



Kaunas University of Technology
Faculty of Mechanical Engineering and Design

Research of Improvement of Phosphoric Acid Production Process

Master's Final Degree Project

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Project author

Assoc. prof. Kazimieras Juzėnas

Supervisor

Kaunas, 2022



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Industrial Engineering and Management (6211EX018)

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Task of the Master's final degree project

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1. Title of the project

Research of Improvement of Phosphoric Acid Production Process

(In English)

Fosforo rūgšties gamybinio proceso tobulinimo tyrimas

(In Lithuanian)

2. Hypothesis:

Phosphate rock raw materials are most efficiently exploited for the production of phosphoric acid using the hemidihydrate process

3. Aim and tasks of the project

Aim: to modernize the phosphoric acid hemihydrate production process to achieve higher P_2O_5 yields

Tasks:

1. to compare phosphorus acid production methods
2. to determine the better phosphate rock raw material
3. to identify the equipment needed for modernization
4. to calculate the payback of a production process project using raw material and yield variables

4. Initial data of the project

N/A

5. Main requirements and conditions

New proposed equipment is integrated consistently with existing

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Summary

During Master's thesis project, the hemihydrate production process of phosphoric acid was modernised. A hemi-dihydrate phosphoric acid production process, which produces phosphoric acid with a higher concentration and a lower impurity content was designed. The production yield of phosphorus pentoxide increases from 95.8 % to 98.9 %. The quantity of the final product is higher with the same amount of raw materials. Phosphoric acid is the main raw material for mineral fertilisers. So far, no substitute for mineral fertilizer has been produced to meet the market demand. As phosphate rock resources are limited, it is important to use them as efficiently as possible. As the demand for fertilisers grows, it is useful not only to improve fertilizer production processes and look for substitutes for mineral fertilisers, but also to pay more attention to the research on fertilizer raw materials. Phosphate rocks from Kirov, Covdor, Morocco-Casablanca and South Africa have been studied for more efficient and cleaner phosphoric acid production. The mass fraction of phosphorus pentoxide in the rocks ranged from 32.3 % to 38.8 %. The phosphate rock from Covdor was selected for the project. The rock was found to contain 36.6 % mass fraction of phosphorus pentoxide, the lowest impurity content, and the finest particle fraction. Considering that the phosphogypsum produced by the phosphoric acid semi-dihydrate process is cleaner, drier and has better processing properties it is more suitable for reuse. The amount of recycled phosphogypsum is expected to increase and the landfill area to decrease. The estimated cost of the project for the modernisation of the phosphoric acid production equipment is EUR 17.8 million. The theoretical savings of EUR 4.7 million per year due to the reduction in phosphate rock consumption and the increase in production yield were estimated, and the project would pay for itself in 3.8 years. In contrast, when the mass fraction of phosphorus pentoxide in the phosphate rock and energy costs are taken into account, the annual savings are reduced to EUR 3.8 million. Therefore, the payback period is extended to 4.7 years. This project is not only viable because of the higher quality phosphoric acid and more efficient use of raw materials. After 4.7 years, the project is expected to add EUR 3.8 million annually to the company's budget. This money is intended to be used for modernisation of the company and improvement of the quality control department, thus making the work of the departments more efficient, and eliminating human error. The thesis consists of 51 pages, 13 figures, 18 tables and 36 references cited to illustrate it.

