European Sustainable Phosphorus Platform

SCOPE NEWSLETTER

With participation of
the European Commission:
DG GROW and
Joint Research Centre

Summary of joint European Commission – ESPP webinar on P_4 (phosphorus) Critical Raw Material, 9th July 2020

This ESPP SCOPE Newsletter summarises discussions at the expert webinar jointly organised by ESPP and the European Commission on 9th July, with participation of the leading companies using phosphorus (P_4) or its derivatives in Europe, *with additional input from the independent industry expert Willem Schipper. The content below has been seen by the participants but does not represent their position, it represents ESPP's own assessment.*

This webinar aimed to provide expert input to the ***European Commission's MSA (Material System Analysis) of the specific industrial form of "Phosphorus", P_4, as a Critical Raw Material****, and to provide an update on potential for production of P_4 in Europe from waste recycling.*

All significant industry sectors using P_4 or P_4 derivatives in Europe were invited, and almost all were present (eleven companies and three industry federations).

Elemental phosphorus

White phosphorus is one of several allotropes in which the element phosphorus occurs. Due to its versatile reactivity, it forms a building block for the production of a wide range of specialty and bulk chemicals.

White phosphorus (P_4, tetraphosphorus, CAS 12185-10-3) is also known as yellow phosphorus, since it can contain a small amount of impurities (tars, partial recomposition to red P), imparting a yellowish hue. Chemically this is however the same substance. The other allotropes of phosphorus are red phosphorus (see below), violet phosphorus (also known as Hittorf's phosphorus), and black phosphorus. These are strongly different in their appearance and reactivity from white phosphorus. Black and violet phosphorus have no commercial applications and are mainly a laboratory curiosity, although black phosphorus might in the future see applications as semiconductor, due to recent progress in its facile synthesis (see ESPP eNews n°36 and Liu et al. 2015).

The industrial scale production of elemental phosphorus always yields the white form. All other allotropes are produced from white phosphorus, and are to be seen as first derivatives.

There are only a few direct uses of white phosphorus: rodenticide (no longer today), in homeopathic formulations, and in military applications, notably in incendiary grenades and smoke screens. The latter application is commercially relevant, but insignificant in terms of yearly volume in the EU.

Almost all white phosphorus is processed in typically two to four steps to end products, via a number of key intermediates (such as chlorides, sulphides, oxides …). These are discussed below.

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ESPP Editorial

*The **European Commission (DG GROW and JRC)** co-organised with **ESPP** (European Sustainable Phosphorus Platform) an expert webinar, 9th July 2020, to **better understand material flows and end-uses of P_4 (White Phosphorus)** – the specific form of phosphorus, produced in phosphorus furnaces.*

Representatives of nearly all the main companies and sectors using P_4 and P_4 derivatives in Europe participated, probably the first time ever that such expertise on this specialist sector has come together.

*ESPP has worked with independent phosphorus industry expert, Willem Schipper, to produce this SCOPE Newsletter Special Issue, which builds on the exchanges at this webinar (respecting anti-trust and Non Disclosure) to produce an up-to-date overview of P_4 chemical applications and uses. In particular, we try to show which industry sectors and **end-uses are dependent on P_4 (that is, where P_4 / P_4 derivatives cannot be replaced by wet-acid route phosphate chemicals)** and why P_4 is non-substitutable in these applications.*

*P_4 is on the EU Critical Raw Materials List (CRM) as "Phosphorus", in addition to "Phosphate Rock". For ESPP, the latter effectively concerns supply and end-uses of P in any form (including fertilisers, animal feeds …). **Both "Phosphorus" and "Phosphate Rock" are maintained on the 3rd September 2020 update of the CRM list** (COM(2020)474).*

*Although P_4 represents only a few percent of world phosphate rock consumption, it is irreplaceable for the production of specialist phosphorus chemicals needed by a very **wide range of high-value end-uses**, including electronics, fire safety, batteries, industrial water and process treatment, technical plastics, pharmaceuticals, lubricants, metal treatment, …*

***Europe has leading companies in phosphorus chemistry, in P_4 derivative chemistry and applications**. Major manufacturing sectors are dependent on these: phosphorus flame retardants - electrical and electronic equipment, engineering plastics, thermal insulation …; phosphonates: oil and gas extraction, drinking water production …; catalysts: pharmaceuticals, petrochemicals, rare earth metal extraction …*

***However, Europe has no P_4 production and is 100% dependent on imports from the four countries** in the world which produce P_4. Production and exports are highly dependent on variable factors such as local electricity prices, export policies or up- and downstream integration.*

*This critical dependency could be addressed by **up-cycling P_4 from wastes in Europe**, in particular sewage sludge incineration ash. The webinar saw several projects working on this. Development of a consortium of industries and stakeholders to take forward an operational project is proposed.*

Ludwig Hermann, ESPP President

ESPP's advisor for this SCOPE Special Issue: Willem Schipper

This Special Issue of the SCOPE Newsletter was prepared thanks to the specialist phosphate industry expertise of Willem Schipper. Willem Schipper has twenty years' experience responsible for research and development at Thermphos, a former white phosphorus producer, and is today an independent consultant to the phosphorus and phosphate industry, working on process development, plant optimization, environmental issues and phosphate recycling. He provides expertise to leading phosphate industry companies in Europe and worldwide. Contact: wsconsulting@zeelandnet.nl

The EU Critical Raw Materials: "Phosphate Rock" and "Phosphorus"

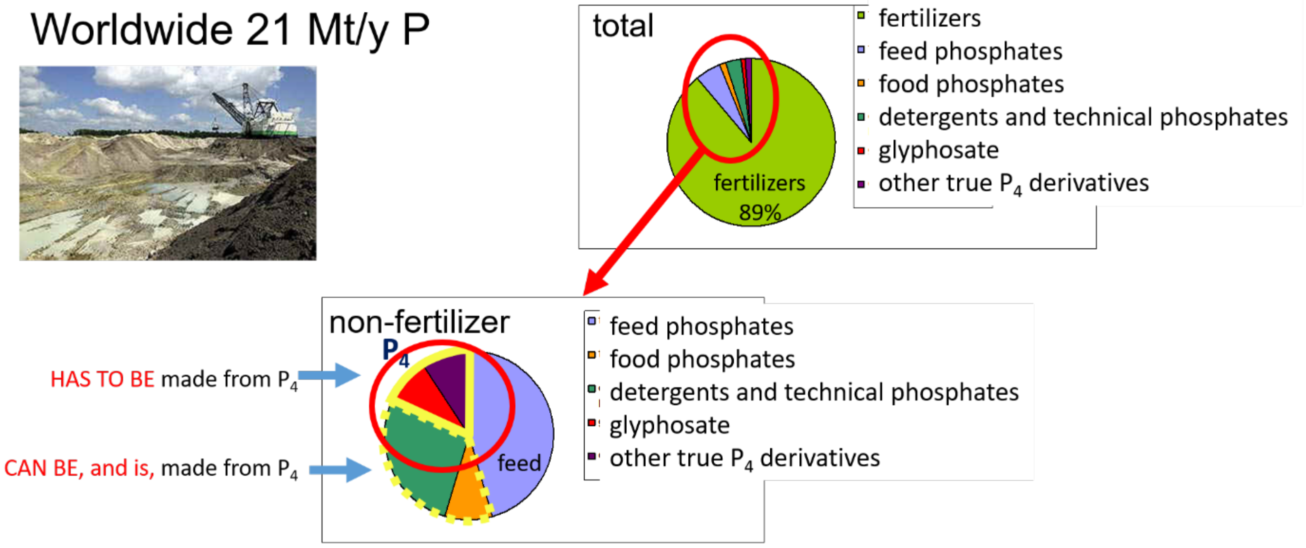
The **EU Critical Raw Material "Phosphorus", that is P_4,** is today essential for the production of

- **organic phosphorus chemicals**, essential for a range of industries and applications, including fire safety, cleaning, industrial water and process treatment, lubricants, metal extraction, industrial catalysts, herbicides …
- **certain specific inorganic phosphorus-chemicals,** e.g. some important industrial chemical intermediates (e.g. for production of vitamin A), specific fire safety applications, specialist metal applications,
- **'thermal' phosphoric acid** which is needed for specific applications requiring ppm or ppb purity (see below).

The third update of the EU Critical Raw Material List (2017) includes both "Phosphate rock" (in effect covering phosphorus P in different forms in fertilisers, animal feed, chemicals and other uses) and "Phosphorus" (referring to elemental phosphorus P_4, often known as white phosphorus). P_4 is produced from phosphate rock in specific furnaces. This is confirmed in the 4th update of the CRM List (3rd September 2020).

