P budgets was the result of an increase in phosphorus outflows over the period (increasing crop production), a slight decrease in livestock numbers, but above all a **significant decrease in mineral fertiliser application**, thus corresponding to a general increase in soil phosphorus efficiency.

#### Livestock concentration in Brittany

Animal excretion phosphorus input to soils depended strongly on the farming system, varying for the four studied regions from 29.1 kgP/ha/year in Brittany





SCOPE Newsletter - nº 93 - May 2013 - Page 8 www.ceep-phosphates.org (livestock concentration) to only 4.2 kgP/ha/year in the Centre region. This resulted in a **high positive phosphorus balance in Brittany** of 18.9 kgP/ha/year. Importantly, soil P input from animal excretion was higher than crop uptake in this region. Nonetheless, an additional 7.9 kgP/ha/yr was applied through inorganic P fertilisers in Brittany, which is questionable.

The regional phosphorus flows and balances differed considerably between the four regions studied, corresponding to the farming system and the **prevalence of livestock** in Brittany. Inflow of phosphorus to Brittany in animal feeds was nearly 29 kgP/ha/year, compared to 2 -6 kgP in the other 3 studied regions. Outputs in animal products were 12.3 kgP/ha/year in Brittany compared to 1 - 2 kgP in the other regions. Losses in leaching and soil erosion were similar in the four regions, totalling 1.2 - 2.1 kgP/ha/year.

Considerable differences between the two mixed farming regions, Aquitaine and Lorraine, for example in mineral fertiliser application rate and phosphorus budget, showed that there are **no simple rules for 'anticipating' phosphorus flows**, which can **depend on local factors** such as the proportion of highfertiliser application crops (eg. fruit and vegetables) or local segregation of animal and crop production areas (preventing local recycling of animal manures).

The authors conclude that **national**, **or even regional**, scale **nutrient flow studies can overestimate recycling feasibilities**, by neglecting local-scale variability. They emphasise the need to study nutrient cycles and budgets at multiple scales.

"Regional-scale phosphorus flows and budgets within France: the importance of agricultural production systems", Nutr Cycl Agroecosyst (Springer), n° 92, pages 145–159, 2012.

K. Senthilkumar, T. Nesme, A. Mollier, S. Pellerin, INRA and Bordeaux Sciences Agro (Univ. Bordeaux), UMR 1220 TCEM, 33883 Villenave d'Ornon, Cedex, Gironde, France senthilkumar.kalimuthu@gmail.com

# **Urban phosphorus flows**

Fate of phosphorus in food and municipal wastes

A P-flows study in Gothenburg, Sweden (published 2012), indicates that around half of phosphorus imported into the urban area is in foods and beverages, and that the amounts of phosphorus in sewage sludge and solid waste residues are similar. Solid waste streams should not therefore be ignored, whereas Sweden's Precycling goal targets only phosphorus in wastewaters (see below). Impacts of five different scenarios for waste management were assessed. In a second study (published 2013) phosphorus extraction for Precovery is tested from municipal waste incineration fly ash by different acid and/or alkaline leaching and precipitation steps.

The P-flows study assessed phosphorus flows into and within the urban area in foods and beverages, detergents and personal care products, pet foods, newspaper and packaging, deposition and runoff, agriculture, food wastes, wastewater collection and treatment, municipal solid waste collection and treatment. The studied Gothenburg urban area has a population of 917 000, and a number of industries including chemicals, food processing and dairies, automobile and metals industries ... and some agriculture.

#### **Urban phosphorus flows**

P in human diets was estimated at 235 tP/year, using figures of 1.2 gP/day for women and children and 1.5 gP/day for men, based on data estimated for the Swedish city of Malmö (Welch et al. 2009). Additionally, food waste was estimated at 5-10% in retail and distribution, and 20 - 33% within households (Skjöldebrand 2008), giving a total of 100 tP/year. Phosphorus in detergents was estimated at 44 tP/year (2010 data, the figure will today be lower), plus 3 tP/year in personal care products. Inflows of phosphorus into the urban area in pet foods are estimated at 28 tP/year. Inputs to the urban area's agriculture as fertilisers was estimated to be 16 tP/year, and in animal feeds and fodder 1 tP/year. Other inputs (newspaper, packaging, atmospheric deposition) total c. 10 tP/year.

