

Dates 2023	1
ESPP dates for 2024	1
SOFIE3	2
Standards & definitions for "Bio-Based" nutrients	2
Policy	2
EU support study for Sewage Sludge Directive published	2
EU evaluation of the Nitrates Directive	3
EU Critical Raw Materials Act trilogue compromise	3
Call for input for evaluation of EU Fertilising Products Regulation	3
Finland publishes new national fertilisers regulation	3
EU Fertilisers Expert Group	4
EU fertilisers market data portal	4
ESPP Member news	5
N2 Applied – GEA Manure Enricher roll out	5
Ragn-Sells "10 Billion Challenge"	5
Fertilizers Europe launches Roadmap for climate neutral fertilisers by 2050	5
German Phosphorus Platform GA, annual Forum and research sponsorship	5
Events	6
Role of plant biostimulants in farmers adaptation to climate change	6
Research into new routes to P ₄	6
Carbothermal reduction of phosphoric acid	7
Attempts to recover P from iron industry wastes	7
Electrolysis of phosphate rock in molten calcium chloride	8
Electrolysis of molten condensed phosphate salts	8
I utorial review on organo-phosphorus chemistry and applications	9
Stay informed	9
ESPP members	9

Dates 2023

- 6-8 Dec 2023: Cambridge UK International Fertilisers Society <u>IFS conference</u>, crop nutrition and fertiliser production
- 11 Dec. 2023: 14h-17h CET, Brussels & online European Commission workshop How to boost consumer demand of bio-based materials and products
- **14 Dec. 2023:** 14h30-16h30 CET **ESPP General Assembly (online)** ESPP members/partners have received link if not contact info@phosphorusplatform.eu
- 14 Dec 2024: 13h-14h30 CET EasyMining webinar on recycled phosphates for animal feed

ESPP dates for 2024

- 16-17 Jan. 2024: Brussels & online <u>SOFIE3</u> (Organic and Organo-Mineral Fertilisers) (with Eurofema, Fertilizers Europe, International Fertiliser Society and SILC Ferilizzanti)
- 18 Jan. 2024: Brussels & online <u>"Bio-Based" nutrients</u> standards & definitions
- 26-28 Feb. 2024: Warsaw CRU Phosphates 2024 ESPP panel on sustainable fertilisers
- 12-14 March 2024: Brussels & online ESPP workshops on Nutrient recycling policy
 - targets for nutrient recovery under the Urban Waste Water Treatment Directive revision
 policy tools to support market pull for recycled nutrients
- 16-17 April 2024: Brussels & online <u>NERM</u> Nutrients in Europe Research Meeting (with Fertimanure, Lex4Bio, Walnut, Sea2Land, Rustica) – call for abstracts extended to 10th December 2023
- 8-10 October 2024: Lleida, Spain ESPC5 (5th European Sustainable Phosphorus Conference)



16-17

2024

January

Brussels

& hybrid

rganic

fertilisers

3rd summit

Europe

SOFIE3

3rd Summit of Organic and organo-mineral Fertiliser Industries in Europe.
 16-17 January 2024, Brussels & hybrid. SOFIE is the only industry meeting place for organic-carbon-based fertiliser producers, distributors, advisory, technology suppliers. <u>SOFIE1</u> (2019) attracted 125 participants, with 230 for <u>SOFIE2</u> (2023).
 Programme now online. Organic fertiliser company showcase pitches are welcome.

Programme <u>www.phosphorusplatform.eu/SOFIE</u>. Registration <u>Eventbrite</u>

Standards & definitions for "Bio-Based" nutrients

Brussels & hybrid, 18th January 2024 Defining "Bio-Based Fertilisers" and FPR "solely biological origin"

The term "Bio-Based Fertilisers" is today being widely used. For market transparency and policy making. It is important to have a clear and agreed definition of what is a "Bio-Based Fertiliser" and how to define the "Bio-Based" nutrient content of fertilising products. Also, the EU Fertilising Products Regulation 2019/2009 uses the term "*of solely biological origin*" for nutrients in criteria of several PFCs and there is today no clarity on how this should be interpreted. CEN and ISO methodologies for "Bio-based products: vocabulary" and for defining bio-based content are based on carbon radio-dating, and are not applicable to nutrients.



Defining "Bio-Based Fertilisers" and FPR "solely biological origin"

> 18th January 2024 Brussels & Online

The meeting will take as starting point the working proposal HERE. Programme: http://phosphorusplatform.eu/BBF2024 Registration Eventbrite

Policy

EU support study for Sewage Sludge Directive published

European Commission "feasibility study" considers two sewage sludge management options: 1 = ongoing land use of treated sludge with tighter monitoring and contaminant limits; 2 =mandatory sludge incineration with P-recovery. The study rejects options for ongoing sewage sludge land use without EU regulatory contaminant limits. The study does not select a preferred option of the two considered because of uncertainties about levels of contaminants and related risk, and with the aim of enabling further stakeholder input. The scenario (1) proposes that sewage sludge from larger sewage works applied in agriculture must qualify under the EU Fertilising Products Regulation and that other quality requirements would be applicable to sludge from smaller sewage works used in agriculture or forestry etc. (p31), and also that all sludge used on land should be applied according to crop phosphorus needs and with good management practice requirements (p34).