These **two distinct EU Critical Raw Materials** correspond ("in effect" if not in vocabulary) to the two distinct processing routes by which mined phosphate rock is processed to useful phosphorus-containing chemicals:

- **"wet acid route":** phosphate rock is reacted with sulphuric acid to produce a phosphoric acid containing various impurities from the rock (called "**MGA**" = Merchant Grade Acid). Impurities present in MGA, depending on the origin of the phosphate rock, can include iron, aluminium, potassium, fluorides, heavy metals such as cadmium … Other acid processes also exist, such as nitro-phosphate route, using nitric or other acids.
- **"thermal route": elemental phosphorus (P_4, also called "White" or "Yellow" phosphorus)** is produced by reducing phosphate rock in a specific phosphorus furnace at high temperatures. This P_4 is then either traded as such, converted to intermediate organic phosphorus chemicals (see below) or reacted with water to produce extremely pure phosphoric acid ("**thermal acid**")



(Fig. i) Overview numbers: from phosphate rock to P4 / P4-derivatives and applications

The question of which phosphorus-containing chemicals can feasibly be produced via the wet-acid route (MGA), and which require P_4, is complex and is discussed below. To simplify,

- **Can only be feasibly produced from P_4 / P_4 derivatives: nearly all organic phosphorus chemicals, and any phosphorus chemical in which the oxidation state is not +5** (some of the latter are organic, some are not). In biological systems, organic phosphorus chemicals (e.g. DNA) are produced from inorganic orthophosphate, and these biological molecules have phosphorus oxidation state of +5. Chemical synthesis of industrial organic phosphorus chemicals, other than via P_4 is, to be optimistic "in its infancy" (see Geeson & Cummins review 2020, in ESPP eNews n°45).
- **Certain specific phosphorus-containing chemicals can only feasibly be produced via P_4,** because of specific chemical structures, technical requirements for low water content (difficult to achieve in production from phosphoric acid), or specific reaction pathways.
- **Where specific applications require ppm or ppb purity (e.g. electronics), this can only be achieved via P_4/P_4 derivatives or via 'thermal' acid. However, a quantitatively significant part of current use of thermal acid could be replaced by MGA, after purification processes.**
  Food additive phosphates are probably today one of the largest end-uses of thermal acid in Europe (metal treatment is also a large use). However, it is ESPP's understanding that a majority of EU producers already use purified "wet acid route" phosphoric acid (solvent purification of MGA) and not "thermal" acid (P_4-derived) to produce food additive phosphates. Some producers continue to use thermal acid, either produced in the EU from P_4, or imported, for reasons of cost or supply chain structure.

Around 240 million tonnes per year of phosphate rock (apatite) are mined worldwide ("beneficiated phosphate rock, USGS data for 2019), containing 17 – 24 MtP/y, see ESPP Phosphorus Fact Sheet. Around 95% of this mined P is used in fertilisers and in animal feed, via the wet acid route, and a further 2 - 4 % is used to produce inorganic phosphates used in detergents, ceramics, fire extinguishers, …. P use in detergents has considerably reduced over recent decades (this concerns "detergent phosphates" = polyphosphates, mainly STPP = sodium tri poly phosphate, not to be confused with phosphonates – see below).

Around 2-3 % of world phosphate rock is used to produce P_4 (Gantner et al. 2014).

ESPP estimates that there are maybe **ten to thirty P_4 plants operating today, in only four countries worldwide**. These furnaces are both small and large, with some operating intermittently. There is no P_4 production in Europe, and Europe is totally dependent for both P_4 and P_4 derivatives on these four countries (see below).

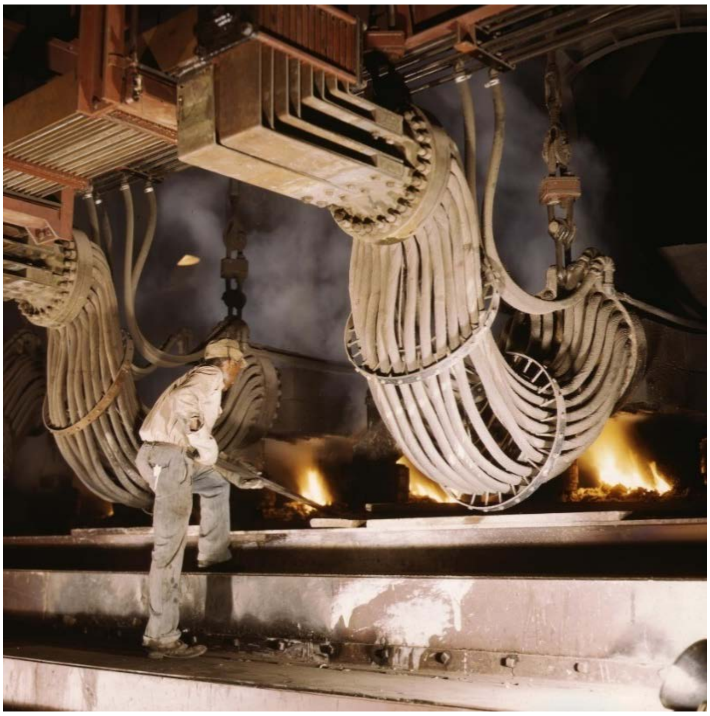
How is P_4 produced? the phosphorus furnace

White phosphorus (P_4) is today produced at high temperatures in arc-type furnaces where heat is generated by passing large electrical currents through the low-conductive furnace feed. Phosphate rock is thus heated to 1500 - 1700 °C in the presence of coke, which reduces the phosphate to elemental P. The process is purely thermal and no electrochemistry is involved. Gaseous phosphorus (actually present as P_2 at elevated temperatures) is drawn out of the furnace with carbon monoxide gas (CO) which is formed as by-product. Liquid P_4 is obtained, filtered, and stored for further use or sale (often kept liquid by heating, or may be allowed to solidify for transport). The remaining CO is often used to pretreat the phosphate rock raw material, which needs to be in a nodular form (not powdery) to prevent the furnace from blocking. Balling pan - sinter grid combinations, standalone sintering machines, or rotary kilns are commonly used to granulate the phosphate rock. Gravel is added to the furnace feed to form a slag with the calcium oxide remaining after reduction and removal of the phosphorus from phosphate rock. This forms a molten calcium silicate slag which is tapped from the furnace and solidified.

This technology is essentially unchanged over the last century and is used in all of the P_4 furnaces operating today.

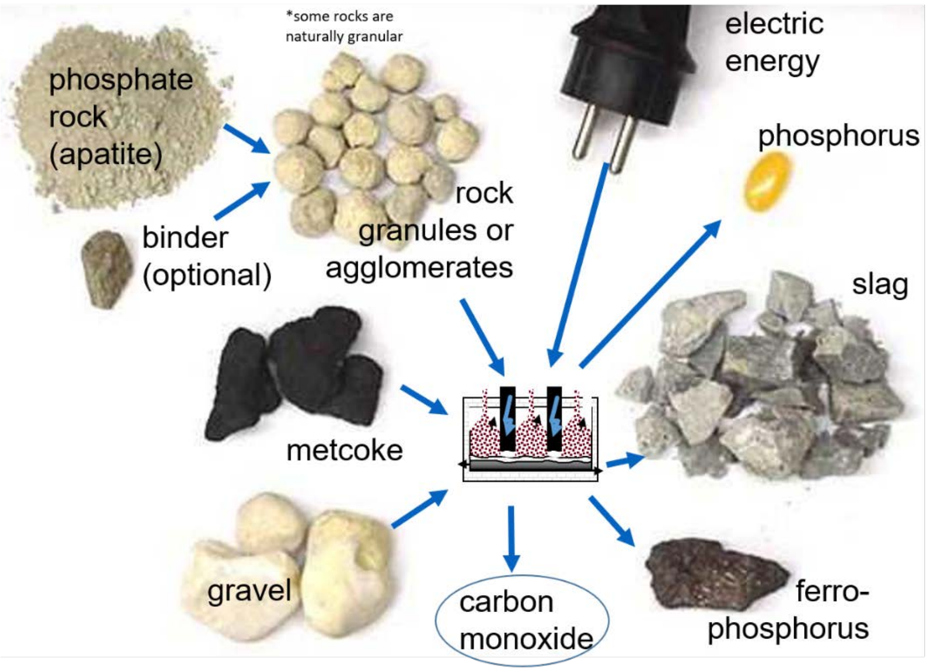
R&D is underway to develop processes to produce P_4 from secondary materials, also using electrothermal furnaces, but with the objective of enabling smaller scale installations. See below.

Photo: P_4 furnace



Electrical power is supplied through sets of bundled connectors to the electrodes which are partly in the furnace. Some escaped phosphorus can be seen burning on the furnace lid. Photos: Wikimedia Commons, TVA, Muscle Shoals, 1942.

Schematic: P_4 manufacture process (simplified)



Which chemicals critically depend on P_4 / P_4 derivatives?