**Phosphorus flows to sewage works** were derived from operator data for connected populations and phosphorus monitoring in sewage, treated sewage (outflow water) and in sludges.

**Phosphorus flows in solid waste** collected and treated by the municipalities were estimated from the phosphorus flow data, local data on collection rates, and national data on waste sorting and separation and on phosphorus concentrations in food wastes (estimated 35% dryness and 0.4% P/dry matter). In the urban area, collected solid waste was treated in one waste-fuelled domestic heating plant (incinerator), one composting plant and two landfills.

Calculation of missing phosphorus flows were used to correct the estimated P-flow figures.



CEEP Centre Européen d'Etudes des Polyphosphates

SCOPE Newsletter - nº 93 - May 2013 - Page 9 www.ceep-phosphates.org

# Importance of P-flows in municipal solid wastes

The assessment concludes that the quantities of phosphorus ending up in municipal solid waste is approximately the same as that in sewage (both c. 40% of total inflows/outflows). This phosphorus is currently lost for the part going to incineration (then landfill of ashes), or recycled for the part going to composting. The largest flow of phosphorus to municipal solid waste is **food waste**: at the time of the study, only c. 20% of food waste was collected separately (this will today have improved with installation of a biogas plant and increasing separate collection).

#### Sweden national P-recycling objective

The authors conclude that **in urban settings the phosphorus flow in municipal solid waste is significant**, and should be taken into account in the Sweden national objective for phosphorus recycling which currently only addresses phosphorus in wastewater as follows:

"By 2015 at least 60% of phosphorus compounds present in wastewater will be recovered for use on productive land. At least half of this amount should be returned to arable land." De Facto 2007 http://www.naturvardsverket.se/Documents/publikatione r/620-1259-2.pdf

#### Waste management scenarios for P-stewardship

Five different scenarios for waste management were assessed for their implications for P-recycling: incineration of all food waste (base scenario, close to the existing system at the time of the study), separate collection of 70% of food wastes, installation of kitchen grinders (consumer food waste mixed into municipal wastewater), urine diversion, separation of blackwater (toilet wastes) and food wastes.

The **separate collection of 70% of food wastes** (retail and consumer) resulted in a 'saving' of 88 tP/year (compared to the base scenario).

A similar quantity of phosphorus could be recovered (additionally to the food waste) by **urine diversion and reuse/processing into fertiliser**. This would also reduce discharges to surface waters from the sewage works by an estimated 10 tP/year.

Widespread installation of **food grinders in households and small businesses** (restaurants, schools, hospitals, etc.) is estimated to divert 80% of food waste into municipal wastewater, that is 72 tP/year, of which 7 tP/year would reach surface waters. This scenario would not increase phosphorus recycling at present, because the sewage sludge is considered too contaminated for agricultural use.

**Blackwater diversion combined with food waste separation** could enable 245 tP/year to be recycled, as well as reducing P losses to surface waters by 20 tP/year. The authors indicated that this assumes the combined stream was processed to produce a fertiliser material, for example by adding urea or ammonia to remove pathogens. This stream would have negligible contaminants and so would be acceptable for agricultural use. Given the limited agriculture within the urban area, this would necessitate the export of most of this fertiliser product to farmland outside the urban area.

#### Phosphorus extraction from fly ash

The 2013 study presents **tests of phosphorus extraction from Gothenburg municipal waste incineration fly ash**. 3 samples of electrostatic filter ash from the solid municipal waste incinerator in Gothenburg indicated above, during normal operation in which lime was not added to the filter system.

**The ashes showed c. 0.6% phosphorus content**, significantly lower than contents of aluminium (3%) and iron (2%). The ash had high calcium content (14%) and only 4.5% silicon.