The study indicates that the EU generates just over 8 Mt/y dry matter (DM) of sewage sludge of which c. 32% is incinerated (based on Eurostat 2021). 10% of EU sewage sludge still goes to landfill, resulting in significant methane emissions.

Table 1 (p8) shows that heavy metal limits are generally lower in current Member State national legislation than in the EU Sewage Sludge Directive (which dates from 1986 and has not been updated), and also that the lowest national heavy metal limits for sewage sludge are in all cases lower than EU Fertilising Products Regulation (FPR) limits (for Organic Fertiliser / Organic Soil Improvers). The average observed heavy metal levels in sewage sludge are also lower than the EU FPR limits for all eight metal contaminants considered. However, JRC note concerns about other chemicals potentially found in sewage sludge, including industrial chemicals, pesticides, pharmaceuticals, personal care chemicals, PFAS, microplastics, and consider (p26) that risk assessments of these chemicals in sludge are inadequate, in particular because they do not take into account local context and combination effects of chemicals in sludge.

The study suggests (p 19-20) that benefits to society are highest for mono-incineration of sewage sludge with phosphorus recovery (option 1). Use of composted or digested sewage sludge in agriculture has net positive benefits (assuming tight contaminant limits and application of nutrients according to crop requirements and not in excess) but significantly lower than for option 1, whereas co-incineration (phosphorus not recovered) has negative net societal impacts and landfilling has strongly negative societal impacts. On the other hand the cost of mono-incineration (option 2) is estimated to be 2-3 x higher than agriculture application (option 1).

Organic carbon returned to soil by use of treated sewage sludge is not considered significant (fig. 5 p 11, p 35) compared to manure and bio-waste.

Short-term agronomic P-efficiency is considered to be higher in mineral P-fertiliser products recovered from sewage sludge incineration ash than in agricultural application of sewage sludge, so leading to lower expected nutrient losses in scenario 2 (p 43-44).

Option 2 (mono-incineration and P-recovery from sewage sludge incineration ash) is estimated to result in additional annualised total EU costs (Capex plus Opex, compared to agricultural sludge application) of 138 – 569 million € per year, depending on the size of sewage works above which this is mandated (138 M€ if sewage works > 500 000 p.e. – 569 M€ if > 20 000 p.e.). If



mandated for sewage works > 50 000 p.e. estimated additional cost is 1.4 – 3.3 €/person/year, that is 1-3% of wastewater treatment costs. Correspondingly, option 2 (> 50 000 p.e.) would generate 3 000 – 4 200 full time job equivalents across Europe.

The study underlines that cost to operators of societally positive sludge management options are higher than for options with negative societal impacts, so that policy action is therefore necessary.

ESPP will make comments to JRC on the content, methodology and conclusions of this study, probably in early 2024. Any input to these comments is welcome, to ESPP info@phosphorusplatform.eu by end 2023.

"Feasibility study in support of future policy developments of the Sewage Sludge Directive (86/278/EEC)", European Commission, JRC Science for Policy Report, L. Egle et al., 2023 <u>https://dx.doi.org/10.2760/305263</u>

EU evaluation of the Nitrates Directive

European Commission opens public consultation for evaluation of the Nitrates Directive, citing climate, food security, sustainability, nutrient recycling and the commitment to reduce nutrient losses by 50% by 2030. The evaluation will assess if the Directive remains "fit for purpose", if it is coherent with EU environmental objectives, whether cost and administration burdens can be reduced. The consultation (in 27 languages) is 16 questions plus possibilities for comments or to submit documents. The accompanying "Call for Evidence" specifically notes the question of whether the Directive is sufficiently promoting the recycling of nutrients, including from processed manure, and the EU commitment at COP15 (Convention on Biological Biodiversity) to reduce nutrient losses by 50% by 2030. Phosphates (which are not mentioned in the current Nitrates Directive text) are mentioned in the online introduction to the questionnaire, but not in the questionnaire, not in the Call for Evidence. Recycling of nutrients is cited in Q2.7. Measures to limit inappropriate manure spreading and the 170 kgN/ha manure nitrogen limit are cited in Qs 3.1, 3.2, 3.4, 3.9. Addressing intensive livestock production is cited in Qs 3.1, 3.9. Questions address which Nitrates Directive measures are effective (Nitrate vulnerable Zones, Action Programmes, manure storage, manure spreading limit ... Q3.2) and relevance to Water Framework Directive Good Ecological Status and to the 50% nutrient loss reduction objective (both Q3.12).

"The protection of waters against pollution caused by nitrates from agricultural sources – Evaluation", public consultation preparatory to evaluation of the EU Nitrates Directive (91/676/EEC) and Call for Evidence. Input requested from the public, farmers, stakeholders. **Open to 8th March 2024.** In all EU languages. <u>HERE</u>.

