

Iron – phosphorus interactions and P stewardship

This special issue **SCOPE Newsletter** is a summary of the webinar "Iron – phosphorus interactions and opportunities for phosphorus stewardship", $13^{th} - 14^{th}$ July 2020, at which over 400 people participated. The webinar was organised in four sessions:

- 1) Iron phosphorus interactions in natural and engineered systems
- 2) Iron phosphate in agriculture
- 3) P-TRAP Poster session
- 4) P release and recovery from iron phosphates -Impact of iron on industrial P-recovery processes

In this Newsletter, all to the webinar content is included, but it is grouped according to the key themes identified during discussion. Webinar speakers' presentations and online discussions are complemented by summaries of some recent relevant scientific papers.

This webinar was co-organised by <u>ESPP</u> with <u>WETSUS</u>, <u>INCOPA</u>, <u>INRAE</u> Rennes and the Horizon 2020 projects <u>P-TRAP</u> and <u>SUSFERT</u>. <u>Slides and other webinar documents</u> are here: <u>https://phosphorusplatform.eu/ironphosphate</u> Full video recordings of the webinar can be seen on ESPP's YouTube channel: <u>https://www.youtube.com/channel/UCMid-39AIMT-3pzjoY58qiQ</u>

Struvite update

This SCOPE Newsletter also includes an update summary of published studies assessing the <u>agronomic value of struvite</u> as a fertiliser (updating information in previous SCOPE Newsletters).

Editorial & Conclusions
Iron salts for P-removal from wastewaters
Industrial applications of iron phosphates
Iron – phosphorus interactions in the aquatic
environment4
Iron – sulphur interactions in aquatic systems
Vivianite in marine coastal sediments5
Trapping P from agricultural run-off5
P-TRAP: perspectives for iron-based P traps
Field testing of iron-based P trap systems
R&D into P-trap systems and materials8
Iron-based P-adsorbents
Recovering P from iron phosphates11
Biological P-release from iron phosphate in sludge 11
Impacts of iron on P-recovery processes
Electrodialysis 12
Phos4Life13
RecoPhos13
"Get More P" 13
Euphore
Parforce
Sulphide14
RAVITA HSY 14
Remondis Tetraphos15
EasyMining Ash2Phos
Outotec Ashdec
Iron – P interactions in soils and plant availability 16
Effects of iron on soil P plant availability

 Availability of P in chemical P-removal sludge
 17

 A new take on iron phosphate: Vivianite (Iron (II)
 18

 phosphate)
 18

 Vivianite recovery
 18

 Vivianite as a fertiliser
 19

 Biological & chemical understanding of vivianite
 20

 Vivianite as a fertiliser
 20

 Vivianite as a fertiliser
 20

 Transformation of vivianite in soils
 21

 Adsorbents: recent review papers
 22

 Update on studies of agronomic value of struvite
 24

 Struvite fertiliser tests – pot trials
 25

 Struvite dissolution and leaching in soil
 26

 Struvite and soil remediation
 27



European Sustainable Phosphorus Platform SCOPE Newsletter info@phosphorusplatform.eu www.phosphorusplatform.eu



Editorial & Conclusions

Iron-based coagulants are key to meet increasingly demanding P-removal requirements, necessary to improve water quality and to meet the obligations of the EU Water Framework Directive (2000/60) - see ESPP workshop on wastewater phosphorus removal 2019 in SCOPE Newsletter <u>n° 133</u>.

Climate change will accentuate these challenges for municipal wastewater treatment, but also for agricultural drainage runoff and for lake restoration. Better understanding of iron phosphate chemistry in different systems will help address this, because **interactions with iron are key to retention or release of phosphorus from sediments in water bodies**.

The effectiveness of iron or aluminium coagulants for chemical P-removal is proven. This is **the most widely used P-removal process in sewage works worldwide**, costeffective, safe, and with the benefit of also improving organic particulate removal.

Literature reviews summarised show **increasing interest in use of adsorbents for P-removal**, both in wastewater treatment and in P trap systems to remove P from agricultural runoff. Because iron offers high P binding capacity, low toxicity and ready availability, many such systems use iron-based adsorbents, e.g. iron-containing secondary materials, or biological secondary materials loaded with iron.

Magnetite (Fe₃O₄) has potential as a P-adsorbent because it can be magnetically separated and regenerated. Papers also suggest that iron-based adsorbents can be made more effective by combining with a second metal, such as manganese or titanium. See e.g. the AquAsZero FP7 project (below) which showed a ten times higher Padsorption capacity than magnetite and good regeneration on/P-recovery potential, or the well-proven GEH specific ferric hydroxide material (also below).

Today, however, the question is raised: **How to recycle phosphorus precipitated as iron phosphate** by coagulants, or from iron-based adsorbent systems?

- When iron coagulants are used for P-removal, is the P in sewage sludge plant available?
- Iron phosphate can be recovered as such: can it be directly used as a fertiliser? Or re-processed?
- In particular, can biological processes be developed to separate the P from the iron phosphate?
- How does iron in sewage sludge impact P-recovery technologies (from sewage sludge, or sludge incineration ash)?
- Can phosphorus be feasibly recovered from adsorbent regeneration solutions?

A significant new interest is in **vivianite**, i.e. **iron (II) phosphate**, whereas the forms produced in chemical Premoval are generally expected to be (amorphous) iron (III) (hydroxy) phosphate complexes. Recent R&D shows that vivianite can be significantly present in anaerobic digesters treating sewage sludge, it can be relatively easily separated and recovered (because it is paramagnetic) and may be effective as an iron and phosphorus fertiliser in some soils. Reprocessing of vivianite to separate and recover phosphorus may be easier than for iron (III) phosphate. Recovery of vivianite is now at a pilot scale and moving towards commercialisation.

Ludwig Hermann, ESPP President

A glossary of some relevant iron and phosphorus compounds

Vivianite = iron (II) phosphate [that is Fe^{2+}] = $Fe_3(PO_4)_2 \cdot 8H_2O$

Iron (**III**) **phosphate** [that is Fe^{3+}] = **strengite** FePO₄ when pure and crystalline, but is more generally found as (amorphous) iron (III) (hydroxy) phosphate complexes, e.g. **Santabarbaraite** $Fe_3(PO_4)_2(OH)_3 \cdot 5H_2O$ (see <u>here</u>) or **metavivianite** $Fe(III)_2(PO_4)_2(OH)_2 \cdot 6H_2O$

Other phosphates: stanfieldite Ca(Mg,Fe)₆(PO₄)₆, **merrillite** Ca₉NaMg(PO₄)₇, **hydroxyapatite** Ca₅(PO₄)₃(OH), **apatite** Ca₅(PO₄)₃(F,Cl,OH) (the same mineral as phosphate rock), a combination of hydroxyapatite, fluorapatite and chlorapatite

Struvite = magnesium ammonium phosphate NH₄MgPO₄· $6H_2O$. **Hazenite** = KNaMg₂(PO₄)₂· $14H_2O$. **K-struvite** = magnesium potassium struvite MgKPO₄· $6H_2O$.

Iron compounds: magnetite = iron oxide $Fe(II)_2Fe(III)O_4$ or simplified: $Fe_3PO_{4;}$ **iron oxyhydroxide** FeOOH; **iron hydroxides**: iron(II) hydroxide $Fe(OH)_2$, bernalite = iron(III) hydroxide $Fe(OH)_3$, lepidocrocite γ -FeOOH, ferrihydrite (Fe)₂O₃·0.5H₂O.



Iron salts for P-removal from wastewaters

Jean-Christophe Ades, <u>Kemira</u> and INCOPA (European Inorganic Coagulants Producers <u>Association</u>, a sector group of Cefic), presented the use of iron and aluminium coagulants in wastewater treatment.

These coagulants are metal salts (e.g. iron chloride or iron sulphate) used for "**chemical phosphorus removal**", enabling reliable respect of discharge consents of 0.2 mgP/l or lower (see summary of ESPP workshop on phosphorus removal and water policy, Liège, 2019 in SCOPE Newsletter <u>n°133</u>), necessary to protect surface waters from eutrophication.

Coagulants are also used in paper manufacturing, fertiliser production, drinking water treatment ...

Environmental benefits

Chemical P removal offers low operating costs, and environmental advantages. Coagulant dosing not only precipitates phosphorus, but also improves removal of small organic particles (COD/BOD and particulates), so further contributing to quality improvement of surface waters.

70% of EU coagulant production comes from secondary materials such as iron oxides or spent metal solutions from industry.

A study by IVL Sweden (see <u>here</u>) compared two chemical Premoval scenarios (pre- and simultaneous precipitation, i.e. dosing iron upstream or during secondary biological water treatment) to biological P-removal (EBPR), with two discharge consent scenarios (standard 1 mgTP/l or more stringent 0.3 mgTP/l).

This study concludes that **pre-precipitation chemical Premoval has significantly lower greenhouse emissions than simultaneous precipitation chemical P-removal, which is again lower than biological P-removal.**

This is largely because **chemical P-removal improves BOD/COD removal, so increasing the amount of carbon going to methane production** (anaerobic sewage sludge digester) in the scenarios studied.



Global Warming Potential ($kgCO_2$ -eq./m³ water treated) related to Premoval from sewage by chemical P-removal (pre- or simultaneous precipitation = PrePrec or SimPrec) or biological P-removal (Bio-P), for two discharge limits (baseline = 1, stricter = 0.3 mgTP/l). Study IVL Sweden, publication pending. The study also concludes that tighter discharge limit nearly doubles greenhouse emissions related to P-removal.

A key question is: how to recycle phosphorus "removed" (transferred to sewage sludge) by chemical P-removal? Because coagulants precipitate the phosphorus in a specific and concentrated chemical form (iron or aluminium phosphates), various P-recovery routes are possible:

- If coagulants are dosed as a 'tertiary' step (not as pre- or simultaneous precipitation), then iron or aluminium phosphate can be recovered directly with low organics content. Some tests suggest that iron phosphate recovered in this way can be an effective fertiliser, but there is ongoing agronomic discussion of this (see below)
- Iron phosphate materials recovered from sewage Pprecipitation can be treated chemically (or possibly biologically) to release phosphorus in a form which can be recovered for fertiliser or industry applications, whilst also recovering the iron salts which can be recycled back for use as a coagulant in sewage treatment
- If sewage sludge is mono-incinerated (incinerated not mixed with other wastes) then phosphorus can be recovered from the resulting sewage sludge incineration ash, where some recovery processes are able to separate P bound to iron in the ash.

Webinar discussion

Q: What levels of *P* and of iron are typically found in sewage sludge?

A: Phosphorus content of digested sewage sludge is usually around 2 – 3 % P (% dry weight), giving 7 – 11% in sewage sludge incineration ash, depending largely on the level of P-removal in the sewage works (see ESPP Phosphorus Fact Sheet)

Iron content of digested sewage sludge is generally 3 – 6 %Fe (% dry weight), but can be up to 8 – 9 % Fe (% dry weight in digested sludge) if iron is used for chemical P-removal to achieve very stringent discharge limits. Data on iron content of sewage sludges in several countries can be found in the following publications, showing iron concentrations from 2 to 300 gFe/kg dry solids. Typical levels may be around 40 – 70 g/kg for sewage works operating chemical Premoval to discharge consents of 1-2 mgP/l, or 100 – 150 g/kg for sewage works with high levels of iron dosing. See Wilfert et al. 2018

<u>https://doi.org/10.1016/j.watres.2018.07.020</u> and Korving et al. 2018 <u>https://doi.org/10.1007/978-981-10-8031-9_21</u>



Willem Schipper, industry consultant, outlined the significance of iron in the phosphate industry.

Iron phosphate, be it ferric = iron (III) or ferrous = iron (II), is not a significant phosphate product: not in any of the main phosphorus industry company's portfolio, not mentioned in market studies. There are however a few niche applications, e.g.:

- ferric phosphate (iron (III) phosphate) as a **molluscicide** certified for Organic Farming (<u>Neudorff Sluggo</u> contains 1% ferric phosphate). The ferric phosphate causes slugs and snails which consume the bait to stop feeding, and so die.
- Lithium iron phosphate, used as a cathode material in certain types of batteries (LFP). This is produced from very pure ferric phosphate. Because of the level of purity required, this ferric phosphate may only be produced from P₄ or would require intense purification for wet-route phosphoric acid.
- **Vivianite**, Fe₃(PO₄)₂.8H₂O, was historically used as a blue pigment for artists paints and is still available today, e.g. <u>here</u> or <u>here</u>.



Vermeer, De Koppelaarster (The Procuress), 1656, the blue-green in the carpet is vivianite (not the jug which is probably lapis lazuli)

It is to be noted that "iron phosphating" (deposit of an iron phosphate film on steel for rust protection, before painting, does not involve iron phosphate, and is achieved by treating the metal with phosphoric acid. The fate of iron present in phosphate rock will depend on the processing route

European Sustainable Phosphorus Platform

- **"Wet acid" route:** iron will either remain in the final product (e.g. fertilisers or animal feeds), or will be removed as a (non-phosphate) waste stream in purification (for final products e.g. detergent or human food phosphates)
- **P**₄ route (only c. 2-3 % of total world phosphate rock use): iron comes out of the P₄ furnace as a metal alloy **ferrophosphorus (FeP)**, a by-product for which markets are limited. If iron is present in significant amounts, it decreases the yield of P4 furnaces, negatively affecting energy use and economics.

Iron phosphate recovered from secondary raw materials is unlikely to find a place in the above niche markets.

Iron – phosphorus interactions in the aquatic environment

Lena Heinrich, Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Germany, explained how iron and phosphorus interact in freshwater systems and sediments, underlining the importance of the oxygen status of water.

She noted the possible **applications of this knowledge to lake management measures** preventing eutrophication by diminishing phosphorus release and stimulating lake sediments as a phosphorus sink.

If lake water is oxic (especially at the sediment – water interface) then iron is oxidised to insoluble iron (III) [hydr]oxides, which bind phosphorus and sink to the sediment. Within the sediment, where anoxic conditions prevail, this is reduced to soluble iron (II) and dissolved phosphate, both of which diffuse deeper into the sediment and also back to the sediment surface and the water. However, so long as the water is oxic at the sediment surface (sediment-water interface), the loss of phosphorus from the sediment will be blocked by oxidation as insoluble iron (III) [hydr]oxides.

Furthermore, the simultaneous release of phosphorus and reduced iron (II) under anoxic conditions in the sediment can lead to an **immobilization of phosphorus by vivianite precipitation**.

The examples of two lakes near Berlin are presented. In Lake Groß Glienicke, iron dosing in 1992 led to a long-term retention of phosphorus in lake sediment, with 80% of phosphorus in the sediments showing to be bound to iron, partly as vivianite. But in Plötzensee, iron dosing in 2000 did not lead to long-term phosphorus retention. In this lake, only 40% of phosphorus in sediment showed to be bound to iron. Instead, sulphur and pyrite (FeS₂) coincided with the accessory iron. Therefore, in order to achieve long-term phosphorus retention in lake sediments, the competing binding reaction of sulphur with iron needs to be included in the planning of lake management measures using iron.

