



UvA-DARE (Digital Academic Repository)

Sustainable use of phosphorus

Capturing the philosopher's stone

de Boer, M.A.

Publication date

2019

Document Version

Other version

License

Other

[Link to publication](#)

Citation for published version (APA):

de Boer, M. A. (2019). *Sustainable use of phosphorus: Capturing the philosopher's stone*. [Thesis, fully internal, Universiteit van Amsterdam].

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Chapter 1

Phosphorus: Reserves, Production and Applications

Abstract: The demand of phosphate fertilizers is growing as a result of a rising population, changing human diets as a follow up of the increasing (meat) consumption per capita, and an expansion in the production of biofuels. Besides the fertilizer industry, there is a steady growth of using phosphorus (P) containing compounds in the chemical industry for applications in, e.g., soft drinks, pharmaceuticals and flame-retardants. To meet this growth, it is important to know if the P reserves are sufficient and what kind of processes are used to produce such phosphorus compounds. Reserves are not equally spread around the world, with three-quarters located in Morocco and The Western Sahara. Furthermore, prices can be volatile, as shown in 2008 with an eightfold price increase. Moreover, the estimated time until depletion of phosphate rock differs substantially between several studies, which resulted in the addition of phosphate rock on the critical material list of the European Commission. An important aspect for the processing of phosphate rock is the quality of the rock, which is dependent on the ore type (sedimentary or igneous), level of radioactivity and hazardous metal contents. The main intermediary compounds for phosphorus products are phosphoric acid and white phosphorus. About 95% of the phosphoric acid is made

via the wet process; acidulation of phosphate rock to create wet phosphoric acid and the main byproducts phosphogypsum and hydrogen fluoride. The purity and thus the reusability of phosphogypsum is dependent on the type of digestion process. However, reusing phosphogypsum is not a common practice at the moment. Wet phosphoric acid can be purified via extraction up to phosphoric acid comparable to that produced with the thermal process. Separation of specific compounds can be done through precipitation. Additionally, cationic impurities can be removed via precipitation, but the product will then be changed into a phosphate salt, which is unfavorable for its use in industrial applications.

Published: M. A. de Boer, L. Wolzak, J. C. Sloopweg, in *Phosphorus Recover. Recycl.*, Springer Singapore, Singapore, 2018, pp. 75–100.

1.1 Introduction

Phosphorus (P) is an essential element for life, our current food production system, manufacturing industries and general economic growth.^[1] P is a key limiting factor for plant growth and is therefore one of the three main elements (N:P:K) in fertilizers. The demand for phosphate fertilizers has grown over the last years due to the expanding production of crops, as a result of the rising population, changing human diets resulting in increased (meat) consumption per capita, and also for biofuel production. However, phosphorus is a finite resource and its global distribution is uneven; almost the entire global P demand is supplied by just four countries, namely China, the United States, Russia and Morocco and with three-quarters of the reserves located in the latter.^[2]

Currently, phosphorus is produced from phosphate rock (PR), which is mined and processed into valuable P-containing products using two main production processes. The first method is the production of phosphoric acid for the fabrication of fertilizers via the wet process, which accounts for 80-90% of the global P demand. The second process converts phosphate rock into elemental (white) phosphorus (P_4), which is then used to produce phosphorus compounds for industrial purposes, including feed additives, detergents, flame-retardants, pesticides and medicines. Both methods will be discussed in this chapter, as well as the application of phosphorus containing products, preceded by giving a geopolitical assessment of the reserves of phosphate rock.

1.2 Reserves and Production of Phosphate Rock – a Geopolitical Assessment

In the beginning of the 19th century, Liebig founded a theory that stated that nutrients, such as nitrogen and phosphorus, were crucial elements to grow crops and that these nutrients were circulating between living and dead material.^[3] During the same time, the value of guano was discovered. This phosphorus containing matter originates from bird droppings deposited over several millennia. Guano soon became a valuable world trade material, however, this phosphate resource was limited and declined at the end of the 19th century.^[4] Soon other sources of phosphate were discovered, most notably, phosphate rock deposits that appeared to be of unlimited quantity and soon became the main resource for phosphorus. However, high grade phosphate rock reserves take millions of years to form via the decomposition of (marine) organisms, and with the current mine production significantly more is being consumed than is geologically replaced. Currently, it is uncertain how large the global phosphate rock reserves are and it is thus unclear when these will be depleted. The estimated time of depletion varies greatly among different studies, ranging from 40 to more than 400 years.^[5] Therefore, several researchers have focused on taking stock of the current global reserves and the quality of these.

1.2.1 Reserves

There are three types of phosphate rock, namely sedimentary rock, igneous rock and metamorphic rock. Since each of these ore types differ in chemical composition, for example the phosphate content and amount of impurities, these three types will be discussed individually and an assessment of the quality of the reserves will be provided.

Sedimentary rock

Sedimentary marine phosphorite is the most common phosphate rock. More than 80 percent of the produced phosphate originates from sedimentary rock, which is often composed of accumulated fossilized shells and aquatic animals. The most favorable deposits to exploit are frequently found as one or more thick beds with a high phosphate-grade that are unconsolidated and have a uniform granular composition with a minimal structural deformation.^[6] Sedimentary rock contains more than 7.8% P_2O_5 , and is called phosphatic sedimentary rock when it contains 7.8% to 19.5% phosphate, and phosphorite above 19.5% phosphate. The largest sedimentary deposits can be found in Northern Africa, China, and the United States (Table 1).

Sedimentary rock consists of the mineral apatite, a calcium phosphate combined with either a hydroxide, fluoride or chloride ion: $Ca_5(PO_4, CO_3)_3(OH, F, Cl)$, with fluorapatite, $Ca_5(PO_4)_3F$, being the most common.^[7] Sedimentary deposits exhibit a wide range of chemical compositions, including pollutants, and great variation in physical form. This results in the formation of several possible byproducts during processing, such as fluorine, cadmium, uranium and rare earth elements. The mineral apatite is sparingly soluble in water. However, the different compositions

influence the solubility of the mineral. Incorporation of hydroxide, for example, results in apatite minerals with a higher solubility than apatite containing fluoride.^[7]

Igneous rock

Igneous rock was formed through the crystallization of cooling lava or magma. Phosphorus concentrations in igneous rocks often range from 0.005% to 0.4% P_2O_5 but higher values (1.5% to 2.0% P_2O_5) can be found in strongly alkaline, low-silica igneous rocks. Igneous rock mainly consists of carbonatites, minerals consisting of more than 50 percent carbonate minerals and alkalic intrusions.^[8] An example of a commonly encountered alkaline intrusion is diopside ($MgCaSi_2O_6$). In addition, the minerals calcite and dolomite can also be present in igneous rock.^[6] These igneous deposits can provide phosphate rock with 35% to 40% P_2O_5 content via beneficiation methods (often grinding followed by flotation to remove quartz and calcination to remove organic impurities). Examples of crystalline fluorapatite igneous deposit regions are Canada, Brazil, Russia, and Finland.

Metamorphic rock

Metamorphic rock deposits are often deep-lying phosphate deposits, which contain both sedimentary and igneous deposits. Metamorphic rock often contains of 0.01% to 1.3% P_2O_5 . These deposits have been subjected to high levels of pressure and heat resulting in a less porous texture, more interlocked crystals, and higher induration compared to igneous and sedimentary rock.^[6] As a result, exploitation of metamorphic rock deposits is not currently economically viable. Metamorphic rock deposits can be found in China and India.

Table 1. Composition of phosphate rock in wt % based on dry material [9]

Phosphate rock	P ₂ O ₅	CaO	F	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CO ₂	SO ₃
Kola (Russia)	39.1	51.5	3.4	2.0	1.2	0.7	0.0	0.0
Phalaborwa (South Africa)	38.4	52.5	2.3	1.9	0.2	0.4	1.3	0.1
Florida (USA)	31.6	47.7	3.9	9.0	1.0	1.6	3.7	1.4
Idaho (USA)	31.2	45.7	3.6	8.5	0.6	0.5	3.1	1.2
Khourigba (Morroco)	34.8	52.5	4.2	0.9	0.5	0.1	4.1	1.5
Togo (Togo)	29.7	40.3	3.9	10.2	4.4	5.3	1.6	0.1

Quality of the phosphate rock deposits

The highest possible apatite (and thus phosphate) content is always the pursuit, both for technical and economic reasons.^[5] Consequently, the ambition is to remove as much of the impurities in phosphate rock as possible. These impurities concern many types of different chemicals. One could distinguish three main types of unwanted impurities in phosphate rock: other non-phosphorus bearing minerals, heavy metals and radioactive materials. Other non-phosphorus bearing minerals need to be removed from PR as much as possible in order to increase the phosphate grade. Heavy metals and radionuclides need to be removed due to health and environmental concerns.