In nature, the P atom is (almost) exclusively in oxidation state +5. This is the case for phosphoric acid and also for most phosphates, which have PO_4 units in their structure, i.e. four oxygens surrounding the central P atom. Such phosphates and phosphoric acid represent some 99% of world phosphate rock consumption and include fertilisers, animal feed phosphates, human food phosphates, and various other technical / industry phosphate chemicals.

These phosphates can all be produced from phosphoric acid (wet acid route MGA), after appropriate levels of purification to remove contaminants (usually by solvent extraction processes). Purity requirements increase from fertilisers, through animal feeds, detergents, industrial phosphate chemicals, human food phosphates through to ppm or ppb purity demanded for some specialist applications such as electronics, pharmaceuticals, catalysts … For example, given the miniaturisation of electronic chips, a few impurity atoms in phosphoric acid used for etching can cause errors in the final chip.

In theory, contaminants can be removed from MGA to even extreme purity levels, but each additional purification step inevitably means increased costs, energy and chemical use, generation of waste streams and loss of phosphorus to these waste streams. Therefore, **ppm or ppb levels of purity are achieved not by purifying wet-acid MGA, but by producing 'thermal' phosphoric acid from P_4** (P_4 is reacted with oxygen and water to produce pure phosphoric acid).

Whether or not P_4 /P_4 derivatives are necessary to produce a given chemical (that is: the chemical cannot feasibly be produced via wet-acid route phosphoric acid) depends on four factors:

- **Oxidation state of the phosphorus atom in the target chemical**
  Chemicals in which the P atom oxidation state of the P atom is not +5 need to be made via P_4 / P_4 derivatives, for example: most organic phosphorus chemicals (including phosphonates), phosphites, hypophosphites, phosphines, phosphides …. This is the main reason why P4 is critical.
- **Degree of purity needed**
  As outlined above, thermal acid (from P_4) is required where near zero levels of impurities are required in either phosphoric acid itself or in PO_4 phosphate chemicals produced from phosphoric acid.
- **Arrangement of other atoms in the target chemical**
  In some phosphorus chemicals, the P atom is not surrounded by four oxygens. These chemicals need to be produced via P_4 / P_4 derivatives. E.g. $LiPF_6$, (used in batteries), where the P atom is surrounded by fluorine atoms.
- **Water content, dehydration or water release**
  - Some applications of phosphorus chemicals require very low water content, e.g. flame retardants and additives used in technical plastics or in electrical applications. This is difficult to achieve for some chemicals if they are produced from phosphoric acid, so for such applications they are produced from P_4 derivatives
  - Phosphorus chemicals used for water removal (chemical dehydration reactions) cannot be feasibly produced from phosphoric acid, e.g. phosphorus pentoxide P_2O_5 (used in vitamin A production), specific grades of polyphosphoric acid …
  - Water can be generated in the use reactions of phosphorus chemicals, e.g. reacting alcohols with P_2O_5 generates water which interferes with esterification, so that $POCl_3$ – derived from P_4 - has to be used to produce phosphate triesters as plastics additives.

EU dependency on P_4 concerns many industry sectors

The workshop confirmed that **there is since 2012 no P_4 production in Europe**, and so all EU industries needing organic phosphorus chemicals or other P_4-derived chemicals are dependent on import of either P_4 or P_4-derivatives (intermediate 'vector' chemicals such as PMIDA, P_2O_5, NaH_2PO_2, red P, H_3PO_4,).

Note that other important P_4 derivatives exist but are not significantly imported into the EU (e.g. because not convenient for transport, generally re-converted locally …): PCl_3, P_2S_5, PH_3 …).

It is ESPP's understanding (see Willem Schipper in SCOPE Newsletter n°123) that the EU today imports these mainly from, and is dependent on, two countries Vietnam and Kazakhstan. The USA and China also have significant P_4 production, but this goes to national / integrated use and is largely not exported (because of vertically integrated producers or export tariffs). However, these two countries do export some P_4 derivatives and/or thermal phosphoric acid.

Note: this information is added by ESPP based on publicly available customs statistics: origins of supply were not mentioned at this workshop for reasons of commercial confidentiality between participating companies and anti-trust.

The criticality of P_4 is accentuated because a significant part of the world's P_4 production is dependent on factors which can vary, such as electricity prices or specific phosphate rock supply sources.

A large range of **EU industrial sectors are dependent on P_4 and P_4 derivatives**. These include not only the chemical sectors present at this workshop (phosphonates, fire safety, specialist organo-phosphorus chemicals …) but also **downstream user industries** such as:

- metal production: e.g. separation of cobalt from nickel during metals production depends on the P4 derivative thiophosphinates
- electronics: P_4 “thermal” phosphoric acid for micro-chip etching, phosphine for semiconductor doping
- lubricants: e.g. lubricant additives, such as ZDDP zinc dialkyl dithiophosphates or alkyl phosphate mono- and di-esters
- oil and gas extraction: phosphonates
- petrochemical industry: phosphorus catalysts
- cooling water circuits: phosphonates
- detergents: phosphonates
- speciality chemicals: e.g. BAPO photo-initiators
- performance metal alloys: cuprophosphorus
- plastics, cables and textiles used in electrical equipment, construction, trains, cars, airplanes, ships, furniture: phosphorus flame retardants, other organic phosphorus chemicals
- …

(Fig. ii) Production via wet-acid or via P_4 / P_4 derivatives / ‘thermal’ acid ?

Which chemicals are (or could be) produced from wet-acid (MGA)? Which critically depend on P4 / P4 derivatives?

Chemically based on phosphoric acid but increasing levels of acid purification are needed.	**Production almost exclusively from wet-acid route.** Thermal acid is generally no longer used for cost reasons.	
	Fertilisers	Together, represent around 95% of total world phosphate rock consumption
	Animal feed phosphates	
	Detergent phosphates	That is: polyphosphates (e.g. STPP). This does not include phosphonates (see below)
	Most other industrial inorganic phosphates	E.g. Ammonium phosphates used in fire extinguishers and in wildfire fighting
	Industrial grade phosphoric acid	E.g. metal treatment (pre-treatment before painting)
	Can be produced from either MGA or P_4	
	Food phosphates Toothpaste phosphates	Some producers continue to use thermal acid for reasons of cost or supply chain structure.
	Phosphoric acid for metal treatment	
	Phosphoric acid for beverage applications	Purity specifications set by some beverage companies make production by MGA purification very complex.
	Can feasibly today be produced only from P_4 / P_4 derivatives	
	Possibly in the future: some specific inorganic phosphorus chemicals for batteries	Such applications require very high purity (ppm or ppb), which can only feasibly be achieved via P_4 (thermal acid, P_4 derivatives).
	Phosphoric acid for electronics applications, etching	
Chemical structure or P oxidation state	Phosphonates. Inc. glyphosate	Also the intermediate PMIDA
	Organic phosphorus flame retardants	DOPO, AlPi …
	Other organic phosphorus chemicals Phosphine	Many different chemicals in a wide range of applications.
	Metal-phosphorus alloys (phosphides)	Cannot be produced from phosphoric acid, but some alloys may be produced as by-products in steel furnaces (phosphorus is present at low concentrations in steel ores).
	Specific non-PO_4 chemicals	E.g. lithium hexafluorophosphate ($LiPF_6$), thiophosphates (such as ZDDP …), hypophosphites (used in e.g. nickel plating)
Water content / release / dehydration	Some phosphorus flame retardants and plastics additives. Some other specific applications.	Production from P_4 ensures near-zero water content in the derivative, or avoids production of water in chemical reactions during use.
	Intermediates required to avoid water release in chemical production reactions	E.g. $POCl_3$ for production of phosphate triesters
	Phosphorus chemicals used for removing water in chemical reactions	E.g. phosphorus pentoxide P_2O_5, specific grades of polyphosphoric acid …

The table represents ESPP’s understanding, and was not discussed at the webinar. It should be considered as a simplification covering most P_4 and P_4 derivative use in Europe today, but there may be exceptions concerning small quantities. Data of companies’ use of MGA or of P_4 derivatives is commercially confidential and anti-trust, so that in any case only an overall outline can be considered.

Objectives of the webinar

The web workshop was opened by **Constanze Veeh, European Commission DG GROW**. She indicated that Critical Raw Materials are considered in key EU policies including the Green Deal, the Industrial Strategy and the post-Covid recovery strategy. The EC publishes every three years the list of critical raw materials for the EU. **P_4 is considered to be critical since 2017, and this is confirmed in the 2020 update**.

A **MSA (Material System Analysis)** is developed for selected Critical Raw Materials by the European Commission JRC to ensure that policy is evidence-based. Industry expert input to this analysis is essential.

Fabrice Mathieux, European Commission JRC, highlighted the importance of organising validation workshops for MSA studies, in order to fill-in data gaps and validate assumptions that were deemed necessary. It was noted that this P_4 webinar is one of the most attended MSA input webinars (JRC is organising these for many different materials). He welcomed the exceptionally wide spread of industry representation, showing significant industry mobilisation around the material P_4 (phosphorus). The initiative of ESPP to enlarge the MSA validation workshop to other related topics to build a common understanding of P4 was also welcomed.