Iron – sulphur interactions in aquatic systems

Caroline Slomp, Utrecht University, The Netherlands, also indicated that sulphur importantly impacts phosphorus retention in coastal marine sediments.

Over the long term, most phosphate in marine sediments is transformed to **carbonate fluorapatite**, a calcium phosphate mineral containing carbonate and fluorine, which is the basis of mined phosphate rock.

On shorter time scales, however, phosphorus in marine sediments is present in a range of additional phosphorus P forms. These are:

- **organic particles** containing phosphorus settled from the water column
- phosphorus bound to iron oxides
- phosphorus in vivianite.

The burial form of phosphorus in sediments is strongly affected by sulphate concentrations in the overlying waters.

When sulphate is reduced in anoxic sediments, S^{2-} can be released, which can transform iron oxide bound phosphate and vivianite to iron sulphides, with phosphate then being released to the porewater, and, possibly, to the overlying water.

Vivianite in marine coastal sediments

Recent studies show that a significant part of the phosphorus in marine sediments can be present as vivianite (iron (II) phosphate): e.g. 40 - 50% of total sediment P was present as vivianite at 20 - 50 cm depth below the sediment-water interface at a location in the Gulf of Bothnia, one of the northern basins in the Baltic Sea (*Egger et al., 2015:* <u>https://doi.org/10.1016/j.gca.2015.09.012</u> Open Access).

Vivianite is difficult to quantify, because standard analysis methods cannot distinguish it from iron (III) phosphates. In this study, a combination of different methods (micro-XRF, XANES, SEM, XRD), and embedding of crystals in resin followed by X-ray fluorescence examination was used to identify and quantify vivianite crystals. This led to a reliable estimation of vivianite as a proportion of phosphorus present in sediment samples.



Blue colour resulting from vivianite present in Baltic marine sediments.

The formation of vivianite in Bothnian Sea sediments may be related to eutrophication and resulting increased organic matter deposition, which has caused the SMTZ (sulphur



methane transition zone in the sediment) to move upwards, nearer to the sediment surface. In the SMTZ, iron oxides will be reduced to FeS (iron (II) sulphide). Below this layer there is available iron (reduced to iron (II) by methane), no competing sulphide and free phosphate, thereby enabling the formation of vivianite.

Note that the elevation of the SMTZ nearer to the sediment surface is also identified as a factor by which eutrophication may lead to increased aquatic methane emissions (see Myllykangas et al. in SCOPE Newsletter $n^{\circ}135$).

Importantly, lower salinities, as generally found in coastal zones, lead to higher rates of vivianite burial in sediments as demonstrated in a recent study by (*Lenstra et al. 2018* <u>https://doi.org/10.5194/bg-15-6979-2018</u>). This is the effect of a lower availability of sulphate when salinity is lower and hence less conversion of Fe(II) to FeS, allowing more Fe(II) to precipitate as vivianite.

Webinar discussion

Q: What levels of sulphur will inhibit iron retention in sediments?

A: Sulphur / iron ratios of 1 to 1.5 can significantly interfere with iron binding of phosphorus in sediments.

Q: how does organic matter in sediments impact iron phosphate retention? Complexation of iron to organic carbon might influence Fe-P coupling: Between 26 and 63 % of reactive Fe was directly bound to C_{-org} in coastal sediments. The proportion of reactive Fe complexed to C_{-org} increases with decreasing oxygen exposure. See Barber et al. 2017, Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. <u>https://doi.org/10.1038/s41598-017-00494-0</u>

Trapping P from agricultural run-off

P-TRAP: perspectives for iron-based P traps

Thilo Behrends, Utrecht University, The Netherlands, summarised the EU Marie Sklodowska-Curie Innovative Training Network <u>P-TRAP</u>, which started in March 2019.

P-TRAP aims to develop new methods and approaches to trap phosphorus (P) in drained agricultural areas and in lake sediments, with the aims of:

- reducing P run-off from ditches to surface waters or reducing internal P loading of eutrophic lakes
- recovering the trapped phosphorus for recycling.

11 projects in 7 countries will look at **using iron-rich byproducts from drinking water treatment**: where iron chemicals are used to purify drinking water (removing organics) and to prevent plumbosolvency.

P-TRAP is testing the use of these materials to remove phosphorus from drainage ditch water and at valorisation of the resulting P-enriched iron-containing materials as fertilisers, e.g. by microbial processes to improve phosphorus plant availability. This will include fertiliser testing of these materials.

The webinar included **short 'poster' presentations by five of the P-TRAP researchers**, these are summarised in the relevant sections of this Newsletter.

Field testing of iron-based P trap systems

The Netherlands

Stefan Jansen, <u>Deltares</u>, The Netherlands, presented experience **using iron oxide coated sand to remove P from drainage ditches** in Dutch flower-growing fields, where legacy P has accumulated in groundwater from past fertiliser use.

The iron oxide coated sand is a by-product of drinking water production and offers: low cost, good P retention and safety (no contaminant release).

Two P-removal systems have been installed in farm drains and operated for around two years, with a layer of iron oxide coated sand of ca 10 cm thickness around the drains.

80-90% soluble phosphorus removal can be achieved from the drain water, but removal of organic P is lower. Potential problems encountered include clogging and reductive dissolution of iron oxide. More knowledge about this is needed to assess robustness. Operating life of the iron oxide sand is estimated to be around 10 years, before it becomes P saturated.

P-TRAP poster

Victoria Barcala, Utrecht University and Deltares, summarised a farm scale field study of how P is transported from its application in the soil to surface waters. Future work on a P-trap system using a sedimentation pond and iron coated sand (ICS) filter was presented.

The installation was set up in 2018-2019 and monitored the main farm drainage ditch, groundwater, soil and ditch sediments. The P concentrations in the soil water were $0.05 - 0.13 \text{ mgP}_{total}/1$. The farm has iron-rich sandy soils and historic high manure application, so that today this phosphorus runoff continues despite balanced P input to crop P uptake. The water flow to the ditch is though the subsurface soil which has a high iron content and adsorbs P. Therefore, the P concentration in the ditch was just 0.02 mg/L



Future work presented included the construction of a P-TRAP system by ARCADIS. The system is a water retention pond with drains covered by ICS in the outlet. The particulate P is settled in the pond and the dissolved P adsorbed in the ICS filter. Iron coated sand is a by-product of drinking water treatment.

The study underway aims to assess this P-removal system fullscale in the field and make complementary column experiments in the laboratory, to better understand P-retention behaviour of ICS and to address challenges in removal efficiency caused by high velocities, low redox conditions, and the possibility of taking maintenance measures to improve the life span of the structure.

Publication summary:

Groenenberg et al. (2013) previously presented results of trials of an iron coated sand (ICS) P trap in a tulip field plant near Egmond aan den Hoef, The Netherlands.

The field was 420m x 200m with pipe drainage. No mineral fertiliser was used, but compost applied resulted in a P-surplus of nearly 20 kgP/ha/year compared to plant offtake. Soluble phosphorus in the pipe drains from the field, before treatment, was 2 - 5 mgDRP/l.

Iron coated sand (by-product from drinking water treatment) was installed within a pipe drain, contained by a coconut fibre cloth.

Results are reported after two years of operation, and for soluble P removal only (no data on particulate phosphorus). Over 90% trapping of soluble phosphorus was achieved.

The authors note that there was no loss of iron from the iron coated sand, and suggest that this may be linked to the manganese content of this sand material (c. 0.3% Mn).

"Reducing Phosphorus Loading of Surface Water Using Iron-Coated Sand" J. Environ. Qual. 42:250–259 (2013) <u>https://doi.org/10.2134/jeq2012.0344</u>

Belgium

Hui Xu, Ghent University, Belgium, presented the NuReDrain project.



@phosphorusfacts

Iron coated sand (by-product of drinking water production from Pidpa) has been tested in P-removal filter box systems (c. 30 L filter medium, to treat max. water flow of $6 - 8 \text{ m}^3$ per day) connected to the end of subfield drainage pipes. The design ensures upward-oriented flow through the filter medium, to optimise sedimentation of particulate materials, and the medium is contained in mesh netting to prevent material losses.

In on-farm testing, 2018-2020, at Zedelgem, Belgium, 80% to 90% total phosphorus removal was achieved, with discharge down to lower than 0.05 mg P_{total}/l . Filter medium material life was estimated to be 2 – 3 years. Costs are estimated at 500 – 1000 restarted = 1000 for a standard operating cost.

See also: "Reducing phosphorus (P) losses from drained agricultural fields with iron coated sand (- glauconite) filters" Water Research 141: 329-339 (2018) <u>https://doi.org/10.1016/j.watres.2018.05.022</u> Video of the filter:

https://www.youtube.com/watch?v=zhfOgH1AnME&list=PLncry667FbdvnNluiBoMt8UDGBUx_5Pg

Denmark

Hans Christian Bruun Hansen, University of Copenhagen, presented experience of the Supreme Tech project.

The project has developed and assessed **P-removing filter materials for agricultural drainage waters**, testing both alkaline media (calcium based) and iron or aluminium oxide based media.

A specific P trapping material was developed, to address challenges of high flow rate and short residence time, using **calcined diatomaceous earth (2-4 mm particles, high internal porosity) coated with iron oxide** (by reaction with FeCl₃ and NaOH). This was tested in the field in 2 m³ circular tank filter installations (treating up to 50 m³/day throughflow).

This material is stable, enables high flow (large particle size) and has high P sorption capacity (> 10 gP/kg depending on the inflow P concentration). There may be possibilities to recover P from the saturated filter material and reuse the filter material.

A challenge is that the filter material can be clogged by particulates, which need to be removed by e.g. settling upstream of the filters.

This system is now being developed for commercialisation by **DiaPure** <u>http://www.diapure.eu/</u>

Germany

Simon Kellmann, GEH Wasserchemie, Germany, presented the iron-based adsorbent GEH[®] for tertiary Premoval from surface or drainage waters, and research into regeneration for P-recovery and adsorbent reuse.

The material is an adapted **synthetic ferric hydroxide**, containing the mineral phases akageneite and ferrihydrite, with particle size 0.2 - 2 mm a specific surface area of $300 \text{ m}^2/\text{g}$.



GEH was developed for arsenic removal from drinking water and is used worldwide for this purpose. The material is also already applied heavy metals, copper and zinc removal from roof and street runoff water, e.g. since 2009 in <u>Switzerland</u>.

Because of chemical similarity, the material also selectively adsorbs phosphorus. Full scale application for P-removal is operational since 2011 at the Phoenix See, near Dortmund, Germany, treating 1 600 m³/day of lake water (photo below). The influent lake water soluble P concentration fluctuates 0.05 – 0.005 mgP-PO₄/l. Outflow target was 0.03 and achieved was 0.01 mgP-PO₄/l.



Research shows that a solution of up to 250 mgP/l can be produced by regeneration using 1 molar sodium hydroxide, with up to four regeneration cycles tested to date. Phosphorus can then be precipitated to produce a high-purity phosphate and to enable reuse of the sodium hydroxide.

Acid rinsing before generation removes calcium (which inhibits regeneration) and other metals. Current investigations are looking at how many regeneration cycles are possible, the challenge of residual calcium even after acid washing, acid rinsing to restore neutral pH for adsorbent reuse and automation of regeneration. The adsorbent bed will also remove some organics and biofouling can also be a challenge.

© @phosphorusfacts



P-TRAP poster

Karel As, Bayreuth University, summarised a project to look at possible use of iron coated sand for lake restoration.

The objective is to **lower lake water P concentrations** by adsorbing P released from sediments (legacy P), and also by stabilising the sediments.

The ICS material (a by-product from drinking water treatment, AquaMinerals, Netherlands) has c. 12% iron content and c. 10% organics. It is expected to be more effective in lower pH or low-buffered lakes (low levels of carbonate).

Initial tests involve sediment incubation in the lab. Tests to date show, as expected, significant release of both soluble phosphate and ammonia in anoxic conditions, but limited release in oxic conditions.

The aim is to then implement full scale in Brombachsee, Bavaria, Germany. This lake is currently mesotrophic and stratified (leading to anoxic conditions in the sediments) and requires restoration to oligotrophic conditions under EU Water Framework Directive objectives.

Publication summary:

Penn et al. (2017) reviewed pilot or field-scale data on the performance of P-removal structures (P traps) from over 40 published studies.

Structures were treating various wastewaters or runoffs, and were either independent filter structures or integrated into constructed wetlands.

Wastewaters treated included from sewage works, livestock, fish farm, landfill, milk parlour and runoff from farmland or golf course. Influent P concentrations varied from 0.2 to 80 mgP/l. P adsorbent materials tested included sands/gravel, limestone, marl, steel slag, mining residuals, Polonite (calcium silicate). The different published results were assessed by residence time, influent P concentration and cumulative P-removal (as %, as mgP/kg).

Conclusions are that **iron-containing materials generally show a higher cumulative P-removal capacity compared to calcium-based materials or slags**, especially in structures with a low residence time or treating low influent P concentrations. Calcium-based materials require structures designed to ensure a longer residence time. **Structure design must strongly take into account material hydraulic conductivity, and therefore particle size**.

The authors note the **need for R&D into adsorbent material** regeneration, to reduce costs by enabling material reuse, as well as for P-recovery.

"A Review of Phosphorus Removal Structures: How to Assess and Compare Their Performance", C. Penn et al., Water 2017, 9, 583; doi:10.3390/w9080583 9(8) https://dx.doi.org/10.3390/w9080583

Webinar discussion

Q: What are the challenges in **recycling the NaOH used for bed regeneration** (reusing for repeated regeneration steps). This is important, as NaOH

chemical costs are a significant factor.

A: Carbon dioxide should be prevented from entering the system, as it will dissolve and decrease the regeneration solution pH and react to form NaCO₃.

regeneration solution pH and react to jorm $NaCO_3$.

A: Calcium is added to precipitate calcium phosphate from the NaOH regeneration solution. If residual calcium remains, this may form a surface precipitate on the adsorbent, reducing its effectiveness for P-removal.

See Kunaschk et al. 2015

https://doi.org/10.1016/j.watres.2015.01.001

and Kumar et al. 2018

https://doi.org/10.1016/j.watres.2018.08.040

R&D into P-trap systems and materials

Changyong Lu, University of Copenhagen, presented lab tests on magnesium – iron LDH (layered double hydroxides). These LDHs showed to be effective in reacting with phosphorus, to produce e.g. magnesium or iron phosphates. However, the **LDH was not stable and tended to dissolve**, so limiting applicability in practice. Work is now underway to identify more stable LDHs, possibly based on calcium.

