

Phosphate industry in the balance of sustainable development and circular economy

K.Gorazda¹, B.Tarko¹, H.Kominko¹, Z.Worek¹, A.K.Nowak¹,

¹Institute of Inorganic Chemistry and Technology, Cracow University of Technology, Cracow, Poland
corresponding author email: gorazda@chemia.pk.edu.pl, 0048 12 628-27-96

Abstract

Characterisation of phosphorus industry and its assessment according to sustainable development rules and circular economy was presented. Non-renewable sources of raw materials, energy consumption and environmental impact was discussed. Examples of recognised solutions divided to groups of strategies were analysed: feedstock flow release (quality), feedstock flow recycling (re-use) and flow replacement (renewable materials) as well as process modification.

Keywords

Sodium tripolyphosphate, sewage sludge ash, poultry litter ash, phosphorus recovery, fertilizers, circular economy, sustainable development, alternative raw materials, phosphorus industry, secondary raw materials

1. Introduction

A rapid increase in human activity which has been taking place since the industrial revolution has resulted in the exploitation of huge amounts of resources and energy in a short time. Mass consumption and an increased production have exerted an impact on ecology and non-renewable resources, and have also become a cause of environmental problems through pollution of the atmosphere, hydrosphere and lithosphere. Apart from the appropriate management, reduction of pollutants at the source of their origin, waste recycling or utilisation of renewable resources, technological innovations constitute one of possibilities of reducing the environmental impact resulting from industrial production.

1.1. Sustainable development and circular economy

Sustainable development concept combines activities in a number of areas, i.e. the ecological, technical, economic, social or political area. The technical area is considered to be the most significant one due to the minimization of environmental destruction through the interference into the essence of the implemented technological process thanks to the achievements of technical sciences [1]. To realise such concept we can use Cleaner Technology - a creative process which through its character decreases emissions and the production of waste, increases the quality of products, maximizes the exploitation of raw materials and energy as well as other components introduced into the process [2]. Cleaner Technologies also constitute a part of Environmental Technologies (ET), whose market is estimated to be worth 478 billion Euros [3]. Cleaner Technologies assume three levels of activity, which may be chosen individually in order to improve the production process: optimization, modification and change of the technological process. In order to better understand the technological process, it is necessary to obtain the data which will permit to determine material and energy balances as well as understand the mechanisms of occurring chemical processes. Therefore, optimization constitutes the first stage in the implementation of cleaner technologies, thus allowing the control and generation of savings in the stream flows of matter, energy and raw materials. The optimization of processes has certain limitations when it comes to the improvement of management, hence the modification of processes that does not interfere with the production and quality of products may be necessary. The basic process remains unchanged, significant modifications are carried out before and, above all, after the main process. These modifications may be realized as recycling, retrieval or regeneration of waste streams, or the utilization of waste as recyclable raw materials. Investments may be considerable, depending on the size of an object but operating costs are balanced by the savings on raw materials, raw materials turnover and waste revaluation. Moreover, the inner recirculation of waste streams also contributes towards lower charges and the closure of

balances of the circulation of particular substances. A change of the existing process may be a result of two previous methods. This is a solution which conditions the best effects and takes advantage of basic research as well as the one from the field of technology. At the same time it requires considerable accessibility of workforce, techniques, finances, and it must be accompanied by an increase in the profitability of a given company [4,5].

Cleaner Technologies as a tool in the realization of sustainable development objectives, find support and justification in all European Union documents referring to the development of industry at the Union, national, sector, regional or local level. Moreover, it has been highlighted in the document „Sustainable growth – for a resource efficient, greener and more competitive economy” that sustainable development means making use of European position to devise new environmentally-friendly technologies and production methods in order to build a more competitive low-emission economy which will take advantage of resources in a rational and economical manner. These activities are also encompassed in the assumptions regarding circular economy which is supposed to boost global competitiveness, foster sustainable economic growth and generate new jobs in Europe [6].

The circular economy assumes that natural resources are exploited in a more sustainable way, and its objective is to maximize added value at every stage of products lifecycle. In accordance with the document accepted by the European Commission on 2 December 2015, re-use and industrial symbiosis will be promoted, i.e. by-products or waste from one industry sector should become a resource for another industry. Recycling and processing of waste as well as used products is supposed to generate energy savings and at the same time decrease the exploitation of natural resources and the amount of waste. Similarly, „A zero waste programme for Europe” emphasizes the fact that durable economic growth is possible through the implementation of assumptions of a more closed-loop economy [7,8].

The principles of sustainable development and circular economy are particularly important for the phosphorus industry that faces significant feedstock problems, excessive energy-consumption as well as negative environmental impact.

2. Characteristics of the phosphorus industry and identification of the most important problems

Phosphorus and its derivatives find application in a number of industrial sectors, such as the production of fertilizers, phosphoric acid, chemical intermediates, batteries, flame retardants, water treatment and the production of detergents. The most commonly applied phosphorus derivatives include phosphate fertilizers, fodder phosphates, foodstuff and industrial phosphates as well as phosphoric acid.

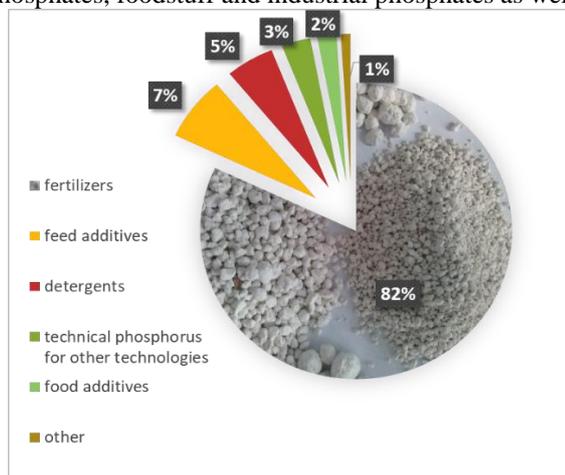


Fig.1. Phosphate rock usage in industrial sectors [9].