Other minerals

Due to its mineral structure, phosphate rock can contain other sparingly soluble minerals which do not contain phosphorus, such as fluorite (CaF₂), magnesite (MgCO₃) and barite (BaSO₄). Substitutes for PO₄³⁻ are CO₃²⁻, As₂O₄, SO₂, SO₄²⁻ and VO₄³⁻, while the calcium ion can be substituted by Mg²⁺, Mn²⁺, Sr²⁺, Pb²⁺, Na⁺, U³⁺, Ce³⁺ and Y³⁺ as well as other rare earth elements.^[7] The substitutes are not all of the same valency. When anionic substitutes cause a gain or rise in valency, this can be compensated with other cationic substitutes of opposite nature.^[7]

The most common minerals in sedimentary phosphate rock are clay minerals, such as kaolinite ($\text{Al}_2\text{SiO}_5(\text{OH})_4$) and sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$), quartz and two types of carbonates, calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). A replacement of PO_4^{3-} by CO_3^{2-} of 25% and of Ca^{2+} by Mg^{2+} of 10% is sometimes found.^[10] Carbonates can lead to complications during the processing of phosphate rock, especially during froth flotation (separating the hydrophobic from the hydrophilic minerals), because of the high similarity between carbonates and phosphate minerals.^[11] A thermal process called calcination can be used to remove the carbonates, but this is economically unfavourable due to the high energy input. The Florida Institute of Phosphate Research points out that a large amount of today's phosphate reserves are left untouched because of a high dolomite concentration. Other common materials found in sedimentary rock are iron, alumina, quartz, montmorillonite, organic matter, and many other elements in trace amounts.

Heavy metals and radioactivity

Russia is the only country of the four main producers with mainly igneous deposits, while the others have sedimentary PR deposits (Table 2). Igneous deposits are mostly low in grade (less than 5% P_2O_5), but both the level of radioactivity as well as the hazardous metal content (e.g. cadmium, arsenic and mercury) are low. This is also the case for the igneous deposits in Russia compared to the sedimentary deposits of Morocco, China and the United States (Table 3). A more in depth comparison of several sedimentary and igneous deposits on cadmium, uranium, and ^{226}Ra contents can be found in Table 4. The United States has the highest level of radioactivity and Morocco relatively has the highest hazardous metal content, which will be discussed in more detail below.

Heavy metals are dangerous because of their tendency to bioaccumulate and therefore be potentially harmful for human health.^[12-13] There are several metallic elements present in PR with an up to 10-100 times higher concentration than in soil, such as arsenic, cadmium, mercury, lead and uranium.^[10] The chemical composition of PR, however, varies largely and depends on its origin. When comparing the most common toxic heavy metals chromium, lead, cadmium, zinc, copper and arsenic in PR from Moroccan and Russian origin, it is clear that the heavy metal content in average Moroccan PR (sedimentary) is significantly higher than in Russian PR (igneous) (Table 3). For these six heavy metals, phosphate rock in Morocco has up to 2 to 30 times higher concentrations than in Russian phosphate rock.

Table 2. Comparing phosphate deposits of the four major countries in phosphate rock production

	Morocco	China	Russia	U.S.
Ore type	Sedimentary	Sedimentary	Igneous	Sedimentary
Level of Radioactivity	Moderate	Low-moderate	Low	Moderate-high
Hazardous metal contents	Moderate-high	Low-moderate	Low	Moderate

Table 3. Comparison of heavy metals in Moroccan and Russian phosphate rock. Average Concentration (mg/kg) ^[10,12,14]

	Type of heavy metal					
	Cr	Pb	Cd	Zn	Cu	As
Morocco	291	7	30	345	22	11
Russia	23.3	3	0.1	19	30	1

The amount of heavy metals is very variable, even within the same deposit. The presence of heavy metals in fertilizers is primarily due to impurities in phosphate rock that have not been removed during the production process.^[15] This creates the

risk for these metals to accumulate in the soil and crops and enter the human food chain. However, this risk is not only influenced by the heavy metal content of the fertilizer, as soil properties and the chemical form of the metal also play an important role. An acidic environment, for example, increases the availability of heavy metals in soils for the uptake in crops. Cadmium has the highest transfer factor (cadmium uptake from soil to crop ratio) for any type of crop and is therefore the element with the highest risk of being detrimental to human health in the phosphate fertilizer field.^[12] Due to the high toxicity of cadmium, it is classified as a class 1 carcinogen (Group B1) by The International Agency of Research on Cancer and the World Health Organization (WHO).^[16,17] If one examines the cadmium, uranium, and ²²⁶Ra concentration in the several deposits, we can see in a single glance that the amounts differ notably depending on origin and are significantly higher in sedimentary phosphate rock mines than igneous phosphate rock mines (Table 4). The incoherency between the data of three different references for the cadmium content for the same deposits shows that it does not only differ between the mines, but also between the researches. A reason can be the variability within the same deposit or different types of measurement.

Table 4. Average concentration of cadmium (mg/kg), uranium (mg/kg) and ²²⁶Ra (Bq/kg) in the major igneous and sedimentary deposits ^[18-21]

Origin	Cadmium content (mg/ kg P ₂ O ₅)			Uranium content (mg/kg)	²²⁶ Ra content Bq/kg
	[18]	[19]	[20]	[21]	[21]
Igneous Rock					
Russia (Kola)	<13	0.3	0.25	20	70
South Africa	<13	0.1	0.38		
Sedimentary Rock					
USA	23-166	19.8-125	24-120	80-150	600-1500
Jordan	<30	12.1-28	18	80-110	800-900

Morocco	46-121	17-63	55	100-160	800-1600
Syria	52	13-46	22		
Algeria	60	42-62.6		100-120	700-850
Egypt	74				
Israel	100	81-112	61	80-140	800-1200
Tunisia	137	94	173	30-50	250-350
Togo	162	164-179	147	100-110	950-1000
Senegal	203	165-180.6	221	100-120	950-1100
Nauru	243				

The high content of cadmium in some PR deposits (Table 4) raised various concerns. As a result, technologies for decadmiation are currently under debate, but have not yet been employed on industrial scale, primarily due to cost issues. Besides this, the current decadmiation processes remove the cadmium from the phosphoric acid and are therefore not a solution for other products as the fertilizers SSP, TSP and NPKs. Due to the numerous, complex factors which can influence the bioaccumulation of cadmium and uptake by crops, it is difficult to quantify the real health risks of the use of P containing fertilizers since it depends on a lot of factors, resulting in controversy among researchers, policies and fertilizer companies.^[19] Nevertheless, human exposure to cadmium resulted in an increased risk for several types of cancer and is related to kidney and renal failure, and bone demineralisation. The diet exposure of average European citizens is close to or slightly exceeding the tolerable intake. People with special diets, like vegetarians, even exceed the tolerable diet with 200%.^[20] Several institutes and companies have advocated limits of cadmium, such as 60 mg/kg (Fertilizers Europe), 80 mg/kg (OCP, Timac Agro), and 90 mg/kg (Grupa Azoty, Fetinagro). The European commission is also debating on setting limits and a maximum level will be put into practice from 2019.

Phosphate rock contains radionuclides of the uranium and thorium natural decay series.^[21] The radioactivity of PR ranges from 70-100 Bq/kg ²²⁶Ra for igneous PR from Russia, to 600-1500 Bq/kg ²²⁶Ra for sedimentary Moroccan PR.^[22] On average, 90-95% of the uranium can be found in the phosphoric acid, while almost the entire ²²⁶Ra content in phosphate rock ends up in the phosphogypsum.^[19] Every year, 10.000-15.000 tons of uranium are deposited on agricultural land.^[19] Through mining and processing of PR, radionuclides are redistributed into the environment and introduced in products and byproducts from the phosphate industry. Naturally occurring radioactive materials (NORM) are found everywhere in our surroundings and consequently we are exposed to it every day. These materials do not pose threats for human health per se. Only when these materials, such as PR, are concentrated to a certain degree then they may pose risks to humans and environment.

The concentration of radionuclides (and their respective decay products) in byproducts is technically enhanced. Therefore, these byproducts are labeled as Technically Enhanced – Naturally Occurring Radioactive Materials (TE-NORM).^[23] One of these byproducts in the phosphate industry is phosphogypsum, which contains calcium sulphate, small amounts of silica, unreacted phosphate rock, radium, uranium and US EPA toxic metals.