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Santrauka

Magistro baigiamojo projekto metu buvo modernizuotas pushidratis fosforo rūgšties gamybos procesas. Suprojektuotas pus-dihidratis fosforo rūgšties gamybos procesas, kurio metu gauta fosforo rūgštis stipresnės koncentracijos, bei mažesnis priemaišų kiekis. Gamybinė fosforo pentoksido išeiga padidėja nuo 95.8 % iki 98.9 %. Galutinio produkto pagamina daugiau, sunaudojus tą patį kiekį žaliavų. Fosforo rūgštis pagrindinė žaliava mineralinėms trąšoms. Kol kas nėra gaminamas mineralinių trąšų pakaitalas, kuris užpildytų rinką. Mažėjant fosfatinių uolienų ištekliams, svarbu juos išnaudoti kaip įmanoma efektyviau. Augant trąšų poreikiui naudinga tobulinti ne tik trąšų gamybos procesus, ieškoti mineralinių trąšų pakaitalų, tačiau taip pat skirti didesnę dėmesį trąšų žaliavų ištyrimui. Efektyvesnės ir švaresnės fosforo rūgšties gamybai ištirtos Kirovo, Kovdoro, Maroko-Kasablankos, Pietų Afrikos Respublikos fosfatinės uolienos. Uolienų sudėtyje fosforo pentoksido masės dalis svyravo nuo 32.3 % iki 38.8 %. Projekto vykdymui išrinkta Kovdoro fosfatinė uoliena. Nustatyta, jog uolienos sudėtyje fosforo pentoksido masės dalis 36.6 %, mažiausias priemaišų kiekis, bei smulkiusia dalelių frakcija. Įvertinus, jog fosforo rūgšties pus-dihidračio proceso gamybos metu susidaranti fosfogipso atlieka švaresnė, sausesnė ir pasižymi geresnėmis perdirbimo savybės, o todėl ji geriau tinkama perdirbimui. Numatoma, jog perdirbto fosfogipso kiekis padidės, o savartynų užimama teritorija mažės. Numatomos fosforo rūgšties gamybos įrangos modernizavimo projekto išlaidos siekia 17.8 mln. EUR. Nustatyta, jog teoriškai sumažėjus fosfatinės uolienos sunaudojimui pagaminant 1 toną fosforo pentoksido, dėl didesnės gamybinės išeigos, kasmet sutaupoma suma siekia 4.7 mln. EUR, o projektas atsipirks po 3.8 metų. Tuo tarpu, įvertinus fosforo pentoksido masės dalį fosfatinėje uolienoje, bei energetines išlaidas, kasmet sutaupoma suma sumažėja iki 3.8 mln. EUR, o atsipirkimo terminas prailgėjo iki 4.7 metų. Šio projekto įgyvendinimas perspektyvus ne tik dėl fosforo rūgšties geresnės kokybės, efektyviau išnaudojamų žaliavų. Numatyta, jog po 4.7 metų kasmet projektas įmonės biudžetą papildys 3.8 mln. EUR. Šie pinigai planuojami panaudoti įmonės modernizavimui, kokybės kontrolės skyriaus tobulinimui, taip su efektyvinant padalinių darbus, bei eliminuojant žmogiškąsias klaidas. Darbo apimtis 51 puslapis, jam iliustruoti panaudota 13 paveikslų, 18 lentelių, cituojama 36 literatūros šaltiniai.

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List of abbreviations and terms

Abbreviations:

AgNO_3 – silver nitrate;

CaO – calcium oxide;

$\text{C}_2\text{H}_5\text{OH}$ – ethyl alcohol;

CO_2 – carbon dioxide;

DH – dihydrate phosphoric acid production process;

HCl- hydrochlorid acid;

HH – hemihydrate phosphoric acid production process;

H_3PO_4 – orthophosphic acid;

H_2SO_4 – sulfur acid;

KH_2PO_4 – dihydrogen phosphate;

K_2O – potassium oxide;

Na_2CO_3 – sodium carbonate anhydrous;

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ – ammonium molybdate;

NH_4VO_3 – ammonium metadate;

N – nitrogen;

O. M. – organic matter;

P_2O_5 – phosphorus oxide;

Si_2O – silica (silicon dioxide).