The phosphorus industry around the world comprises leading companies: the OCP Group, the Prayon Group, Innophos Holdings Inc., PhosAgro, Yuntianhua Group Co. Ltd, EuroChem, CF Industries Holdings Inc, United Phosphorus Limited, Jordan Phosphate Mines Company PLC, Chemische Fabrik Budenheim KG, Solvay-Rhodia, Ojsc Phosagro AG and Yara International. Its value in 2019 is estimated at 73,217.55 million USD. The main growth stimulus will be increasing agricultural demand aiming at meeting the needs for food of the rising population as well as increasing demand for water treatment [10].

According to the report [9] the USA, China and Vietnam are considered to be the biggest producers of phosphorus and its derivatives. At present Asia and the Pacific Countries dominate the

phosphorus market, and the demand for its derivatives is also perceived as very high because it is not yet regulated by stringent rules regarding the environmental protection. India and China demonstrate the highest demand for phosphorus compounds in this region. China alone is the largest producer as well as consumer of phosphorus compounds in the world. The USA is the second largest region where the demand for phosphorus compounds is high, and these are principally used by the chemical industry, for flame retardants production as well as by chemicals producers. This market is estimated to grow by 3.66%, and its value in 2019 is forecast to reach the level of 41,382.56 million USD. The main factor on the market is a great consumption potential, growing production capacities, competitive production costs and a high pace of the economic growth.

The report [9] estimates the size of the European phosphorus market at 8,244.29 million USD in 2019, with the assumption of 2.59% growth of in relation to the year 2014. Europe is the second largest market of phosphoric acid, with a 24% share in the total income from phosphoric acid in 2013. Kazphosphate LLC is one of the largest global exporters of phosphorus compounds, and its exports are most of all headed for Europe, where Great Britain and Germany import its major part. The European market participants are companies such as: Solvay-Rhodia (France), Chemische Fabrik Budenheim KG (Germany), Lanxess AG (Germany), EuroChem (Russia), PhosAgro (Russia), Acron Group (Russia), Italmatch Chemicals (Italy) and the Prayon Group (Belgium)[10].

Analyzing the phosphorus industry from the viewpoint of the assumptions of sustainable development, special attention should be paid to the application of non-renewable feedstock in the production, a negative environmental impact of generated solid and liquid waste as well as energy-consumption of the applied processes.

2.1. Non-renewable resources as an input material

Phosphorus raw materials belong to a group of non-renewable resources, and until recently it was estimated that the demand for phosphorus ore would be higher than the amount of the extracted resource already in the years 2030-2033 [11]. The successive reports signalled a correction that the real amount of phosphorus deposits reserves would permit their continuous exploitation for another 300-400 years, on condition that the exploitation includes ores with a lower concentration of the main component, with a higher level of impurities, and in places requiring the use of more advanced technologies [12]. As a result of this situation, there will be a gradual increase in the price of the feedstock, which stood at USD 115 per ton in the first quarter of 2016 [13]. At present most of the resource is extracted in China (100 million Mg) and Morocco (30 million Mg), however this is Morocco, which is in the possession of as much as 75% of the global reserves of phosphorus resources. Analyzing the so-called average remaining lifespan of resources (Fig.2), which is expressed as a ratio of reserves to current production, further destabilization should be expected, as this ratio amounts to only 37 years for China, whereas in the case of Morocco and Western Sahara it is as much as 1667 years [14-16].

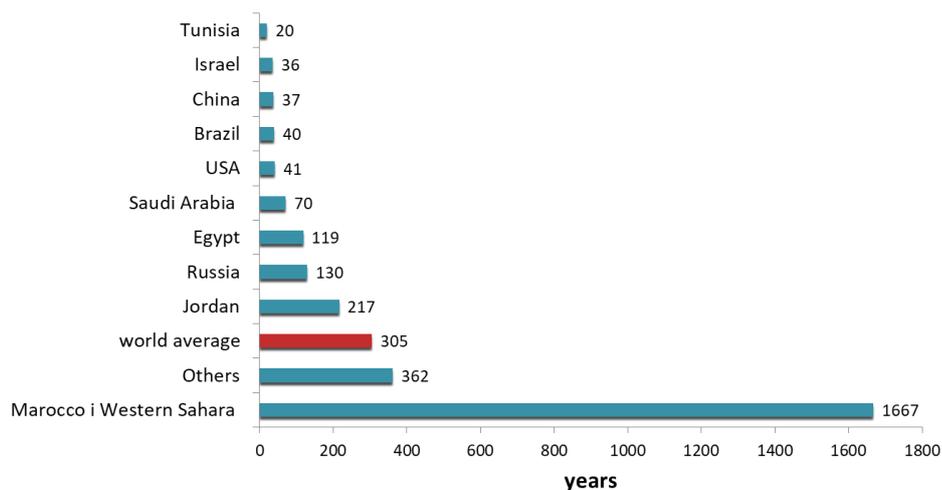


Fig.2. Static resource lifetime [16]

Even negligible changes referring to the export policy on the feedstock market exert a considerable influence on the prices of this resource, which is confirmed by the example of China. When the government imposed a 20% tax on the exported ore with the aim of slowing down the exploitation of national reserves, the price of the resource on the global market increased eightfold. The prices stabilized in the successive years due to the negotiations conducted by the global fertilizer industry and ore suppliers [17,18]. Europe is strongly dependent on imported raw materials (6.4 mln Mg in 2014) from Morocco, Russia, Syria and Algeria (Fig.3.), and the prices dictated by the world's leading mining industry [19,12,20]. Non-renewable raw materials imported by EU-27 countries was used for production of 10.5 mln Mg of N, 2.4 mln Mg of P₂O₅, and 2.7 mln Mg of K₂O in 2012 [21].