Two leaching – phosphorus recovery processes were tested:

- Acid leaching, using hydrochloric acid at varying concentrations (1 3 molar) and times (2 24 hours), followed by sequential precipitation of phosphate from the leachate at pH 3 and 4 (by sodium hydroxide titration)
- Acid leaching at pH4 (using 1M hydrochloric acid), followed by alkaline leaching of the remaining ash residue at pH 11 13 (using 1M sodium hydroxide) to generate a phosphorus-rich solution

In the first method, acid leaching generated leachates with phosphorus concentrations of up to 6%, the optimum being with 2M HCl and 24 hours, that is over 90% leaching of phosphorus from the ash. However, heavy metals such as arsenic, cadmium, copper, lead and zinc were also leached at high % levels.

The objective of the pH3 and pH4 precipitation in the first method was to first precipitate iron and aluminium, and then (at pH4) phosphate. However, although 67% of initial ash phosphorus was precipitated in the second precipitate, so were also 22% of aluminium and 60% of iron, and also high





SCOPE Newsletter - n° 93 - May 2013 - Page 10 www.ceep-phosphates.org proportions of arsenic, tin, chromium and zinc (but only low proportions of cadmium, copper, lead). The final precipitate produce contained around 3% phosphorus, which comparable to very low grade phosphorus rock.

The second method showed to be ineffective, in that only 0.1% of the phosphorus in the ash (after acid leaching) was released by the alkaline leaching phase, even at very high pH (pH 13).

"Pathways and Management of Phosphorus in Urban Areas", J. Industrial Ecology (Wiley), vol. 16, n° 6, pages 928-939 http://onlinelibrary.wiley.com/doi/10.1111/j.1530-9290.2012.00541.x/pdf open access

Y. Kalmykova, R. Harder, H. Borgestedt, I. Svanäng, Water Environment Technology, Civil and Environmental Engineering, Sven Hultinsgata 8 Gothenburg, 41296, Sweden. yuliya@chalmers.se

"Phosphorus recovery from municipal solid waste incineration fly ash", Waste Management (Elsevier), in print 2013: http://dx.doi.org/10.1016/j.wasman.2013.01.040 open access

Y. Kalmykova, as above, K. Fedje, Renova AB, SE-401 22 Gothenburg, Sweden

# Life cycle assessment Sewage sludge and P-recovery

Four existing routes for utilisation of digested sewage sludge from the Henriksdal municipal works, Stockholm, Sweden, sewage were subjected to Life Cycle Assessment (LCA) looking at primary energy, global warming impacts, acidification, eutrophication and finite resources consumption: land restoration after mining (Boliden), composting with other materials then application on golf courses (Econova), agricultural spreading after storage to ensure sanitation (Ragn-Sells) and supercritical water oxidation followed by acid extraction to produce iron phosphate (Aqua Reci - Chematur AB, Feralco AB).

The sewage treatment and sludge digestion processes are not considered in this LCA, which starts with the Henriksdal digested sewage sludge. This digested sludge has a dry solids content of 27% (73% water) and 56% of solids are organics. For specifications of the Henriksdal sewage works and sludge, see the full inventory report available on request, in Swedish.

In the **Boliden** case (land restoration after mining), the digested sludge is spread without further treatment in a 20 cm layer on mined land, replacing the use of excavated moraine material. Nutrients (N, P) present in the digested sludge are considered to substitute mineral

fertilisers which would be required to build up fertile soil from the moraine.

In the **Econova** case (composting for use on golf courses), the digested sludge is co-composted with biofuel combustion ashes and forestry industry wastes (bark, fibres, biosludges) then transported to golf courses and spread in a 10 cm layer. It is considered to replace excavated topsoil with added mineral fertilisers.

In the **Ragn-Sells** case, the digested sludge is stored for 7-10 months to ensure hygienisation then transported to farmland where it is spread. The digested sludge nutrients are considered to replace mineral fertilisers, calculated on the basis of an assumed plant availability of 70% for the sludge phosphorus.