1.2.2 Geopolitics and Reserves

Currently, there is speculation on the amount of global phosphate reserves. The estimated time until depletion differs substantially between the several studies. The time left before depletion will rise according to the '*Qui quaerit, reperiet*' (He who seeks, will find) principle. When the prices of these finite sources will rise,

previous uneconomic reserves become economically profitable and more reserves will be discovered. This could be compared to the oil reserves; nowadays oil is extracted from the ocean floor, which was first considered as an uneconomic/unavailable resource. Thus, the volume of phosphate rock reserves is dynamic. The precursor of the USGS (USBM) developed a classification method with which four types of PR deposits could be distinguished:

1. Current economic deposits as reserves;
2. Marginally or sub economic deposits as the reserve base;
3. Uneconomic deposits, which have a reasonable potential of becoming economic in the future as resources;
4. Deposits with no reasonable prospect of economic viability in the foreseeable future, as occurrences.

This classification method is not universally required by law.^[24] The lack of a universal classification method for PR deposits caused speculations on the amount of phosphorus left. An example occurred in 2010, when the reserves and resources as reported by the USGS were reassessed by the International Fertilizer Development Centre (IFDC). The USGS reported in 2010 the global PR reserves as being 16,000 Mt (million tonnes), of which 5,700 Mt of PR are located in Morocco. In the same year, the IFDC issued a report in which the global reserves were increased to 60,000 Mt PR with an estimation of 51,000 Mt found on Moroccan territory, which is an increase of almost 4 times within one year. In the USGS reports, reserves are defined as upgraded (beneficiated) concentrate. This term is used by the mining industry for upgraded ore that is upgraded to such an extent that it is ready to be sold on the market. The phosphate (P_2O_5) content for this

beneficiated ore needs to be at least 30%. However, from the IFDC report it does not become clear what factor is used to calculate this beneficiated ore back to phosphate reserves. In the report of IFDC, the term 'phosphate rock' deposit is used for both unprocessed rock and beneficiated concentrates. Despite the fact that both institutes used different definitions, the USGS has adopted the reserve estimation of IFDC.

The difference in estimated reserves in Morocco can be clearly seen in Fig.1, which shows the estimated world reserves in 2007 and in 2017. Besides Morocco and Western Sahara, also the estimated reserves in the Middle East significantly increased, while the estimated reserves for China is only half of what has been estimated in 2007. In 2017, the world resources of phosphate rock are estimated around 300,000 Mt and reserves around 68,000 Mt, and 75% of the total estimated reserves can be found in Morocco and the Western Sahara (see Fig.1).^[2]

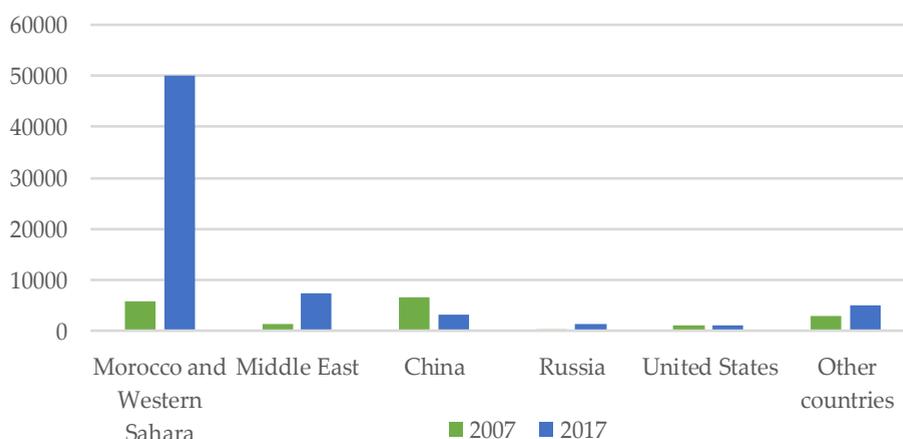


Fig.1 The estimated world reserves in million tonnes according to USGS in 2007 and 2017 ^[2,25]

1.2.3 Mines in EU

In 2010, Europe imported 7,518,000 tonnes of phosphate rock, and the remaining ~10% of the current European phosphate rock demand is produced in Europe, in Finland.^[26] The Siilinjärvi phosphate mines in Finland are currently mining phosphorus at a rate of 1,000,000 tonnes per annum and are expected to be operational until 2035. Several other phosphate deposits are located in Europe, with the largest in Turkey, and minor deposits in, for example, Belgium, Germany, Spain, France, Italy and Greece. However, these are no longer exploited. The Terres Rouges Mine in Lorraine was the last phosphate mine in France and was closed in 1998, due to the increasing criticism of environmental damage. The United Kingdom also has significant phosphate resources in former tin mines and widely dispersed deposits, but these are not economically viable to mine. Belgian and Italian phosphate mining plans received similar criticism. Greek Phosphate mines, although functional for a short time, are deemed as economically unviable due to the scattered phosphate resources and the low grade of 2%.^[27]

1.2.4 Phosphate Rock Production

The mining of phosphate rock is mainly concentrated in four countries, namely Russia, The United States, China and Morocco (including the Western Sahara). Together, they accounted for 79% of the global phosphate rock production in 2016.^[2] Compared to 2006, China increased their production by 450% from 30,700 to 138,000 tonnes, primarily to keep up with the growing domestic demand in agriculture. The Middle East increased their production from 22,870 in 2006 to 26,300 tonnes in 2016. Mainly due to the Arabic spring, changes in the production size occurred in the Middle East. Syria produced 3,600 tonnes in 2006, but in 2016

the production came to a complete halt due to the civil war. Moreover, Tunisia lowered their production from 8,400 in 2006 to 3,500 tonnes in 2016. Other countries in the Middle East have increased their production, such as Egypt, which doubled their production and Jordan increased their production from 6,400 to 8,300 tonnes in these 10 years.

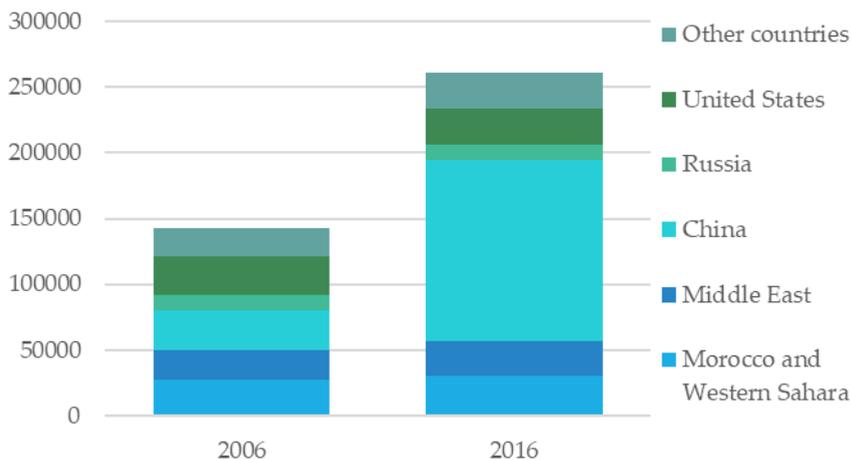


Fig.2 The world production of phosphate rock in 2006 and 2016 [2]

The world consumption of phosphate rock in 2016 was 44.5 Mt and is expected to increase to 48.9 Mt in 2020. The estimated global phosphate rock reserves contain around 68,000 Mt of phosphate rock, which indicates that there is no urgent geological scarcity in the coming decades.

1.2.5 Price Volatility

The price of phosphate rock was stable until 2008, when suddenly a price peak occurred. The price for one tonne of phosphate rock was around 50 dollars before 2008, but after the price peak in 2008, prices rose over 800%.^[26] After this price

peak, the price dropped, but is still on average more than two times higher than prior to 2008. Besides this, with increasing scarcity of P, countries are likely to implement protectionist policies to protect their reserves, which can subsequently increase the price.^[26] China for example has added phosphate as third on the list of most important strategic resources and protects the domestic demand via export quotas on phosphate fertilizers. In 2008, China imposed an export quota of 135% on phosphate rock, which is one of the reasons of the price peak in 2008.