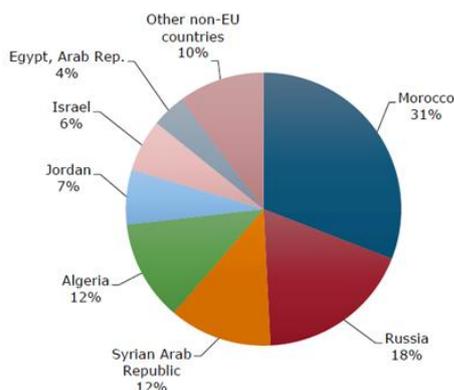


Fig.3. Origin of raw materials imported by EU-27 countries [22,19].

These activities emphasize the necessity for securing the resources in Europe, which possess limited access to own resources. This need may be satisfied through the introduction of alternative phosphorus feedstock originating from wastewater stream and solid waste [22-24]. The search for alternatives for phosphorus raw materials is justified not only because of the principle of sustainable development or circular economy, but mostly for safety reasons due to rapidly changing geopolitical situation in the world. Also, the analysis of the phosphorus flows shows that the largest losses of this element brings the waste streams. The development of methods for the recovery of phosphorus from waste is therefore a key measure aimed at improving the balance of phosphorus, both globally and locally [25-29].

2.2. Energy consumption

Agriculture spent near 2% of total energy consumed in 2011-13 with highest share in Turkey, Poland, Denmark and the Netherlands. In Japan, Luxembourg, Switzerland and the UK this consumption is lower than 1% [30]. 1.2% of the world's energy is used by inorganic fertilizers sector [21].

In the phosphate production plants energy is used for raw materials preparation section (milling drying, sizing, compression), a reaction section (neutralization, evaporation, calcining section), a drying section and a grinding and sieving section. For products, especially those like sodium tripolyphosphate (STPP), high-temperature around 400-550°C is applied. Fertilizers are also indirect energy consumers, especially for transport and application (Fig. 4) [30].

Comparing nitrogen, potassium and phosphorus fertilisers, energy consumption is concentrated in the ammonia production. Ammonia plants uses 28-48 GJ/Mg NH₃ while nitric acid production 10kWh/ Mg of 100% HNO₃. It was estimated that – on average production of 1 kg NPK (15-15-15) 9.81 MJ of energy is required where 90% associates N fertilizers production. In feed phosphates 547 – 1145 kWh per Mg of dicalcium phosphate 18 % is used in hydrochloric acid process route, while 37 – 348 kWh /Mg DCP when phosphoric acid rout is applied. [21].

Sodium tripolyphosphate plants uses energy for spray drying (4.65 GJ/Mg of product), calcining (0.38 GJ/Mg of product) and charge preheating 0.53 GJ/Mg of product) [31-33].

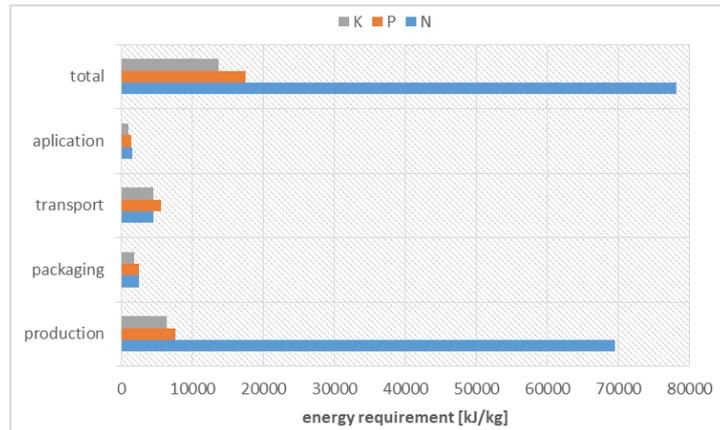


Fig.4. Energy required from NPK nutrients production [34].

2.3. Environmental emissions

The environmental impact of a fertilizer plant depends on nature of the plant, the processes and raw materials or feedstocks, location with surroundings as well as regulations to which it must conform. In fertilisers production plants there are several environmental emissions: gaseous emissions (fluorides, NO_x, N₂O, NH₃, CO₂), dust, solid waste (phosphogypsum, neutralization pulps), wastewaters rich in nutrients. 2.7 Mg of CO₂ per 1 Mg of nitrogen is produced when natural gas is used as the feedstock to ammonia production. Annual share of fertilisers industry in CO₂ release is estimated on 0.1-0.2% of global emission. Nevertheless, the projected growth of fertilizer use makes more necessary keeping CO₂ emissions as low as possible as well as including CO₂ capture by fertilized plants in the future assesment [35-37].

N₂O emission from nitric acid, ammonium nitrate and nitrophosphate fertilizers production varies from 1-10 kg N₂O per 1 Mg of 100% nitric acid. N₂O released from nitric acid pfacilities was 0.23 CO₂eq/Mg of nitric acid in 2013. Fertilizer production is responsible for about 6% of anthropogenic N₂O emissions. N₂O accounts for 7.5% of the calculated anthropogenic global warming effect. Consequently, fertilizer production is responsible for less than 0.5% of this effect. It needs to be pointed out that 87% decrease in N₂O emissions was noted during 11 years (17% per year) [38-42].

Nitrogen oxides (NO_x) are also emitted from ammonia and nitric acid facilities. It is about 1-2 kg NO_x per Mg of N for ammonia plants and 6-9 kg N per Mg of converted nitrogen in case of nitric acid [36,43].

About 4-5 Mg of phosphogypsum are produced for each Mg of P₂O₅ converted into phosphoric acid. Phosphogypsum mainly consists of different form of calcium sulphate (gypsum, hemihydrate or anhydrite), undissolved phosphate rock as well as arsenic, nickel, cadmium, lead, rare earth element, radium and aluminium. A crucial production problem of the sodium tripolyphosphate (STPP) technology constitutes phosphorus loss in waste stream of post-neutralization sludge accounted for 11% of P introduced to the neutralization [40-43].