Ludwig Hermann, Proman and ESPP President, underlined that this webinar is probably the first time that nearly all the European companies needing P_4 / P_4 derivatives for their production have come together, and that this should improve understanding of key uses and applications. The objective is also to inform on possibilities to reshore P_4 production back to Europe, using secondary materials as inputs, using new technologies applicable in smaller units than the "furnaces" of the past, in order to address the criticality of P_4.

Data and boundaries of MSA for P_4

Cristina Torres de Matos, European Commission JRC, outlined difficulties encountered in developing the MSA (Material System Analysis) for P_4. The MSA uses standardised methodology, applied to all materials studied as critical or potentially critical, in order to enable comparison. In particular, the MSA results are used to calculate summary indicators for "dependency" and for the (current) "recycling rate". This is the first MSA study for P_4. The MSA includes only aggregated data, in order to fully respect commercial confidentiality and anti-trust.

The MSA for P_4 poses significant **difficulties of access to data**:

- **no P_4 production in Europe**
- the **limited number of user companies** of P_4 and P_4 derivatives means that all direct data on quantities, sources, use routes, is commercially and anti-trust confidential
- **customs statistics provide only limited information** because they:
    - group together white phosphorus (P_4), which is an intermediate (nearly no final use itself) and red phosphorus, which is a final product (used e.g. as a flame retardant)
    - do not enable to identify some P_4 derivatives (vector chemicals listed above) which are grouped together in the same chemical class despite being different in origin and applications;
    - do not distinguish between thermal phosphoric acid (from P_4) and wet acid route
    - do not separate different grades of chemicals, whereas in some cases some grades can be produced from wet-acid route phosphoric acid whereas other grades are dependent on P_4 derivatives (e.g. APP, polyphosphoric acid).
- **poor knowledge of the material use routes and of the different phases of the value chain** (P_4 – intermediates – derived chemicals – final use applications) – this webinar and this document aim to address this
- a market study exists (IHS, 2016) but is sold commercially with content subject to non-disclosure by purchaser, and is not expert reviewed

Customs data indicate imports into the EU of around 60 – 90 ktP/y of white phosphorus and red phosphorus (total). Participants considered this to be realistic, or maybe an underestimate, but note that this fails to include a significant part of imports which are not in the form of P_4 but as intermediate 'vector' chemicals and which effectively 'replace' P_4 by bringing the needed properties (reactive phosphorus) to chemical manufacturing processes.

P_4 and P_4 derivatives

It was agreed by webinar participants that these P_4 derivative intermediate 'vector' chemicals must be considered in the same way as import of P_4 itself in the MSA. **Total net EU consumption of phosphorus in 'P_4 and derivatives' is probably thus somewhere around 100 – 130 ktP/y.**

JRC clarified that the MSA will look at P_4 and its derivatives and at data for the chemical industries using these (e.g. for the production of flame retardants). The downstream end-user industries which are dependent on these chemicals produced will be identified: e.g. phosphorus flame retardants are essential for the manufacture of plastics, technical textiles, electrical equipment, cars, trains …, or phosphonates are essential for oil and gas extraction ….

It should be noted that EU Customs Codes (trade statistics) are somewhat illogical, with several distinct chemical categories joined under one code (e.g. phosphonates and phosphinates) whereas other codes are reserved for rarely-traded, non-existing, or unstable chemicals (e.g. P chlorides other than tri- penta- or oxychloride, or triammonium phosphate). Also, some categories cover multiple compounds with varying P content, so that only an approximation of their P content is possible.

(Fig. iii) Summary list of P4 derivatives

P_4-derivatives (intermediate vector chemicals) are mainly as in the table below.

These intermediates can only be produced, today, from P_4 (not from purified wet acid route MGA phosphoric acid).

	Oxidation state of P	***Used as intermediates?*** **Or used in final chemical applications?**
Thermal phosphoric acid	**+5**	*Intermediates for production of inorganic phosphates where very high levels of purity are required* Needed for e.g. electronics (micro-chip production)
P_2O_5	**+5**	*Intermediate* Used as chemical drying agent
P_2S_5	**+5**	*Intermediate*
Chlorinated second derivatives made from PCl_3: - $POCl_3$ - PCl_5	 **+5** **+5**	*Intermediates only, either for organic phosphorus chemical production or for chlorinated chemical production*
PCl_3	**+3**	
PMIDA = N-(phosphonomethyl) iminodiacetic acid $C_5H_{10}NO_7P$.	**+3**	*Intermediate only, principally for glyphosate production*
Phosphites (organic)	**+3**	*Intermediates* Used in plastics processing / as additives
Phosphonates - not inc. PMIDA (see above).	**+3**	Not used as intermediates (for final uses, see below)
Hypophosphites, e.g. NaH_2PO_2 (sodium hypophosphite).	**+1**	*Intermediates* Used as anti-oxidant, reduction agent
Red P	**0**	Used as flame retardant *Intermediate for onsite use, but not traded for use as an intermediate*
Phosphine oxides. Phosphine (PH_3), organic phosphines, phosphonium compounds.	**-1** **-3**	*Intermediates* Used for fumigation
Phosphides	**-3**	*Metal intermediates* Metal alloys

For memory, the oxidation state of P in inorganic phosphates P_2O_5 or in phosphoric acid is +5. The oxidation state of P in biological phosphorus molecules is also +5, both organic (e.g. DNA, phospholipids, ATP and ADP …) or inorganic (bone phosphates). In white phosphorus P_4 the oxidation state of P is zero (0).

Production and uses of different P_4-derivatives

Willem Schipper presented in detail his expert understanding of the **different derivate chemicals, flows and final applications of P_4-derived chemicals**.

Chlorinated P_4 derivatives:

The largest group of derivatives is formed by PCl_3, and its secondary derivatives $POCl_3$ and PCl_5, with many applications and used in the production of many organo-phosphorus chemicals.

$PlCl_3$ offers reactivity (able to deliver a P atom into an organic chemical molecule) and versatility and many organo-phosphorus chemicals are made via this intermediate. However, the reactivity and toxicity of PCl_3, and its relatively lower P content, mean that it is not traded much over longer distances. Instead it is locally produced from P_4 in chemical complexes where Cl_2 infrastructure exists, enabling recycling of the chlorine after reaction. EU imports and exports do take place but are minor.

Important uses of PCl_3 and its second derivatives include production of phosphonates (via H_3PO_3, see uses of phosphonates below), of agrochemicals (glyphosate is a phosphonate) and of phosphines and phosphites, and as a chlorination agent.

Around 15 – 20% of PCl_3 worldwide is reacted with oxygen to $POCl_3$, used to produce various organo-phosphorus flame retardants (e.g. halogenated or non-halogenated phosphorus esters, resorcinol bis (diphenylphosphate) = RDP), organo-phosphorus chemicals used in pharmaceuticals, lubricants, hydraulic fuels, mining, in starch modification, as a chlorination agent in the chemical industry (that is, as an intermediate to add chlorine into different chemicals or pharmaceuticals, e.g. production of acyl chlorides).

The P_4-derivative phosphorous acid (phosphonic acid, H_3PO_3), which is imported into Europe as such (solid chemical), is produced from PCl_3, and is used in particular to produce phosphonates.

PCl_5 is produced in smaller volumes, with two main applications, in pharmaceuticals production and to produce $LiPF_6$, the electrolyte in lithium ion batteries.

Phosphonates

This class of compounds, made from PCl_3 (via H_3PO_3 generated in-situ, or from H_3PO_3 acquired on the market), are used as sequestering agents water treatment and in other applications (see below), but are not used as an intermediate for the production of other chemicals.

The intermediate PMIDA and glyphosate (both, see below) are chemically phosphonates but are not included here because they have distinct industry circuits.

PMIDA (N-(phosphonomethyl)iminodiacetic acid):

PMIDA, made from PCl_3, is an intermediate in glyphosate production, and is often traded.

Phosphites

Phosphites, derived from PCl_3, serve as intermediates in e.g. production of the phosphonate PBTC manufacture (2-phosphonobutane-1,2,4,-tricarboxylic acid), but are also used directly as plastic additives as antioxidants and to improve plastics processing.

Phosphine and derivatives:

Many organo-phosphorus chemicals can be produced from P_4 via via phosphine PH_3 and its secondary derivatives.

Phosphine is produced from P_4 in reactions yielding either hypophosphite or phosphoric acid as a co-product.

Phosphine can be reacted with formaldehyde and mineral acids to form tetrakis(hydroxymethyl)phosphonium salts (THPC, widely used as textile flame retardants) and biocides (THPS, e.g. for oilfield applications).