In the Aqua Reci process (Chematur, Feralco), the digested sludge is treated in a reactor at temperature (>370°C), pressure (>220 bars), under oxygen addition, and with energy recovery. Exhaust gas is treated to remove NO<sub>x</sub> emissions, but all nitrogen nutrient value of the sludge is lost. Sulphuric acid and magnesium oxide (to raise pH) were then considered to be used to extract phosphate from the process residue, resulting in 0.18 tonnes of ferric phosphate per tonne of dry sludge solids treated. This iron phosphate is considered to be a phosphate fertiliser, with 70% plant availability of the phosphorus: this figure is based on Pettersson G (Master Thesis, 2001, see references below).

#### **Greenhouse emissions**

Although most **biogas emissions** will have taken place and been collected as methane production during the sludge digestion (upstream of this LCA), the three digested sludge spreading / composting scenarios nonetheless result in some methane emissions and these are calculated in this LCA.

On the other hand, the value of the organic carbon addition to soil is not taken into account.

Possibly more important are **emissions of N<sub>2</sub>O** to air from digested sludge (global warming potential). In the study they are considered in one high emissions scenario and in one low emissions scenario. For these spreading / composting scenarios, part of the digested sludge nitrogen will result in NH<sub>3</sub> losses to air (acidification and eutrophication) or NO<sub>3</sub> losses to water (eutrophication).

However, the **replacement of mineral nitrogen fertilisers** avoids the nitrogenous greenhouse gas emissions from soil related to their use, and this is estimated.





SCOPE Newsletter - nº 93 - May 2013 - Page 11 www.ceep-phosphates.org

#### **Best environmental options**

The Boliden case shows a positive environmental assessment, largely through avoidance of moraine extraction and transport. This is however a specific mine, and not generalizable.

The Aqua Reci process offers the lowest impacts, in particular because of energy recovery from the digested sludge. The energy is assumed to be utilized as district heating in the surrounding areas.

One key finding from the study is that **biogeochemical emissions of, for instance methane and N<sub>2</sub>O from digested sludge may have much larger impact** on the impact assessment results than the core technical systems. In all core systems, digested sludge transport was a key factor of overall environmental impact. This, in combination with the energy recovery contributed strongly to the advantages of the Aqua Reci process where the digested sludge was treated on site.

#### **Nutrient recycling**

Recycling rates for the sludge nitrogen content range from 0% (Aqua Reci) to 42% (agricultural spreading). P-recycling rates were generally considered to be 70%.

A P-resource index of 0.005613/year (B. Albertsson et al. 1997) was used, because no index is included in the base data set for phosphorus.

The additional P-recovery stage implies a significant environmental burden in the Aqua Reci process, principally because of the ecological impacts of producing magnesium oxide, used to increase pH.

"Sewage sludge handling with phosphorus utilization - life cycle assessment of four alternatives", Journal of Cleaner Production, 16, pages 135 -151, 2008 www.elsevier.com/locate/jclepro

K. Johansson, M. Perzon, M. Svanström, Chemical Environmental Science, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. M. Fröling, Laboratory for Energy and the Environment, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA. A. Mossakowska, Environment and Development, Stockholm Water Co., SE-106 36 Stockholm, Sweden magdalena.svanstrom@chalmers.se

G. Pettersson, Master Thesis, Chalmers University of Technology, Göteborg, Sweden, 2001 "Life Cycle assessment of four sludge treatment methods" (Livscykelanalys av fyra slamhanteringstekniker, in Swedish) http://boffe.com/rapporter/Avlopp/Slam/ESA2001\_4.pdf

# Food waste aerobic composting Struvite precipitation and nitrogen loss

Aerobic compositing of food wastes is an efficient route to convert to a stable humus-like form, which can be used as a soil amendment. Nitrogen losses during aerobic composting (mainly as NH<sub>3</sub>) can however be considerable, resulting in decreased agronomic value of the compost, odour problems and greenhouse emissions. Addition of soluble phosphate and magnesium to induce struvite precipitation in the compost has been shown to be a route to reduce nitrogen losses (Jeong & Kim, 2001).

In this study, four 30 litre laboratory composters were tested, using real mixed foods. Compost stabilisation was achieved after 25 days.