EU Critical Raw Materials Act trilogue compromise

Political agreement between Council and Parliament adds only aluminium to the "Strategic" materials list. Phosphorus is not added to the 'Strategic' materials list but remains on the 'Critical' raw materials list. The 'Strategic' list is 16 raw materials identified as supply-critical for 'strategic technologies' defined as "green and digital transitions ... defence and space applications". Both phosphate rock and "phosphorus" (meaning P_4 = white phosphorus) remain on the EU list of "Critical" raw materials (34 materials). Graphite, already on the "Strategic" list, is extended to both synthetic and natural graphite. The trilogue agreement is not public. It will lead to detailed compromise amendments which then go back to European Parliament and Council for validation votes. To ESPP's understanding, only "Strategic" materials are concerned by the main tools of the CRM Act (EU sourcing, processing and recycling targets; Strategic Projects) but all "Critical" raw materials will benefit from monitoring of supply and uses, programmes to develop recovery and recycling, and stress tests every three years.

European Commission: "Commission welcomes political agreement on the Critical Raw Materials Act", <u>13th November 2023</u>. <i>Council: "Council and Parliament strike provisional deal to reinforce the supply of critical raw materials", <u>13th November 2023</u>.

Call for input for evaluation of EU Fertilising Products Regulation

DG GROW asks for input on which issues to consider in preparing the upcoming evaluation of the EU Fertilising Products Regulation. The Commission notes that the evaluation must be completed by July 2026 and expects to assess impacts on markets, trade and companies, health and environment (levels of cadmium and of other contaminants) and at the wider context as to whether the Regulation brings added value compared to national fertiliser regulations. Comments are invited in particular as to what aspects should be assessed concerning markets and definitions of PFCs, coherence of the FPR, interactions with REACH, Animal By-Produces Regulations, Nitrates Directive, Farm-to-Fork Strategy, conformity assessment procedures, contaminants, effectiveness of the FPR and interactions with national regulations, or to indicate other questions which should be considered in the evaluation. Comments can be submitted only via members of the EU Fertilisers Expert Group (inc. ESPP).

Deadline for comments is 31st December, so please send any comments you wish ESPP to submit to ESPP before mid December.

Finland publishes new national fertilisers regulation

Finland's new national fertiliser regulation defines criteria for different fertiliser types and inputs, covering composts, digestates, biochars and ashes. Sewage and industrial sludges are authorised for use in agriculture and in biochars, subject to specified conditions. This Finland national regulation enables fertilisers to be sold in Finland, not on the EU market. The overall structure and product and input families show similarities to the EU Fertilising Products Regulation, with product categories and component materials, but criteria are in some cases stricter or different, and are less comprehensive. Sewage sludge can be included in biochars subject to minimum 500°C x 5 minutes pyrolysis, and subject to the criteria defined for all biochars. Sewage



sludge after certain other specified treatments (e.g; specified composted, digested, limed, aged) can be used in agriculture with limitations of quantities (per five years) and subject to analysis of metals in soil. Combustion ashes are authorised under conditions, with specific conditions for forest ash (minimum K and P contents). Cadmium limits at 22 mgCd/kgP₂O₅ (= 50 mgCd/kgP) are the same as those in the existing 2006 EU derogation for Finland (see ESPP eNews n°59): this derogation allows Finland to limit cadmium not only in national fertilisers but also in EU fertilisers sold in Finland. It is ESPP's understanding that authorisation of a material under this national regulation authorises use in agriculture but does not give End-of-Waste status.

Finland national fertilisers regulation 964/2023, 6th October 2023 (Maa- ja metsätalousministeriön asetus)

EU Fertilisers Expert Group

Meeting updated on: EU Fertilising Products Regulation (FPR) evaluation, product Conformity Assessment, standards development, FAQ guidance document, animal by-products ("Processed Manure"), CMCs, biodegradability criteria ...

ESPP participated in the European Commission official fertilisers working group meeting 28-29 November. The summary below is not officially validated and is provided for information only, and may contain inaccuracies.

Giel Tettelaer (ECFI), chair of the Notified Bodies coordination group, explained work underway on CE-product certification (Conformity Assessment) processes, including challenges of how to rationalise audit of multiple decentralised sites supplying recycled materials and how to apply "batch" audit requirements to liquid flows.

An updated list of standards under development to support the FPR was circulated here. New standards needed for animal byproducts and "Processed Manure" in CE-fertilisers are not yet mandated because CEN does not have sufficient human resources to take these on.

A number of additional question-answers were validated for the living Commission FAQ guidance document (here). Questions concerning the use of plants as inputs to "production processes" in CMC15, the definition of "nutrients ... of solely biological origin", animal by-products, sewage sludge were not resolved pending further discussion.

Biodegradability criteria for fertiliser polymers, mulches, etc. are pending finalisation (following the AIMPLAS report here) and should be published for public consultation in January 2024.

The Delegated Act amending the FPR to enable used of "Processed Manure" (as defined in the Animal By-Products Regulation) is finalised here and is expected to be published in coming months. ESPP requested clarification in the FAQ guidance document concerning application for manures used as inputs for composts, digestates, ashes and pyrolysis materials (biochars) when the ABP process criteria can be achieved simultaneous with the FPR CMC process criteria. An external consultant (QLab, Greece) has been commissioned by the Commission to carry out studies on other Cat 2-3 animal by-products cited in the DG SANTE ABP Regulation amendment 2023/1605 prior to integrating these into the FPR CMC10.

NMI, The Netherlands, has been contracted by the Commission to study possible new CMC materials or changes to CMC processing and other criteria. This study will centre on the materials and requests submitted to the survey (ESPP eNews n°69) A second study is being contracted to assess additional biostimulant microorganisms.