Phosphine is also used to produce organic phosphines of PR_3 type. Some of these can also be produced via PCl_3. These are not a large volume use of P_4, but their use as catalyst ligands is crucial in many chemical and petrochemical transformations. Phosphine oxides serve as photo-initiators in polymerisation reactions (e. BAPO), as well as extraction agents (e.g. TOPO).

Pure phosphine gas is also used as a dopant in semiconductors (adding phosphorus to semiconductor material to modify its electrical or optical properties).

Phosphine itself is also used for agricultural fumigation.

Aluminium phosphide can be used for this purpose, as it releases phosphine gas progressively.

Phosphorus sulphides

P_2S_5 is the dominant compound of this type of P_4-derivative. It is produced from P_4 and liquid sulphur. A number of grades exist, with varying reactivity and granulometry.

P_2S_5 is used to make compounds requiring both P and S atoms in one molecule. Applications include thiophosphates (e.g. ZDDP zinc dithiophosphate) lubricant additives, the main application of P_2S_5 in Europe and thion type insecticides, such as parathion and malathion.

Phosphorus pentoxide P_2O_5

This compound is produced from phosphorus and dry air. A significant application is as an intermediate to production of ammonium polyphosphate (APP), a flame retardant. APP can also be produced from phosphoric acid (via wet acid route MGA), but in this case it is not industrially feasible to achieve the very low water content necessary for many flame retardant applications (especially in plastics). Plastics grade APP is therefore produced via P_4 derivatives, whereas APP for some other applications can be produced from phosphoric acid (for example fire treatment of wood products).

APP is thus one example of a chemical for which some grades can be produced from wet-acid route phosphoric acid, but other grades are dependent on P_4 derivatives. The two grades are not distinguished in customs statistics.

When phosphorus pentoxide is reacted with concentrated phosphoric acid, polyphosphoric acid is formed which is more or less a liquid form of P_2O_5 in terms of reactivity and applications. It finds use as a reactive solvent in many dehydration reactions e.g. in pharmaceutical applications. Concentration of phosphoric acid at high temperatures into polyphosphoric acid is possible but challenging and is no longer practiced in the EU. As for APP above, the P_4 route is necessary for production of some grades of polyphosphoric acid, in order to achieve low water contents.

Other uses of phosphorus pentoxide include as an intermediate (by reaction with alcohols) to production of phosphate mono-and diesters, which have many uses including antistatic agents, extraction agents, lubricant additives and wetting compounds. Polyphosphoric acid also finds application in this field.

Phosphorus pentoxide P_2O_5 is also used directly itself as a powerful drying and chemical dehydration agent, used for example in the pharmaceutical industry to produce vitamin A.

Red phosphorus

This allotrope of phosphorus is produced from white phosphorus by heating it in an inert atmosphere. It is much less reactive and less toxic than white phosphorus.

It is used onsite as an intermediate to produce phosphine and hypophosphites, but is generally not traded for use as an intermediate.

Its main use is in flame retardant formulations. Other uses include pyrotechnics and the striking surface of matchboxes.

Hypophosphites (phosphinates)

Hypophosphites, also termed phosphinates, are based the ion $(H_2PO_2)^-$ or hypophosphorous acid H_3PO_2 (also known as phosphinic acid). They include NaH_2PO_2 (sodium hypophosphite) and its organic derivatives. They can be produced directly from P_4 by reaction with caustic soda, producing also phosphine gas and phosphite. The phosphine compound is often the main product.

A significant use of sodium hypophosphite is as an intermediate to the production of phosphinates such as flame retardants (e.g. aluminium salts of diethyl phosphinate) or organic phosphinates and thiophosphinates used as extraction agents in mining (e.g. for the separation of nickel or cobalt).

The main direct use of sodium hypophosphite is as the reducing agent in electroless nickel plating, to apply nickel layers onto complicated shapes and/or nonconductive materials.

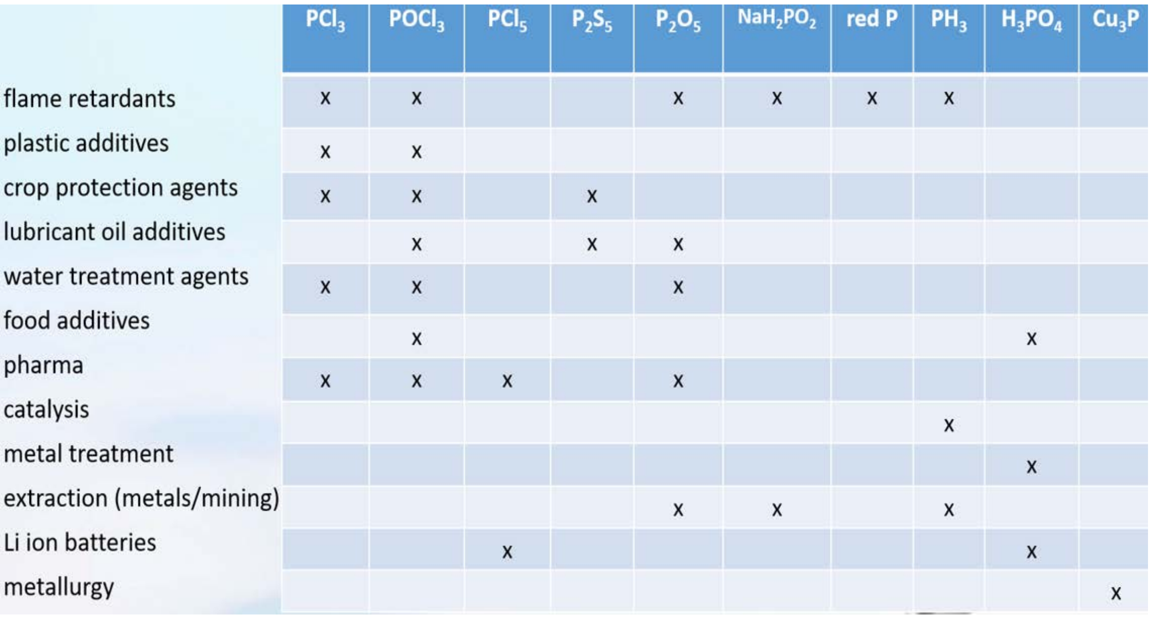
Phosphorus metal alloys and phosphides

Cuprophosphorus (Cu_3P), produced by reacting copper and P_4, is a necessary precursor to specialised alloys such as phosphorus bronze.

Ferrophosphorus, a byproduct from P_4 manufacture, is used as an alloying agent in certain special steels.

Aluminium phosphide is used for fumigation for its ability to slowly release phosphine gas in moist air.

(Fig. iv) Main final end-use applications reached via different P_4 derivatives:



	PCl_3	$POCl_3$	PCl_5	P_2S_5	P_2O_5	NaH_2PO_2	red P	PH_3	H_3PO_4	Cu_3P
flame retardants	x	x			x	x	x	x		
plastic additives	x	x								
crop protection agents	x	x		x						
lubricant oil additives		x		x	x					
water treatment agents	x	x			x					
food additives		x							x	
pharma	x	x	x		x					
catalysis								x		
metal treatment									x	
extraction (metals/mining)					x	x		x		
Li ion batteries			x						x	
metallurgy										x

Some key use sectors of P4 and P4 derivatives

P4 and agrochemicals

Laurent Oger, ECPA (European Crop Protection Association), indicated that organophosphorus insecticides have largely disappeared from the European market, either having been banned (e.g. parathion, chlorpyrifos) or with a ban currently under consideration (fenamiphos) and because companies are moving to other products. The list of authorised agrochemicals is here and today includes few organophosphorus compounds*.

Some organophosphorus herbicides are also now banned in Europe (e.g. glufosinate) but glyphosate is still used (glyphosate is a phosphonate). Despite difficulties related to commercial confidentiality of data, ECPA can indicate that glyphosate and/or other organo-phosphorus herbicides are still today produced in Europe. ESPP estimates that this production probably uses less than 10 ktP/y. This is probably thus not now the biggest use of P_4 or P_4 derivatives in Europe.

Note: the ESPP Phosphorus Fact Sheet estimated world use of phosphorus in glyphosate (alone) at 150 ktP/y. This is entirely from P_4 or P_4 derivatives.

The organophosphorus crop protection chemicals authorised in the EU today are: glyphosate, fosthiazate, fenamiphos, ethephon, phosmet, fosetyl, pirimiphos-methyl Insecticide, tolclofos-methyl, malathion, phosphine

P_4 and fire safety

Adrian Beard, Clariant and President of pinfa (Phosphorus, Inorganic and **Nitrogen Flame Retardant Association, a sector group of Cefic)** explained why P_4 supply is critical for fire safety, and thus for the wide range of industries in Europe which need to ensure safety of their products: electrical and electronic equipment, cables and optical fibres, transport vehicles and infrastructure, buildings, textiles and furniture (depending on applications), renewable energy and energy storage, …

Fire kills around 6 000 people each year in Europe and injures ten times more, and modern materials, comfortable homes and ubiquitous electronics mean that "escape time" from a furnished room in case of fire is today as low as 1½ to 10 minutes.