Introduction

These days, the demand for phosphoric acid is growing, as the demand for fertilizers is growing accordingly. Fertilizers is a substance used to supply the soil and, at the same time, the plant tissues with the various nutrients that plants need. The global demand for fertilizers is growing as world population is increasing and natural resources are decreasing. This is because of soil depletion and the fact that consumers has become accustomed to a wide choice of products and only a part of them are paying more attention to sustainability, recycling, reuse, and efficiency. Therefore, it is necessary to saturate the soil with substances, such as nitrogen, phosphorus oxide and potassium oxide, as crops have higher yields with optimal amounts of these substances. In almost all of life's activities, there are ways in which they can be improved and renewed. The incentive for these actions is not just to make work easier for employees. It can lead to more efficient work results, reduce the number of staff required, contribute to the preservation of nature, and increase profits. Phosphoric acid production is no exception. This production covers many areas. The use of non-renewable phosphate rock, the high energy costs, the storage of phosphogypsum waste in landfill sites, which is a sensitive topic in environmental studies. However, without phosphoric acid, agro-culture would not be supplied with necessary fertilisers. Therefore, in order to minimise the negative impact on the environment a variety of solutions are being sought to replace mineral fertilisers and to upgrade and modernise the acid production stages. The types of processes used to produce phosphoric acid: hemihydrate, dihydrate, di-hemihydrate and hemi-dihydrate. To improve phosphoric acid processes, it is first necessary to define the expected result. Companies are increasingly using the hemi-dihydrate process. The acid produced by this process is stronger and cleaner. The phosphogypsum by-product is purer, making it more suitable for recycling, as recycling is currently hampered by the presence of phosphoric acid residues and impurities from phosphate rock. If more phosphogypsum is recycled, landfills are less likely to be filled, which would make a significant contribution to sustainability. In order to obtain a cleaner acid, efficient use of the raw material and a higher yield of phosphorous oxide production, the selection of the phosphate rock raw material must be appropriate. Phosphate rock compositions vary in phosphorus oxide content, impurity content and particle fraction. The production of phosphorous acid consumes huge amounts of electricity and steam power. The modernisation of processes needs to take into account changes in these indicators, as the moderate use of resources is a principle of sustainability. The most important indicator in the production of phosphoric acid is the production yield of phosphorus oxide. It is influenced by the choice of the right production process and the composition of the phosphate rock. Higher production yields lead to higher profits with the same amount of raw materials and contribute to the efficient use of natural resources.

Aim: to modernize the phosphoric acid hemihydrate production process to achieve higher P_2O_5 yields

Tasks:

1. To compare phosphorus acid production methods
2. To determine better phosphate rock raw material
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1. Mineral fertilizers

Table 1 data presents that from 2016 to 2022, the demand for nitrogen (N), phosphorus oxide (P_2O_5) and potassium oxide (K_2O) for the production of fertilizers has been increasing every year. It can be seen that the need for nitrogen is the greatest. However, with the growing demand for all elements, the demand has increased by an average of 3,000 thousand tons annually since 2018.

Table 1. World demand for nitrogen, phosphorus and potassium for fertilizer use (thousand tons) [1]

Substances	2016	2017	2018	2019	2020	2021	2022
Nitrogen (N)	105 148	105 050	105 893	107 424	108 744	110 193	111 591
Phosphate (P_2O_5)	44 481	45 152	45 902	46 587	47 402	48 264	49 096
Potash (K_2O)	35 434	36 349	37 171	37 971	38 711	39 473	40 232
Total (N+ P_2O_5 + K_2O)	185 063	186 551	188 966	191 981	194 857	197 930	200 919

Mineral fertilizers – fertilizers that are produced industrially from minerals and rocks. They are divided into macroelemental and microelemental. Macroelemental fertilizers are used more widely because plants require higher amounts of them, their main elements are nitrogen, phosphorus and potassium, while microelemental fertilizers consist of copper, manganese, zinc, boron, and other elements. During fertilization 99 % of phosphorus from the granules is distributed over a tiny area and not deeper than 5 cm from ground surface. After fertilizing phosphorus is no longer depleted from the soil by biological and chemical processes, the only way for phosphorus to reach the plant's roots is through diffusion, which is a slow process. Therefore, it is advisable to apply phosphorus fertilizer as close to the root zone as possible and to apply it to the soil as soon as it is required by plants. Other elements in the fertilizer are not absorbed by the plant immediately, so it is necessary to properly select the concentration of the fertilizer during fertilization so that it does not reach drinking water. In order to minimize the negative impact on the environment, fertilizers must be selected responsibly, taking into account the condition of the soil and the type of the plant, so that all macro- and microelements used during fertilization enter the plant and do not pollute the environment.