#### **Different phosphate salts**

Three different soluble phosphates were tested for phosphate addition, in each case along with MgSO<sub>4</sub> (soluble magnesium), and compared to a control (no phosphate or magnesium added):

- K<sub>3</sub>PO<sub>4</sub>
- K<sub>2</sub>HPO<sub>4</sub>
- KH<sub>2</sub>PO<sub>4</sub>

The three phosphate compounds release zero, one or two  $H^+$  ions per molecule of struvite (hydrate) formed MgNH<sub>4</sub>PO<sub>4</sub>.6H<sub>2</sub>O. This results in **different pH developments in the composters, significantly impacting NH<sub>3</sub> emissions**: at higher pH, NH<sub>4</sub><sup>-</sup> ions tend to take up H<sup>+</sup> ions, releasing NH<sub>3</sub> gas and decreasing NH<sub>4</sub> available for struvite precipitation.

Temperatures also differed in the composting vessels: higher temperatures are likely to lead to increased NH<sub>3</sub> volatisation, and also to higher struvite solubility (reduced struvite precipitation).

**Microbial activity is also important** and the results show that this activity (as measured by OCR – oxygen consumption rate) was correlated to temperature and to N losses.

Results show that nitrogen losses with  $K_3PO_4$  were higher than the control (no P or Mg addition), as was the % degradation of organic matter (loss of organic carbon). With  $K_2HPO_4$ , nitrogen losses were reduced from c. 21% (control) to 13%, and with  $KH_2PO_4$ nitrogen losses were even lower (<4%).



SCOPE Newsletter - nº 93 - May 2013 - Page 12 www.ceep-phosphates.org



X-ray diffraction confirmed that **struvite crystals** were precipitated in the three composters to which P and Mg were added, but not in the control.

"Nitrogen Conservation in Simulated Food Waste Aerobic Composting Process with Different Mg and P Salt Mixtures", Journal of the Air & Waste Management Association, n° 61-7, pages 771-777, 2012 http://dx.doi.org/10.3155/1047-3289.61.7.771

Y. Li,B. Su, J. Liu, X. Du, Research Academy of Energy and Environmental Studies, North China Electric Power, University, Beijing, People's Republic of China. G. Huang, Environmental Systems Engineering Program, Faculty of Engineering, University of Regina, Regina, Saskatchewan, Canada liyuxx@jlu.edu.cn

References cited: Y. Jeong & J. Kim, "A New Method for Conservation of Nitrogen in Aerobic Composting Processes", Bioresource Technol., 79, pages 129-133, 2001.

## Zirconium ferrite

# P-recovery by adsorption/desorption and magnetic separation

Zirconium ferrite can be used to remove soluble phosphate from solution (by adsorption), then release the phosphate potentially for phosphorus recycling (desorbtion in sodium hydroxide). It offers the advantage that it can be used as a powder, offering a high surface area and avoiding the need for structural support resins used with most ion exchangers, because it can be separated from treated wastewater using a magnetic field.

Laboratory experiments using 100 ml flasks of phosphate solution were carried out. 0.9 mgP/l pure potassium phosphate solution and **treated sewage effluent** (before chlorination) with 1.1 mgP/l phosphate concentration were tested.

Zirconium ferrite (ZF) was tested in two forms: particles with a resin binder, powder. Before use, the ZF was magnetised by exposure to a magnetic field. The magnetised ZF was then stirred in the phosphate solution, to adsorb phosphate. It was then separated from the solution in a separate vessel using a 10T high magnetic gradient superconductor magnetic field.

The powdered ZF showed better phosphate removal and adequate **magnetisation and magnetic separation**, and so was used for the principal experiments.

500 mg/l of ZF enabled **91% phosphate removal** from the solutions in 15 minutes and 80% in just one minute. Performance was similar in the real wastewater plant effluent to with the pure solution, suggesting that the process was not significantly hindered by other ions present in the wastewater. Magnetic separation of the ZF (with bound phosphate) was demonstrated to be effective by filtering the residual solution and showing lack of magnetisation.

#### 84% of the adsorbed phosphate could then be recovered by desorption using 7% sodium hydroxide (in 60 minutes).

The authors conclude that using zirconium ferrite as a ferromagnetic adsorbent/desorbent can enable reduction of phosphorus concentrations in wastewater discharge effluent from >1 mgP/l to 0.1 mgP/l and **recovery for recycling of the removed phosphorus**.