NMI presented work underway (interim report for comment and input) to develop guidance on Technical Documentation to support Conformity Assessment, including an IT support tool.

Input was requested by the Commission to identify guestions for evaluation of the EU Fertilising Products Regulation (see above).

The 3rd SOFIE (Summit of the Organic Fertilisers Industry in Europe), 16-17 January, Brussels and online, will offer opportunities to discuss these different points, for organic-carbon based fertilisers: SOFIE.

EU Fertilisers Expert Group documents (CIRCABC public) HERE.

EU fertilisers market data portal

European Commission launches fertilisers pages on the EU Agri-food Data Portal. Industry and stakeholder comments are welcome. This follows the commitment, in the Commission Communication on fertiliser supply and price (November 2022, see ESPP eNews n°72), to improve data access. The newly launched fertiliser sector pages on the EU Agri-food Data Portal present data and visualisations on fertiliser price trends (by month, average prices aggregated by nutrient N, P and K), fertiliser production in Europe (by fertiliser type and raw material, by Member State, per year) and fertiliser trade (import export, by Member State and trade partners, by fertiliser type and raw material, per month). Statistics on fertiliser production and trade are also available for a selected number of products. The data shown suggests that phosphorus fertiliser prices increased by nearly 4x from 2020 to early 2022, before falling back, with today's prices still nearly 2x the 2020 level. Phosphate fertiliser production in the EU is indicated to be 500 000 - 700 000 t-fertiliser/year since around 2011, with main producers since 2016 being Poland, Italy and France. However, if "mixed" fertilisers are also included, the production is much higher (c. 12 000 t-fertiliser/year) with main producing countries Finland, Spain, Belgium, Poland, Italy, Greece, France.

European Commission Agri-food date portal: Fertiliser https://agridata.ec.europa.eu/extensions/DataPortal/fertiliser.html See also: Fertilisers (europa.eu) and European Commission call for experts for EU Fertilisers Market Observatory in ESPP eNews n°74.



ESPP Member news



N2 Applied – GEA Manure Enricher roll out

Plasma nitrogen fixing and stabilisation technology from N2 Applied, rolled out with GEA, is nominated for the Boerenbusiness Agribusiness Awards 2023 and is now rolled out into Germany in addition to installations in Norway, Sweden, Denmark, Netherlands, UK. The first installation in Germany, rolled by GEA, is treating dairy manure digestate on a farm in Meschede, Northern Germany.

Boerenbusiness Agribusiness award: <u>https://www.boerenbusiness.nl/award/genomineerden</u> N2 Applied news: <u>https://n2applied.com/latestnews/</u>

Ragn-Sells "10 Billion Challenge"

How will we feed ten billion people in the world ? Ragn-Sells calls for action on nutrient recycling. Food waste could feed 1 ¼ billion. Recycling of sewage nutrients is essential to sustain food production and reduce environmental impacts. Ragn-Sells state that without phosphorus and nitrogen inputs, agricultural crop production would be cut by half. The company is developing nutrient recycling with EasyMining technology for phosphorus, nitrogen and potassium recovery from sewage, aquaculture wastes and municipal waste incineration ash. "We want to accelerate change, scale circular models and create synergies that reward innovative companies."

Ragn-Sells 10 Billion Challenge "Changing food together" https://www.10billionchallenge.org/

Fertilizers Europe launches Roadmap for climate neutral fertilisers by 2050

The European fertilisers industry fixes ambitions to reduce GHG emissions 70% by 2040 and to net-zero by 2050 through decarbonising existing fertiliser technologies and green hydrogen for ammonia. Decarbonising strategies include electrolysis, carbon capture and storage and biomethane. Green ammonia is produced with hydrogen from electrolysis using renewable energy. Estimated costs include 17 billion \in for electrolysers, 3 billion \in for hydrogen pipelines and 64 billion \in to supply green electricity from offshore wind. The roadmap underlines the need for varied approaches adapted to specific local contexts (logistics, infrastructure, raw materials, energy ...). Five prerequisites are identified as access to competitive green energy, boosting market demand for climate-neutral fertilisers (through a labelling system accompanied by a mandatory purchasing target for all EU nitrogen fertiliser purchasers), de-risk support for early investments, protection against unfair competition from imported fertilisers (Carbon Border Adjustment Mechanism) and a legal and funding framework. The roadmap documents point to the need for "availability of nutrients for recycling" and for an industry strategy combining organic and mineral nutrients, nutrient recycling, improved nutrient efficiency fertilisers, soil organic matter and carbon farming. The roadmap was launched by Fertilizers Europe at an event in Brussels, 14th November 2023, with 100+ participants, including a panel discussion with representatives from the European Parliament, European Commission, the fertilizers and agriculture businesses.

"Decarbonising Fertilizers by 2050 - Fertilizers Europe", 14th November 2023 <u>https://www.fertilizerseurope.com/decarbonising-fertilizers-by-2050/</u> and "Roadmap for the European Fertilizer Industry" (Guidehouse for Fertilizers Europe), <u>22nd September 2023</u>.