3. Potential solutions

3.1. Feedstock flow release in technological processes

Environmental technologies, which include cleaner innovations, introduce a constant improvement on processes, products and services through the protection of raw materials. Four groups of strategies regarding raw materials were defined: the limitation of feedstock flow (decreased exploitation), feedstock flow release (quality, longer exploitation), feedstock flow recycling (re-use) and flow replacement (renewable materials)[3].

Both thermal and wet-process phosphoric acid is used for the production of sodium tripolyphosphate. In general economic and commercial considerations matter as to a choice of phosphoric acid. Thermal phosphoric acid used for the STPP production allows to obtain an ultra-high purity product. In current technologies the thermal acid is used only in the STPP production for consumption purposes. A cheaper and available raw material is wet-process phosphoric acid (WPA). However, due to impurities it contains the acid cannot be used without previous purification, hence in this case the production process is more complicated and material-consuming.

The methods for phosphoric acid purification compared in literature are the methods relying only on decreasing impurities concentrations to a level which is acceptable in a particular production method (table 1).

Table 1. Methods for phosphoric acid purification.

Purification method	Description	Industrial use	References
Precipitation	making use of precipitation of impurities in a form of compounds which are sparingly soluble in phosphoric acid	TVA, FMC, Prayon,	[44-47,18]
Extraction	with the use of organic solvents	United States Steel Corporation, Azotes et Produits Chimiques, Prayon, FMC, TVA, ALBRIGHT & WILSON, Chemische Fabrik Budenheim, IMI, Monsanto, Pennzoil, Luwa	[48-61,18]
Phosphoric acid crystallization	in a form of urea phosphate, melanine orthophosphate or freeze crystallisation	Produits Chimique Mazal SA, TVA	[62-65,18]
Sorption	with the use of ion exchange, dialyses or activated carbon, applied mainly as supplementary techniques for purification	Chemische Fabrik Budenheim, R.A.Oetker, Kemira	[66-75,18]

The methods for phosphoric acid purification can be applied as pre-treatment methods like: desulfation (<0.5%SO₄), crude defluorination (0.15%–0.5% F), crude dearsenication by sulphiding (<5 ppm As, <1 ppm Cd), organic reduction (100-250 ppm TOC), or solvent extraction (most impurities reduced to <1 ppm for food grade acid). Post-treatment methods can also be applied: dearsenication (<3 ppm As), decolorization (TOC <10 ppm, color to waterwhite <5 APHA/Hazen/Pt–Co colour scale), defluorination (<10 ppm F), freeze crystallization (most impurities <50 ppb) or ultrafiltration[18].

In case of sodium tripolyphosphate an issue has arisen then to what level, justified technologically and economically, wet-process phosphoric acid should be purified so that its impurities do not influence phase composition and a quality of the obtained product.

Concentrated wet-process phosphoric acid contains such impurities as sulphates (2-2.5% SO₄²⁻), fluorides (>0.2% F) or silicates, as well as Al³⁺, Fe³⁺, Ca²⁺, Mg²⁺ cations present in the amounts of 0.1-0.5%, respectively. It was confirmed that these impurities influence the course of the condensation process to sodium tripolyphosphate, especially the phase composition of the obtained pyro- and polyphosphates. It indicates that it is possible to potentially employ the impurities as crystallization nuclei, which consequently leads to enhancing the parameters for sodium tripolyphosphate production[76-78].

In the work [79] it was shown that the presence of Fe³⁺ in phosphoric acid is conducive to the formation of Phase I, which, in negligible amount, occurs already at a temperature of 400°C, i.e. by a 100°C lower than in a material free from impurities. The iron impact occurs within the range of calcination temperatures of 400-450°C at a concentration greater than 0.5%, while during calcining at temperatures of 500-550°C its impact disappears. Both in the presence of iron compounds and without them the final calcination product at a temperature of 550°C is STPP Phase I (more than 80%), which is accompanied by a small addition of sodium pyrophosphate (Na₄P₂O₇). The presence of Al³⁺ in phosphoric acid influences calcination products quite similarly to iron ions, yet at a higher concentration (1% Al by weight) an additional phase, i.e. Na₃PO₄, emerges in a final product (calcined at 550°C). The presence of both elements at once works synergistically, increasing the share of Phase I at lower calcination temperatures. In this case Phase II disappears almost completely at a temperature of 450°C. Unlike Fe³⁺ and Al³⁺, the presence of sulphates inhibits the transition of Phase II to Phase I, which was shown in the figure 6 [80]. This impact disappears at a calcination temperature of 550°C. The above impurities must be ingrained in the crystal structure of a final product or be present in an amorphous form. The principles of STPP production process provide for the use of concentrated extraction phosphoric acid containing 54% P₂O₅, 2-2.5% SO₄²⁻ and <0.2% F.