"Removal and recovery of phosphorus in wastewater by superconducting high gradient magnetic separation with ferromagnetic adsorbent", Physica C, vol. 470, pages 1818–1821, year 2010 www.elsevier.com/locate/physc

T. Ishiwata, O. Miura, K. Hosomi, K. Shimizu, D. Ito, Graduate School of Science and Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan and Y. Yoda, Bureau of Sewerage Tokyo Metropolitan Government, 2-8-1 Nishishinjyuku, Shinjyuku, Tokyo 163-8001, Japan. T. Ishiwata, current address: Applied Superconductivity Lab., Tokyo Metropolitan University, 315, Bldg#9, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397 offspring0210@yahoo.co.jp

### Novel P-recovery from wastewaters Amorphous calcium silicate hydrates (A-CSHs)

Amorphous calcium silicate hydrates (A-CHSs) can be readily synthesised from readily available, cheap siliceous sands and calcium hydroxide. A-CSHSs were tested for phosphorus recovery from anaerobic sludge digester liquor (from Toyonaka City wastewater treatment plant, Osaka, Japan) and from pure chemical solutions, looking at Premoval and at dewatering/filterability of the phosphorus containing product generated. The recovered product could be directly used as a Performance compared fertiliser. was to autoclaved lightweight concrete ALC particles (crystalline calcium silicate).

A-CHSs were synthesised from M-rite (a **natural** siliceous shale, containing cristobalite / porcelanite, a high temperature polymorph of silica) and calcium hydroxide Ca(OH)<sub>2</sub>. The M-rite was treated with 0.5% sodium hydroxide to release soluble silicates, to which calcium hydroxide was added at a Ca:Si molar ratio of 3.5. After 3 hours reaction, the precipitate was filtered and dried at 100°C. Free calcium hydroxide was removed from the A-CHSs by washing then drying. The A-CHS and ALC particles were characterised by X-ray diffraction, transmission electron microscopy and for calcium release (stirring in water).



SCOPE Newsletter - nº 93 - May 2013 - Page 13 www.ceep-phosphates.org



The A-CHS-s showed slightly smaller particle size than the ALC, but surface area 1.3 - 1.8 times greater. The Ca:Si ratio in the washed A-CHSs was around 2, that is 4 times higher than for ALC.

#### **Phosphorus adsorption**

A-CHS and ALC were tested for phosphorus removal in stirred beaker tests using 1.5g of product per litre, in both **anaerobic sludge digester liquor** (soluble phosphorus concentration c. 90 gP-PO<sub>4</sub>/l), and in synthetic liquor made of potassium phosphate, ammonium chloride and sodium carbonate in solution adjusted to pH 7.6.

After the 20 minute P-adsorption phase, the beakers were settled for 10 minutes, 90% of supernatant drawn off, and the remainder filtered at  $0.45\mu$ m. Dewaterability was assessed by then drying the filter cake at 100°C for two hours and measuring weight loss.

At 1.5g/l dosage, A-CHSs achieved **55% P-removal from the real sludge liquor after 5 minutes stirring,** increasing to 59% with 20 minutes stirring (73% P-removal from the synthetic liquor). ALC particles also achieved good P-removal rates, but only at much higher doses (80% P-removal after 20 minutes, for 10x higher dosage: 15g ALC/l) but this would correspond to 10x lower phosphorus content in the recovered product.

Experiments with the synthetic liquor showed that increasing the carbonate concentration did not significantly reduce the phosphorus adsorption by the A-CSHs (13% reduction for 5 g NaHCO<sub>3</sub>/l).

#### **Phosphorus recycling**

The washed A-CHSs (removal of free calcium) showed slightly lower phosphorus removal rates, indicating that the key mechanism was indeed adsorption and not calcium phosphate precipitation.

The experimentally derived Langmuir adsorption isotherms corresponded well to the results in real and synthetic sludge digestion liquors, with a phosphorus adsorption capacity of around 87mgP/gA-CSH (that is 8.7%P by weight) and 20 mgP/gALC (2%P).