German Phosphorus Platform GA, annual Forum and research sponsorship

The annual forum of DPP, the German Phosphorus Platform, gathered nearly 100 participants in Frankfurt and online, discussed P-recycling implementation, and awarded a new 1 000 € research prize. The day before, the DPP's general meeting took place and members elected a new board for the next two years: Simone Apitz, Hessian Ministry for the Environment, remains DPP Chair, and the Board includes members from Dechema, SWW Wundsiedel, Veolia, EasyMining, MSE and Justus Liebig University Giessen. At the DPP Forum, projects on recycled nutrients in Organic Farming (nureq4org: final report here) and on sewage sludge incineration and P-recovery capacity (Refoplan) were presented. The new DPP research prize of 1 000 € for a thesis addressing phosphorus recycling, sponsored this year by Remondis (member of DPP), was awarded to Jannik Mühlbauer (TU Dresden) for his thesis "Laboratory studies on thermochemical sewage sludge (Contact). At the end of the event, participants answered the key question "P-Recycling - stagnation or progress?" with a show of hands. The majority voted "progress". Simone Apitz appealed to all stakeholders to act now and discuss the topic across networks so that the implementation of a sustainable phosphorus economy can succeed.

DPP Forum 16th October 2023 https://www.deutsche-phosphor-plattform.de/aktuelles-forum/



Events

Role of plant biostimulants in farmers adaptation to climate change

Webinar, organised by the European Biostimulants Industry Council (EBIC), discusses how biostimulants can support farmers in adapting to changing environmental conditions and extreme weather events. The meeting, 8th November 2023, gathered more than 500 participants in presence and online, and was moderated by Kevin Bosc, EBIC, who introduced the challenges faced by farmers and food production companies in adapting to climate change and highlighted the importance of building resilient and sustainable food systems, presenting biostimulants as part of the solution.

Jens Boyen, Permanent Representation of Belgium to the European Union, highlighted how extreme events disrupt the food system and the food supply chain, impairing farmers' possibility to plan their harvests, causing the spread of pests and diseases, reducing biodiversity and soil health. Many technologies are trying to face these problems, including genomic techniques to develop adapted crop varieties, biocontrol as an alternative to chemical pesticides, biostimulants to strengthen plants' adaptation to abiotic stressors, and new types of irrigation systems. Policy actions are essential for these new tools to reach the farmers, as well as financial support, funds to research and innovation, and proper tools for risk management for farmers like insurance policies.

Felipe Cortines, a farmer from Andalucía, emphasised that the main problems faced by farmers are extreme and random climatic events and market disruptions increasing costs and threatening farmers' profitability. In his opinion, biostimulants are a useful tool, as they are tailor-made for specific functions, although their cost is high and they are not easy to use: more knowledge and training on how to use these products are needed to make the best use of them.

Lisa Boulton, Purina PetCare (Nestlé), introduced the company's Regenerative Agriculture initiative and work with seaweedbased biostimulants. Field trails started in the UK in 2022 to test the improvement in plant performance, including nutritional content of the grains and resistance to abiotic stress, the possibility to reduce the use of traditional fertilisers while maintaining or increasing the yield, and the impact on biodiversity and on the carbon stored in the soil. More trials planned in France, Italy and Hungary. For these solutions to be taken up, a systemic approach is needed, including incentives for farmers, regulatory frameworks, farmers' education and relevant stakeholders' engagement. She also presented a project where seaweed amendments and biostimulants are produced from seaweed grown on nutrients absorbed from coastal waters where excess N and P deriving from land may threaten ecosystem health.

Carlos Rodriguez-Villa Förster, EBIC, pointed out that many biostimulant products are currently not covered by the FPR, and regulatory barriers remain for some of these products to gain access to market. Policy and regulatory coherence, as well as education, training and incentivisation for farmers are required. He remarked that biostimulants are not a standalone solution but part of a broader toolbox that farmers can use, and concluded the meeting by highlighting the need to continue engaging with agri-food chain, policymakers, academia and other stakeholders to raise awareness on biostimulants and on how they can support common objectives.

"Farmers and food chain actors debate the role of plant biostimulants in helping farmers adapt to climate change": <u>EBIC summary here</u>. "A seaweed aquaculture imperative to meet global sustainability targets" Duarte et al. (2022) Nature Sustainability <u>DOI</u>

Research into new routes to P₄

We here summarise a number of recent scientific studies proposing possible future routes to produce elemental phosphorus (P₄),. Elemental phosphorus is on the EU Critical Raw Materials List, because there is today no production in Europe and the EU is dependent on imports from only 3-4 countries.

P₄ is today produced by carbothermal reduction, using coke in furnaces operating at c. 1400°C, with high electricity consumption and greenhouse gas emissions.