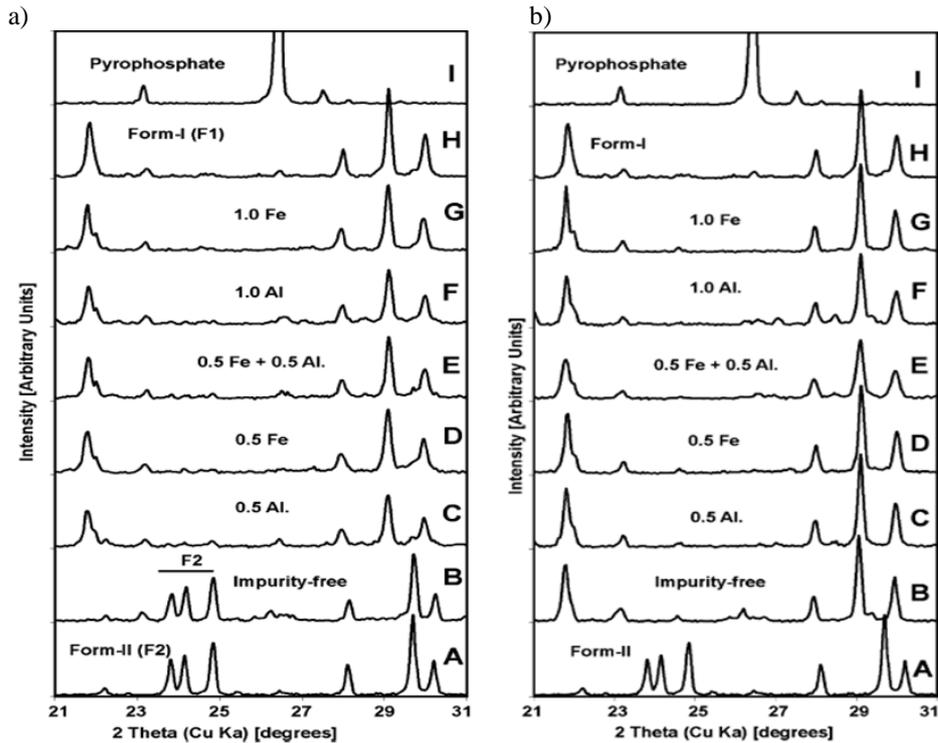


Fig. 5. XRD analysis of STPP products (B-G) in temperature 450°C (a) and 500°C (b) in comparison with standards (A, H, I) [79].

As a result of the conducted research it was established that making use of wet-process phosphoric acid impurities, i.e. Fe^{3+} and Al^{3+} , leads to lowering the temperature parameters of polycondensation and thus decreases the energy-consumption of production processes. Non-purified WPA may be successfully used for the production of a low-temperature form of STPP (Phase II) at a temperature of 400°C, while for the production of a high-temperature Phase I it is necessary to purify the acid of SO_4^{2-} ions to the level of 0.1% by weight. This level also ensures lowering the polycondensation temperature to 400-450°C (in relation to the applied 550°C) as it influences the reduction of heat consumption in a rotary kiln.

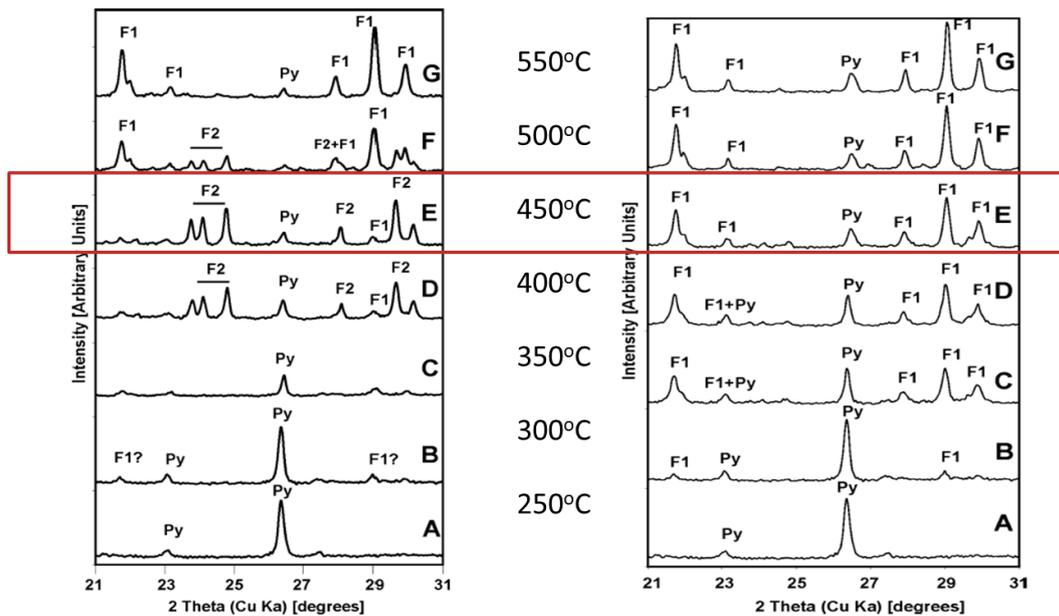


Fig.6. XRD analysis of STPP products in temperature range 250-550°C (a) for not purified WPPA (a) and purified WPPA to 0.1% SO_4^{2-} [80]

3.2. Feedstock flow replacement in technological processes

The analysis of the phosphorus flows shows that the largest losses of this element brings the waste streams. The development of methods for the recovery of phosphorus from waste is therefore a key measure aimed at improving the balance of phosphorus, both globally and locally [81].

An alternative for non-renewable raw materials used for phosphoric acid production by conventional methods may be the use of industrial waste.

Ash from the incineration of meat and bone meal (MBM) and bone pulp constitutes a great alternative for phosphorus feedstock due to a high content of phosphorus compounds exceeding the content of the element in currently exploited deposits. Highly important is also negligible amounts of heavy metals introduced into the reaction environment together with this waste. Ash after the incineration of meat and bone waste may be successfully used for the production of wet-process phosphoric acid of foodstuff quality, free from fluorine compounds and heavy metals [82].

Bone pulp, calcined in two stages, was used for the production of phosphoric acid by wet extraction method. Clear orthophosphoric acid of 62.7% H_3PO_4 concentration was obtained. The comparison of raw acid obtained from bone pulp ash with a food-grade commercial acid points to a lower concentration of phosphorus compounds by 13%. Whereas the application of pure alternative feedstock - bone pulp ash-results in a considerably lower content of Fe, Pb, Cd, Al, Cr and Zn in the produced acid. Sodium tripolyphosphate (STPP) was then prepared with the use of the method of single-stage neutralization of the produced phosphoric acid with soda until the molar ratio $Na/P=5/3$ was achieved. STPP recirculation was used in order to obtain the appropriate loose consistency of a mixture dosed to the kiln and the addition of ammonium nitrate in order to obtain the required colour of calcination products. On the basis of the conducted research it was confirmed that STPP can be produced based on alternative phosphorus raw materials by single-stage method. The most favourable production parameters, i.e. the amount of ammonium nitrate (0.17g/g of acid), the amount of recycled STPP (1.7g/g of acid) and calcination temperature (500°C), were determined. Product quality parameters were determined, the product being powdery (P) first-rate quality, with a high content of high-temperature Phase I; as far as impurities were concerned, the product satisfies the quality of a purified type. With regard to bulk density equal to 1.06 kg/dm³ the product is classified as 'heavy'[83].