June 2017, Grenfell tower flats, London. The fire is reported to have started in a fridge-freezer with flammable insulation foam, spread across the building through cladding insulation materials (recently installed in renovation but not conform to fire regulations) and into flats as uPVC windows deformed. 72 people died and over 200 families lost their home.

Flame retardants are essential to enable compatibility of combustible materials with safety regulations or industry safety standards. This concerns plastics and composites, 3D-printing, insulation materials (both synthetic and recycled or natural), textiles … Phosphorus based flame retardants often offer the best performance (fire safety and maintaining of material properties, low smoke) to replace halogenated flame retardants (organochlorine and organobromine chemicals), which are under increasing pressure for phase-out from regulators, industry and consumers.

Because of demand for fire safety in sectors such as construction and electronics, and substitution of halogenated flame retardants, there is currently considerable science and industry R&D into new organic phosphorus flame retardants (OP FRs). OP FRs today represent around one fifth of world FR use, with expected growth rate of 5 to 7 % p.a. over the coming decade.

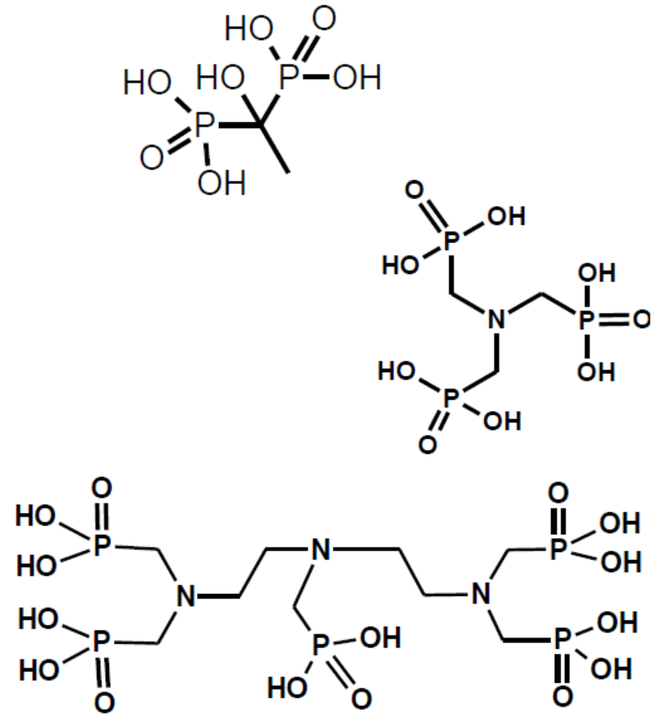
Phosphorus flame retardants include a very wide range of different chemical families with different properties. Some phosphorus flame retardants are inorganic phosphates and can, for some applications, be produced from phosphoric acid ('wet acid' route, not via P_4), e.g. melamine polyphosphate, (poly-)phosphates used in fire extinguishers or wildfire fighting, but red phosphorus, high-grade ammonium polyphosphate and many organophosphorus flame retardants can only be produced via P_4 (from P_4 derivatives).

Webinar participants agreed with JRC's estimate that probably around 10 ktP/y are used in flame retardant production in Europe, but noted that part of this will be in inorganic phosphate FRs, so not from P_4 / P_4 derivatives

Note: this is coherent with the estimate of 50 ktP/y in flame retardants worldwide in the ESPP Phosphorus Fact Sheet 2019

Phosphonates

Stephan Liebsch, Zschimmer & Schwarz Mohsdorf GmbH & Co. KG. and President of **Phosphonates Europe (a sector group of Cefic),** presented typical (non agro-chemical) phosphonates and outlined the main application sectors.



Typical phosphonates (from top downwards): hydroxybisphosphonates (e.g. HEDP), aminomethylenephosphonates (e.g. ATMP, DTPMP)

Key applications of phosphonates include

- at low concentrations, prevention of incrustations or fouling in systems such as cooling circuits (important for electricity generation), membranes in drinking water production or desalination, oil and gas extraction
- as additives in domestic and industrial detergents, ensuring stain removal and anti-greying in "phosphate-free" formulations. Phosphonates are typically used at 0.1 to 0.7 %

P in the detergent formulation, compared to 5 -15 % P in phosphate-based detergents (STPP).

In all cases, the function of phosphonates is to prevent detrimental effects of ions of alkaline earth (e.g. magnesium, calcium …) or transition metals (e.g. Manganese, iron, copper, zinc …).

Phosphonates are organo-phosphorus molecules, and there is no industrially feasible route for their production today other than from P_4 / P_4 derivatives.

Total production of phosphonates in Europe is estimated by EPA (Cefic) at around 50 kt/y of phosphonate (active ingredient), that is around 16 ktP/y. Around 2/3 of this is for detergent applications.

Note that PMIDA and glyphosate are chemically phosphonates, but are not considered here because they have distinct industry circuits, not covered by Phosphonates Europe.

Batteries

P_4 is used, via the derivatives PCl_3 then PCl_5, to produce ***lithium hexafluorophosphate, $LiPF_6$, the electrolyte used in today's lithium ion batteries****, in combination with various carbonate chemicals.*

However, lithium ion batteries pose a recognised fire risk, because they combine high energy densities and flammable organic electrolyte. In case of incidents such as overcharging, internal faults, physical damage or overheating, this can lead to thermal runaway, fire and explosion. For example, lithium iron phosphate (LFP) batteries, which ***differ by using $LiFePO_4$*** *(instead of lithium cobalt oxide $LiCoO_2$ and manganese oxides) as cathode materials, offer better fire safety, for UPS applications (uninterruptible power supply). LFP batteries also have a longer life time and a better voltage / discharge pattern. However, lithium iron phosphate is poorly conductive, so has to be processed to specific forms (e.g. nano structure with conductive coating) and LFP batteries, to date, achieve significantly lower levels of energy storage (Wh/kg) than lithium ion. This is less of an obstacle in batteries in non-mobile applications, in particular for storage of irregular renewable energy, or back-ups for data centres, and development of these applications could lead to considerable growth in lithium iron phosphate demand.*

The world market for LIFP batteries is currently estimated at around 8 billion US$ and may grow to 34 billion by 2026, that is maybe around 25% of the world lithium ion battery market.

The ESPP Phosphorus Fact Sheet 2019 estimates potential world demand for phosphorus in lithium ion batteries (electrolyte) and in lithium iron phosphate batteries (cathodes) at c. 90 ktP/y 2025.

Lithium ion phosphates can be produced from phosphoric acid*, but as batteries are increasingly energy-concentrated, even a few molecules of impurity can cause malfunction, so it is possible that 'thermal' phosphoric acid (that is, produced via P_4) may be required, if sufficient levels of purity cannot be achieved by solvent-extraction purification of 'wet acid' phosphoric acid.*

The ***lithium hexafluorophosphate, $LiPF_6$, used in lithium ion batteries can only be produced from P_4-derivatives****.*

P_4 and recycling

The final end products produced from P_4 eventually end up dispersed or discarded, depending on their use as plastic additive, agrochemical, lubricant additive, etc. Mapping the detailed life cycle would be a major task, but generally for the largest types of uses, a distribution is given on the following page.