Other proposed routes to P4 are presented in

- <u>ESPP eNews n°64</u>: 'Spodophos' process using aluminium scrap to provide energy rather than coke and operating at around 600°C.
- <u>ESPP eNews n°57</u>: FlashPhos project to produce P₄ from sewage sludge and other wastes by thermo-chemical reduction (University of Stuttgart, Italmatch)
- <u>ESPP eNews n°45</u>: "Replacing P₄ is still in its infancy", review of possible future processes to produce P₄ (Geeson & Cummins, <u>2020</u> and <u>2018</u>)



Carbothermal reduction of phosphoric acid

Study suggests that P₄ could be produced at c. 1000°C by reducing phosphoric acid with activated carbon, instead of c. 1400°C using phosphate rock and coke. Lab-scale experiments by Yoshida, Yu et al. (reactor tube 1200 cm x diameter 32 cm) containing a layer of activated carbon and a layer of activated carbon soaked in phosphoric acid (85% acid / 15% water). With the activated carbon at c. 1000°C and the P-acid soaked carbon at c. 700°C, under argon gas, yellow phosphorus (white phosphorus = elemental P₄ with some impurities) was recovered by bubbling the offgas through hot water. The authors state that the phosphoric acid is first vaporised as P_4O_{10} then reduced to gaseous P₄. In this lab experiment, after heating the reactor for several hours, around 50% of the phosphorus in the input phosphoric acid was recovered as P₄.

"Yellow Phosphorus Production from Phosphoric Acid by Carbothermic Reduction", H. Yu et al., REWAS 2022: Developing Tomorrow's Technical Cycles (Volume I), The Minerals, Metals & Materials Series, <u>https://doi.org/10.1007/978-3-030-92563-5_31</u>

See also "Carbothermic Reduction of Phosphoric Acid Extracted from Dephosphorization Slags to Produce Yellow Phosphorus", Int. J. Materials and Metallurgical Engineering Vol:13, No:11, 2019, summarised in <u>ESPP eNews n°39</u>.

This is not a new approach and was presented for example in the **2010** <u>US patent WO 2010/029570</u> for production of elemental **phosphorus (P4)** from phosphoric acid and carbon. This patent notes that obstacles to achieving this are the release of water from phosphoric acid, which requires excess carbon to react with this water, and the sublimation of phosphoric acid to gaseous metaphosphates without reacting with carbon. The latter obstacle is addressed in the patent by selective different heating in different parts of the reactor.

In a more recent **patent from Université Mohammed VI Polytechnique**, **Morocco**, **EP 3891099 2023**, **production of elemental phosphorus from phosphoric acid is proposed using different (hydrophilic) carbon sources**: biomass, sewage sludge organic polymers, kerogen (geological carbon deposits). The phosphoric acid is first reacted with the carbon source (at 80 – 150°C) then carbothermal reduced at 550 – 950 °C to produce elemental phosphorus (P₄).

ESPP comment: these processes may enable P_4 production at a lower temperature than the existing industrial furnace route (1000°C vs. 1400°C) and possibly with lower energy consumption (no silicate slag production), but total energy consumption needs to be calculated taking into account the production and concentration of the phosphoric acid, activation of carbon, *P*-recovery rates, furnace design and elimination of impurities from the carbon source and from the phosphoric acid (or purification of the phosphoric acid).

Attempts to recover P from iron industry wastes

Matsubae-Yokoyama et al. have estimated that 4% of global phosphorus flows are in steel industry wastes (<u>SCOPE Newsletter</u> $n^{\circ}122$). However, to date, despite a number of research publications (as ESPP sees things) there seems to be no suggestion of an effective process to recover the phosphorus in such slag, in which iron is present from which the phosphorus must be separated to so recover it in a useful form, and in which the phosphorus is at very low levels (1 – 1.5% P). Phosphorus is deliberately left in slag from existing phosphorus furnaces at concentrations of a few % in steel slag in order to avoid unwanted reactions in the furnace (silicon reduction).

Lab tests (Liu et al. 2023) seem to show failure to recover phosphorus from calcium phosphate doped iron slag: less P was recovered than was added. The "industrial converter slag" used initially contained 1% P and 25% iron. Calcium phosphate (Ca₃(PO₄)₂) and silicon dioxide (SiO₂) were added to up to 1.7, 2.6 and 3.4 %P. This was heated to 1450°C then carbon was added (to 1.5x theoretical reduction requirement) and temperature maintained for 60 minutes. At the higher calcium phosphate doping rates, the level of P in the slag remained considerably higher than in the initial (non P-doped) slag, and at the lower P addition rate, the final P concentration in the slag after one hour of reaction time was still >90% that of the initial slag P level suggesting none or nearly none of the initial slag P level was potentially recoverable (only the added calcium phosphate P was being released from the slag).

Lab tests (Tong et al. 2023) of carbothermal P-removal from converter slag show that although phosphorus is partly released as P_2 gas, most of the phosphorus ends up as ferrophosphorus (P_xFe_y). The authors indicate that China's iron and steel industries produce around one billion t/y of converter slag, much of which ends up stockpiled as waste because it cannot be recycled back into the iron furnaces because of its chemical characteristics. Lab-scale tests (100 g batch) used converter slag with c. 1.3% P, heated at c 1500°C with coke for one hour. Nearly 30% of P was removed from the slag.

Lab tests (Wang et al. 2022) heating converter slag with coke at 1600°C with different contents of iron oxide (FeO) show that FeO up to c. 30% increases P gasification, but above this may decrease P gasification. The converter slag contained 1.3 %P. Around one third of the P in the slag was removed by gasification after one hour at 1600°C with coke with 15% FeO increasing to nearly three quarters with 30% FeO.