Taking into account the principles for circular economy which should be the basis for the EU economics, waste from the meat industry, i.e. post-production bones should be directed for the production of phosphoric acid by the wet method and, subsequently, its neutralization with the formation of STPP.

Fulfilling consumption of nutrients like N, P and K (world: 170 mln Mg, EU: 12 mln Mg) recovery from waste streams will only be possible from concentrated renewable sources. Therefore only specific nutrient-rich materials (animal by-product, sewage sludge, nutrient-rich biomass etc.) after thermal treatment or salts precipitated from nutrient-rich streams (solutions after anaerobic digestion, composting, enriched wastewater streams, industrial streams or wastewaters) could play important role for fertilizer production. It was estimated that present potential of phosphorus substitution by renewable concentrated inorganic sources is only 17-38%. [23,84,24,85]

A promising alternative sources of phosphorus are by-products of wastewater treatment like sewage sludge and ashes after its combustion, as well as sewage side-streams. Many European countries develops technology in this area, with an emphasis on local solutions [86-90,25]. Sewage sludge ash seems to be promising alternative as phosphorus source with maximum efficiency of phosphorus recovery between 80-90% [91-93]. During the thermal conversion phosphorus concentration in mineral fraction takes place and its content in ashes is more favourable (7-11% P) and can be compared with poorer natural ore (Fig. 7) [89,94,95].

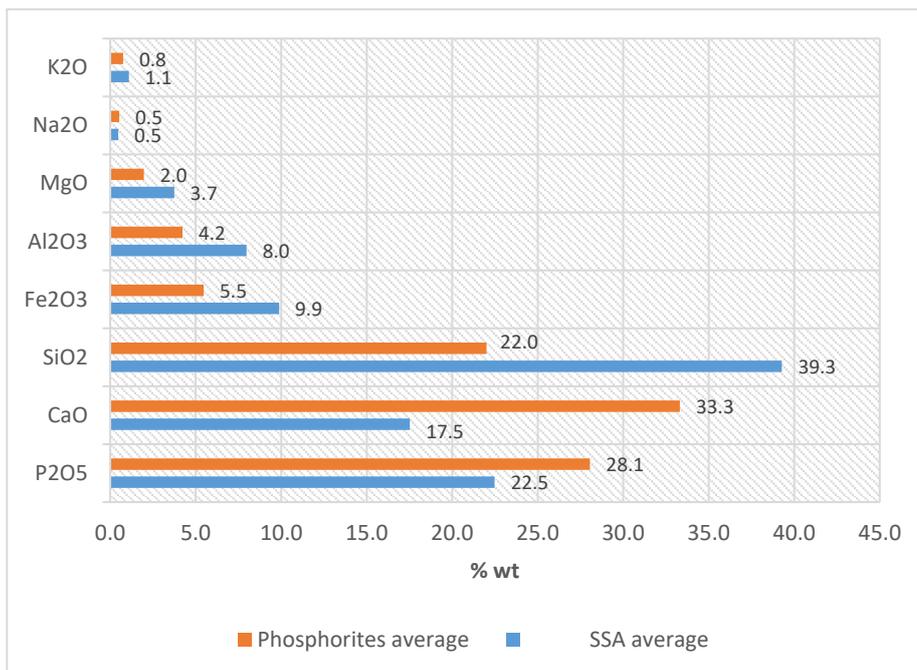


Fig.7. Comparison of main components in European SSA and marketable phosphorites

Numerous technologies have been developed to recover phosphorus from waste water, sewage sludge, sewage sludge ash or other wastes (bones, meat-bone meal) to close broken phosphorus cycle [92,96,97,93,98,99].

Phosphorus wastewater treatment plant as well as from liquid fraction after anaerobic digestion and industrial streams can be precipitated in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), calcium or ammonium phosphates. Technologies like AirPrex, ANPHOS, ELOPHOS EXTRAPHOS, GIFHORN, NASKEO, REPHOS (NuReSys), Perl (OSTARA), PHORWater, PHOSPAQ, PhosphoGREEN (Suez), STRUVIA Stuttgart, NuReSys and PHOSPAQUE are introduced to produce phosphate salts with fertilising value similar to inorganic fertilisers [23,100].

In case of sewage sludge ash (SSA) two ways of dealing with ash from incineration of sewage sludge may be distinguished: wet chemical extraction methods and thermochemical methods.

Thermochemical methods, which include the process of phosphorus production in an electric furnace and ash calcination with a chlorine donor, require a low content of iron in ash. Hence, the solutions suggested in the literature in the case of Polish ashes will have a limited application. In the thermochemical method, which consists in ash calcination with a chlorine donor, heavy metals constituting volatile forms are removed, however iron and aluminium compounds still remain in the solid phase. The process is energy-consuming since ash requires additional heating to a temperature of approximately 1000°C. Moreover, it is necessary to implement a system of treatment of waste gases which contain volatile chlorides of heavy metals. The content of available phosphates in obtained products at the level of 82% means that approximately 18% of phosphorus contained in fertilizer still remain in the form unavailable for plants [101].

The main idea behind extraction methods is carrying out the extraction of ash with the application of solutions of acids, alkalis or their sequence, or water in its supercritical state, as leaching agent [102-105,91,106,94]. The most frequently encountered solution is the extraction of ash with the application of the following acid solutions: H_2SO_4 , HCl, HNO_3 , H_3PO_4 with pH below 2 (table 2). The extraction of ash with the application of hydrochloric acid and sulphuric(VI) acid is connected with generating additional waste in the form of calcium chloride or phosphogypsum (apart from the remains left after ash extraction). Moreover, calcium, which is a secondary component in fertilizers, is lost together with the waste.