See also: "Stability of magnetic LDH composites used for phosphate recovery", C; Lu et al., J. Colloid and Interface Science, vol. 580, Nov. 2020, pp. 660-668 <u>https://doi.org/10.1016/j.jcis.2020.07.020</u>

Denise Roberts, LKAB Minerals UK & Ireland, and **Derrick Emms, Sustainable Water Company**, presented use of **magnetite** (iron oxide Fe₃PO₄), a mineral mined in Sweden. This material is chemically inert (pH neutral), stable, does not contain problematic contaminants, and does not tend to release iron. Magnetite is already used for P-removal in both <u>Filterclear</u> and <u>BioMag</u> installations. LKAB and Sustainable Water Company are now developing a pellet form for Premoval from discharge of small sewage works or in reed-bed sewage treatment systems.

Phos-Fate is an iron oxide by-product from the drinking water treatment industry. Treatment with a specific binder **avoids increases in alkalinity** which are can be associated with some other solutions.



Iron-based P-adsorbents

In complement to the webinar content, several recent studies on use of iron-based adsorbent materials for Premoval are summarised below.

Publication summary

Kumar et al. (2018) tested three **different regeneration methods for three iron-based adsorbent materials** in real wastewater.

Municipal wastewater treatment effluent (Leeuwarden, Netherlands) was used and was spiked to have an orthophosphate concentration of 2 mg P/l. Three different commercial iron oxide based adsorbents were used: <u>GEH</u>, <u>Ferrosorp</u> and <u>BioPhree</u>. The adsorption and regeneration were done as small-scale column tests, with adsorbent bed volume of 10 ml and an empty bed contact time of 5 minutes. The adsorption was stopped when the phosphate level at the effluent reached more than 0.1 mg P/l. At that point, the adsorbent was regenerated and tested for reuse.

For the adsorbent regeneration, an acidic (HCl) and alkaline solution (NaOH) were needed. Alkaline solution was used for phosphate desorption, and acidic solution was used to release calcium-based surface precipitates. Based on the sequence of using these two solutions, different regeneration strategies were tried out, and it was found that using acidic solution followed by alkaline desorption worked the best for adsorbent reuse.

Effects of adsorbent properties like particle size, surface area, type of iron oxide, and effects of some competing ions on adsorbent reusability were also determined. Amongst all these parameters, calcium had the greatest influence on phosphate adsorption and adsorbent reusability.

Phosphate adsorption was enhanced by co-adsorption of calcium, but the **calcium formed surface precipitates such as calcium carbonate, which affected adsorbent reusability** and needed to be removed by the acid wash step.

ESPP notes that challenges identified include chemical use (alkali and acid, especially if neutralisation is needed between the two regeneration steps), reuse of alkali and acid regeneration solutions (to reduce chemical consumption) and regeneration for a large number of cycles (only three cycles were tested here).

"Understanding and improving the reusability of phosphate adsorbents for wastewater effluent polishing", P. Kumar, L. Korving, M. van Loosdrecht et al., Water Research (2018), Water Research, vol. 145, 2018, pp. 365-374 https://doi.org/10.1016/j.watres.2018.08.040

Publication summary

Kalaitzidou et al. (2016) tested P-removal for final sewage works effluent polishing using several ironbased adsorbents with a 7 000 l/day pilot.

The AINEIA sewage treatment works (near Thessaloniki, Greece) was not operating P-removal and had effluent with 4 - 6 mg P-PO₄/l, whereas expected future discharge limit is 1 mg P-PO₄/l.



Pilot-plant located (and used) in "AINEIA" WWTP.

After listing the P-adsorption capacity of over 30 adsorbents, five were selected for lab testing: synthetic iron oxyhydroxide (FeOOH), commercial materials GFH (iron, akageneite), Bayoxide (iron, goethite) and AquAsZero (iron + manganese: Mn-ferroxyhyte, EU FP7 project) and Purolite A200ZMBLC ion-exchange resin.

AquAsZero was then selected for tests in a continuous-flow 7 000 I/day capacity pilot plant including a hollow fibre membrane filter (to remove particulates from incoming sewage works effluent), an adsorption bed (2 m high, 184 mm diameter), NaOH regeneration and calcium phosphate precipitation (Ca addition) from the P-enriched regenerate. The precipitate was recirculated to increase P-enrichment and improve separation.

Six regeneration cycles were assessed in the pilot. This at first showed significant reductions in P-adsorption capacity, but this was largely resolved by increasing the pH of regeneration to pH 12.8, thus **achieving 95% P-desorption in < 5 hours**.

The recovered calcium phosphate material showed over **10% phosphorus content (P)** and 33% calcium (Ca), with significant carbonate content and very low heavy metal levels (mostly below detection limit), and could be recycled as a fertiliser.

Iron and manganese levels in the recovered phosphate were c. 4% and 200 mg/kg, suggesting low losses from the AquAsZero adsorbent (these levels are not from the treated effluent).



In a previous study (Raptopoulou et al. <u>2016</u>), recovery of phosphorus was tested in batch lab tests, by iron(III) salt precipitation and by FeOOH adsorption, and characteristics of the recovered P materials were analysed.

This study used the effluent of the AINEIA wwtp as above.

Firstly iron (III) solution was dosed at Fe/PO₄ mass ratio of 0.8, stirred, filtered at 0.45 μ m, then dried at 100°C.

Secondly, a 50 cm column of FeOOH adsorbent was used at 350 ml/h until P-removal ceased to achieve the 1 mgP-PO₄ objective. The adsorbent was then regenerated using NaOH, (pH 12.5) so recovering a phosphate solution. Calcium or magnesium chloride was then added to **precipitate a calcium or magnesium phosphate**, which was dried at 100°C.

Plant availability of the phosphorus in the different precipitates was tested using Mehlich-3 or Olsen methods in soils at pH 4.5 and pH 7.8. The magnesium precipitate showed good bioavailability in both soils, the calcium good in acidic soil and the iron poor in both soils.

Phytotoxicity was tested on cress and sorghum showing no negative effects on seed germination or root elongation, except for iron phosphate precipitate inhibition of cress root growth in alkaline soil.

"Pilot-Scale Phosphate Recovery from Secondary Wastewater Effluents", K. Kalaitzidou et al., Environmental Processes volume 3, pages 5–22 (2016) https://doi.org/10.1016/S0008-8846(02)00888-8

"Phosphate removal from secondary effluent of wastewater treatment: characterization and potential re-use as fertilizer of recovered precipitates", C. Raptopoulou et al., Waste Biomass Valor. volume 7, pages 851–860 (2016) https://doi.org/10.1007/s12649-016-9516-2

Publication summary

Xiao et al. (2016) tested magnetite (Fe_3O_4) for P-removal from sewage works effluent with up to 30 regeneration cycles.

Magnetite was supplied by Sichuan Scimee, particle size $10-60 \ \mu m$. Effluent was taken from the secondary settler in Xiaohongmen sewage works, Beijing (operating biological Premoval, effluent $1-2 \ mgP_{total}/l$, in 100 ml beaker tests. Regeneration used 1M NaOH. The magnetite was removed from the both effluent and from the regeneration solution by magnetic separation.

Change in magnetite dry weight after 30 cycles showed <5% loss.

Phosphorus in the treated effluent was reliably reduced to $< 0.1 \mbox{ mgP}_{total}/l.$

Phosphate was recovered from the regeneration solution as calcium phosphate, by dosing CaCl₂.

The authors conclude that although the magnetite tested had relatively low P-adsorption capacity (0.5 - 0.8 mgP/kg), it showed **high removal selectivity for phosphorus**, can **reliably achieve low P discharge levels**, can readily be extracted by magnetic separation and **can be very effectively**

regenerated, enabling phosphorus recovery. This could make magnetite a cost-effective route for P-removal from sewage works effluent and P-recycling.

"Phosphorus removal and recovery from secondary effluent in sewage treatment plant by magnetite mineral microparticles", X. Xiao et al., Powder Technology, vol. 306, Jan. 2017, pp. 68-73 https://doi.org/10.1016/j.powtec.2016.10.066

Publication summary

Park et al (2017) tested mixed iron and titanium oxide fixed on sulfonated copolymer beads for P-removal for P-removal from a membrane bioreactor treating sewage.

The mesoporous beads were metal loaded by soaking in metal oxide solutions, then placed in alkaline solution, to achieve a metal content of 4 - 6%.

Addition of titanium oxide (compared to iron only) significantly improved the P adsorption rate (up to 3 mol% Ti), adsorption capacity and selectivity for phosphate (versus e.g. nitrate, sulphate).

After testing with pure ionic solutions, a 31 ml volume laboratory column was used for continuous flow testing on membrane reactor effluent. Around 1 000 bed volumes of effluent (at 0.5 mgP/l) could be treated before adsorbent regeneration was necessary.

Regeneration used 0.2M NaOH. P-removal improved after the first regeneration, and this was shown (using pure ionic solutions) to be because of calcium incorporation onto the beads during the first cycle.

It is not specified how many regeneration cycles were tested.

The authors note a reduction of % iron in the beads after regeneration and indicate that further research is needed to assess whether this is due only to accumulation of e.g. calcium on the beads or whether also iron is being lost to the effluent.

"Mixed metal oxide coated polymer beads for enhanced phosphorus removal from membrane bioreactor effluents", H-S. Park et al., Chem. Eng. J., vol. 319, July 2017, pp. 240-247 https://doi.org/10.1016/j.cej.2017.03.017

Publication summary

Sibrell et al (2016) compared two iron-based adsorbents for P-removal and regeneration, in pilot-scale long-term trials treating fish farm effluent.

Materials used were GFH (Granular Ferric Hydroxide Media, a commercial adsorbent based akageneite, a chloridecontaining iron (III) oxide/hydroxide) and mine drainage residuals (generated by limestone neutralisation of acid mine drainage.

The fishery effluent had 0.1 - 0.2 P/l.

Pairs of continuous flow adsorption columns were used, c. 1 m high, 152 mm diameter, treating a flow of c. 5 500 l/day. Flow was switched between columns every 12 hours, to allow a resting time to enable assimilation of adsorbed P. In some trials, effluent was filtered ($20 \mu m$) and UV treated upstream



Publication summary:

Shemer et al. (2019) tested, at lab scale in pure chemical solutions, regeneration of iron oxyhydroxide agglomerates for phosphorus removal.

The paper refers to "secondary effluent" whereas in fact a pure synthetic solution of orthophosphate with several mineral ions was used for the tests, including sulphate but no nitrogen ions, no soluble organics (e.g. humics) and no particulates.

Iron oxyhydroxide was lab synthesised to produce nano particles which then aggregated (IOA). The phosphate solution was passed in batches through a suspension of the IOA in an air bubble mixed reactor in which outflow of the IOA was prevented by a 0.04 μ m pore membrane. The reactor was then stopped, and the settled IOA regenerated using 1M sodium hydroxide.

The iron oxyhydroxide synthesised in this way showed **high P adsorption capacity** (c. 60 mgP/gFe), probably because of high surface area resulting from agglomeration of nanoparticles, and **good regeneration capacity**, with loss of <10% of P adsorption capacity after 5 regeneration cycles.

Challenges to implementation in real wastewater are possible interference by substances such as humics, clogging of the IOA by organic particles, and separation of IOA from the wastewater after P-adsorption.

"Reusability of iron oxyhydroxide agglomerates adsorbent for repetitive phosphate removal", H. Shemer et al., Colloids and Surfaces A 579 (2019) 123680 https://doi.org/10.1016/j.colsurfa.2019.123680

Recovering P from iron phosphates

Several technologies under development for P-recovery from wastes (such as sewage sludge or sewage sludge incineration ash) were presented, indicating to what extent P could be recovered from iron phosphate present in these materials.

Biological P-release from iron phosphate in sludge

Marie-Line Daumer, INRAE Rennes, France, summarised lab-scale investigations into biologicallyinduced release of phosphorus from chemical Premoval sewage sludges (P-removal using iron and/or aluminium salts, sludge after dewatering, before anaerobic digestion).

See also SCOPE Newsletter $\underline{n^{\circ}134}$.

Sugar production by-products are used to 'feed' lactic acid producing bacteria, whose metabolism causes a pH decrease. In the tests, pH is not controlled: bacterial activity takes the pH

of the columns. The three trials were of 107, 175 and up to 223 days operation.

The third trial included three regeneration cycles (using 0.5M NaOH) during operation and a final one at the end, treating a total of nearly 90 000 bed volumes of effluent.

Overall, 50 – 70% P-removal was achieved over the first hundred days or so. The GFH showed better performance at first, but reached saturation more rapidly. Regeneration enabled to achieve around 50% P-removal over longer periods, with several regeneration cycles, and recovery of around 60% of the removed phosphorus.

Reuse of the regeneration NaOH was not effective, and new chemicals were required for effective regeneration. The authors suggest acid and alkaline regeneration should be investigated (cf. Kumar et above).

"Phosphorus removal from aquaculture effluents at the Northeast Fishery Center in Lamar, Pennsylvania using iron oxide sorption media", P. Sibrell & T. Kehler, Aquacultural Engineering, vols. 72–73, 2016, pp. 45-52 http://dx.doi.org/10.1016/j.aquaeng.2016.04.003

Publication summary:

Scott et al. (2020) present tests of regeneration of three commercial Al- and Fe-based phosphorus sorbents.

Sorbents tested were:

- ActiGuard AAFS50: Alcan, Fe-enhanced Al,
- Biomax: ABS Materials, containing both Al and Fe,
- PhosReDeem, iron oxide based.

Maximum P sorptions were assessed using pure phosphate solutions at 0.5 and at 50 mgP/l and P-removal longevity curves are shown for each material.

Regeneration was tested using 1M potassium hydroxide at various residence times, number of pore volumes and number of regeneration cycles.

Conclusions are that low volumes of KOH are needed for regeneration, and that P-sorption is again functional after regeneration. Pore volume was important for regeneration, which implies higher chemical costs and larger treatment tanks. Recirculation of regeneration solution was not effective. PhosReDeem is identified to function mainly through sorption to calcium (not to iron or aluminium) and regeneration was not effective for this material, whereas **around 80% P-recovery was achieved from the Alcan and Biomax materials by KOH regeneration**. However, results may prove to be not so good in real wastewater, where other ions and organic impurities may interfere with both phosphorus sorption and regeneration.

"Development of a Regeneration Technique for Aluminum-Rich and Iron-Rich Phosphorus Sorption Materials", I. Scott, C. Penn, C-H. Huang, Water 2020, 12, 1784, <u>https://dx.doi.org/10.3390/w12061784</u>



P-TRAP poster

Lordina Eshun, University of Manchester, presented work with Fertiberia aiming to select and implement microorganisms able to convert iron (III) oxide to vivianite (i.e. iron (II) phosphate).

The microorganisms use organic carbon or hydrogen as an electron donor (oxidation to CO_2 or H_2O) in the presence of phosphate. Formation of vivianite is favoured by high iron levels (vivianite iron/P ratio = 1.5), neutral pH, anoxic conditions. Presence of carbonite may instead favour siderite (FeCO₃).