Lab tests (Nakase et al., 2017) possibly showed up to 50% extraction of P from steel slag by thermochemical reduction with coke at 1400°C. The trials used 100g of different steelmaking slags with graphite as reducing agent in a lab-scale induction furnace (30 minutes), with fifteen different tests (temperature 1200° C – 1400° C, initial iron content 1.7% - 16%). Phosphorus not found in different forms in the slag is assumed to have been removed as vaporised P offgas (this is not confirmed). In nearly all



tests, most or all P stayed in the slag, either chemically remaining in the slag or as phosphorus droplets not separated from the slag. In one case only was a significant part of the P (1400°C, low initial iron content of <2%).

Already fifteen years ago (Yokoyama et al. 2007, Kubo, Matsubae-Yokoyama & Nagasaka 2010) published results of lab scale (1g) tests of magnetic separation of simulated steel slag (mixtures of iron, calcium, silicon, aluminium and manganese chemicals). This showed improvement of the P:Fe ratio from c.0.2 (initial mixed chemicals) to c. 0.8 (after magnetic separation). However, the magnetically separated material still contained more iron than phosphorus.

"Study on the recovery of phosphorus and iron from molten modified high-phosphorus industrial slag by carbothermal reduction", Y-Q. Liu et al., Metall. Res. Technol. 120, 307 (2023), <u>https://doi.org/10.1051/metal/2023035</u>

"Behavior of Carbothermal Dephosphorization of Phosphorus-Containing Converter Slag and Its Resource Utilization", S. Tong et al. Processes 2023, 11, 1943. <u>https://doi.org/10.3390/pr11071943</u>

"Effect of iron oxide content on dephosphorization behavior of slag gasification", S. Wang et al., Metalurgia 61 (2022) 3-4, 595-598, ISSN 0543-5846 <u>https://hrcak.srce.hr/file/396846</u>

"Effect of Slag Composition on Phosphorus Separation from Steelmaking Slag by Reduction", K. Nakase et al., ISIJ International, Vol. 57 (2017), No. 7 <u>http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-071</u>

"Magnetic Separation of Phosphorus Enriched Phase from Multiphase Dephosphorization Slag", H. Kubo et al., Tetsu-to-Hagané, Vol. 95 (2009), No. 3, pp. 300–305) - ISIJ International, Vol. 50 (2010), No. 1

"Separation and Recovery of Phosphorus from Steelmaking Slags with the Aid of a Strong Magnetic Field", K. Yokoyama et al., to-Hagané, Vol. 92, 2006, No.11, pp. 683–689) ISIJ International, Vol. 47 (2007), No. 10

ESPP comment: these lab studies confirms what is already known from the P₄ industry, that P is difficult to separate from iron by carbothermal reduction. For industry, the remaining ferrophosphorus is a low or zero value by-product, decreases yield and increases energy consumption.

Electrolysis of phosphate rock in molten calcium chloride

 P_4 production by electrolysis, without carbon reduction, by dissolving phosphate rock in liquid calcium chloride (molten at 850°C) was demonstrated at lab-scale (electrolysis cell with 300g of liquid CaCl₂. The calcium chloride was heat dried under vacuum, then heated to 850°C to melt, under argon, in an aluminium oxide crucible within a silicon oxide vessel. 2% mass of calcium phosphate Ca(PO₄)₂ was dissolved in the molten CaCl₂. Silver cathode and graphite anode electrodes were used for electrolysis, causing phosphate to dissociate to P (moving to the cathode) and oxygen. Phosphorus was shown to have accumulated on the cathode (by dismantling at the end of the experiment) and on the surface of the silicon oxide vessel above the melt bath: the boiling point of P₄ is around 280°C, significantly lower than the 850°C electrolysis temperature, so these deposits may be allotropes of phosphorus other than P₄. Erosion of the graphite anode suggested that oxygen generated by electrolysis had combined with graphite to CO or CO₂. The authors note that the rate limiting factor would be diffusion of the P and O ions in molten CaCl₂, that other liquids could be used on condition that they dissolve calcium phosphate.

Patents by Gruber 1957-1960 and Caton 1963 showed successful production of P₄ by electrolysis of molten metaphosphates, pyrophosphates or polyphosphates, or lithium and sodium phosphates, possibly with borates.

"A New Concept for Producing White Phosphorus: Electrolysis of Dissolved Phosphate in Molten Chloride", X. Yang & T. Nohira, ACS Sustainable Chem. Eng. 2020, 8, 13784–13792, <u>https://dx.doi.org/10.1021/acssuschemeng.0c04796</u>

"Method for the Preparation of Pure Elemental Phosphorus", B. Gruber, (Monsanto), U.S. Patent 2955552, 1960, <u>https://patents.google.com/patent/US2965552A/en</u>

"Polarography in Fused Alkali Metaphosphates", R. Caton et al., Anal. Chem. 1963, 35 (13), 2103–2108, https://pubs.acs.org/doi/abs/10.1021/ac60206a035