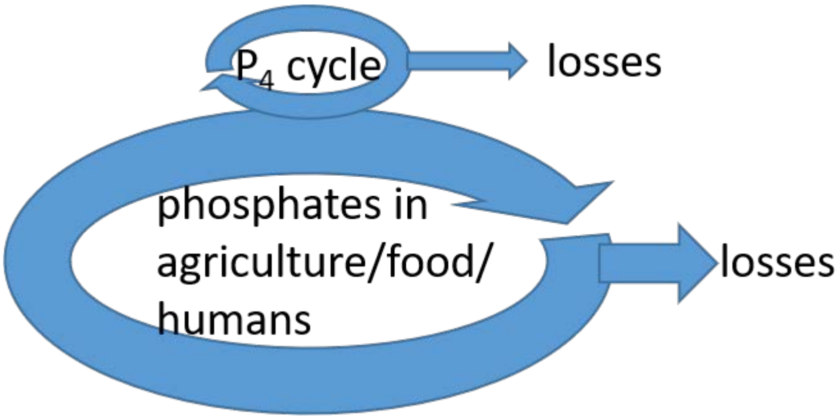
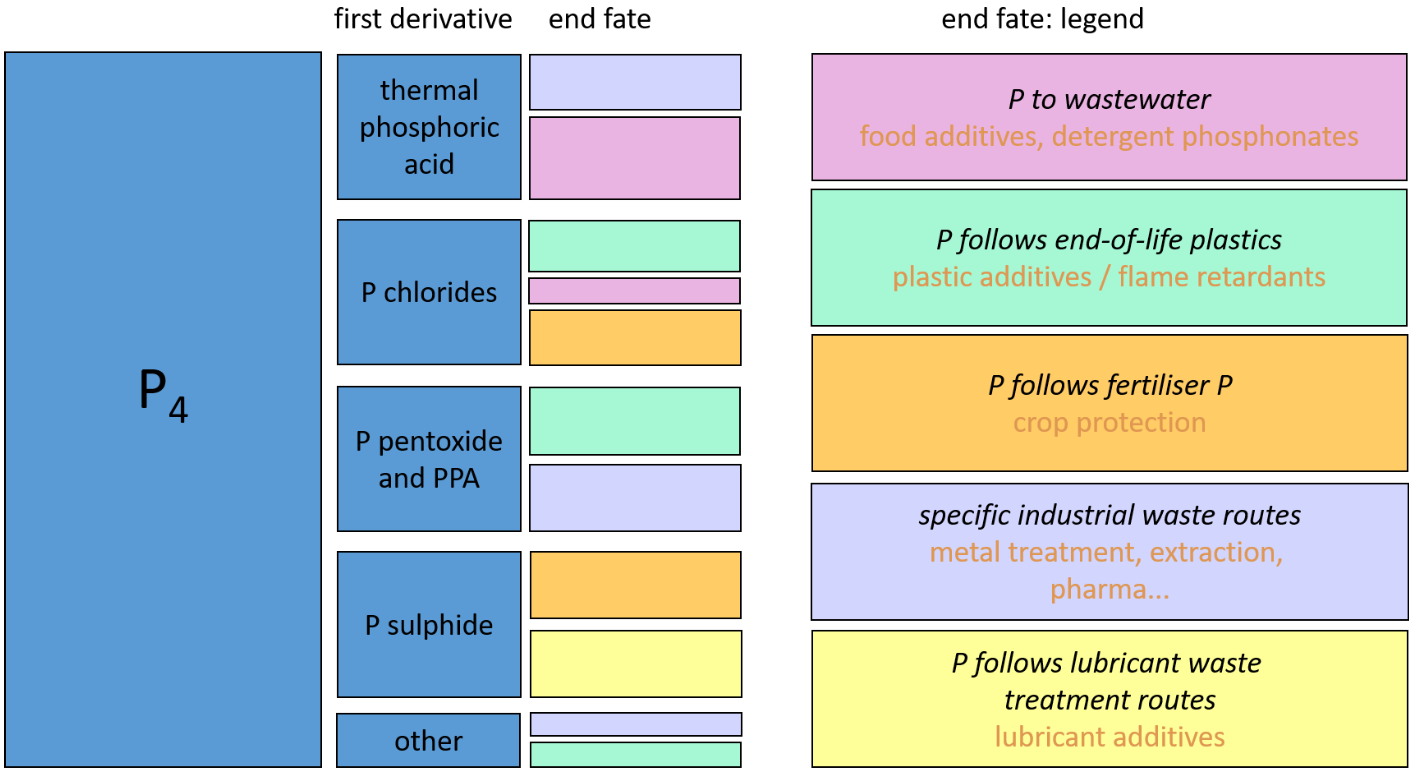


Diagram:
the P_4 cycle and the overall phosphorus cycle

(Fig. v) End-of-life fate of P_4 derived phosphorus

Estimates by Willem Schipper of end-of-life fate of P_4-derived end products, classified per major first derivative. The right half of the figure specifies what is represented by each colour. The sizes of the "end fate" bars indicate the relative importance of each end point for that category. The bar sizes for "first derivative" are not scaled.



When considering P_4 recycling, it needs to be kept in mind that **almost all P flows in society are not derived from P_4**.

Additionally, the number of sectors and applications where P_4-derived chemicals are found is enormously diverse. Whereas some end uses, such as flame retarded plastics, could see a form of re-use as such (e.g. via mechanical recycling of end-of-life plastics), recycling of P from many P_4 end-uses is either complicated, or represents just a very small part of the larger cycle of fertilizer, feed and food phosphorus (e.g. detergent phosphonates reaching wastewater will represent probably <2% of P in sewage, the rest coming from faeces, urine, food waste, etc.).

Much work has been devoted to map phosphorus (in the form of phosphate) in society, and many efforts are under way to recycle phosphate in some form. Manure, municipal wastewater, slaughterhouse waste and food waste are identified as entry points for such recycling. Recycling from sewage sludge incineration ash or meat and bone meal ash is one relatively advanced sector, with a number of technologies under development or implementation to recycle P in some form (e.g. as fertiliser or as phosphoric acid), technologies are also being proposed to produce P_4 from such ashes. This would be **upcycling, in that a higher value and higher quality material (P_4) would be produced** than that initially (fertiliser phosphates or organic phosphates).

It therefore makes sense to consider producing P_4 out of the agricultural/food/waste cycle rather than back from the multitude of chemical specialties originally derived from P_4.

Circular Economy: possible future production of P_4 in Europe

ESPP contacted and invited to present, all projects known to us to be working on P_4 production from waste materials which have reached the pilot scale:

- Italmatch industrial project
- RecoPhos, Austria
- MITechnology, Austria

If there are other projects who are developing P_4 production from secondary materials of which ESPP is not aware, and who have reached at least laboratory pilot testing scale, please contact info@phosphorusplatform.eu ESPP's objective is to be inclusive and to ensure objective information on all projects.

RecoPhos

Christoph Ponak, Montanuniversität Leoben Austria, presented the **RecoPhos EU FP7** R&D project (2012-2015, website, final project Cordis summary and in ESPP SCOPE Newsletter n°112). The InduCarb electrical induction heated reactor was adapted to produce elemental phosphorus (P_4) by reduction of phosphates in sewage sludge incineration ash or dried sewage sludge with coke. The pilot constructed and successfully demonstrated in the RecoPhos FP7 project had reactor dimensions around 0.2m diameter, 1 m height, with capacity 10 kg secondary material input per hour and enabled proof of feasibility of the design concept and collection of indicative initial data on operating parameters and energy consumption (at this test pilot scale).

Around 75% of the phosphorus in sewage sludge was recovered as P_4, and it is hoped that process adjustment could significantly increase this.

Further tests since the FP7 project, with a newly constructed lab-scale plant, have demonstrated the feasibility of recovery of materials from lithium ion batteries (from processing waste): recovery of phosphorus, lithium, iron, cobalt and nickel.

Studies are also underway into possible phosphorus recovery from steel slags using the reactor.

Currently, a larger pilot is in the planning phase (again in Leoben) with an industry partner, capacity 50 kg secondary material per hour, to be operational within 1 -2 years. This should provide the data necessary for construction of a semi-industrial scale pilot of 2 500 – 3 500 tonnes secondary material per year (c. 150 tonnes P_4 production per year).

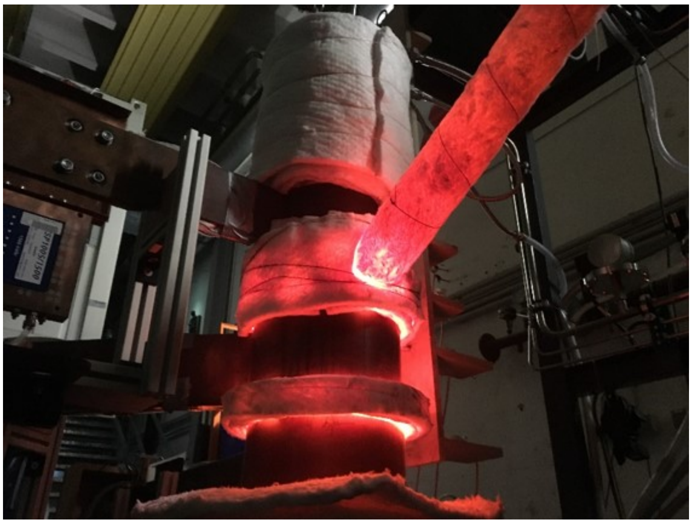


Photo: the RecoPhos FP7 pilot reactor demonstration, 2015, Leoben

FerroPhos

Alfred Edlinger, MITechnology, Austria, presented research into adapting the **FerroPhos process** to recover P_4 from secondary materials. This combines a FerroPhos Reduction Reactor and a Ferrophos FlashOxidator.

A downflow furnace is heated by carbon-containing biomass or charcoal plus hydrogen. Phosphate and iron oxide containing materials are reduced. Molten iron phosphide (Fe_2P) is reacted with lime (CaO) and aluminium oxide (Al_2O_3) and oxygen to release gaseous phosphate P_2O_5 and Brownmillerite ($Ca_2(Al,Fe)_2O_5$ - which can be used in cement production). The concept is to then reduce the P_2O_5 to elemental phosphorus in the same or in a second furnace using again biomass carbon and hydrogen as reduction agents.