Geobacter and *Shewanella* microorganisms have been identified which can bio-reduce soluble iron (III) oxide to vivianite at moderate temperatures (mesophilic). The project will test different electron donors, redox mediators and buffer systems and use of secondary iron material as substrates.

Webinar discussion

Q: What factors inhibit conversion of iron (III) phosphate to vivianite in bioreactors?

A: Challenges can include **crystallinity of iron (III) phosphate** (less easily oxidised), **adsorption of phosphate to other materials in the substrate** (so reducing phosphate availability), and **adaptation of the microorganisms** to the specific forms of electron donor present.

Impacts of iron on P-recovery processes

Electrodialysis

Lisbeth Ottosen, Technical University of Denmark, presented lab-scale batch tests of phosphorus dissolution from sewage sludge incineration ash (SSIA) using an electrodialysis cell (c. 1 litre volume).

The SSIA is from the mono-incineration ash landfill near Copenhagen, with 10% - 12% total P content, and shows very variable particles and visible iron oxides under electron microscopy (photo below).



down to and stabilises at **pH4.** The sugar by-products are fed at approx. 0.5 to 1 gCOD/gVM in sewage sludge

"**Lactic acid bacteria**" are an order of gram-positive, acidtolerant bacteria which produce lactic acid by carbohydrate fermentation. Such bacteria are naturally widespread and are present in sewage sludge.

20 different sewage sludges from 10 municipal waste water treatment plants (wwtp) were tested. Results showed to up to **70% solubilisation of phosphorus in sludge from wwtp using well-controlled iron dosing for chemical P-removal** (as % of total P in the sewage sludges), potentially sufficient to achieve the obligations of the German Phosphorus Recycling Regulation (see SCOPE Newsletter <u>n°129</u>), including for small wwtps. This is a higher solubilisation than achieved using mineral acids even at very low pH.

However, the results are very variable, with no clear correlation to iron or aluminium, nor to pH. although P-solubilisation was higher in chemical P-removal sludges than biological P-removal sludges (bio-P) and often not good where aluminium salts were used for P-removal (to be confirmed). Also, excess iron or aluminium, compared to P levels in sludge (inadequately controlled dosing for P-removal), led to poor solubilisation.

Sequential extraction methods were used to identify the form of iron phosphorus in the sludges received, suggesting that generally most P is iron (III) phosphates or linked to Iron (III) hydroxides, with significant iron (II) phosphate (vivianite) in only two sludges. Most P was generally as iron (III) forms, even in sludges where most of the iron was generally present as iron (II), e.g. as iron (II) (hydr)oxides (that is iron not bound to P).

Sequential extraction after bio-acidification showed that **P** and iron are solubilised from both iron (III) and iron (II) phosphate. Bio-acidification also increased iron (II) phosphate (reducing effect).

Copper and zinc are not significantly solubilised.

Sugar industry by-products are readily available, and the process results in a considerable increase (up to 2x) in methane production, that is +10 to +20% more than the sum of both sludge and sugar by-product methane production potential. This is because of acid sludge hydrolysis in the bio-acidifier.

Further work is underway to investigate how phosphorus and also iron could be recovered after solubilisation (in the <u>Phos4You</u> project), and how bio-acidification and overall wwtp management (C,-, N- and P-removal, chemical dosing control, sludge dewatering, anaerobic digestion / methane production) could interact to optimise costs and environmental impacts.



RecoPhos

Christoph Ponak, University of Leoben, Austria, summarised the **RecoPhos** inductively heated thermal reactor process to produce white phosphorus (P₄) from secondary materials.

This is presented in the SCOPE Newsletter Special $\underline{n^{\circ}136}$, 2020, on P₄.

This has been tested on sewage sludge incineration ash (SSIA) in an EU FP7 project (10 kg/h input) and **industrial development is now planned by** <u>Italmatch</u>, who have acquired patents. University of Leoben is working on scale up to a research installation of 50 kg/h, for which construction is planned for 2021, and which will be tested on sewage sludge incineration ash or dried sludge or other secondary materials.

In the reactor, at c. 1600°C, liquid iron and gaseous, elemental phosphorus are generated by reduction of iron phosphate and other iron and phosphate compounds, and are separated because gaseous phosphorus is continuously removed from the reactor. The process must be managed to avoid the formation of ferrophosphorus.

Around 75% (from sewage sludge incineration ashes) to 85% (from steel slags) of input phosphorus is gasified and recovered as P_4 .

A lab-scale pilot reactor is currently being tested for treatment of waste lithium-ion batteries, with the objective of recovering lithium, phosphorus (present in electrolyte flame retardants or in lithium iron phosphate batteries) and other metals such as cobalt, nickel and manganese.

"Get More P"

Alexandre Wavreille, <u>Prayon</u>, outlined the "Get More **P**" process under development by the company.

Low-grade phosphate material is attacked with dilute sulphuric acid, then neutralised using a calcium compound, precipitating gypsum and impurities. After filtration, a second calcium neutralisation stage enables production of animal feed grade DCP (di calcium phosphate). This process has been tested at lab and small pilot scale for several years in Prayon R&D premises in Belgium. Semi-industrial tests are planned in the recently acquired Technophos Facility.

Tests with calcium-rich secondary materials showed 90% P-recovery and low levels of impurities in the final product. However, lab scale **tests with iron phosphate showed only 60% P-recovery**, and also higher calcium consumption (no calcium in input material).

A suspension of SSIA in water is placed in the stirred anode compartment of the electrodialysis cell, which is separated from the cathode compartment by a cation exchange membrane (CEM). A DC current is applied (50 mA, <5 V). **This causes acidification at the anode, which, after 5 – 10 days, releases over 95% of phosphorus to solution** (c. 85% of P in SSIA stays in solution in the anode compartment) and releases metals which migrate through the CEM to the cathode compartment.

Most heavy metals (including lead) stay undissolved in the ash, with copper and zinc mainly concentrating in the cathode compartment.

The objective is P-recovery from the anode compartment solution and removal of heavy metals.

The anode solution showed cadmium levels <2 mgCd/kgP₂O₅ (much lower than the new EU Fertilising Products Regulation limit of 60 mgCd/kgP₂O₅). Potentially c. 1.5 kg zinc per tonne ash and 0.6 kg copper could also be recovered from the cathode compartment.

Around 50 - 60% of ash (dry weight) remains after electrodialysis, and **the economics depend on valorisation of this residue, in order to recover landfill tax on the ash removed from landfill**. This residue is high in iron (iron oxides do not significantly dissolve in the electrolysis) and so could be used as an additive to concrete to impart stable red colour to imitate bricks.

Grinding of ash before electrodialysis was tested but was found not necessary. Operating challenges include physical wear, due to stirring, and in particular the membrane requires protection.

Phos4Life

Ángel Galindo Carbajo, Técnicas Reunidas, presented the **Phos4Life** <u>technology</u>, currently in pilot testing, with a full-scale installation planned in Soluthurn, Switzerland.

This process starts with acid leaching of sewage sludge incineration ash SSIA (using sulphuric acid), solid-liquid separation, then uses **solvent extraction to remove iron, aluminium** and also metal contaminants from the resulting phosphoric acid, before concentrating the acid by evaporation. For further details, see ESPP P-Recovery <u>Technology</u> Catalogue.

SSIA tested has <10% P and >15% iron, and the iron hinders the solvent extraction process. The iron and phosphorus streams are interconnected, and two process options are currently considered:

- 'soft' leaching, enabling 90% P-recovery, but only 5% recovery of iron
- 'strong' leaching, enabling 95% P-recovery and 65% recovery of iron (as 40% ferric chloride solution)

The 'strong' leaching option is complex, involving several more processing steps, resulting in a higher cost, but also a residue of better quality (gypsum of quality useable in construction products).

Euphore

Siegfied Klose, Euphore, summarised the **Euphore** <u>process</u> which incinerates sewage sludge in a rotary kiln, at around 1 000 °C, and uses hot gases to ensure reducing conditions in the reactor. Chlorides are added to bind heavy metals and remove them in gaseous form.

For further details, see ESPP P-Recovery Technology Catalogue.

A majority of the iron present in the sewage sludge remains in the resulting phosphate-rich ash (20 - 30% of iron is removed) by the chlorides to offgas, with the heavy metals). In the resulting ash, the iron is mostly present as magnetite (Fe₃O₄) and partly as stanfieldite (Ca(Mg, Fe)₆(PO₄)₆).

Phosphorus is present in the resulting ash as merrillite $Ca_9NaMg(PO_4)_7$ (which is plant available), **stanfieldite** (above) and **apatite** (the same material as phosphate rock).





Pot trials with rye grass suggest that the Euphore ash has P-fertiliser effectiveness up to 90% that of superphosphate (dry matter yield, <u>HGoTech 2017</u> and S. Klose / University Gießen, 2020).

Parforce

Jürgen Eschment, Parforce, the **Parforce** <u>process</u> for P-recovery from different materials.

This process, a spin-off from the Freiberg University of Mining and Technology, Saxony, Germany, involves four steps: acid leaching (HCl or HNO_3) to solubilise phosphorus, solid-liquid separation to remove siliceous residues, an electrodialysis step to separate mono- and di-valent ions (sodium, calcium, magnesium, copper, ...) then finally concentration of the remaining phosphoric acid.

The siliceous residues contain heavy metals and must at present go to landfill. Reuse is however being researched.

The electrodialysis generates 10% to 20% phosphoric acid which is concentrated to 75% for commercialisation. Because of P losses across the electrodialysis membranes, an additional P precipitation step (using lime) is necessary to achieve 80% P-recovery as required by German legislation. For further details, see ESPP P-Recovery <u>Technology Catalogue</u>.



However, **presence of iron or aluminium necessitates an additional solvent extraction step prior to electrodialysis**, then the iron or aluminium is recovered from the organic solvent (using hydrochloric acid), to generate iron or aluminium salts which can be recycled.

The Parforce process is currently at R&D TRL6, with testing of a 1000 kg material input batch reactor at Freiburg University, Germany.

Sulphide

Sarah Bluteau, McGill University, Canada, presented lab-scale batch tests of dissolution of phosphorus in biosolids using sodium sulphide.

The pH increase was achieved by dissolution of sodium sulphide nonahydrate in reslurried biosolids.

Tests used digested sewage sludge, after centrifuge dewatering, from the Ottawa WWTP (which applies chemical P-removal using iron chloride), with 3.5 % P_{total}/DM (by mass).

Around 30 – 45 % of total phosphorus was dissolved (compared to c. 10% of total P in soluble form initially), at pH 11, after 24 hours, with sodium sulphide dosed at S²⁻ / P_{total} ratio of 4. Sodium and sulphide were found to increase in the solid fraction, while iron decreased. These S²⁻/P_{total} ratios correspond to extreme redox of -500 to -600 mV.



Effect of sodium sulphides nonahydrate on o-Pi dissolution.

See however the comments on feasibility of application of sulphide for P dissolution in Leon Korving's presentation.

RAVITA HSY

The RAVITATM HSY process recovers iron phosphate, after using iron or aluminium coagulants for tertiary P-removal (post precipitation) see SCOPE Newsletter n°132.

Helsinki Region Environmental Services Authority (HSY), Finland, has been developing this nutrient recovery process since 2015. The driver is that HSY wants to be able to recover and utilize the nutrients in wastewaters without compromising effluent quality in WWTPs.

The RAVITATM process enables the recovery of phosphorus as phosphoric acid, which can be further processed into ammonium phosphate for fertiliser. The current technical

European Sustainable Phosphorus Platform SCOPE Newsletter info@phosphorusplatform.eu www.phosphorusplatform.eu

@phosphorusfacts



readiness (TRL) is estimated to be on level 5 or 6. In 2019 a RAVITATM demo plant, 1 000 p.e., was built in the Viikinmäki WWTP in Helsinki, Finland.

In the RAVITA process, the phosphorus is recovered in the effluent wastewater with post-precipitation followed by disc filtration. The chemical sludge that is produced in the filtration is then further processed in order to separate the phosphorus, by leaching with phosphoric acid, releasing metals and phosphate into solution for the following recovery step. In the recovery step, the phosphoric acid is separated by solvent extraction process, as the first end product. RAVITATM process is able to recover more than 50% of the total influent phosphorus of the wwtp.

The research has been carried out on both lab scale and pilot scale. At the pilot scale, the chemical sludge production has been robust and over 80 % of the wwtp inflow phosphorus can be transferred to the recovery step. At the lab scale, the recent focus has been on both dissolution and solvent extraction. The extraction process is now optimized at bench scale, and 85 % of the precipitation chemical (using aluminium) and 95 % of phosphorus can be dissolved.

HSY were unable to participate in the webinar but provided the text above.

Remondis Tetraphos

This process uses phosphoric acid to solubilise phosphorus and calcium from sewage sludge incineration ash. Most of the iron and heavy metals remain in the ash. Sulphide dosing and ion exchange systems then enable removal of heavy metals, purification of the generated phosphoric acid and production of a dilute ferric chloride solution which can be recycled to sewage works for phosphorus removal. For details see <u>SCOPE</u> Newsletter n° 129.

Remondis declined to participate or provide information for reasons of protection of process know-how. The general text taken from information previously supplied by and validated with Remondis.

EasyMining Ash2Phos

The EasyMining Ash2Phos process recovers phosphorus from sewage sludge incineration ash (SSIA), separating iron and aluminium as recyclable salts, removing heavy metals.

Full-scale installations are planned in Sweden and Germany: https://www.easymining.se/article-startpage/gelsenwasser/

In the process, sewage sludge incineration ash is first leached with diluted hydrochloric acid. After separation by filtration of the insoluble fraction, the filtrate is subjected to a series of precipitation reactions and filtrations at different pH conditions, during which **iron and aluminium are separated as products**, and the heavy metals are removed for disposal. The sand-like residue is suitable for use in concrete. Finally, phosphorus is precipitated from the purified solution as calcium phosphate of high purity and low heavy metal content. In the Ash2Phos process **10-20% of Fe, 60-80% of Al and**

In the Ash2Phos process 10-20% of Fe, 60-80% of Al and 90-95% of P are recovered from SSIA as commercial products.

Typical content of SSIA is up to 10% P, 15-20% Fe and below 5% Al. The process is able to accommodate for significant variations in the content of elements. Both iron and aluminium rich and poor SSIAs can be handled with the same resulting high degree of P recovery.

A process variation allowing for recovery of over 80% of Fe is possible though not currently included in current projects.

EasyMining were unable to participate in the webinar but provided the text above. For further details on the process see <u>https://www.easymining.se/technologies/ash2phos/</u>

Outotec Ashdec

The AshDec® electrothermal process transforms sewage sludge incineration ash into a plant-available fertiliser material, whilst removing most heavy metals.

The AshDec process was developed in joint research with the German Federal Institute for Materials Research and Testing (BAM) and Outotec. (see <u>SCOPE Newsletter $n^{\circ}132$ </u>).