Electrolysis of molten condensed phosphate salts

P₄ production by electrolysis of molten sodium tri metaphosphate melting point 628°C) was demonstrated at lab scale suggesting potential to achieve 95% Faradaic efficiency and to develop direct electrolysis to P₄ from phosphoric acid. The tests used alumina reactor tubes of c. 460 mm x 13 mm diameter (then replaced by quartz for better oxidation resistance), under nitrogen flow, with glossy carbon and graphite electrodes. The sacrificial graphite anode was oxidised in electrolysis mainly to CO₂. Elemental phosphorus (P₄) was collected in a cold water bath through which offgas flow was bubbled. The authors indicate that the electrolysis breaks down the sodium trimetaphosphate (STMP) as follows: 6 (NaPO₃)_n -> P₄ + 2 Na₃PO₄ + 5 O₂ and that if phosphoric acid is added it is reacted and dehydrated 2 Na₃PO₄ + 4 H₃PO₄ - 6 H₂O -> 6 (NaPO₃)_n so potentially enabling continuous electrolysis of phosphoric acid to P₄. The authors note that this process benefits from the high ionic strength of the molten condensed phosphates which ensures high electrical conductivity, but the low proton content which avoids risk of hydrogen (H₂) generation. The electrochemical cell ensures separation of the P₄ generated at the cathode from O₂ generated at the anode. The high phosphate content of condensed phosphates ensures high diffusion-limited current densities and their phosphoryl anhydride linkages are hypothesised to facilitate breakage of the strong P-O bonds (Lux acid effect, analogous to that of SiO₂ in carbothermal P furnaces). The authors conclude that electrolysis in molten condensed phosphates can potentially produce P₄ from phosphoric acid with high Faradaic efficiency and low overpotential.

"Towards Sustainable Electrosynthesis of Industrially Valuable Small Molecules", J. Melville, PhD thesis Massachusetts Institute of Technology (MIT), Une 2021 <u>https://dspace.mit.edu/handle/1721.1/139141</u>



"Electrolytic Synthesis of White Phosphorus Is Promoted in Oxide-Deficient Molten Salts", J. Melville, A. Licini, Y. Surendranath, ACS Cent. Sci. 2023, 9, 373–380, <u>https://doi.org/10.1021/acscentsci.2c01336</u> and MIT News 21st February 2023 <u>https://news.mit.edu/2023/more-sustainable-way-generate-phosphorus-0221</u>

First reactions short summary: "Electrochemistry Cracks the P–O Bond: Sustainable Reduction of Phosphates to Phosphorus", E. Nichols, ACS Cent. Sci. 2023, 9, 343–345 <u>https://doi.org/10.1021/acscentsci.3c00056</u>

See also J. Melville et al., 2021, summarised in ESPP eNews n°62.

ESPP comment: as a route to produce P_4 , electrolysis (even in hot molten salts) could potentially be more energy efficient and have lower GHG emissions than carbothermal reduction as currently used in P_4 furnaces (using electrical energy and coke at c. 1400°C). Energy used to melt the electrolyte bed would not be lost in a continuous operation, and heat losses would be low in an insulated industrial-scale installation. There are however major challenges to scale-up to industrial implementation, including high temperature operation and durability (including avoiding oxidation), maintenance of electrodes and recovery of P_4 (ensuring that P_4 evolves as a gas and does not coalesce on the cathode or in the reaction chamber) in a continuous system without cooling the molten electrolyte. The possible effects of water if phosphoric acid is added (risk of H_2 production) need to be assessed. The overall energy balance must take into account energy needed to produce phosphoric acid and to synthesise the salts used as electrolytes.

Tutorial review on organo-phosphorus chemistry and applications

Ung & Li (2023) 27-page detailed overview of organophosphorus (OP) chemistry, applications and synthesis routes, including information on different OP chemical families by oxidation state and valency ($P_{III} - P_V$). Summary of uses of OPs as drugs (osteoporosis, cancer, anti-bacterial, anti-viral, hypertension ...), both existing today (fire safety & flame retardants, plasticisers, catalysts – e.g. for uranium extraction) and under development (compact and flexible organic electronics, improved energy-efficiency phosphorated LEDs ...). Two possible routes to OP chemicals from phosphoric acid (not via P₄) are mentioned: esterification of phosphoric acid or polyphosphoric acid (this is a route to some OP chemicals only, not all); use of trichlorosilane to reduce trimetaphosphates (see Cummins et al. see <u>ESPP eNews n°45</u>).

Tutorial review "From rocks to bioactive compounds: a journey through the global $P_{(V)}$ organophosphorus industry and its sustainability", S. Ung, C-J. Li, RSC Sustainability, 2023, 1, 11–37 <u>https://doi.org/10.1039/D2SU00015F</u>

ESPP note: trichlorosilane is currently produced from silicon, itself from a reducing furnace, so with similar energy costs to P₄ and poses operational and chemical efficiency challenges.

Stay informed

SCOPE Newsletter: <u>www.phosphorusplatform.eu/SCOPEnewsletter</u> eNews newsletter: <u>www.phosphorusplatform.eu/eNewshome</u> If you do not already receive ESPP's SCOPE Newsletter and eNews (same emailing list), subscribe at <u>www.phosphorusplatform.eu/subscribe</u> LinkedIn: <u>https://www.linkedin.com/company/phosphorusplatform</u> Slideshare presentations: <u>https://www.slideshare.net/phosphorusplatform</u> - Twitter: <u>@phosphorusESPP</u> YouTube <u>https://www.youtube.com/user/phosphorusplatform</u>

ESPP members