It is suggested that the whole process could be carbon dioxide neutral in that the use of carbon and hydrogen could be balanced by waste heat recuperation (from transformation of e.g. wood by-products to charcoal) and hydrogen production by pyrohydrolysis of biomass/charcoal or by electrolysis using renewable electricity.

The FerroPhos FlashOxidator furnace has been tested at laboratory scale, with promising results for e.g. reaction of iron phosphide (Fe_2P) with elementary sulphur or sulphur-containing reactants to elementary phosphorus (P_4,) + iron sulphide (FeS_2).

Italmatch

Carlos Galeano, Italmatch Chemicals, explained that the company is a leading phosphorus speciality chemicals producer, with 18 plants and 6 R&D centres worldwide. Italmatch produces P_4-derived phosphorus chemicals for markets including fire safety, plastics, water treatment, lubricants, detergents, …

Italmatch acquired Thermphos' technology knowhow in 2014 and the RecoPhos technology (via ICL) in January 2020, and is also working on the company's own technology concepts for P_4 recovery. Italmatch's objective is to **develop P_4 production in Europe, from waste / secondary materials, to supply all P_4 and P_4 derivative user industries in Europe**. The aim is to develop a best-in-class technology, producing a prime quality product at market conditions, and to enable a fully integrated value chain in Europe, with production and processing of P_4, P_4-derivatives and final phosphorus speciality chemicals. Additionally, the by-products from such P_4 production will offer better quality and are more readily recyclable than those produced from phosphate rock.

To achieve this, **engagement needs to be agreed between relevant companies and stakeholders:** secondary raw material producers (in particular, local authorities and water industry for sewage sludge / sludge incineration ash, rendering industry for meat and bone meal), regulators and policy makers, phosphorus chemical industry (P_4 / P_4 derivative user companies), engineering suppliers and logistics operators / waste traders.

Looking to the future

Chris Slootweg, Van't Hoff Institute for Molecular Science, University of Amsterdam, gave a Green Chemistry view of a future for phosphorus.

He emphasised the need to implement the circular economy for phosphorus, and that production of P_4 from secondary materials would be upcycling, producing a high-value, high-purity product from waste.

He also underlined the research interest to find routes to organo-phosphorus chemicals other than via P_4. He cited in particular the Geeson & Cummins 2020 paper (see ESPP eNews n°45) which summarises a number of possible processes which are being researched at the lab scale, or are achieved in nature by enzyme pathways. This review paper however concludes that "the only industrially practicable way" to produce organophosphorus chemicals is today via P_4 (white phosphorus).

Perspectives and next actions

Participants noted several sectors with potential for considerable development of needs for P_4-derived chemicals in the near future:

- **fire safety of insulation materials and green construction materials** (wood, recycled materials), in particular in the context of the EU Green Deal and "Renovation Wave". Inorganic phosphate flame retardants are widely used in cellulosic insulation materials (e.g. based on recycled paper or textile fibres) but organo-phosphorus FRs are essential for non-halogenated fire safety solutions for synthetic polymer insulation foams
- **batteries**: phosphorus is a component of current standard lithium ion batteries as an electrolyte component ($LiPF_6$), but 'lithium iron phosphate batteries' may develop rapidly in coming years (see box). The $LiFePO_4$ used in their anodes can chemically be produced from phosphoric acid, however, if electronics purity is required, then 'thermal' acid (from P_4) may be necessary. Also, organic phosphorus compounds can be used to improve fire safety of lithium ion batteries. They are already widely used in the plastic components of batteries and battery systems (separators, battery cases …) and may also in the future be integrated into battery electrolytes.
- **circular economy**: the possible future production of P_4 from wastes in Europe would be a major strategic breakthrough. On one hand, it would end Europe's dependency on import of P_4 and P_4 derivatives (CRM: "Phosphorus") for critical downstream industries. On the other hand, it would ensure upcycling (to a higher value material) of secondary phosphorus streams (CRM: "Phosphate Rock")

As next steps, **all concerned companies, experts or stakeholders are invited to send information** relevant to the EU JRC Material System Analysis study (MSA) to info@phosphorusplatform.eu (in case of confidential data, we can indicate to you an email to send directly to the European Commission). Information submitted should include reference sources where possible.

To **address the objective of P_4 production from secondary materials**, it was proposed to organise a half-day event, with the European Commission, in order to discuss how to move projects forward towards implementation, including possible policy support and R&D funding, and to engage dialogue with all stakeholders concerned: concerned companies, secondary material producers (in particular, for sewage sludge incineration ash), researchers and experts …

ESPP overall conclusions on EU P_4 / P_4-derivative use

Note: these conclusions represent ESPP's own analysis and may differ from the EU JRC MSA calculation.

As indicated above, JRC conclude and webinar participants validated, **EU imports of P_4 (customs data for white + red phosphorus) of 60 - 80 ktP/y.** This number has varied over time, and in particular was modified by the demise in 2012 of the last EU producer of P_4.

To this should be added the significant imports of P_4-derivative chemicals. P_4-derivatives are however also exported out of Europe, so **total net use of P_4 + P_4-derivatives in Europe can be estimated at maybe around 80 - 120 ktP/y**.

This refers to processing in Europe of P_4 or P_4-derivatives to phosphorus speciality chemicals. That is, it includes use of P_4 or PCl_3 in Europe to produce a flame retardant (e.g. DOPO), even if this DOPO is then exported out of Europe. It does not include phosphorus in DOPO imported into Europe as DOPO, nor imported into Europe in a finished product (e.g. DOPO contained in plastic in a computer part).

On the other hand, the largest user industries for P_4 / P_4-derivatives (phosphonates, fire safety, agrochemicals) estimate a total of around 45 ktP/y respectively.

There is no data on other uses of P_4 / derivatives, such as production of catalysts, metal extraction chemicals, pharmaceuticals, electronic-grade phosphoric acid, fireworks, … nor for lithium ion nor lithium iron batteries (see box). These uses are however probably quantitively small, despite their high importance for some downstream industries (e.g. electronics, catalysts, rare metal production). An "arbitrary" 5 - 15 ktP/y may cover these other uses.

ESPP therefore suggests that probably the apparent difference between the ‘top down’ estimate for P_4 + P_4-derivative use in Europe (80 – 120 ktP/y) and a bottom up estimate (50 – 60 ktP/y) is likely to be due to **continuing use today of P_4 in Europe to produce ‘thermal acid’ used in food phosphate production and in some other applications (e.g. metal treatment, toothpaste).** Technically, however, as discussed above, this could be replaced by ‘wet acid’ phosphoric acid, after purification by solvent extraction.

ESPP suggests that the EU’s **real import dependency for P_4/P_4-derivatives may thus be around 50 – 60 ktP/y today** (assuming food phosphate production could move to purified ‘wet acid’ route).

This may decrease in the short-medium term as certain organo-phosphorus agro-chemicals are under regulatory question (in particular glyphosate).

However, it could also increase in the medium-long term with a consistent growth in phosphorus-based fire safety and possibly with a significant development in use in batteries (if this ‘thermal acid’ quality materials are needed).

List of participants at the webinar:

European Commission:
- DG GROW: Constanze Veeh, Fleur van Ooststroom Brummel, Milan Grohol
- DG JRC: Fabrice Mathieux, David Pennington, Cristina Torres de Matos

ESPP: Ludwig Hermann, President; Chris Thornton

Willem Schipper, industry consultant

Laurent Oger, ECPA (European Crop Protection Association)

Adrian Beard, Clariant, for pinfa (Phosphorus, Nitrogen & Inorganic Flame Retardants Association), Cefic

Martin Sicken, Global Head of Innovation Flame Retardants, Clariant

Stephan Liebsch, (Zschimmer & Schwarz Mohsdorf GmbH & Co. KG., for EPA (Phosphonates Europe), Cefic

Chantal de Cooman, Sector Group Manager for EPA (Phosphonates Europe), Cefic

Christoph Ponak, Montanuniversität Leoben Austria

Alfred Edlinger, MITechnology – Metallurgy & Inorganic

Carlos Galeano, Norberto Gatti, Italmatch Chemicals Group:

Chris Slootweg, Van’t Hoff Institute for Molecular Science, University of Amsterdam

Herbert Neumann, Director, Perimeter Solutions Germany

Jerzy Kowalski, PCC Rokita

Denis Przybylski, Markus Streitberger, ICL

Rolf-Michael Jansen, Lanxess

Valeria Oldani, Bozzetto Group SpA, member of EPA (Phosphonates Europe)

Susanne Petrovic, BASF

Olivier Vallat, Febex

Svatopluk Valusek, Michel Henrotin and Dalibor Kuchar, Fosfa

Input also kindly received from Carol-lynne Pettit, the Cobalt Institute.