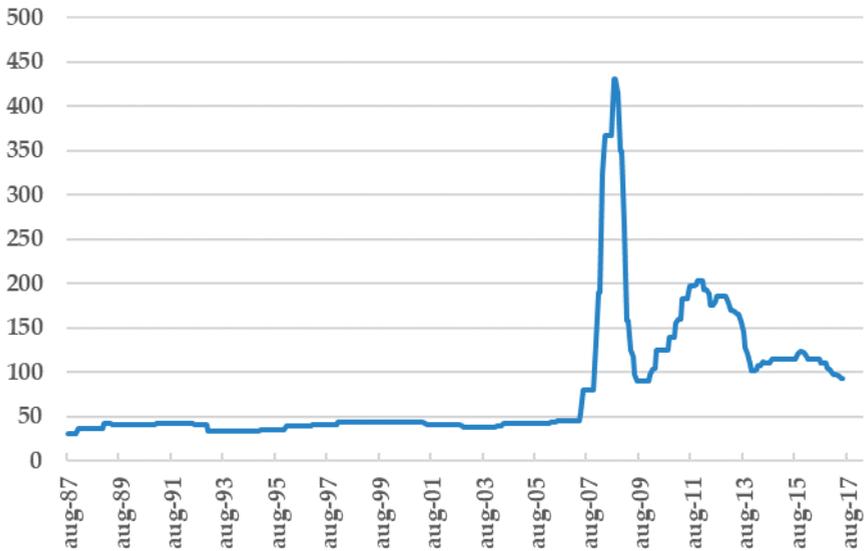


Fig. 3 The price for phosphate rock from August 1987 until August 2017 in dollars ^[28]

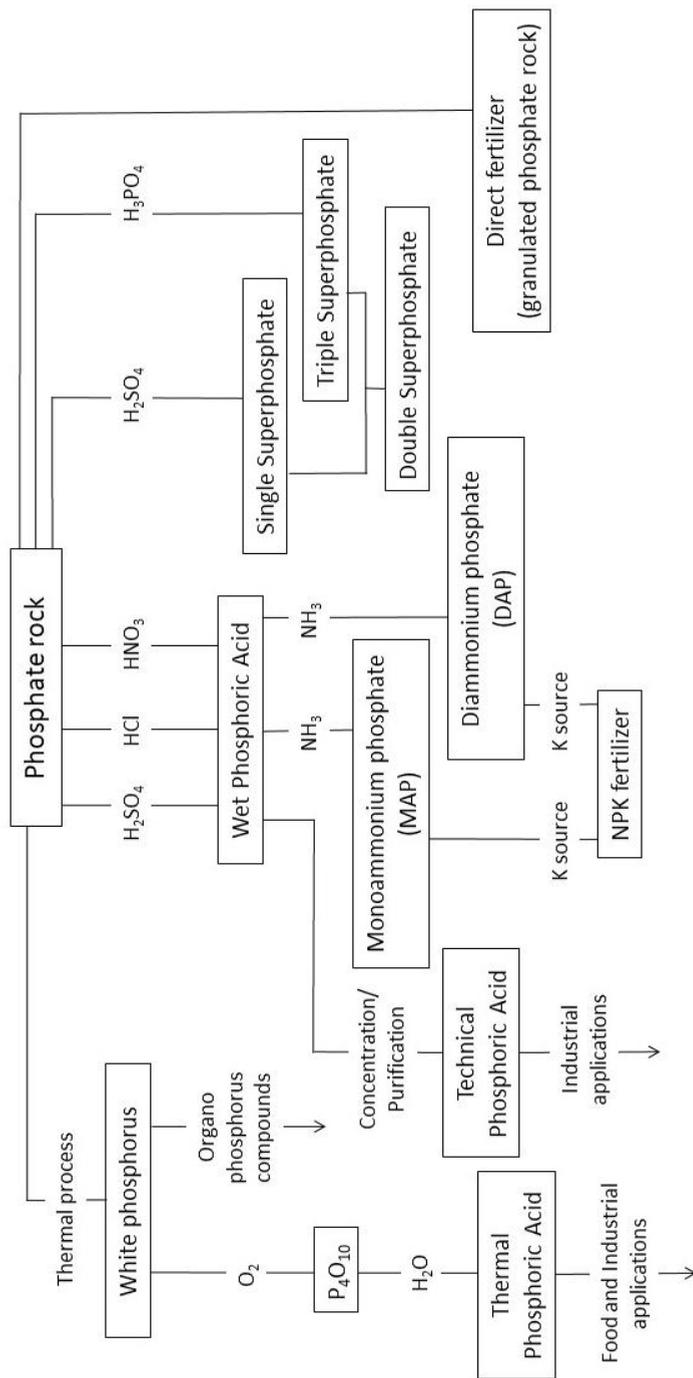
1.2.6 European Critical Material List

The European Union is highly dependent on P import. The main suppliers of phosphate rock in 2011 of Europe were Morocco, Russia and Algeria.^[26] According to the European Commission, the management of P is of critical importance for the development of circular economies and sustainable development. For this reason, P was added to the list of the 20 critical raw materials for Europe, where materials are rated on economic importance for the EU and the possible supply risk.^[29] Phosphate rock has been considered as having a high supply risk since the high corporate concentrations in production, meaning a small amount of producers (four countries, China, Morocco, U.S. and Russia) all with a large market share.

1.3 Phosphate Processing

Following mining, phosphate rock is primarily processed to intermediary products including phosphoric acid (PA) and white phosphorus (P_4), which together form the basis of the industrial phosphorus chemistry. All the production processes from phosphate rock are given in Fig.4. The reduction of phosphates to elemental phosphorus at elevated temperatures is the route to many high-grade phosphorus products, while the production of phosphoric acid through the wet processes is closely related to the manufacturing of fertilizers.^[10] The wet process is the common treatment for the production of phosphate fertilizers and the production of technical phosphoric acid. About 95% of all the phosphoric acid is produced through the wet process, since this is the route towards readily available phosphorus based fertilizers.^[30] In this process, strong mineral acids react with the phosphate ore, where in most cases sulfuric acid is used and on a smaller scale nitric acid or hydrochloric acid. The resulting product is wet phosphoric acid. The type of added acid in the wet process, possible purification steps and the addition of other macro nutrients (for fertilizer production) determine the final type and quality of the product.

Fig. 4 An overview of the production processes for white phosphorus, phosphoric acid and common fertilizers



An alternative route is the thermal process where crude phosphate, coke and silica are heated to over 1500 °C in an electrical resistance furnace to produce elemental phosphorus (P₄); the starting material of many high grade phosphorus compounds in food and industrial applications.^[31] This process is very energy-intensive, and for the production of various compounds hazardous chemicals like chlorine are required as intermediates. On the upside, however, the product contains hardly any impurities. The wet process to obtain several qualities of phosphoric acid and the thermal process to obtain white phosphorus will be both described in more detail below.

1.3.1 Wet Process

The most commonly used method to produce phosphoric acid is via the wet process using sulfuric acid (H₂SO₄) for the acidulation of phosphate rock. The wet process consists of two basic steps: digestion of phosphate rock in a reactor and filtration of the created gypsum (CaSO₄). A third step can be added to reduce the liquid content afterwards and purify the product. In the first step, fluorapatite (Ca₅(PO₄)₃F) is digested with sulfuric acid, resulting in phosphoric acid (H₃PO₄) and the main byproducts phosphogypsum (CaSO₄) and hydrogen fluoride (HF).

Different types of digestion processes exist for phosphate rock, namely the dihydrate process (DH), the hemihydrate process (HH) and combinations of the two (DH/HH and HH/DH). The most applied technology for the production of phosphoric acid, the classical dihydrate process, can be operated at large volumes. It does not have corrosion issues due to the low reaction temperature of 70-80 °C, and is applicable with most grades of phosphate rock.^[30] However, the quality of the phosphogypsum (CaSO₄·2H₂O) is low and the impurities are high, which

disqualifies it as a precursor in other industries. The need for a more concentrated stream of phosphoric acid, less impurities and reduced losses of phosphorus to phosphogypsum led to the development of the hemihydrate (HH) process. This process works at an elevated temperature of 100 °C, which gives rise to the formation of calcium sulfate hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, a very pure gypsum and a higher concentration of phosphoric acid, 40-48% of P_2O_5 with a yield of 90-94%.^[30] The HH process is not often used due to the low process yield, but a combination of the DH and HH process is used, for example in Japan, because of the advantage of the production of pure gypsum for the manufacturer of plasterboard and cement. Nevertheless, the traditional dihydrate process remains the primary dihydrate wet process to obtain phosphoric acid, with more than 90% of the production of the wet phosphoric acid.^[32]

During the digestion step, phosphogypsum is formed; a slurry of solid particles of gypsum (CaSO_4), unreacted phosphate rock and other impurities. The second step involves filtering out this solid phosphogypsum in a partial vacuum resulting in a 28-31 wt% P_2O_5 (50% phosphoric acid) yield. The remaining acids on the solids can be washed off and used again in the process.