Fertilizers are focused on specific targets: strengthening of seedlings, formation of flowers and intensity of green color. They have different compositions, in which N or P_2O_5 is the main constituent. In Fig. 1 it is shown that in 2019, the highest consumption (in terms of P_2O_5 consumption) was the one of ammonium phosphate. In second place there was the NPK compound, which consumption was almost twice lower. In third place there was NP compound, which consumption was almost 6 times lower than ammonium phosphate. Thus, it can be concluded that the greatest demand for the market is for N and P_2O_5 macroelements.

Improper use of fertilizers causes ecological problems: unabsorbed plant fertilizers enter groundwater, cause eutrophication of surface water reservoir, act on microorganisms that affect plant growth, soil moisture retention deteriorates, soil degradation occurs, and soil fertility decreases [2]. Excess of some nutrients has been scientifically proven to impair the uptake of others, and irresponsible and unpredictable use of mineral fertilizers reduces the amount of humus in the soil.

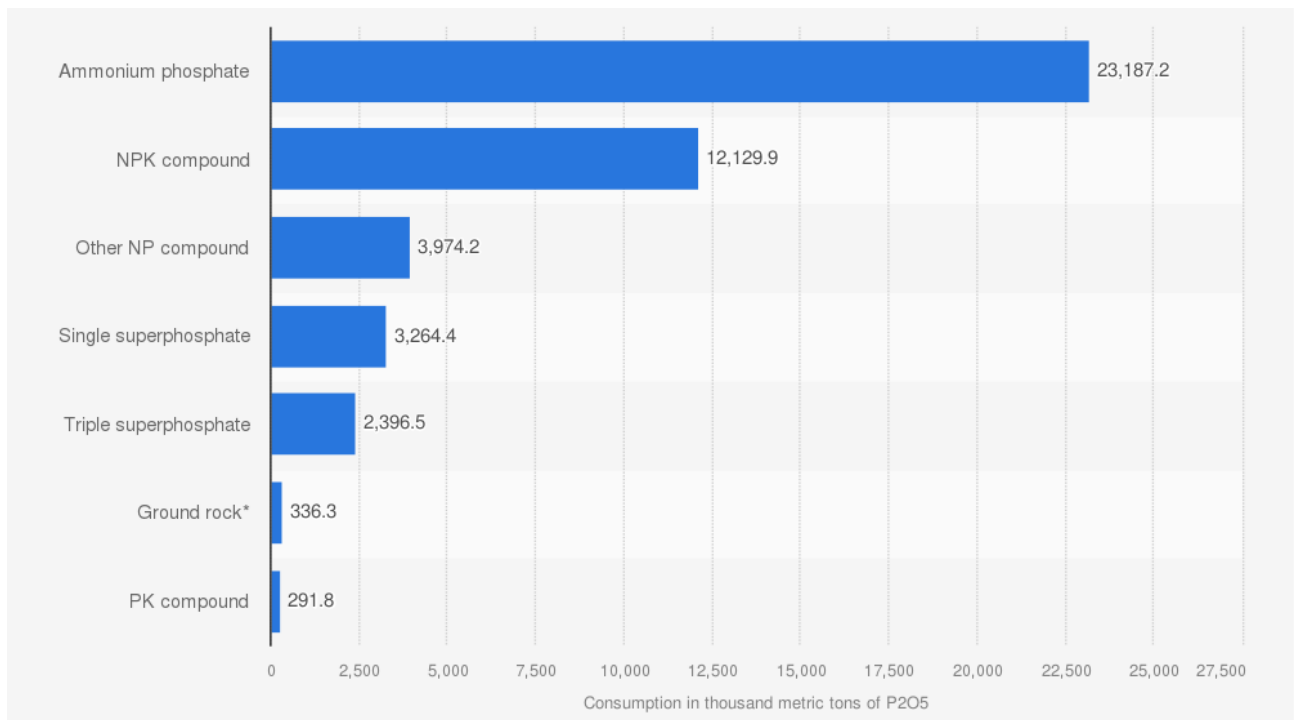


Fig. 1. Consumption of phosphate fertilizers worldwide in 2019, by select product (in 1000 metric tons of phosphorus oxide) [3]

Phosphoric acid is the main raw material in the production of phosphate fertilizers, so it is very important to ensure that all possibilities are used during the production of acid to achieve the efficiency of the production process, maximum yield, economy, and the quality of the final product. With a wide choice of fertilizers, consumers have a choice of fertilizers for a variety of applications.

Ways are also being sought to produce organic fertilizers that are less likely to have a negative impact on the environment compared to mineral fertilizers. Studies have been carried out to use coffee grounds waste to produce organic fertilizers, as coffee grounds are a great source of plant nutrients and soil improver. Coffee grounds are quite rich in organic carbon, which soils are severely lacking because of heavy chemical agriculture and naturally occurring processes. However, it has been found that granules are not formed during the granulation of coffee grounds and phosphorus acid without additional binders [2]. Thus, it is promising to search for new fertilizers from existing waste in order to reduce existing waste and reduce the environmental impact of mineral fertilizers.