The A-CSHs after phosphorus adsorption showed good settling and dewatering properties, with nearly all the adsorbed phosphorus being settled after 10 minutes, and faster dewatering and a lower water content after filtration than for phosphate precipitated as hydroxyapatite using calcium carbonate addition.

The authors conclude that A-CHSs can adsorb phosphorus effectively from wastewater liquors in a reasonably short reaction time, and can then be recovered because of good settling and dewatering properties. No use of chemical coagulants or expensive ion exchange resins is necessary. Because the A-CHSs can be produced cheaply from widely and unlimitedly available materials, **they can be used directly as a phosphate containing fertiliser** (a phosphorus desorption step is not necessary).

A pilot scale demonstration plant is now being constructed in a municipal wastewater treatment plant.

"Novel technique for phosphorus recovery from aqueous solutions using amorphous calcium silicate hydrates (A-CSHs)", Water Research (Elsevier), in print, 2013 http://www.sciencedirect.com/science/article/pii/S0043135413001 05X

K. Okano (a), M. Uemoto (a), J. Kagami (a), K. Miura (b), T. Aketo (b), M. Toda (c), Kohsuke Honda (a), H. Ohtake (a). a = Dept. Biotechnology, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. b = Research & Development Center, Taiheiyo Cement Co., 2-4-2 Osaku, Sakura, Chiba 285-8655, Japan. c = Research & Development Laboratory, Onoda Chemical Industry Co., Ltd., 39-13 Miyamoto-cho, Itabashi-ku, Tokyo 174-0054, Japan. okano@bio.eng.osaka-u.ac.jp

# Sewage sludge incineration ash Acid extraction from ashes

Municipal sewage sludge incineration ash products from two Danish mono-incineration plants (that is incinerating sewage sludge only, not mixed with other wastes) were used to test phosphorus extraction using sulphuric or nitric acid at room temperature and pressure. Results showed differences between the two ashes, related to the use of aluminium or of iron for phosphorus removal in the sewage works, and of mixing of bottom ash with flue gas cleaning residues. Heavy metals contents in the ashes were low but were extracted by the acids, and would require a separation process.

The ashes tested came from the MRL Molleavaerket Renseanlaeg Lundtofte facility, mono-incinerating sludge from a 135 000 person equivalent sewage works using aluminium salts for phosphorus precipitation, and SAH Spildevandscenter Avedore Hvidore, mono-incinerating sludge from a 330 000 pe sewage works using iron salts. In both cases, flue gas cleaning residues are mixed with the ash containing sodium bicarbonate and activated carbon (MRL) or lime (SAH).

#### **Phosphorus content**

The ash products contained 7 - 10% phosphorus (P). The LoI (loss on ignition = organic content) was very





SCOPE Newsletter - n° 93 - May 2013 - Page 14 www.ceep-phosphates.org low in the SAH ash (0.2%), indicating good incineration performance, but higher in the MRL ash (5.7%, probably because of the activated carbon in the flue gas cleaning residues).

The SAH ash contains 5.8 % iron, the MRL ash 6.7% aluminium.

Both ashes had pH of around 10, but the MRL ash was 10x more soluble in water and produced 10x more gas when reacted with acid.

#### pH for acid P extraction

With nitric acid, the pH needed for phosphorus extraction from the ashes was significantly different. For the MRL ash (aluminium rich), nearly no P-extraction showed down to pH of around 2, but 80% extraction of P and 50% of aluminium were noted at pH 1.7. For the SAH ash (iron rich), on the other hand, some P extraction occurred even at pH5 increasing to nearly 100% at pH1. At pH2, phosphorus extraction was higher from the MRL than the SAH ash.

The MRL ash showed a significantly higher buffering capacity, so **requiring more acid to achieve extraction pH**, and this may be due to both the presence of aluminium (rather than iron) and the presence of c. 5% activated carbon from flue gas cleaning.

Longer extraction times tended to increase heavy metal extraction more than it increases P extraction, but in any case **it is expected that a heavy metal separation process will be required** if the extracted phosphorus is to recycled.