The concentration of 28-32 wt% P_2O_5 is too low to be used as a fertilizer and has to be concentrated to 40-55% (or even 70% if superphosphate is the desired product). Therefore, the dihydrate process can be followed by reducing the liquid content via evaporation with submerged combustion burners and vacuum circulation evaporators resulting in merchant grade phosphoric acid, 54% P_2O_5 (70% phosphoric acid).^[30]

Byproducts of this concentration process are SiF_4 and HF. When concentrating from 30% to 55% P_2O_5 , 50-60% of the hydrogen fluoride evaporates. Emissions to the atmosphere are prevented by reacting the gaseous HF with a byproduct SiF_4 to form H_2SiF_6 , which is a liquid at room temperature (boiling point 108.5°C). Roughly, 90-95% of the HF is captured this way, which complies with the fluorine emission limits.

The byproduct phosphogypsum is produced in large quantities, and leads to enormous amounts of waste. For the production of 1 tonne of phosphoric acid roughly 5 tonnes of phosphogypsum are produced, resulting in an estimated production of 100-280 Mt per year.^[34] In theory, phosphogypsum could be a source of gypsum for construction works but the presence of trace metals, such as thorium, radium, cadmium and uranium, prevent extensive use and turn it into a material classified as hazardous.^[33] About 85% of the phosphogypsum is disposed without any treatment, which poses storage problems and provokes environmental concerns.^[34] The gypsum produced via the HH/DH and DH/HH process can be used in the cement or plaster industry. Depending on the digestion process, the gypsum formed can be a dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), a hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) or a mixture of the two. Anhydrite (anhydrous CaSO_4) can be formed, but the required conditions ($120\text{-}130^\circ\text{C}$) cause excessive corrosion problems, which makes it an insufficient method for industrial processes.

1.3.2 Purification Process of Wet Phosphoric Acid

Many of the impurities in the phosphate rock are still present in the phosphoric acid product. The amount of impurities in the phosphoric acid and phosphogypsum is not only dependent on the type of digestion process, but also on the origin of the phosphate rock. The phosphoric acid produced with phosphate rock from Russia contains 5-10 mg/L uranium compared to 120-160 mg/L in the phosphoric acid from Morocco. The amount of ^{226}Ra is even negligible in the phosphoric acid produced with the PR from Russia, compared to 30-60 Bq/L from Morocco (see Table 6). Most of the uranium is taken up by the phosphoric acid, while most of the ^{226}Ra ends up in the phosphogypsum. Roughly, 87-92% of the uranium ends up in the phosphoric acid and 8-13% in the phosphogypsum. In the case of ^{226}Ra it is the other way around, 5-10% ends up in the phosphoric acid and 90-95% in the phosphogypsum.

Table 6. Uranium and radium concentrations in phosphoric acid and phosphogypsum ^[19]

Origin	Phosphoric acid		Phosphogypsum	
Phosphate Rock	Uranium mg/L	^{226}Ra Bq/L	Uranium mg/L	^{226}Ra Bq/L
Igneous Rock				
Russia (Kola)	5-10	-	-	60-100
Sedimentary Rock				
Florida	120-140	40-70	10-20	500-1200
Jordan	80-100	30-50	5-10	500-1000
Morocco	120-160	30-60	10-15	600-1300
Israel	90-110	40-50	10-20	600-1200

Tunisia	40-60	40	5-8	300-400
Togo	100-110	60	10	700-1100

Impurities in phosphoric acid can be partially or completely removed by extraction and precipitation. Typically, the wet phosphoric acid contains impurities such as sulphites, fluorine, silicon and calcium. The full list and general quantities can be found in Table 5.^[30] Purification is a major challenge and can be performed via precipitation, ion exchange, adsorption, membrane technologies, nano-filtration, reverse osmosis and extraction processes.^[35] The two most common purification processes for phosphoric acid, extraction and precipitation, will be discussed below in more detail.

Table 5. Wet phosphoric acid composition in wt% ^[30]

P ₂ O ₅	30.0
F	2.17
SO ₃	2.1
Ca	0.45
Si	0.41
Mg	0.13
Fe	0.08
Al	0.04
Cr	0.022
Zn	0.019
V	0.013
Ni	0.0034
Cu	0.0027
Mn	0.0009
As	0.0007
Pb	0.00002

Extraction

Different extraction processes have been designed to remove various impurities, ranging from the removal of specific compounds to almost complete purification. Extractive purification processes of wet phosphoric acid contain the following steps: purification of the crude wet phosphoric acid, phosphoric acid extraction, extract wash, phosphoric acid recovery and, if necessary for the final product, a post treatment. Firstly, in a pre-purification process, arsenic, sulfate and organic components are removed by precipitation or adsorption from the crude wet phosphoric acid (40-50% P₂O₅). The pre-purified phosphoric acid is then dissolved in an organic solvent (such as methyl isoamyl ketone and diisopropyl ether) through countercurrent distribution. While most impurities remain in the aqueous phase, the phosphoric acid ends up in the organic phase. Additionally sulfuric acid (H₂SO₄) can be used to react with cationic

impurities to form sulfates, which remain in the aqueous phase when a yield of 95-98% of phosphoric acid is preferred. After treatment, the purity of phosphoric acid is comparable with the food-grade phosphoric acid produced via the thermal process.

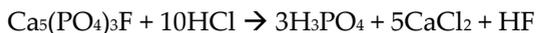
Precipitation

Separating arsenic and to an increasing frequency cadmium (decadmiation) from wet phosphoric acid is crucial when it is used in the fertilizer industry. Arsenic can be removed by addition of Na_2S to the acid and filtration of the precipitated arsenic sulfide. Cadmium can be removed after adding complexing agents, such as dialkyl dithiophosphoric acid ester.^[36] If necessary, cationic impurities (e.g. Fe, Al, Mg, Ca) can be removed by neutralizing the acid with caustic soda, sodium hydroxide. This will however change the product in a phosphate salt solution and metal hydroxides instead of an acid, thereby limiting its use to only detergent phosphates.

Acidulation with hydrogen chloride or nitric acid

The other two types of acidulation processes of phosphate rock besides sulfuric acid are with the use of hydrochloric acid and nitric acid. The nitrophosphate process is an alternative route to form phosphoric acid with the significant advantage of the formation of the marketable calcium nitrate instead of phosphogypsum. But, due to the price difference between sulfuric acid and nitric acid, only 10% of all the fertilizers are produced via the wet process with nitric acid.^[30]

Another process for the treatment of phosphate rock without the production of phosphogypsum involves HCl, the solvent extraction process (SX process), which produces calcium chloride and hydrogen fluoride as byproducts via the following chemical reaction:



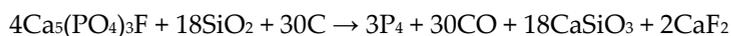
The phosphoric acid is extracted and concentrated via distillation to obtain food-grade phosphoric acid. The advantage of the HCl method is the high concentration and low impurity of the product (>50 wt% P₂O₅), but the disadvantage is the relatively high cost. The wet process (with H₂SO₄) and the SX process can be combined via mixing both slurries and extracting the phosphoric acid with an aliphatic alcohol afterwards.

1.3.3 White Phosphorus

Elemental phosphorus has 10 allotropic forms, but only two of them are industrially important, namely white (P₄) and red phosphorus (in an amorphous network). Examples of other allotropic forms are diphosphorus (P₂), violet phosphorus (in a tube structure) and black phosphorus (a puckered sheet structure).^[10] White phosphorus is extremely reactive with air and is therefore stored in heated vessels (so P₄ remains a liquid) and always covered with water and on top of the water nitrogen to exclude any contact with air. Red phosphorus is less reactive and stable in air and is, for example, used as the striking surface of a matchbook. White phosphorus, P₄, accounts for 99% of the global elemental phosphorus demand with 850,000 tonnes per year and is required for the production of important organophosphorus derivatives such as PH₃, PCl₃, P₄S₁₀

P_4S_3 and P_2O_5 .^[37] White phosphorus is the starting material of almost all high-end industrial and food products containing phosphorus, such as flame-retardants and acidification of soft drinks.

The industrial manufacturing of white phosphorus is primarily done via the Wöhler process, in which phosphate rock is mixed with coke and silica, and heated by electrodes. White phosphorus is commonly produced from phosphate rock (apatite) and to a lesser extent from guano, manure, and recycled phosphates. Overall, the Wöhler process proceeds according to the following equation:

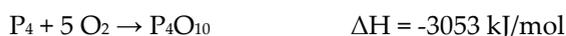


The first step in this process is to reduce the size of the rock in order to avoid blocking of the furnaces.^[38] Carbon monoxide provides 85-90% of the heat needed for roasting the pellets after the sintering process and the dust is removed through scrubbing and recycled into the process. The pellets are mixed with cokes, which act as a reducing agent, and SiO_2 pebbles, a liquid slag, which has its use in road construction and other applications. This mixture is heated to 1500 °C in an electric resistance furnace. At these temperatures, silica is a strong acid that is able to release phosphate from fluorapatite, and form molten calcium silicate that binds fluoride, yielding CaF_2 . In addition, some of the silica also combines with fluoride to form SiF_4 gas. In the furnace, the phosphates are reduced to diphosphorus. The furnace gas, containing the P_2 , is cleaned with electrostatic precipitators to remove dust. To obtain P_4 , two condensation steps, above and below the boiling point of phosphorus (280 °C), are performed to condense the P_2 vapors to solid P_4 .