The core process feeds ash to a rotary kiln where sewage sludge incineration ash is mixed with sodium compounds and a reducing agent, preferably dried sewage sludge (used at c. 10 – 20% input). The amount of sodium compounds needed depends on the phosphorus and silicon content in the ash, since sodium reacts with both components. The material is treated at 850° C - 900°C for 15-20 min. A high proportion of heavy metal compounds evaporates at this temperature, and so are removed so that cadmium and uranium levels in the AshDec product are 80% - 99% lower than in most mineral phosphate fertilisers. Over 95% of the phosphorus removed to sewage sludge in wastewater treatment plants can be recovered in the AshDec fertiliser product by the process.

In principle, ashes from sewage sludge incineration from all types of municipal wastewater treatment plants can be handled by the AshDec process, regardless of whether iron or aluminum are dosed for chemical P-removal. The AshDec process breaks the chemical Fe-P and Al-P bonds in the sewage sludge incineration ash and produces new Ca-Na-P bonds. The process thus converts the low plant available P-compounds in the sewage sludge incineration ash (e.g. $Ca_3(PO_4)_2$ as Whitlockite, AlPO₄ or iron phosphate compounds) to the plant available compound CaNaPO₄ (that is, "Rhenania" phosphate fertiliser, <u>known</u> for nearly a century).

The iron present in the sewage sludge incineration ash is present in the resulting AshDec fertiliser product, but mostly not as iron phosphate but as magnetite Fe₃O₄. See <u>Peplinski et al. 2006</u>.

Consequently, the presence of iron or aluminium in the ash are expected to have no influence on the fertiliser plant availability of the AshDec product.

The AshDec process has to date been tested for several years with continuous production campaigns in a 0.3 t input/hour pilot. Construction of a full-scale plant is planned in the German national <u>RePhoR programme</u>, "R-Rhenania" project.



Iron – P interactions in soils and plant availability

Ruben Sakrabani, Cranfield University, UK, underlined that the usefulness of P in soil to crops (to support growth) depends on its plant availability, and that this varies considerably between different forms of P in soils.

He presented the various **different analytical methods available to measure soil P availability** (Bray 1, Mehlich-3, Modified Kelowna, Truog, Morgan, Warren and Cooke, Dyer, H3A-2, Calcium Acetate Lactate (CAL), AB-DTPA, Assubaie, Olsen-P, Colwell). Additionally, some tests use sinks for P analysis, e.g. Diffusive Gradient in Thin Films (see SCOPE Newsletter <u>n°112</u>). The critical soil P value, used by agronomists and farmers to identify whether soil needs phosphorus fertilisation to enable crop performance (growth, quality), varies depending on the crop and on the analysis method used. Each analytical method for P analysis has boundary conditions where it operates best which need to be considered when selecting which method to use.

Effects of iron on soil P plant availability

Erik Smolders, Catholic University of Leuven, Belgium, outlined current understanding of how iron in soil impacts P availability, based on literature knowledge and on recent studies on P-deficient soils in Africa and in Asia.

Such studies enable to provide understanding of nutrient dynamics which is difficult in nutrient rich soils in Europe.

Iron in soil, present as oxyhydroxides (FeOOH) binds phosphorus strongly. As a result, the "Phosphate Saturation Index" increases as soil iron content increases (oxalate extractable iron Fe_{ox}). This P Saturation Index represents the amount of P which has to be added to reach 0.2 mgP/l in soil solution, that is adequate for plant needs. This can be up to 1gP/kg soil. Six et al. 2013 (in SCOPE Newsletter $n^{\circ}112$) showed that the yield of maize increases with increasing soil soluble phosphorus.

Increased iron (III) in soils thus binds phosphorus, meaning that higher inputs of P in fertilisers are needed.

However, **organic matter can make phosphorus more plant available** at the time scale of a few weeks (Vermeiren et al., unpublished), especially in more acidic soils. This can be because:

- organic molecules (e.g. citrate) compete with phosphorus sorption to FeOOH (<u>Kleber et al. 2015</u>).
- phosphorus is sorbed onto organic particles, where it is more readily available then when inorganically bound.
- Microbial activity can mineralise (render available) phosphorus in organic matter.

Increasing soil organic matter can thus improve crop P availability at equal soil iron levels.

Webinar discussion

Q: What is the definition of "Critical" soil P?

A: This is generally taken to be the amount of plant available P needed to obtain expected optimal crop yield.

Q: Why does agricultural P use contribute to eutrophication if P is 'fixed' in soils?

A: Ensuring "Critical" P for crops means that some phosphorus is poorly fixed, and can move through soil with rainwater. Additionally, 'fixed' soil P is lost to surface waters with particulates lost from soil (soil erosion).

Q: Can 'slow-release' or 'controlled release' fertilisers reduce eutrophication risks whilst maintaining crop productivity?

A: If phosphorus is released progressively, according to crop needs over time, it is more likely to be taken up by crops and not lost. However, P-release and crop needs are both dependent on e.g. weather, and so difficult to predict. A study using Ostara struvite (progressive release) with soluble MAP shows that optimal crop productivity is obtained with a combination of the two (Hall et al. <u>2020</u>).

Q: How can plant P availability be best measured for different materials?

A: participants referred to Duboc et al. (2017). This paper is summarised below

Guy Kirk, Cranfield University, UK, discussed mechanisms by which crops access phosphorus from highly-weathered iron-rich soils.

This is in particular based on studies with upland rice in ironrich soils in Asia and Africa where P deficiency is a major constraint to yields.

A number of genetic traits have been identified for rice with better tolerance of low soil phosphorus. The mechanisms include both internal effects, whereby growth differs for the same amount of P in the plant; and external effects, whereby plants differ in their ability to extract P from the soil through:

- **Root geometry effects**, e.g. development of fine, hairy lateral roots and root proliferation close to fertiliser sources.
- **Root-induced P solubilisation**, especially through pH changes in the rhizosphere linked to nitrate uptake and balancing release of bicarbonate ions.

Differences in root infection with mycorrhizal fungi do not account for genetic differences in P efficiency in upland rice.

@phosphorusfacts

Root geometry and solubilisation effects can potentially be enhanced by plant breeding and by fertiliser management. For example, by **adapting fertiliser formulations to facilitate root access to P fertilisers concentrated by placement, and to manipulate rhizosphere chemistry to solubilise P**.

Publication summary:

Duboc et al. (2017) investigated plant P-availability of thirteen different fertiliser materials (plant growth, P-uptake), comparing results with several P solubility test methods.

The materials tested included: digestate solid fraction, chicken manure, chicken manure biochar, meat and bone meal (MBM), MBM biochar, several gasified or pyrolysed (biochar) sewage sludges, struvite, rock phosphate and single super phosphate (SSP).

Fertiliser effectiveness was tested in 6-week pot trials, soil pH (CaCl₂) 6.2, using rye (*Secale cereale*), applying 85% of the P-dose required for maximum biomass production (that is phosphorus limited conditions).

Of the materials tested, only struvite, chicken manure and chicken manure biochar gave shoot dry matter production comparable to SSP (**slightly better with struvite**).

Fertiliser P was tested using different standard solubility methods: 2% citric acid, 2% formic acid, neutral ammonium citrate, water, CAL (calcium acetate lactate) and Olsen-P, as well as by DGT (diffusive gradient in thin films, see Six et al, in SCOPE Newsletter <u>112</u>) and by "iron bag".

The "iron bag" uses an iron oxide filled membrane as a phosphorus sink (Freese et al. 1995) extracting fertiliser P for 37 days in a pH-buffered solution, and assesses the amount of phosphorus taken up by the iron oxide.

The authors conclude that, of the different P-solubility test methods, this **"iron bag" gave the best correlation to plant uptake** (R^2 c. 0.8), better the other extraction methods performed on the fertiliser without soil, and similar to DGT (diffusive gradient in thin films) or to Olsen-P extraction (both performed on fertilised soil).

"Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers", O. Duboc, J. Santner et al., Science of The Total Environment, vols. 599–600, Dec. 2017, pp. 1160-1170 https://doi.org/10.1016/j.scitotenv.2017.05.054

Availability of P in chemical P-removal sludge

Bengt Hansen, <u>Kemira</u>, summarised current understanding of the plant availability of phosphorus in sewage sludge, where iron is used from chemical P-removal.

This question continues to be strongly debated. Discussions are not new, see e.g. McGeorge & Breazeale 1932 "investigations showed that the precipitated phosphates ... are readily available sources of phosphorus for plants. This aroused a certain amount of controversy ...".



Other more recent studies confirm plant availability of iron (III) phosphate complexes:

- Richards & Johnston, <u>2001</u>, a three month pot trial of synthetic iron phosphate with rye grass showed that plant uptake is lower initially than for MCP (mono calcium phosphate) but **equivalent after 2-3 months**.
- A WERF study, USA (O'Connor et al., 2004) concluded however a **lower plant availability compared to triple super phosphate for most sewage sludge (biosolids)**, especially those containing high iron or aluminium (Fe or Al:P ratio >2). The study also showed that high iron or aluminium levels in sludge applied to land resulted in reductions in phosphorus losses to surface waters.
- A major field trial study by Hushållningssällskapet (Swedish Rural Economy and Agricultural Societies), on two different farms is testing two different sewage sludges (applied every 4th year) with 0, 1 or 3 tDM/ha and with or without NPK mineral fertiliser, for five different crops. After 34 years, **iron-containing** (chemical Premoval) sludge increased yields by average +16% compared to no fertiliser, and +7% compared to fertiliser only (please indicate the DOI link to publication). This study also shows that heavy metal levels in sewage sludges have been reduced considerably over recent decades and no longer significantly modify soil heavy metal levels, and that crop uptake of heavy metals is not increased when sewage sludge is applied to land.

Webinar discussion

Q: In what form is iron generally present in sewage sludge when iron is used for chemical *P*-removal?

A: Iron phosphate in sewage sludge will generally be **amorphous iron (III) hydroxyphosphate**, but may be significantly transformed to iron (II) phosphate (vivianite) in anaerobic digesters.

Q: When is iron phosphate more likely to be plant available?

A: The iron phosphate mostly present in chemical Premoval sewage biosolids, as **iron (III), is more likely to become crop available in aerobic soils**; if it is **amorphous** (not crystalline); or in presence of **organic matter** (which can facilitate reduction to iron (II)). **Lower soil pH, or release of H⁺ ions** (e.g. from ammonium inputs) can facilitate phosphorus uptake, but there may be **interference from sulphates**.

Q: How will iron (III) phosphate evolve in soils? A: With weathering, amorphous iron (III) phosphate may become crystalline, and so have a lower surface area, and lower plant availability.

A new take on iron phosphate: Vivianite (Iron (II) phosphate)

Vivianite recovery

Leon Korving, <u>Wetsus</u>, Netherlands, and Philip Wilfert, IPP Kiel, Germany (water engineering company) and previously at Wetsus, explained why there is today significant interest in recovery of vivianite (iron(II) phosphate) from digested sewage sludge.

He noted that, even without chemical P-removal, there is always iron in sewage sludge, coming from groundwater intrusion, metal corrosion or from iron dosing in sewers to prevent odours or H_2S (**up to 20% of sewage works input P can be iron-bound**, more if iron is dosed to drinking water to avoid plumbosolvency). Iron is also added in sludge digesters to reduce sulphide in biogas (which leads to engine corrosion and to SO_2 emissions in the engine exhaust).

P is known to be released from iron phosphate by sulphide (produced by bacteria) in natural systems. However, tests showed **sulphide use to be not feasible in sewage** (see Bluteau above) because (a) the released phosphorus tends to bind to other elements (calcium, magnesium, aluminium), and not be solubilised (b) dewaterability of the sludge is significantly deteriorated (organic bound iron may lead to smaller flocs).

Investigation of the form of iron in digested sewage sludge found a significant part to be present not as iron (III) but as iron (II) phosphate (vivianite):

- **30 70% of total P as vivianite** in both undigested and digested sludge with Fe/P ratios > 0.5 (40 to 60% + for Fe/P ratio >1)
- up to 90% of total P as vivianite in digested sludge with Fe/P ratio > 1.5
- visible free crystalline vivianite particles of size 10 400 μm.

Full-scale tests in a wwtp sludge digester showed that increased iron dosing led to an increase in the proportion of total P present as vivianite.

Because vivianite is paramagnetic, existing wet mining electro-magnetic equipment can be used to separate the vivianite out of sewage sludge (ViviMag process, see SCOPE Newsletter $n^{\circ}132$). Full scale tests at one wwtp show recovery of 80% of the vivianite present (60% of wwtp influent P), resulting in a 95% purity material (after washing). In wwtps with a high enough Fe dosing this could lead to an overall recovery of 60% of wwtp influent P.

The recovered vivianite has generally low heavy metal levels, except there may be challenges with nickel levels, and levels of organic carbon below 5 - 10 % C_{-org} (after washing). The particle size of the recovered vivianite is 100 – 400 μ m, resulting in a vivianite concentrate after magnetic separation, which can be easily dewatered mechanically due to the high density of vivianite. The material can probably be directly used as a Fe-fertiliser without further purification



Pilot scale magnetic separator



Recovered vivianite crystals

The process is technologically simple, using existing industrial equipment, and **relatively low-cost** compared to other P-recovery processes. An advantage is that sludge disposal costs are reduced: lower sludge volume, lower sludge P-content, higher calorific value.

Further R&D is needed to:

- better define the interaction between **levels of iron dosing** and vivianite formation
- understand how vivianite formation is affected by **crystal growth** mechanisms, **microbial activity**, **organic** matter
- identify valorisation routes for the recovered vivianite, e.g. directly as an iron/phosphorus fertiliser (see discussion in this Newsletter), for reprocessing in the fertiliser industry, by solubilisation (e.g. using potassium hydroxide) so enabling recovery for recycling of the phosphorus and of salts, separately, or for specific use routes (possibly as a paint pigment, in LiFePO₄ production for batteries, as a flame retardant component ...)

The vivianite recovery process is moving towards commercialisation with Kemira (22/7/20)

@phosphorusfacts

European Sustainable Phosphorus Platform





Webinar discussion

Q: Can vivianite recovery in sewage works **reduce works scaling problems** (in the same way as does struvite recovery)?

A: This is possible, in that vivianite recovery (at the anaerobic sludge digester) takes P out of 'recirculation', if digestate filtrate is returned to the sewage works. However, vivianite recovery is mainly applicable in sewage works using iron for chemical P-removal, where scaling problems occur much less often than in biological P-removal sewage works.

Vivianite itself can spontaneously precipitate and cause scaling in some specific cases in sewage treatment: e.g. in dewatering centrifuges, but only if the sludge is not digested, or in heat exchangers. Because of small particle size, settling in digesters is not an issue.

Publication summary:

Martin et al. 2020 precipitated P from simulated semiconductor industry wastewater in a beaker-scale electrochemical reactor with a sacrificial iron anode, resulting in easily settled vivianite particles.