Sulphuric acid is the cheapest mineral acid, but when it is used for acid extraction, calcium is also released from the ash, producing gypsum (calcium sulphate) precipitation, which increases waste volumes.

"Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminium" Chemosphere, vol. 91, Issue 7, pages 963– 969, May 2013 http://www.sciencedirect.com/science/journal/00456535

L. Ottosen, G. Kirkelund, P. Jensen, Dept. Civil Engineering, Building 118, Technical University of Denmark, 2800 Lyngby, Denmark lo@byg.dtu.dk

### Conferences

# Agadir, 6 – 10 May 2013 SYMPHOS

#### www.symphos.com

OCP is organizing the **2nd International Symposium on Innovation and Technology in the Phosphate Industry**. This symposium aims at becoming a leading event for the industry, manufacturers and equipment suppliers, technology and services, and R&D in areas related to the transformation of phosphates and derivatives.

Topics: phosphate extraction, enrichment and handling, sulphuric and phosphoric acid processing, fertiliser and phosphate chemical technologies, environment and sustainable development, water and energy consumption, management and use of by-products (sludge, phosphogypsum) ...



# Antwerp, 6<sup>th</sup> June 2013 Nutrient and Recycling RRB-9

#### http://www.rrbconference.com/call-abstractsnutrient-energy-cycling

- Nutrient (N-P-K) recovery from waste(water) / manure / digestate
- Renewable biobased fertilizers in substitution of conventional fossil-based mineral fertilizers
- Closing loops by decentralized processing of wasteto-energy in small-energy-systems
- Optimizing nutrient & energy cycling in the modern agro-industry
- Sourcing inorganic bulk chemicals from organic based waste(water)stream
- Biogas installations as renewable refineries
- Recovery of organic carbon for valorization as soil enhancer
- Recovery and re-use of water from wastewater treatment systems





SCOPE Newsletter - n° 93 - May 2013 - Page 15 www.ceep-phosphates.org



# Beijing, 18-20 June 2013 Global TraPs world conference



#### www.globaltraps.ch

The Global **Transdisciplinary Processes** for Sustainable Phosphorus Management (Global studying phosphorus TraPs) project is 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



Agenda

- 14-16 May, Washington DC: US National Science Foundation Research Coordination Network (RCN)
  Coordinating Phosphorus Research to Create a Sustainable Food System
  http://sustainability.asu.edu/research/project.php?id=704
- 31 May, Basel, Switzerland: P-Rex WA5 Europe wide implementation of P-Recovery market, legislation, regional & societal barriers www.p-rex.eu
- ✤ 4-6 June, Fulda, Germany : Klärschlammtage http://de.dwa.de/klaerschlammtage.html
- 5-7 June, Antwerpen: "Renewable Resources & Biorefineries" conference (RRB-9) http://www.rrbconference.com/call-abstracts-nutrient-energycycling
- 18-19 June, Strasbourg: Efficient Sludge Treatment (VDI = Ass. German Engineers) http://www.vdi.eu/media-services/article/efficient-sewagesludge-treatment/
- \* 18-20 Jun, Beijing: Global Traps www.globaltraps.ch
- 25-28 June, Santiago de Compostela, Spain: 13° world congress on anaerobic digestion – Recovering (bio) resources for the world www.adl3.org
- 28 31 July, Vancouver: IWA Nutrient Removal and Recovery http://www.wef.org/nutrients/
- ✤ 16-17 September: Poderbrady, near Prague: P-REX assembly (16<sup>th</sup>) and (17<sup>th</sup>) stakeholder workshop 'Market and Legislation' www.P-REX.eu
- 5-6 December, Bruges: ManuResource 2013 (International conference on manure management and valorisation) http://www.manuresource2013.org/registration
- 2014 25 Aug 3 September (to be defined) 4th world Sustainable Phosphorus Summit http://sustainablepsummit.net/

### **Nutrient Platforms**

Europe: www.phosphorusplatform.org Netherlands: www.nutrientplatform.org Flanders: dh@vlakwa.be



Centre Européen d'Etudes des Polyphosphates SCOPE Newsletter - n° 93 - May 2013 - Page 16 WWW.ceep-phosphates.org