The production of P₄ is energy intensive with a consumption of 12.5-14 MWh per metric tonne of white phosphorus. Around 55% of the energy is lost as heat in the slag, ferrophosphorus, furnace gasses and radiation, and electrical and cooling losses.^[39] The furnace CO gases, after P₂ removal, containing less than 0.1% of the phosphorus product, are used as fuel for power generation that is needed for the sintering process. Applications for the furnace slag are limited, since it can contain radionuclides out of the phosphate rock. The water used in the phosphorus condenser and for storage contains a substantial amount of phosphates, up to 1 g/L that can be recovered via filtration. P₄ gas (P₂ as a precursor in between) is formed along with CO, some dust and calcium oxide. The P₄ gas leaves the furnace and is subsequently condensed.

Iron impurities in the phosphate rock are reduced in the furnace and form a separate slag: ferrophosphorus. Ferrophosphorus contains about 75% iron and 25% phosphorus with trace amounts of other metals and can be used as an additive in steel manufacturing. The radioactivity of the ferrophosphorus is constantly measured and depending on the level of radioactivity, it can be decided if it has to be stored (temporarily or indefinitely depending on the radioactivity) or sold.

The oxidation of P₄ followed by hydrolysis to yield P₂O₅, used for the production of thermal phosphoric acid, is the most prominent application of P₄ with 70% of the production volume. This production of thermal phosphoric acid from P₄ contains of the two steps:



The phosphoric acid that is obtained is very pure due to the use of elemental phosphorus as a starting material. Its H_3PO_3 content is no more than 0.1% and it barely contains traces of impurities. Only arsenic (5-30 ppm) subsequently needs to be removed via the precipitation of arsenic sulfide by the addition of hydrogen sulfide and filtration. This is necessary, since arsenic replaces phosphorus in the phosphorus lattice resulting in an almost impossible separation on an industrial scale.

The industrial production of white phosphorus in Europe disappeared in 2012 with the bankruptcy of Thermphos B.V. The current P_4 producers worldwide are located in the U.S., China, Kazakhstan and Vietnam (Table 7). The producer with the biggest capacity is located in China, with a yearly capacity of 1,900 kt P_4 . All the P_4 produced in The United States is used for domestic consumption, while just 40% of the Chinese production is used for domestic use. China also protects their internal demand with an export tariff of 20% on white phosphorus.^[40]

Table 7. Overview of the current producers of white phosphorus and their characteristics ^[40]

		USA	China	Kazakhstan	Vietnam
Capacity in kt P_4		80	1900	120	45
Production in kt P_4		80	750-900	80-120	38
P	PR-Supply	Self-Supply			
	Labour Cost (monthly average in USD)	High (70-80)	Low (650-750)	Medium (1000-1100)	Very low (200-300)
Utilities	Coal (USD/tonne)	High (70-80)	High (105-115)	Low (60-70)	Very low (25-35)
	Electricity (cents/kWh)	Medium (6-7)	Low (4-5)	Low (4-5)	Medium (6-7)

	Transportation	Convenient	Inconvenient	Inconvenient	Convenient
Domestic consumption in kt P₄		80	750	60	k.A.
Export Tariff		-	20%	-	

Currently, white phosphorus is exclusively produced out of phosphate rock, but several companies investigated the process to produce white phosphorus out of waste products too. Thermphos had developed a method to produce P₄ out of sewage sludge ashes, but this never went into practice. In 2014, a new technology called RecoPhos has been developed to produce P₄ from sewage sludge ashes. This technology was acquired in 2016 by ICL, Israel Chemicals Ltd., a multinational specialized in chemicals for agriculture, food and engineered materials purposes.

1.4 Industrial Applications of Phosphoric Acid and White Phosphorus

Most phosphoric acid is used for fertilizers, but also in a broad range of industrial and food products.^[31] Different concentrations and impurity levels of phosphoric acid are required for diverse purposes, resulting in various production methods. For fertilizers, merchant-grade phosphoric acid, with a concentration of 55% P_2O_5 , 74% H_3PO_4 (phosphoric acid) is the standard. As for food purposes, food grade phosphoric acid with an 85% concentration of H_3PO_4 is commonly used. The 85% food-grade phosphoric acid is a viscous and corrosive liquid and must therefore be stored in stainless-steel containers with a resistant inner lining. The different forms of commercial phosphoric acid and the concentrations and impurity levels in ppm are listed in Table 8.

The main application of wet phosphoric acid is in fertilizers. With this process, the main fertilizers used in agriculture are diammonium phosphate (DAP), monoammonium phosphate (MAP), single superphosphate (SSP) and triple superphosphate (TSP). DAP and MAP are made via the wet process and SSP via treatment of phosphate rock with sulfuric acid and TSP with phosphoric acid (see Fig. 4). To produce MAP and DAP, an ammonium source is added to the wet phosphoric acid and a potassium source when NPK-fertilizers are the desired final product. The nutrient ratio of the four fertilizers can be found in Table 9. The nutrient grade ratio of the fertilizers differs among the four fertilizers and it depends on the demand of the crop and soil type which of these fertilizers suits best.

Table 8. Commercial phosphoric acid is sold in different forms [39]

Acid Group	Concentration P₂O₅ (%)	Concentration H₃PO₄ (conversion factor 1.381) (%)	Impurity level in ppm
Filter Acid (Dihydrate- Process)	28	39	5.000-25.000
Fertilizer/ Merchant Grade Acid MGA (concentrated)	42-54	74	10.000-50.000
PWA Feed Acid (Green Acid)	54-59	81	5.000-25.000
Raffinate Acid	25-45	62	20.000-50.000
Technical Acid	50-61.6	76	500-5.000
Food Grade Acid	61.6	85	0,5-250
Cola/Pharma Acid	61,6	85	0,5-100
Thermal (from P₄)	61,6	85	
SEMI LCD Acid	61,6	85	0,1-1
Semiconductor Grade Acid	61,6	85	0,01-0,1

Table 9. Common phosphate fertilizers and nutrient grades [6]

Fertilizer	Nutrient grade ratio, N:P:K
Diammonium phosphate (DAP)	18-46-0
Monoammonium phosphate (MAP)	10-50-0
Single superphosphate (SSP)	0-18-0
Triple superphosphate (TSP)	0-46-0

The demand for fertilizers is still emerging due to the rising population, the upcoming biofuel demand and the changing standard of living in developing countries (Fig. 5). The global fertilizer P₂O₅ production steadily increased from

1973 to 2011 with 166% from 25.6 Mt to 42.6 Mt, with a downward trend in the 90s. This trend was mainly a result of the fall of the USSR.

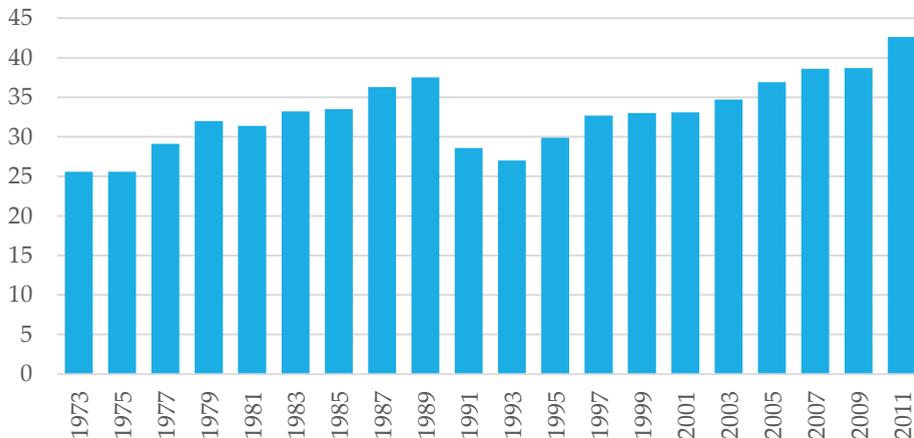


Fig.5 The global fertilizer P₂O₅ production from 1973 to 2011 [41]