Anode and cathode were iron plates of surface c. 41 cm²; current of 2.45 A (equivalent to 60 mA/cm² per anode surface) was applied; pH was adjusted by dosing sulphuric acid; levels of DO (dissolved oxygen) were modified by bubbling either air or N_2 , which also ensured reactor mixing.

The semiconductor industry wastewater is spent phosphoric acid after use for microchip circuit etching and contains traces of calcium and aluminium, as well as significant levels of COD (dissolved organic carbon).

Up to 100% P-removal was achieved at an Fe:P molar ratio of 1.5 (measuring total iron in the reactor), in conditions of low dissolved oxygen (DO) and pH6, resulting in a precipitate analysed to be 82% vivianite (10% silica sand, 8% water).

At higher DO levels, strengite (FePO₄) tended to be formed, but more slowly than vivianite, so that P-removal was less effective. At Ph higher than 6, precipitated P settled less well, probably because of amorphous ferrous hydroxide formation.

The authors conclude that the electrochemical process with sacrificial iron anode can be cost-effective for P-removal from such industry wastewater, removing near 100% of P and precipitating a fairly pure vivianite.

"Electrochemical crystallization for phosphate recovery from an electronic industry wastewater effluent using sacrificial iron anodes", N. Martin et al., Journal of Cleaner Production 276 (2020) 124234, https://doi.org/10.1016/j.jclepro.2020.124234

Vivianite as a fertiliser

Kees Langeveld, <u>ICL Fertilizers</u>, outlined the position of Fertilizers Europe, the EU fertiliser producers' <u>association</u>.

The EU fertilisers industry has been developing circularity for decades, with by-products as key fertiliser production inputs, e.g. ammonium sulphate or sulphuric acid. New developments include projects to use ammonia from biogas stripping, use of sewage sludge incineration ash or meat and bone meal ash to partly substitute phosphate rock, use of struvite, manure processing.

Iron is used in a number of industry products, including iron fertilisers to address chlorosis, or in moss killers (e.g. for lawns).

- R&D is underway to see how vivianite could be used in the fertiliser industry. However, because it is not water soluble, chemical processing is needed: although the iron and phosphorus may be slowly plant available, water solubility is often needed in commercial fertilisers.
- The mineral fertiliser industry would **generally prefer a 'clean' iron phosphate material** to secondary materials containing organics.

P-TRAP poster

Rouven Metz, University of Vienna, presented work on plant availability of P and iron from vivianite in soils.

Many factors in soils, including pH, ionic strength, interfering ions, phosphate sinks, organic ligands and humic substances will impact the bioavailability of P and Fe from vivianite, and thus the applicability as a fertilizer.

Moreover, vivianite itself might evolve significantly in soil. Since vivianite is only a metastable phase at oxic conditions, the mineral will oxidize over time, which leads to a destruction of the structure, accompanied by a change in its physical and chemical properties, including evolving into towards (amorphous) iron (III) complexes.

Preliminary experiments showed that within a few hours ~30% of the iron was already oxidized, and mobilization of Fe and P decreased significantly along with the oxidation.

In turn, different interfering ions could increase solubility of vivianite, even in oxic solutions. Ligands have shown to significantly accelerate P and Fe release (e.g. citrate), as have humic substances and "siderophores".

Siderophores are ligands with a high and targeted affinity for iron(III), e.g. DFOB = desferrioxamine B; a complex organic oligomer, naturally produced by the bacteria *Streptomyces pilosus*.

P-TRAP poster

Tolulope Ayeyemi, University of Sevilla, presented plans to test different vivianites as fertilisers.

Lab-synthesised vivianite, vivianite collected from natural environments and vivianite from wastewater treatment or digesters (both recovered and from spontaneous vivianite scaling) will be tested.

Different vivianites will be tested in pot trials, then some forms will be selected for field trials with different crops. Separate tests will assess P-uptake and iron uptake.

The objectives include to assess impact of organic matter, to identify microorganisms which can improve vivianite mobilisation in soil, to assess whether slow release reduces P leaching risk and to determine the form in which vivianite is most effective as a fertiliser.

Biological & chemical understanding of vivianite

Jonathan Lloyd, Manchester University, UK, discussed microbial actions on iron and phosphorus.

Many soil microorganisms can reduce iron from Fe(III) to Fe(II), so rendering the iron available for cellular uptake. They are unusual in that the respire an electron receptor on the outside of the cell, using protein nano-wires which take protons right into mineral particles.

Studies show that amorphous iron oxides can be metabolised by such microorganisms, but not crystalline iron oxides.

Considerable lab and commercial work have been carried out on production of magnetite (Fe_3O_4) from iron oxide by-products in bioreactors using geobacter microorganisms.

Phosphorus can slow down iron reduction in laboratory systems, whereas in biological and natural systems, vivianite (iron (II) phosphate) is found: e.g. in coastal sediments, see Caroline Slomp, or in anaerobic digesters, see Leon Korving, both in this webinar.

Further research and understanding are needed both on how, and in which conditions, iron oxides can be reduced to vivianite, and also how vivianite can be oxidised to release phosphorus?

Carlo Belloni, Wetsus, summarised **Mössbauer spectroscopy** as a tool to investigate iron compounds, to improve the understanding on vivianite formation and recovery, and to characterize and monitor iron-based adsorbents for phosphate recovery.

This is a highly sensitive gamma-ray based technique, and the highest resolution nuclear technique. It collects signals from all iron atoms and **has the advantage to work also with amorphous species** (not only crystalline). It can detect iron down to 1-2% wt. (lower using ⁵⁷Fe), providing information on the oxidation state, character of bonds, magnetic properties, structural (a)symmetry, particle size and above all a

quantitative speciation of the iron present (each phase down to 3% wt.).

Whereas **XRD** fails to detect oxidized vivianite (amorphous) even up to 40% oxidation, Mössbauer is able to identify it, quantifying the oxidation contribution.

Moreover, Mössbauer provides a **complete characterization of the iron species in phosphate adsorbents**, monitoring their transformations during regeneration, so enabling understanding of changes in performance. Finally, Mössbauer can improve and resolve characterisation of iron-based adsorbents, misinterpreted in some previous studies.

Vivianite as a fertiliser

Cinta Cazador, <u>Fertiberia</u>, presented studies showing the fertiliser value of vivianite (iron (II) phosphate).

Vivianite has been shown to be effective as an iron-providing supplement, to prevent chlorosis (chlorophyll deficiency in leaves caused by insufficient iron), which is especially a problem in calcareous soils (defined as > 15% CaCO₃, FAO)

Map of calcareous soils in Europe: https://esdac.jrc.ec.europa.eu/public_path/CaCO3.png



A range of crops has been tested including lupins, chickpeas, pear trees, olive trees, cucumber, pepper (Fertiberia inhouse know-how, not published).

• A five-year field trial near Valladolid, Spain (2011-2015), soil pH 8.34 and 70.3 % CaCO₃, with sunflower, wheat, barley and vetch showed a general increase in crop yields and SPAD index (Soil Plant Analysis Development, an indicator of chlorophyll), even in the

fifth year when no vivianite was applied, showing that it remains in the soil as an iron salt providing P and Fe for plant nutrition.

• A field trial in Huelva, Spain, soil pH 7.94 and 29.58 % CaCO₃, with wheat, showed that vivianite (plus N) gave slightly better results than MAP (mono ammonium phosphate) and other NP fertilisers commonly used by farmers prepared to similar granulometry, showing that vivianite can also provide phosphorus to crops in relevant soil conditions.

Fertiberia is developing a commercial fertiliser formulation using vivianite, for Mediterranean soils (high pH, high calcium). This will involve readjusting all micro-nutrients (iron, zinc, magnesium, boron) to optimise crop value.

Fertiberia consider that vivianite constitutes an effective iron source in calcareous soils (high pH), as P and Fe are available in long term applications. Moreover, in acidic soils, P and Fe in vivianite can be available for plants more quickly. Therefore, vivianite nutrients can be taken up by plants in both acidic and basic soils.

Webinar discussion

Q: How much vivianite could the European fertiliser industry potentially use?

A: Kees Langeveld suggested maybe around **5 000 t/y** of iron

Transformation of vivianite in soils

Antonio Delgado, University of Sevilla, Spain, confirmed that tests on the fertiliser value of vivianite concern only calcareous soils and address mainly its effect in providing iron.

The availability of iron in vivianite is considered to be depend on its dissolution near the plant root (iron and phosphorus will not move through the soil), then oxidation of the iron to poorly crystalline lepidocrocite, a form of Fe(III)O(OH). This is believed to be related to mobilisation and uptake of phosphorus by plants and to be specific to calcareous soils. This means that vivianite will not be an effective fertiliser in anaerobic soils.

Mobilisation in this way will not occur if the vivianite has already evolved to iron (III) phosphate complexes in the soil.

Further assessment of the phosphate fertiliser value of vivianite is thus needed and will be undertaken in the P-TRAP project (above).



Webinar discussion

Q: Where vivianite can be an effective P fertiliser, does this depend on it not transforming to iron (III) phosphate in the soil?

A: **Oxidation to iron (III) may be limited in acidic soils**, which is the case in most of Europe.

In calcareous soils and if oxidation of vivianite does occur, then **up to 30% - 40% of iron in vivianite can be oxidized from iron (II) to iron (III) without modifying the crystal structure**, so still showing as vivianite under XRD, and maybe without significant reduction of the solubility / plant availability.

Q: How will vivianite evolve over time in soils?

Q: In pure systems, oxidation of vivianite will generally lead to amorphous iron (III) (hydroxy) phosphate phases, such as Santabarbaraite. These **amorphous phases are still plant available**, for both P and Fe. Their crystallisation, to less plant available crystalline iron (III) forms, is inhibited by the presence of phosphorus. In soil systems, however, minerals and organic matter present and plant uptake will remove phosphorus, so that **crystalline iron (III) forms, with low plant availability,** are likely to form.

R&D is needed to ensure that vivianite used in fertiliser is either delivered close to the plant roots, or is treated so that it cannot transform to iron (III) phosphate complexes in the soil.

Q: Could the application of vivianite lead to long-term immobilisation of P in soils by oxidation to iron (III) phosphate (three iron atoms bind two phosphorus in vivianite, but three in iron (III) phosphate)?

A: The change in iron / phosphorus molar ratio for iron applied in a fertiliser is unlikely to significantly modify the overall soil P-binding. Part of the iron (III) will be bound to hydroxides, so not binding P.

Q: What is the role of soil organic matter and soil microbes in plant availability of Fe and P in vivianite? A: The role of organic matter and microbes for vivianite bioavailability is still not clear. An increase in availability or a decrease, are possible, depending on functional groups and microbial community. However, preliminary experiments suggest an increase in availability.

Q: Is there a risk of iron toxicity to plants?

A: Vivianite application in Europe will generally not pose iron toxicity problems, because this occurs only in anaerobic soil conditions.

Adsorbents: recent review papers

Summarised here are several recent publications reviewing data and literature on use of different adsorbents for P-removal. These demonstrate the increasing interest in adsorbents for removal of phosphorus in wastewater treatment, reducing P in agricultural runoff or for lake restoration.

Publication summary:

Gubernat et al. (2020) review reactive materials for Premoval, considering those in use today in wastewater treatment, and those offering R&D potential.

Materials discussed include:

- natural materials containing Al, Fe, Mg, Ca;
- various secondary materials: metal slags and hydrated calcium silicate (CHS) from slag, biochars, coal ash, concrete, brick dust, iron oxide coated sands, acid mine drainage wastes ...
- specifically manufactured P-sorbent materials:
- **Polonite**, **Rockfos** both based on the carbonate-silicate mineral opoka,
- Leca, Filtralite both based on clays,
- Pollytag,
- Filtratrap.

Data on P-sorption capacity, P-removal, pH, etc and literature sources are given.

Conclusions are that these commercial materials achieve better P-removal than unmodified natural or secondary materials. Rockfos adsorbs over 250 gP/kg (after 1 hour, P from 5 – 100 mgP/l). However, P-removal of natural or secondary materials can be significantly improved by modifications, such as coating with metals, calcining to increase porosity and surface area.

Challenges in implementation are avoiding that the material modifies the pH of the treated water, and **selecting materials which can be used as a fertiliser after P-sorption** (plant availability of the phosphorus, low levels of contaminants).

"Reactive Materials in the Removal of Phosphorus Compounds from Wastewater—A Review", S. Gubernat, A. Maslon, J. Czarnota, P. Koszelnik, Materials 2020, 13, 3377, <u>https://dx.doi.org/10.3390/ma13153377</u>

Publication summary:

Ahmed et al. (2019) reviewed 141 papers and 22 patents on P-adsorbents (2012-2017).

The number of papers per year showed a +25% increase over these five years, indicating increasing interest, with the most covered materials being metal oxides, LDHs (layered double hydroxides) and natural materials (together these made up over $\frac{34}{4}$ of publications).

Many LDHs identified combine Mg and Al, and some also Ca, Fe, Zr.

A wide range of natural materials are identified as possible Psorbents, including shells, zeolites, fruit peel, chitosan, and also processed materials such as biochars or metal slags. These are often modified by loading with metals, e.g. zirconium.

Metal oxides included iron, magnesium, zinc, zirconium, lanthanum, silicon and aluminium.

The authors note interest in porous materials. They underline the challenges in implementing adsorbent systems in wastewater, in particular the need to ensure easy separation to avoid sludge generation.

"Recent Progress on Adsorption Materials for Phosphate Removal", S. Ahmed et al., Recent Patents on Nanotechnology, 2019, 13, 3-16, https://dx.doi.org/10.2174/1872210513666190306155245

Publication summary:

Bacelo et al. (2020) also review publications on phosphorus adsorbents, referencing nearly 170 papers.

They show a nearly 100% increase in the number of annual publications from 2008 to around $1\ 000$ / year in 2018, indicating increasing interest and knowledge.

Information on adsorbents reviewed covers synthetic metal oxides / hydroxides (e.g. Al, Ca, Ce, Fe, La, Mg, Mn, Zn, Zr), carbonates, clays, zeolites, porous silica, activated carbon and biochars, polymers, bio-derived and industrial secondary materials. Approaches for P-recycling are discussed: elution to recover P from adsorbents, or use of the P-enriched material as a fertiliser.

Maximum adsorption capacities are reported for a large number and range of materials (specifying experimental conditions).

Overall, adsorption is identified to be an easy-to-operate technology for nutrient removal, with potential for P recovery by elution (regeneration of adsorbent).