Nowadays, companies have developed the view that the face of a company in society is an important part of business. Research has been done to develop technology plans that would be used to develop eco-friendly technologies in the building materials industry. According to the authors of the research, the technology plan is not actively used and researched in the environmental industry, therefore its social contribution is higher, as it can be a means to find technological trends and offer directions for technological development in all other industries [4]. One of the results of this study can be described as the development of a series of guidelines outlining the current challenges in the medium and long term for the industries concerned, considering technical, market needs and product development aspects [4]. Sustainability, which is now an integral part of Industry 4.0, is gaining popularity, as is eco-friendly manufacturing. It is established that the ISM model explains how Industry 4.0 contributes to sustainable innovation. It is also explained how each function interacts with the other in the Sustainable Innovation Capacity Development Plan (Fig. 2) [5]. It can be seen that in the ISM

model, it all starts with inter-functional collaboration and learning and value chain integration, when all the remaining functions are included, the ultimate goal, green product innovation capacity is achieved. This model was developed to enable companies to implement green product innovations. It helps to understand the sequence of future plans, goals, and objectives in order to develop the idea of sustainability in the organization. Thus, eco-friendly production is gaining popularity, because people and companies understand that it is necessary to live not only by this day, but to look to the future and anticipate the consequences if society does not make changes in the areas of efficiency, ecology, and sustainability. There is a tendency in society that the choice of supply must be abundant and very diverse in all areas. However, it is already clear to the majority of society that excessive consumption can lead the world to ecological and economic disasters. So, researchers are looking for ways to incorporate sustainability, efficiency, and environmentally friendly thinking into corporate governance in a variety of industries. Such thinking is also an integral to the industry 4.0 ideology. Of course, the return on investment is not just about profits but also about the future. There is a tendency that sustainable, eco-friendly companies are more attractive to young people in the 21st century. In summary, even the vision and mission of a company determines its popularity as an employer.