Different applications for each of the phosphoric acid types exists, such as an acidifying food additive (i.e. in soft drinks), rust remover for metals, etching agents, and catalysts. An overview of all the applications of phosphoric acid can be found in Fig.6.^[10]

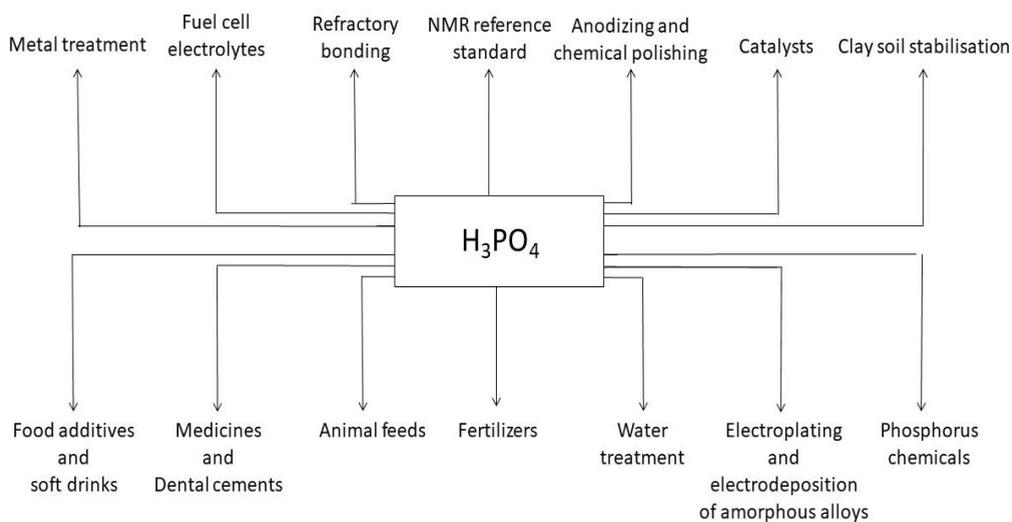


Fig.6 Overview of the use of phosphoric acid

Both (highly purified) merchant grade phosphoric acid and thermal phosphoric acid derived from P_4 can be used. Which one is suitable depends on the cost and level of purity requirements. Recent numbers of industrial phosphate demand do not exist, but in the most recent research in 2015 they assume that around 38% of the industrial phosphate demand is for detergents and cleaners (Fig. 7). Currently there is a ban in several parts of the world for the use of phosphates in detergents to reduce the amount of phosphates ending up in surface waters and lakes, thereby resulting in eutrophication.^[42] This ban has resulted in a decline of the use of phosphates in detergents in the last decade. Besides the application in detergents, around 23% of the phosphoric acid demand is for the production of food additives, 10% in metal treatment, 10% in water treatment, 3% in toothpaste, 2% in special fertilizers, and the other 14% is used for other purposes like medicines and fuel cell electrolytes. For the segments beside detergents, a moderate growth is expected for the coming years.

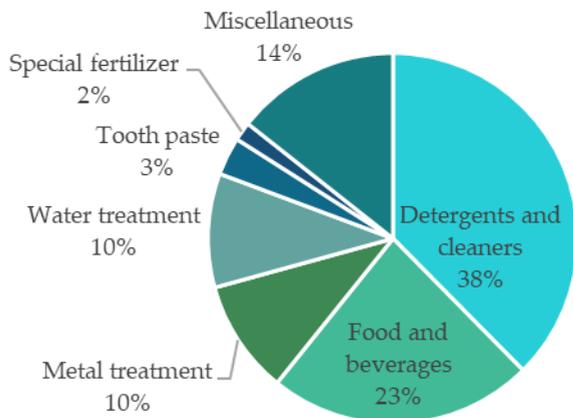


Fig 7. Demand for industrial phosphates in % by application area in 2011 ^[40]

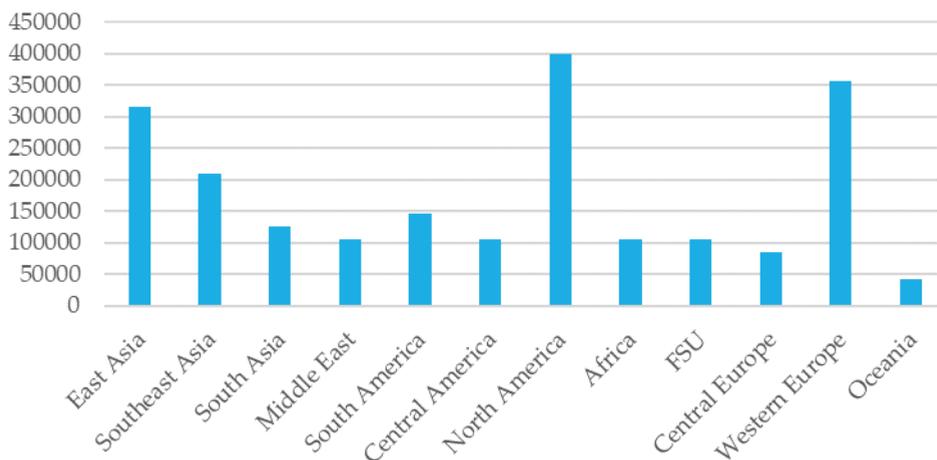
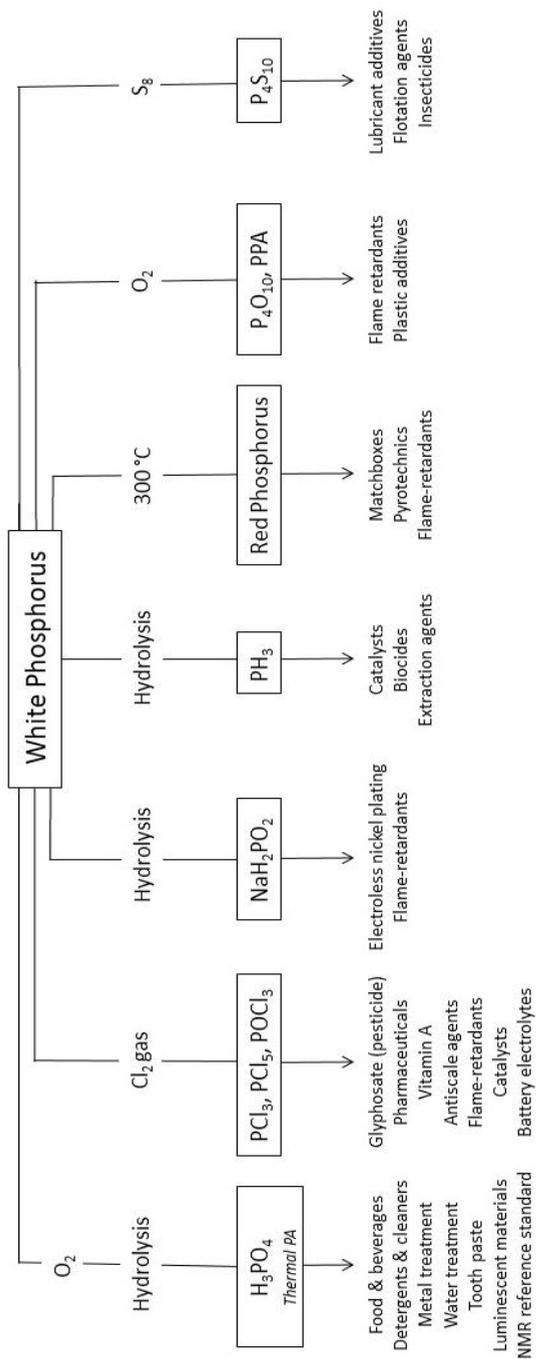


Fig 8. Demand for industrial phosphates in t P₂O₅ in 2011 ^[40]

The highest industrial phosphate demand in 2011 is in North America (19%, 40.000 tonnes), Western Europe (17%, 36.000 tonnes) and East Asia, particularly China (15%, 32.000 tonnes) (see Fig. 8).

Besides phosphoric acid, white phosphorus is a precursor for many inorganic phosphorus compounds (Fig. 9). White phosphorus has to be the starting material, since these cannot be prepared otherwise. White phosphorus has a small direct application as a chemical weapon, but it is mainly a precursor for several organophosphorus compounds. Organophosphorus compounds derived from white phosphorus are PCl_3 , red P, P_xS_y , PH_3 , NaH_2PO_2 and ferro-phosphorus.^[31] The derivative from P_4 with the largest market share is PCl_3 , which for example is used as a derivative glyphosate (a pesticide). Around 1% of the global P-usage is for the production of glyphosate. Examples of other phosphorus containing products manufactured from P_4 are catalysts, battery electrolyte, flame-retardants, vitamin A, plastic additives, doping, matches, antioxidants, water treatment, and reducing agents.^[31]

Fig.9 The production routes and applications of the white phosphorus derivatives.