Further research is needed into:

- Effective use of low-cost, secondary adsorbent materials
- Use of **Ca and Mg based materials**, which offer low cost and low toxicity, but pose performance challenges in real wastewater
- Improving **selectivity** for P for adsorbents based on carbonates, porous silica, activated carbon / biochars
- Scale-up and economy of production of modified or calcined adsorbents
- Better understanding of and optimisation of **adsorbent** regeneration / P-recovery processes, and adaptation of adsorbent materials to improve P-recovery
- Testing of use as fertilisers of P-enriched adsorbent materials, where appropriate, including verifying both fertiliser value and safety (esp. avoidance of transfer of contaminants from wastewaters)

"Performance and prospects of different adsorbents for phosphorus uptake and recovery from water", H. Bacelo et al., Chemical Engineering Journal 381 (2020) 122566 <u>https://doi.org/10.1016/j.cej.2019.122566</u>

@phosphorusfacts





Kumar et al. (2019) review adsorption technologies to achieve low discharge levels in wastewater treatment (0.01 - 0.15 mgP/l), based on some 200 publications, looking particularly at research gaps and cost aspects.

Adsorbents can achieve very low levels of soluble phosphate, but need to be supplemented with other technologies to achieve low total phosphorus (removal of particulate P): either oxidation upstream of the adsorbent to solubilise P, or combination with filter technology to remove particulates.

Costs of adsorption depends on: adsorbent cost, operation costs (installation, loading with adsorbent, maintenance) and adsorbent regeneration costs. Operating costs are also related to the P-adsorption capacity of the material, its specific affinity for phosphorus and the adsorption kinetics, because these impact adsorbent quantity required, and so installation size, adsorbent effective life, regeneration and maintenance.

Various scenarios for adsorbent cost, regeneration chemical cost, energy and capital costs were modelled.

Conclusions are that the key cost elements are the adsorbent cost, practical aspects of installation loading and adsorbent reusability (regeneration), because this can reduce both adsorbent overall cost and operation costs (longer times between changing adsorbent material).

The authors note that research tends to concentrate on adsorption capacity, and that insufficient data is available on effects of competing ions, operation in real wastewater and real operating conditions, and regeneration (adsorbent reusability) in these conditions.

"Adsorption as a technology to achieve ultra-low concentrations of phosphate: Research gaps and economic analysis", P. Kumar, L. Korving, M van Loosdrecht, G-J. Witkamp, Water Research X 4 (2019) 100029 https://doi.org/10.1016/j.wroa.2019.100029

Publication summary:

Pohkrel et al. (2019) reviewed use of metal-loaded agricultural or food processing waste materials as P-adsorbents, with c. 100 references.

Lignocellulose materials generally have more negative than positive functional groups, so are not very effective for Padsorption. These materials are therefore modified, e.g. by metal loading (quaternisation), sulphate loading (anionisation) or thermal activation. High-valent metals generally used are: iron (II) or (III), lanthanum (III), cerium (III), zirconium (IV) or zinc (II).

Important aspects are the P-adsorption capacity for phosphate, low toxicity and avoidance of loss of (leakage) of the metal.

Although raw materials will bind metal ions (due to negatively charged functional groups, e.g. OH or COOH), prior chemical modification of the material will improve P-removal and reduce metal loss. Modifications include grafting carboxyl groups (esterification or carboxymethylation) or saponification (alkali treatment). P-adsorption mechanisms and factors influencing adsorption are discussed. P-removal capacity data for different metalloaded materials are provided, including wood particles, orange wastes, coir pith, okara (soy waste), pine needles, *Phragmites* reeds, litchi seeds, tree bark ...

The authors note the importance of regeneration, with difficulties of loss of metal ions, or deterioration of the material's cellulose structure.

"Removal and recovery of phosphate from water and wastewater using metal-loaded agricultural waste-based adsorbents: a review", M. Pokhrel et al., Journal of Institute of Science and Technology 2019, 24(1): 77-89 http://doi.org/10.3126/jist.v24i1.24640

Publication summary:

Liu et al. (2018) review adsorbents for P-removal, centring on metal-based materials, with over 140 references.

Materials considered are metal oxides/hydroxides, metalloaded carbon-based materials (graphene, carbon nanomaterials, biochars), silica materials and agricultural byproducts metal hybrids such as metal organic frameworks (MOFs) or polymers, industrial by-products and natural or modified minerals.

Interactions with pH, redox, temperature, competing ions, ionic strength, P-concentration, P-species (soluble phosphorus molecules other than orthophosphate ions), adsorbent size are discussed, as well as adsorbent regeneration.

The authors conclude that **iron** (**hydr**)**oxides offer cost effectiveness**, **low toxicity and effective P adsorption**, **but are sensitive to redox conditions**, and can release P in reductive conditions. Other metals tested in reviewed publications include Ce, Mg, Mn, Ti, Zn and in particular La and Zr. However, these can be difficult to separate after P-adsorption, whereas iron (hydr)oxides can be separated using magnetic properties.

The authors note the potential of materials with high surface areas and porosity, after loading with metals, to improve Padsorbency

They underline the need to ensure that adsorbent materials are stable under the variable conditions (pH, temperature, redox) which occur in wastewater treatment, in particular the **risk of leakage of loaded metals**.

Further research needs are underlined concerning regeneration of adsorbent materials, again in particular regarding loss of loaded metals.

"Review of Metal (Hydr)oxide and Other Adsorptive Materials for Phosphate Removal from Water", R. Liu et al., J. Env. Chem. Engineering, vol. 6, Issue 4, Aug. 2018, pp. 5269-5286 https://doi.org/10.1016/j.jece.2018.08.008

@phosphorusfacts



Publication summary:

Liu et al. (2019, 2020) showed the effectiveness of aluminium or iron containing amine MOF (metal organic framework materials) and lab tested in the cathode of an electrolysis cell, as a route to enable effective phosphate adsorption then release whilst ensuring stability of the adsorbent material.

The iron- or aluminium- amine-MOFs showed (2019 paper) rapid P adsorption kinetic and very high P adsorption capacity (> 80 mgP/g), were effective in a pH range 3-11 and showed low sensitivity to competing ions (Cl, F, SO₄, HCO₃). The aluminium based material had faster P-sorption kinetics but the iron-based material had higher phosphate selectivity. The materials could be regenerated using 1% salt solution, retaining 80% adsorption capacity after three regeneration cycles.

In the second study, the aluminium-amine-MOF material was integrated into a stable electrode material, by



carbonisation of nickel foam. This was then used as the anode in an electrolysis cell, and with 1 Volt phosphate was effectively adsorbed (testing at soluble phosphate concentrations of 5 to 200 mgP/l). Good selectivity was shown (versus chloride, sulphate, humic acid). The phosphorus could be desorbed by reversing the current (-2V) in 0.01M salt or 0.01M sodium hydroxide solution.

The authors suggest that integrating aluminium- or iron- amine MOF into an electrolysis anode offers a promising solution to remove and then desorb phosphorus, potentially enabling Precovery, with a high performance, high selectivity material which is fixed and stabilised.

"Effective and selective adsorption of phosphate from aqueous solution via trivalent-metals-based amino-MIL-101 MOFs", R. Liu et al., Chemical Engineering Journal 357 (2019) 159–168 https://doi.org/10.1016/j.cej.2018.09.122

"MOFs-derived conductive structure for high-performance removal/release of phosphate as electrode material Received 5 May 2018; Received in revised form", R. Liu et al., Water Research 184 (2020) 116198 https://doi.org/10.1016/j.watres.2020.116198

Update on studies of agronomic value of struvite

This overview of recent publications of struvite fertiliser tests provides an update, to be taken as additional to the 50+ publications, over the last sixty years, which show the effectiveness of struvite (magnesium ammonium phosphate) as a phosphate fertiliser for a wide range of different crops and plants (see ESPP SCOPE Newsletter n°s <u>122</u>, <u>121</u> and <u>43</u>).

Struvite fertiliser value reviews

Several studies are summarised (indicated with * below) in **Plant Nutrition Courier**, showing yet again that struvite is an effective fertiliser.

Hertzenberger, Cusick and Margenot (5) (2019) provide a meta-analysis of publications on struvite fertiliser value. Their literature review (1962 - 2019) identified 82 publications involving tests with plants/crops, of which 59 were selected (387 data points on struvite). Conclusions of this review, are that struvite is as effective a fertiliser as ammonium phosphates or superphosphates in soil pH < 6. The authors underline that struvite's fertiliser effect is related to both soil pH and to struvite particle size. They note that most studies measure biomass production and P-uptake above to aboveground biomass, whereas crop yield and biomass production and P-uptake below ground should be assessed. They note that results can be unclear if plants need to access N from struvite (which is slowly available), and that most studies employ soils with high to excessive soil available P and/or unrealistically high struvite application rates. Additionally, further field-scale studies evaluating struvite at realistic P application rates are needed to fully evaluate the potential of struvite as a fertilizer.

Römer & Steingrobe (6) (2018, see also **Römer et al**. in SCOPE Newsletter n°s <u>68</u> and <u>97</u>) summarises results of fertiliser tests by five institutes on 32 different recycled P

materials (from 17 German Government funded P-recovery projects 2004 – 2011). Results of 16 different fertiliser tests are presented, nearly all of which were pot trials, using a range of crops: maize (mostly), *Lolium perenne*, wheat, barley and rye. Struvite showed the same fertiliser effectiveness as TSP (triple super phosphate), whereas other recycled P materials were less effective except in some specific test conditions: Seaborne, Mephrec, iron phosphates, sintered sewage sludge incineration ash or meat and bone meal ash.

Struvite fertiliser tests - field trials

Benjannet et al. (7) (2020) conducted potato field trials with potatoes at 4 sites x over 3 years in Canada, comparing TSP (triple super phosphate) to TSP+struvite, with five P application rates (0 - 105 kgP/ha) and 4 different ratios of TSP/struvite (100% TSP, 75%, 50% and 25% TSP + 75% struvite). Trials had six adjacent randomised 8m rows with four replicates. Struvite used was Ostara CrystalGreen. N in struvite was not taken into account. Potato crop yield, Puptake and soil P availability (3 methods: Mehlich-3, anion exchange membrane and petiole orthophosphate) were measured. All sites were low or medium P-fertility soil class (P saturation < 8%) and soil pHs ranged from 4.8 to 6.2. Potato tuber yield and soil available P showed no significant difference when 25% to 75% of TSP was replaced by struvite (except at one site, at 75% struvite, for 2 years, when soil was pH 6.2 - in all other cases, soil pH was < 5.7). The authors conclude that except at one site, struvite mixed with (partially replacing) conventional P fertilizer performed equally as the conventional P fertilizer but that under cold and/or P deficient conditions, struvite at higher proportion may be associated with lower yield than a pure conventional P fertilizer.

Christiansen et al. (15) (2017) and Holton Rubæk et al. (16) (2018) tested wastewater-recovered struvite (Åby sewage treatment plant in Aarhus, Denmark) with spring barley in three month pot trials and in field trials at two sites in Jutland, Denmark. The pot tests used three soils with low P status and pH c. 5.8. As well as struvite, other secondary materials were also tested: sewage sludge with iron or with aluminium used for chemical P-removal, sewage sludge ash, straw ash, composted organic wastes, MBM (meat and bone meal) and MBM biochar. These were compared to soft rock phosphate and to TSP (triple super phosphate). Struvite showed the best fertiliser performance of any of the secondary materials, at 99% - 137% fertiliser effectiveness, compared to TSP. The sewage sludges and sewage sludge ash generally showed fertiliser effectiveness around one quarter to one third that of TSP, as did also the MBM biochar. The least effective material was soft phosphate rock with 5 - 20% fertiliser effectiveness compared to TSP. The field trials, with soil pH c. 5.7, tested struvite, two sewage sludges (with coagulants Fe³⁺ and alum), compost (of green waste) and biomass ash. At one site, only struvite gave grain yields comparable to triple super phosphate, whereas at the other site all materials and even the control were similar, suggesting that the soil already had sufficient phosphorus.

Struvite fertiliser tests – pot trials

Degryse et al. (1) (2017)*, southern Australia, showed that ground struvite mixed through soil quickly dissolved and its agronomic effectiveness was similar to that of MAP (mono ammonium phosphate). In six-week pot trials, they showed (see fig. 6) that fertiliser effectiveness for wheat (dry matter yield, P-uptake) was similar for ground struvite and ground MAP, both in slightly acidic (pH 5.9) and in significantly alkaline (pH 8.5) P-responsive soils. Granular struvite, on the other hand, showed much lower fertiliser effectiveness than granular MAP in both soils, suggesting the importance of struvite granule size on release patterns. Incubation studies indicated that 2 to 50% of pure granular struvite dissolved in 4 weeks depending on the soil pH. This study was sponsored by Mosaic (fertilizer company).

Robles-Aguilar et al. (2) (2020)* showed, in pot trials with maize and lupin, **higher growth after four weeks with struvite compared to triple super phosphate (TSP)**, suggesting progressive phosphorus availability from struvite. They also showed that ammonium sulphate, used as nitrogen fertiliser, can increase plant phosphorus uptake from struvite, probably by acidification of the rhizosphere.

Gómez-Suárez et al. (3) (2020)* also showed similar growth of ryegrass after 12 days in laboratory tests, soil pH 7.8, when comparing struvite with TSP. However, differences from control were only small, probably because the soil was not P deficient.

In a related study, **Watson et al.** (4a) (2019)* compared several struvites to TSP and to magnesium sulphate (Epsom salt) for ryegrass in pot trials, soil pH 5.5, concluding that the **struvites offered comparable or better effectiveness. particularly with regard to struvite's much-overlooked Mg**



content. Nevertheless, P uptake from struvite was reduced in the first harvest in the presence of a nitrification inhibitor, suggesting that nitrification inhibitors may 'indirectly' inhibit release of phosphorus and magnesium from struvite because of struvite's ammonium content.

The same authors (2020) also tested hazenite $(KNaMg_2(PO_4)_2.14H_2O)$, a compound similar to struvite, n pot trials soil pH 5.5. The hazenite was recovered from dairy industry wastewater. Hazenite showed to be as effective a provider of K, Mg and P to ryegrass as the respective conventional fertilisers: muriate of potash, kieserite and TSP (4b).

Oliveira et al. (8) (2019) tested struvite recovered from anaerobically digested organic fraction of municipal solid waste in six week pot trials in acidic sandy loam soil (pH = 5.1) and rye seeds (*Secale cereale*). The struvite showed fertiliser effectiveness similar to (biomass production and agronomic efficiency) or better than (P-uptake) SSP (single super phosphate). Struvite granulometry is not specified.

Hall et al. (9) (2020) compared six struvites from wastewater to TSP (triple super phosphate) and MAP (mono ammonium phosphate) in pot trials with perennial rye grass. The struvite materials were from Xiamen China, Ostara CrystalGreen, Berlin Wasser and three Phosphogreen struvites from Åby, Herning and Helsingor. Three different soils were used with pH 4.8, 5.4 and 6.2, all with P-Index of zero (Olsen-P < 9mgP/kg). Analysis showed that all the struvite materials were indeed mainly struvite, with mineral impurities at low levels (e.g. Newberryite Mg(HPO₄)3H₂O in the Berlin Wasser struvite). All six struvites showed fertiliser performance comparable to TSP / MAP (plant growth, Pbioavailability) despite somewhat different solubilities between struvites. Heavy metals present in the struvites (in all cases < 8 mg/kg) were at lower levels than in the TSP sample and were non-detectable in the grown biomass.