Therefore, it was confirmed that the application of leaching ash with nitric(V) acid and phosphoric(V) acid, still remains the most favorable solution for the reason of producing extracts rich in nitrogen and phosphorus compounds, without generating additional waste. Tetra-Phos (Remondis) [107], Leachphos

BSH Umweltservice [108], Ecophos® or SESAL-Phos were scaled up and are available at pilot or industrial scale [91,93].

Table 2. Selection of the extraction agents used in the SSA leaching

Extraction agents	Conducted research
Acids	
H ₂ SO ₄	[109], [97], [102], [110]
HCl	[104], [109], [97], [102], [110], [111]
HNO ₃	[94,112] [110]
H ₃ PO ₄	[94,112,95],[110]
C ₂ H ₂ O ₄ , C ₆ H ₈ O ₇	[102] [113]
Base	
NaOH	[114], [102], [110]
Combination of acid and base	
	[114], [55], [61]
Bioextraction and others	
<i>Acidithiobacillus Ferrooxidans</i>	[52][99,98]
Extraction of ashes after SCWO – supercritical water oxidation	[46]

In the PolFerAsh technology (Polish Fertilizers from Ash), sewage sludge ash is leached with the use of phosphoric and nitric acid or its mixture to dissolve phosphorus compounds from SSA and achieve high phosphorus recovery rate (ca. 70-99%) without additional purification of leachates. Such agents were proposed because of a high phosphorus concentration and no additional by-product in the form of CaSO₄ or CaCl₂ formed during the extraction with sulfuric or hydrochloric acid [112,115,105,95]. In the second stage after filtration, extracts are neutralized with the use of hydrated CaO or ammonia or biomass ashes like poultry liter ash, to produce solid fertilizers in the form of calcium phosphates, ammonium phosphates or mixture of both as well as liquid fertilisers [116,117].

The same acids or its combination is used in process RecoPhos and Tetra-Phos [92]. However, due to the lack of a decontamination step, RecoPhos process can be apply for high quality ash with low heavy metal content. In Tetra-Phos process diluted phosphoric acid, nitric acid or its mixture (70% H₂O, 15% HNO₃ and 15% H₃PO₄) is used to produce RePacid® - phosphoric acid, gypsum as well as iron and aluminium salts. [107].

On the basis of the conducted attempts of leaching phosphorus from industrial ashes described in it was concluded that the application of the same technology of thermal processing of sewage sludge does not guarantee that the obtained materials will have a similar feedstock potential.

The origin of sewage sludge as well as the kind of methods applied in sewage treatment plant play a crucial role. The processes of phosphorus chemical precipitation at the stage of removing biogens and the final treatment of sewage sludge prior to the process of thermal utilization are of particular importance [94,118,89,119,120].

The application of a grate furnace for the incineration of sewage sludge reduces the utilization of ash in extraction processes of phosphorus recovery. The main reasons for low degrees of leaching are a different microstructure, in particular a small specific surface area of ash in the form of slag (1.7 m²/g) as well as the smallest total volume of pores, which significantly changes the kinetics of the extraction process. Moreover, preparation of the material for extraction requires an initial process of fragmentation, thus imposing additional energy expenditure [94].

It was proved that a high content of Al and Ca in ash reduces the utilization of ash in extraction processes of phosphorus recovery. The mass ratio of Al/P in ash applied as feedstock not higher than 0.7 was accepted as the limit value. Ashes originating from the incineration of sewage sludge obtained from wastewater treatment plants, where simultaneous treatment of sewage with biological and chemical methods with the use of iron and aluminium coagulants in large amounts is applied, is characterized by the mass ratio of Al/P equal to 0.97 and the Al content at the level of 7.14%. It cannot be used as an alternative phosphorus raw material in the suggested extraction methods since the resulting extracts transform into a gel form, which renders further stages of processing impossible. High Ca content (20.71%), results in a considerable change of the extraction process conditions: an increase in the temperature of the system, the pH of the initial stage of extraction (pH=4) and of the final stage of extraction (pH up to 8). The process yield reaches 7%, hence it may be concluded that extraction is

inefficient. Mass ratio of Ca/P in ash applied as feedstock, which is not higher than 1.4, was accepted as the limit value[94,95,120].

It was confirmed in the publication that differences in the composition of ashes obtained at different periods of sewage treatment plant operation remain without a significant impact on the extraction parameters. Ash dating from various periods (spring and winter) differs in the contents of some metals (Ca, Zn, Fe, Al) and phosphorus. A higher content of iron in winter time results from the application of biological enhancement while treating sewage with an iron coagulant during the period of a lowered activity of activated sludge, whereas in spring time with an Al coagulant, which also exerts an influence on the appropriate development of microorganisms in activated sludge, thus facilitating further processing of excessive sludge. Very high yields of the leaching process were achieved, both for the winter time ash and spring time ash (yield of 95%)[121].

3.3. Modification of the production process of sodium tripolyphosphate due to the improvement of phosphorus balance in waste streams

Raw materials used for the production of sodium polyphosphate may be mixtures of sodium phosphates (e.g. NaPO_3 and $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Na}_3\text{HP}_2\text{O}_7$ and Na_2HPO_4), phosphoric acid and sodium chloride, hydroxide or carbonate. The technological process consists of a wet and dry phase. In the wet phase phosphoric acid is neutralized with soda. The molar ratio $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ (TM) for neutralization process is roughly 1.67. As a result of the process sludge is obtained which is separated on pressure drum filters in order to get a clear mixture of orthophosphates in which per 1 mole of sodium phosphate there are 2 moles of disodium phosphate. After the process the solid phase is subjected to repulping with water, and after filtration it is deposited on a landfill site. In the dry phase of production installation drying and calcination of phosphates take place. Single-stage and two-stage method may be distinguished here. The mixture of sodium phosphates condenses to pyrophosphates upon drying. The obtained mixture of sodium pyrophosphates (disodium dihydrogen pyrophosphate and tetrasodium pyrophosphate) condenses in the calcination process forming pentasodium triphosphate[122]. A crucial production problem of the STPP production technology constitutes phosphorus loss in waste stream of post-neutralization sludge. The studies proved that using the acid solution instead of water in the repulping process makes it possible to recover 98% of soluble phosphates present in the sludge, increasing twofold the yield to date. On the basis of balances and production volume it was agreed that applying a modified repulping process will increase the amount of soluble phosphorus recycled into the production process to 1,601 tons a year, decreasing the amount of phosphorus headed for the landfill site to approximately 69 tons of P_2O_5 in sludge dry mass. Phosphates in the stream can be recycled into the production process, contributing to the improvement of process balance by closing the loop and reducing the amount of waste[123].