1.5 Conclusion

The world consumption of phosphate rock in 2016 was 44.5 million tonnes and will increase to 48.9 Mt in 2020. The estimated global phosphate rock reserves contain in total around 68,000 Mt of phosphate rock. This indicates that there is no urgent scarcity in the coming decades. Yet, reserves are not equally spread around the world, with three-quarters located in Morocco and Western Sahara. Moreover, the price for phosphate rock can be volatile and Europe is reliable for 92% on import (see Fig. 3), therefore phosphate rock is added to the critical material list of the European Commission.

The reserves located in Russia, mainly contain igneous ore, and relatively have the lowest levels of radioactivity and hazardous metal contents. Morocco and Western Sahara reserves, mainly sedimentary ore, have on average the highest hazardous content out of the four main phosphate rock producers. Moreover, the amount and type of other mineral structures besides apatite are important to assess the suitability for phosphate production.

Phosphate rock is mainly processed as intermediary products including phosphoric acid and white phosphorus. About 95% of the phosphoric acid is made via the wet-process, which includes acidulation of phosphate rock for creating wet phosphoric acid and byproducts including phosphogypsum and hydrogen fluoride. Five times more phosphogypsum as phosphoric acid is produced during this process. The purity and thus the reusability of phosphogypsum is dependent on the type of digestion process and can be as pure as necessary for reuse in the

plaster industry. However, at the moment reusing phosphogypsum is not yet common practice.

Wet phosphoric acid can be purified via several processes. The most commonly used processes are extraction and precipitation. Via extraction, phosphoric acid comparable to phosphoric acid produced through the thermal process can be obtained. Separation of specific compounds can be done through precipitation. Also, cationic impurities can be removed via precipitation, but the product will then be changed into a phosphate salt which is unfavorable for its use in many industries besides detergents. Production of white phosphorus is primarily done through the Wöhler process. The production of white phosphorus is energy intensive, but amount of impurities is low, which is necessary for certain applications such as in the food and high-tech industry.

1.6 References

- [1] P. J. A. Withers, K.C. Van Dijk, T. S. Neset, T. Nesme, O. Oenema, G.H. Rubaek, O.F. Schoumans, B. Smit, *Ambio*, **2015**, *44* (2), 193–206.
- [2] USGS, ‘Mineral Commodity Summaries of Phosphate Rock 2007’ can be found under https://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2017-phosp.pdf, last retrieved at 28/08/2017
- [3] J. Liebig, *Die Organische Chemie in Ihrer Anwendung Auf Agricultur Und Physiologie / von Justus Liebig*, F. Vieweg, Braunschweig :, **1841**.
- [4] J. T. Sims, A. N. Sharpley, W. M. Stewart, L. L. Hammond, S. J. Van Kauwenbergh, **2005**.
- [5] S. J. Van Kauwenbergh, *World Phosphate Rock Reserves and Resources*, **2010**.
- [6] S.J. Van Kauwenbergh, *Fertilizer Raw Material Resources of Africa*, **2006**.
- [7] V. E. Mckelvey, *Phosphate Deposits*, United States department of the interior, Washington, **1967**.
- [8] K. Bell Carbonatites: Genesis and Evolution. *Unwin Hyman*, London, **1989**.
- [9] H. Diskowski, T. Hofmann, in *Ullmann’s Encycl. Ind. Chem.*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2000**.
- [10] D. Corbridge Phosphorus 2000. Amsterdam, The Netherlands: Elsevier Science B.V., **2000**.
- [11] D. McConnell D. *American Mineral*. **1938**, *54*, 1379-1391.
- [12] S.T. Mehmood, M.M. Chaundhry, M. Tufail, N. Irfan. *Microchemical Journal*. **2009**, *91*, 94-99.
- [13] S. Kratz, F. Godlinski, E. Schnug, in *New Uranium Min. Boom*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2011**, pp. 755–762.
- [14] S.S. Mar, M. Okazaki, *Microchemical Journal*. **2012**. *104*, 17-21.
- [15] E. Schnug, B.G. Lottermoser, *Environ. Sci. Tech.* **2013**. *47*(6), 2433-2434.
- [16] International Agency for Research on Cancer., World Health Organization., *Beryllium, Cadmium, Mercury, and Exposures in the Glass Manufacturing Industry.*, IARC, **1993**.
- [17] WHO, Cadmium, *Environ. Health Criteria*. **1992**. *134*. 1-280.
- [18] A. Davister, *OECD*. **1996**, 21–30.
- [19] T. M. Cioroianu, F. Bunus, D. Filip, G. Filip, *Environmental Considerations on Uranium and Radium from Phosphate Fertilizers*.
- [20] European Commission, *Cadmium in food*. **2017** can be found under https://ec.europa.eu/food/safety/chemical_safety/contaminants/catalogue/cadmium_en, last retrieved at 04/09/2017.
- [21] D. I. T. Fávoro, *J. Radioanal. Nucl. Chem.* **2005**, *264*, 445–448.
- [22] J.P. Pérez Natural radionuclides in the fertilizer industry. *Ph.D. Thesis*, University of Seville, **2005**.
- [23] E. M. El Afifi, M. A. Hilal, M. F. Attallah, S. A. EL-Reefy, *J. Environ. Radioact.* **2009**, *100*, 407–412.
- [24] J. D. Edixhoven, J. Gupta, H. H. G. Savenije, *Earth Syst. Dyn.* **2014**, *5*, 491–507..
- [25] USGS, ‘Mineral Commodity Summaries of Phosphate Rock 2017’ can be found under https://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/phospmcs07.pdf, last retrieved at 28/08/2017
- [26] M. De Ridder, S. De Jong, J. Polchar, S. Lingemann, *Risks and Opportunities in the Global Phosphate Rock Market*, The Hague, **2012**.

- [27] A. J. G. Notholt, R. P. Sheldon, D. F. Davidson, *Phosphate Rock Resour.* **1989**, 2.
- [28] Indexmundi 'Rock Phosphate Monthly Price – US Dollars per Metric Ton.' **2017**, can be found under <http://www.indexmundi.com/commodities/?commodity=rock-phosphate&months=360>, last retrieved at 05/09/2017.
- [29] European commission *Report on critical raw materials for the EU.* **2015**,1819503.
- [30] K. Schrödter, G. Bettermann, T. Staffel, F. Wahl, T. Klein, T. Hofmann, in *Ullmann's Encycl. Ind. Chem.*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2008**.
- [31] O. Gantner, W. Schipper, J.J. Weigand, *Sustainable phosphorus management*, Springer, Berlin, **2014**.
- [32] H. Du, A. Chen, L. Yang, *J. Mater. Sci. Chem. Eng.* **2014**, 02, 7–11.
- [33] R. U. Ayres, J. Holmberg, B. Andersson, *MRS Bull.* **2001**, 26, 477–480.
- [34] H. Tayibi, M. Choura, F.A. López, F.J. Alguacil, A.J. López-Delgado, *Environmental Management.* **2009**, 90(8), 2377–2386.
- [35] A.A. El-Asmy,H.M. Serag, M.A. Mahdy, M.I. Amin, *Sep. Purif. Technol.* **2008**, 61(3), 287– 292.
- [36] H. Von Plessen, G. Schimmel, *Chemie Ing. Tech.* **1987**, 59, 772–778.
- [37] G. Kongshaug, B. A. Brentnall, K. Chaney, J.-H. Gregersen, P. Stokka, B. Persson, N. W. Kolmeijer, A. Conradsen, T. Legard, H. Munk, et al., in *Ullmann's Encycl. Ind. Chem.* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2014**, pp. 1–49.
- [38] W. J. Schipper, A. Klapwijk, B. Potjer, W. H. Rulkens, B. G. Temmink, F. D. G. Kiestra, A. C. M. Lijmbach, *Environ. Technol.* **2001**, 22, 1337–1345.
- [39] R. Gilmour, *Phosphoric Acid: Purification.* CRC Press, **2014**.
- [40] O. Gantner, Ressourcenstrategische Betrachtung der Kritikalität von Phosphor. *Ph.D. Thesis*, Universität Augsburg, **2015**.
- [41] IFA, Phosphate Rock and Phosphoric Acid, **2014**, can be found under http://www.fertilizer.org/En/Statistics/PIT_Excel_Files.aspx, last retrieved at 07/09/2017.
- [42] European Commission, EP supports ban of phosphates in consumer detergents, **2017** can be found under http://europa.eu/rapid/press-release_IP-11-1542_en.htm , last retrieved at 05/09/2017.