Rech, Withers et al. (10) (2019) compared three different struvites to TSP (triple super phosphate) in 38-day pot trials with wheat and soybean. The struvites tested were Ostara CrystalGreen, struvite spontaneously precipitated in a swine manure installation (Brazil) and struvite precipitated in a lab. experiment from chicken manure (by solubilising in sulphuric acid then neutralising with potassium hydroxide). The pot trials used struvite in granular form, dosed at 25 mgP/1.4 g soil pot, with additional nitrogen, potassium and sulphur. Soil pH was 5.3. Fertiliser effectiveness of struvite was not significantly different from TSP for soybean, but was significantly lower for wheat for some criteria (shoot biomass, P-uptake), with PUE (phosphorus use efficiency) 55 - 85% that of TSP, possibly because of the short duration of the pot trials compared to the known slow-release properties of granular struvite. Struvite solubility and 28-day soil mobility tests were also carried out.

Min et al. (11) (2019) tested struvite from wastewater (from an anaerobic digester treating livestock wastewater, South Korea) and lab-synthesised struvite (median particle size $50 - 120 \mu$ m) in 23-day pot trials with chili pepper, Chinese cabbage and cucumber. The struvites tested contained significant levels of potassium and of organic matter. Struvite

was dosed at the agronomic recommended fertiliser rate and at 2x and 4x this rate, that is 1 - 8 g struvite / kg soil. Struvite fertiliser effectiveness was compared to control (no fertiliser) and to a commercial fertiliser containing urea and magnesium sulphate (it is not indicated if this commercial fertiliser contained phosphorus). For all three crops, **struvite proved as affective or better fertiliser than the commercial fertiliser** at the recommended agronomic dose level. Struvite showed growth inhibition at 4x this dose, but less so than the commercial fertiliser.

Horta (12) (2017) tested struvite (NuReSys from potato processing plant) and composts (one composted digested sewage sludge, one composted chicken manure) in 36-day pot trials with rye (*Secale cereale*). In this test, the struvite and composts were first incubated in soil for 75 days before planting the rye. Soil pH was 5.1. Both of the composts and struvite, after soil incubation, resulted in rye growth and **P-uptake not significantly different than for SSP** (single super phosphate), but considerably better than control (no fertiliser). The authors note that these results may be related to the acidic soil and the use of rye, which is known to have a high P uptake.

Duboc et al. (13) (2017) **tested 11 recovered P materials**: struvite, digestate solid fraction, chicken manure, chicken manure biochar, meat and bone meal (MBM), MBM biochar, several gasified or pyrolysed (biochar) sewage sludges. These were compared to rock phosphate and single super phosphate (SSP) in 6-week pot trials, soil pH (CaCl₂) 6.2, using rye (*Secale cereale*), with P-application 15% lower than estimated (by previous testing) for maximum biomass production. **Struvite, chicken manure and chicken manure biochar showed dry matter production comparable to SSP (slightly higher for struvite**) whereas the other materials showed significantly lower results.

Vanden Nest et al. (20) (2021) carried out soil incubation tests and/or pot trials with over 50 different recycled fertiliser materials. The 65-day pot trials used rye grass in soil pH 5.3 with materials dosed so that phosphorus was applied at 39 kgP/ha. N, K and Mg were added to bring application rates up to 120 + 60 kgN/ha, 150 kgK/ha and 43 kgMg/ha, including the contents in the materials. Tested products included two struvites (recovered from municipal wastewater, crystals c. 1mm, and from pig slurry, fine powder). Other products tested were 5 biochars (from biomass and from manure or manure digestate), composts, manure/slurries and manure-based or mixed digestates and various blends. Phosphorus Use Efficiency (PUE) was calculated as the ratio between total P content in the rye grass biomass grown with a given material to that in the rye grass grown with triple super phosphate (TSP). PUE for the two struvites were 95% and 100%, suggesting P fertiliser effectiveness over this time period the same as TSP. For the other materials, PUEs ranged from 56% to over 180%. The biochars tested all show PUEs significantly lower than TSP, whereas PUE results for composts, manures and digestates are variable. The authors suggest that the PUE seems to be mainly determined by the amount of ammonium nitrogen (NH₄-N) present in the product.



Five of the materials tested (all manures) show PUEs significantly higher than 100%, that is they result in higher P uptake by the rye grass than did does triple super phosphate. The authors believe that this is related to the NH₄-N concentration in the manure, which prevents P adsorption on soil particles.

Gong et al. (14) (2018) tested recovered struvite as fertiliser in 35-day pot trials with three fast-growing vegetables: water spinach *Ipomoea aquatica*, amaranth and choy sum *Brassica rapa var. parachinensis*. The struvite was precipitated in a 7litre lab reactor from anaerobically digested cattle manure. Soil pH was 7.7. No mineral fertiliser was tested for comparison. For amaranth and brassica, struvite at agronomic fertiliser recommended dose led to marginally increased biomass production, whereas for water spinach the increase was considerable (c. 3x control). For water spinach, struvite was also dosed at up to 4x agronomic fertiliser recommendation doses, showing little further biomass increase, but **no inhibition nor burning**.

Ehmann et al. (2017) (21) carried out pot trials of germination and crop growth, using cress (2 weeks), spring barley and faba beans (6 weeks) at soil pH8. They tested a precipitated phosphate material recovered from pig manure (Fraunhofer BioEcoSim) which is a mixture of struvite, magnesium and calcium phosphates, at different application rates, and in combination with biochar from dried solid fraction of pig manure. Conclusions are that this mixed recovered phosphate salt offered **similar or better growth for tested plants compared to single super phosphate**, and that fertilising effect can be enhanced by biochar.

Ehmann et al. (2019) (22) further tested similar **mixed phosphate salts**, recovered from pig manure and digested pig manure, in pot trials with sunflower, marigold and Chinese cabbage, this time comparing to triple super phosphate (TSP), at soil pH 5.8. In this set of trials, results were somewhat less clear: for marigolds, biomass and plant P content with no phosphate (control), were similar to results with TSP; results with sunflower were also marginal, suggesting no P deficiency in control soil; results with Chinese cabbage showed similar biomass with TSP, the mixed P salt or also dried solid fraction of digestate.

Struvite dissolution and leaching in soil

Anderson et al. (17) (2020) studied dissolution of struvite (Ostara Crystal Green), both as supplied (granules) and finely ground powder in four Arkansas soils incubated for six months. Soil pHs were 6.2 to 6.7. The ground struvite resulted in significantly increased water and weak acid extractable P after two weeks, whereas these increased progressively over the six months for the granular struvite, so confirming progressive release properties.

Worwag & Sobik-Szoltysek (18) (2019) assessed leaching of P from soils fertilised with lab-synthesised struvite at 0.1 - 1 g struvite / 250 g soil. Soil was pH 7.6 with 3.6% organic matter. 1m depth (5 cm diameter) lysimeters were subject to the equivalent of 650 mm rainfall (corresponding to local climate) divided over 12 days. Phosphorus content in the leachate reached maxima of 4.6 mgP/l (at the lowest struvite dose) to



58 mgP/l (highest dose) but showed a reduction of <25% in the soil. The authors conclude that **most of the P applied in struvite is not leached out** in these conditions and over this time scale.

Struvite and soil remediation

Gu, Gates and Margenot 2020 (19) (2020) demonstrated that struvite can be used to immobilize soil lead (Pb) as effectively as can phosphate rock and triple superphosphate, but without excessive soil available P build-up for the latter and without the risk of secondary contamination of the former (e.g. cadmium in sedimentary phosphate rock). Struvite used was Ostara, recovered from wastewater. P amendments were added to two Pb-contaminated soils with contrasting clay contents at a rate commonly used for Pb immobilization based on the soil elemental molar ratio of 4:1 (P/[Cd + Zn + Pb]). Greater immobilization efficacy of Pb (up to 19%) occurred for granular (2-4 mm diameter) than ground (<0.5 mm) struvite. For a given particle size, Pb immobilization and plant tissue Pb decreased in the order of PR \geq struvite > TSP, but the order reversed for P loss risk, with up to nearly 200x greater waterextractable P for TSP than PR and struvite. Greater immobilization for granular PR and struvite could be caused by lower dissolution rates which may better synchronize P dissolution and desorption of Pb.

(1) Dissolution rate and agronomic effectiveness of struvite fertilizers – effect of soil pH, granulation and base excess, F. Degryse et al. Plant Soil (2017) 410:139–152, <u>https://doi.org/10.1007/s11104-016-2990-2</u>

See also: Everaert, M., da Silva, R.C., Degryse, F., McLaughlin, M.J. and Smolders, E., 2018. Limited dissolved phosphorus runoff losses from layered double hydroxide and struvite fertilizers in a rainfall simulation study. Journal of environmental quality, 47(2), pp.371-377 https://doi.org/10.2134/jeq2017.07.0282

(2) Phosphorus uptake from struvite is modulated by the nitrogen form applied, A Robles-Aguilar et al., J. Plant Nutr. Soil Sci. 2020, 183, 80–90, https://doi.org/10.1002/jpln.201900109

(3) Fertilizer Potential of Struvite as Affected by Nitrogen Form in the Rhizosphere, A. Gómez-Suárez et al., Sustainability 2020, 12, 2212; <u>https://doi.org/10.3390/su12062212</u>

(4a) Plant availability of magnesium and phosphorus from struvite with concurrent nitrification inhibitor application, C. Watson et al., Soil Use Manage. 2019; 00:1–8, <u>https://doi.org/10.1111/sum.12527</u>

(4b) Hazenite: a new secondary phosphorus, potassium and magnesium fertiliser, C. Watson et al., Plant Soil Environ. 2020; 66(1), 1-6. https://doi.org/10.17221/492/2019-PSE

(5) A review and meta-analysis of the agricultural potential of struvite as a phosphorus fertilizer, A. Hertzberger et al., Soil Sci. Soc. Am. J. 2020;1–19, https://doi.org/10.1002/saj2.20065

(6) Fertilizer Effect of Phosphorus Recycling Products, W. Römer et al., Sustainability 2018, 10, 1166; DOI:10.3390/su10041166 and see SCOPE Newsletter n°97 <u>www.phosphorusplatform.eu/Scope097</u>

(7) Potato Response to Struvite in Comparison with Conventional Phosphorus Fertilizer in Eastern Canada, R. Benjannet et al., Agronomy Journal, Volume 112, Issue 2, 2020, <u>https://doi.org/10.1002/agi2.20118</u>

(8) Fertilizing potential of struvite recovered from organic fraction of municipal solid waste, V. Oliveira et al. 2019, NAXOS2018 n°146

European Sustainable Phosphorus Platform SCOPE Newsletter info@phosphorusplatform.eu www.phosphorusplatform.eu http://uest.ntua.gr/naxos2018/proceedings/pdf/146_NAXOS2018_Oliveira_et_al.pdf

(9) Phosphorus speciation and fertiliser performance characteristics: A comparison of waste recovered struvites from global sources, R. Hall, L. Staal, K. Macintosh, J. McGrath, J. Bailey, L. Black, U. Nielsen, K. Reitzel, P. Williams, Geoderma 362 (2020) 114096, https://doi.org/10.1016/j.geoderma.2019.114096

(10) Solubility, Diffusion and Crop Uptake of Phosphorus in Three Different Struvites, I. Rech et al., Sustainability 2019, 11, 134, https://doi.org/10.3390/su11010134

(11) Characteristics of vegetable crop cultivation and nutrient releasing with struvite as a slow-release fertilizer, K. J. Min et al., Environmental Science and Pollution Research, (2019) 26:34332–34344, https://doi.org/10.1007/s11356-019-05522-2

(12) Bioavailability of phosphorus from composts and struvite in acid soils,
 C. Horta, Revista Brasileira de Engenharia Agrícola e Ambiental, ISSN 1807-1929, v.21, n.7, p.459-464, 2017, <u>https://doi.org/10.1590/1807-1929/agriambi.v21n7p459-464</u>

(13) Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers, O. Duboc et al., Science of the Total Environment 599–600 (2017) 1160–1170, https://doi.org/10.1016/j.scitotenv.2017.05.054

(14) Application of Struvite-MAP Crystallization Reactor for Treating Cattle Manure Anaerobic Digested Slurry: Nitrogen and Phosphorus Recovery and Crystal Fertilizer Efficiency in Plant Trials, W. Gong et al., Int. J. Environ. Res. Public Health 2018, 15, 1397; <u>https://doi.org/10.3390/ijerph15071397</u>

(15) Recirkulerede gødningsprodukter og deres P-virkning, N. Christiansen et al., Plantekongres 2017 n° 72.1,

https://www.ft.dk/samling/20161/almdel/mof/spm/398/svar/1380995/172009 2.pdf or

https://sp.landbrugsinfo.dk/Planteavl/Plantekongres/Sider/pl_plk_2017_res_ 72_1_nina_hoej_christiansen.pdf

(16) Gødningsværdi af fosfor i restprodukter G. Holton Rubæk et al., DCA Rapport nr. 141 December 2018 https://dcapub.au.dk/djfpublikation/djfpdf/DCArapport141_2.pdf

ппрыласариоланая адраонканов адрадо сптарронт н _2.рај

(17) Chemically Precipitated Struvite Dissolution Dynamics over Time in Various Soil Textures, R. Anderson et al., Agricultural Sciences, 2020, 11, 567-591, <u>https://doi.org/10.4236/as.2020.116036</u>

(18) The Influence of Soil Fertilization with Struvite on Water Efficiency – Lysymetric Columns, M. Worwąg & J. Sobik-Szołtysek, Rocznik Ochrona Środowiska, voL; 21, 2019, ISSN 1506-218X, 894-905 https://ros.edu.pl/images/roczniki/2019/055_ROS_V21_R2019.pdf

(19) Phosphate recycled as struvite immobilizes bioaccessible soil lead while minimizing environmental risk, C. Gu, B. Gates, J. Margenot, Journal of Cleaner Production 276 (2020) 122635, https://doi.org/10.1016/j.jclepro.2020.122635

(20) Renewable P sources: P use efficiency of digestate, processed animal manure, compost, biochar and struvite, T. Vanden Nest et al., Science of the Total Environment 750 (2021) 141699, https://doi.org/10.1016/j.scitotenv.2020.141699

(21) Can Phosphate Salts Recovered from Manure Replace Conventional Phosphate Fertilizer?, A. Ehmann, I-M. Bach, S. Laopeamthong, J. Bilbao, I. Lewandowski, Agriculture 2017, 7, 1; https://doi.org/10.3390/agriculture7010001

(22) Phosphates recycled from semi-liquid manure and digestate are suitable alternative fertilizers for ornamentals, A. Ehmann, I-M. Bach, J. Bilbao, I. Lewandowski, T. Miiller, Scientia Horticulturae 243 (2019) 440–450, https://doi.org/10.1016/j.scienta.2018.08.052