4. Conclusions

The research carried out for many years in the area of technologies of phosphate salts contributed to the development of modern solutions creating an opportunity for a further significant progress regarding the reduction of the impact of industrial production on natural environment. An advantage of presented solutions is also the fact that the progress was achieved principally due to the application of new technological, design and equipment solutions, which are the basic elements of activities proposed in the area of cleaner production methodology. Figure 8 illustrates a scheme of the range of developed modifications.

Developed cleaner innovations ensure:

- possibility of the internal recirculation of post-neutralisation sludge within the process of STPP production with simultaneous soluble phosphates recovery 98%, increasing amounts of phosphorus introduced to the process by 1601 Mg annually, what generates raw material savings up to 1 135 ton of H_3PO_4 ;
- the possibility of using untreated wet process phosphoric acid to produce a low temperature STPP (Phase II) with simultaneous lowering of the polycondensation temperature, which leads to a reduction of energy consumption in production processes;
- the possibility of producing high temperature phase of STPP from wet process phosphoric acid purified from SO_4^{2-} ions to the level of 0.1% by weight with simultaneous lowering the polycondensation temperature by 100-150°C, thus reducing the heat consumption in the rotary kiln;

- possibility of using phosphoric acid produced from renewable alternative raw materials, i.e. bone pulp for single-stage STPP production with high bulk density and meeting the requirements of the standard for grade I, purified;
- the possibility of using renewable phosphorus raw materials, i.e. ash after combustion of sewage sludge from Thermal Stations of Sewage Sludge Utilization for the production of mineral fertilizers enabling the recovery of the critical element - phosphorus from waste with a yield above 80%, which now allows recirculation to the environment of approx. 4000 tonnes of P being the equivalent of 31 thousand Mg of imported phosphorus ore in Polish case;

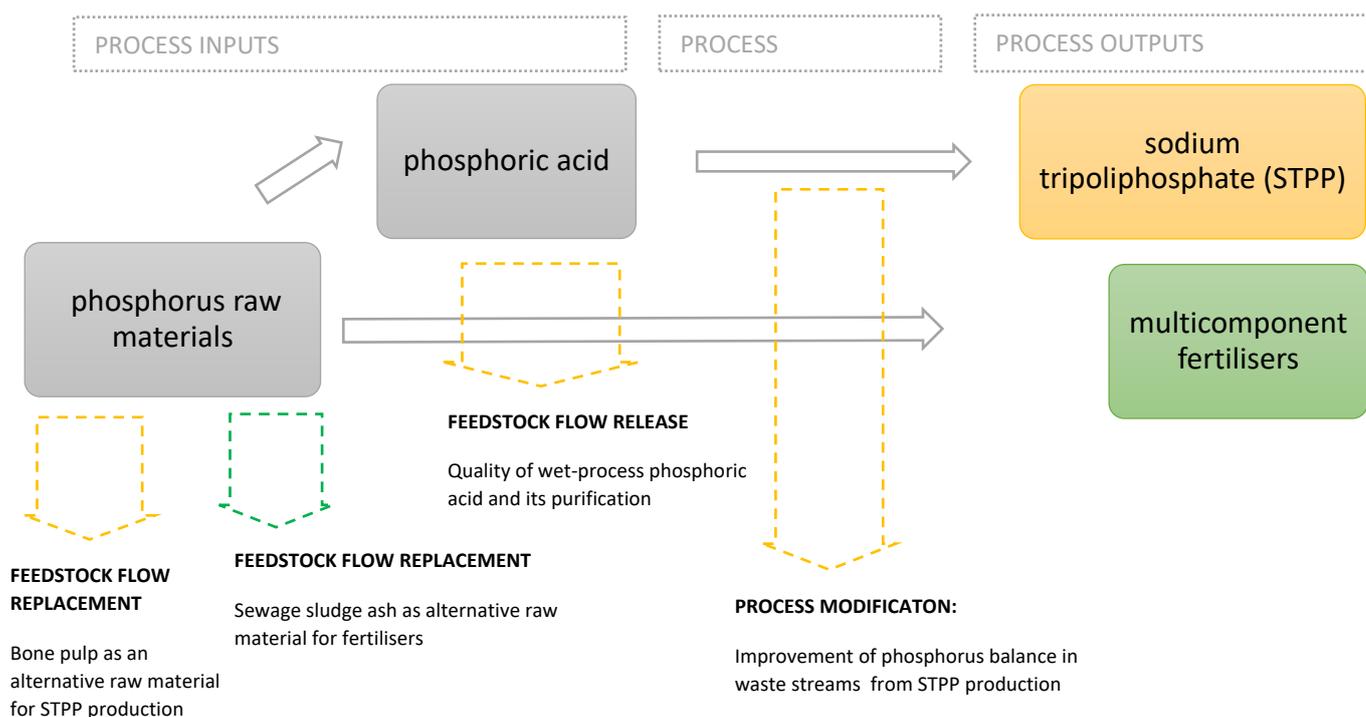


Fig. 8. Cleaner innovations in the production of phosphate salts

The proposed solutions have been covered by patent protection and constitute an innovative complex technological offer for the industry and producers, who may combine the care for the environment with technical or financial decisions. They will play an important role on the market increasing their competitiveness through taking into account all the elements of increasingly international chain of values, from raw materials to intelligent products.

It should be noted that similar activities are supported by European initiatives, which contributes to their high commercial potential and ensuring a better condition and higher competitiveness for enterprises.

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