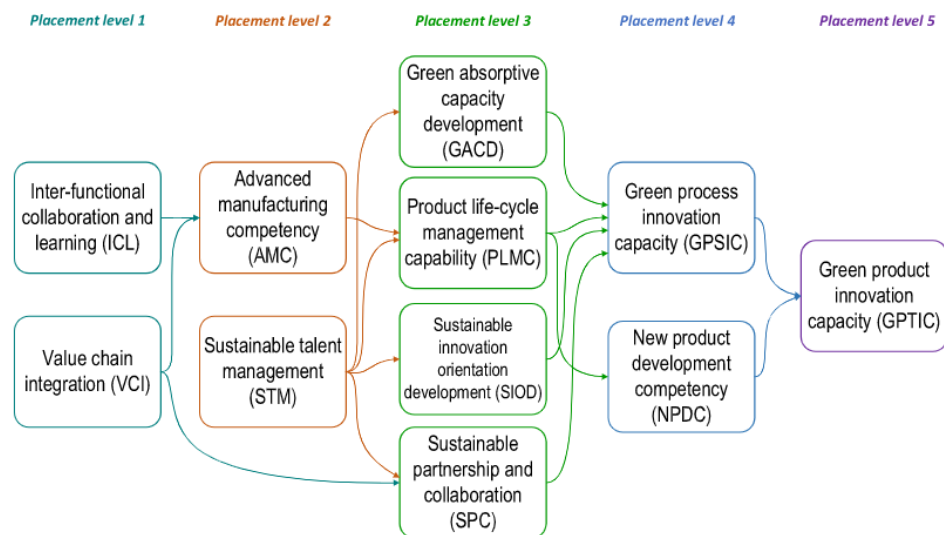


Fig. 2. ISM model of Industry 4.0-enabled sustainable innovation [5]

It should be noted that consumers, who must use this product responsibly in order to make full use of it without harming the environment, also play a key role in the production of fertilizers. The main goal of fertilizer management practices is to balance the supply of nutrients to crops with their needs in order to achieve better yields and minimize the release of nutrients into the environment. The implementation of this practice requires the application of the 4Rs principle, which consists of four areas of nutrient management: right source, right rate, right time and right place. Studies investigating this principle have been conducted in the Midwestern United States to reduce phosphorus losses. The identification of overlapping areas of high P source has been found to enhance the implementation of best management practices in fields and basins [6]. It can be concluded that fertilizer users must also strive to maintain knowledge for sustainability and ecology.

The production of organic fertilisers is expensive. As a result, the product cost of organic fertilisers is higher than that of inorganic fertilisers. Consumers tend to choose and buy more economically

viable product. Even if public opinion were to change and switch to organic fertilisers, the amount of organic fertilisers currently produced could not reach required amount in the market, as the demand for fertilisers continues to grow every year. Therefore, the improvement and development of inorganic fertiliser production, such as the development of environmentally friendly production, the efficient use of raw materials, and the incorporation of renewable energies into the production process are required.

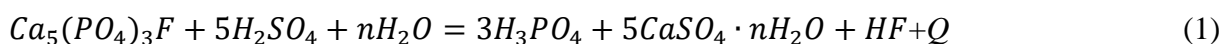
2. Phosphoric acid

Phosphoric acid (orthophosphic acid) is a weak inorganic acid with the chemical formula H_3PO_4 . This acid is non-toxic and is in solid form (at room temperature and normal pressure). Melting point $42.35^\circ C$, density 1870 kg/m^3 , freely soluble in water. Heated phosphoric acid interacts with metals, is a weak oxidant, and does not decompose [7]. H_3PO_4 acid is produced in industry by extraction or thermal method. The use of phosphoric acid is wide: in the production of phosphorus fertilizers, phosphates, phosphatized metals, and as an ingredient in electrochemical and chemical polishing solutions. In the food industry, phosphoric acid is used as a food supplement E338, to acidify foods and beverages. It is also used in the production of beer and wine for pH adjustment and washing of equipment. Studies have been carried out to use phosphoric acid and sugar liquid for fermentation [8]. The acid hydrolysis with H_3PO_4 is a conceivable method to fractionate sugar cane bagasse. Thus, in the future, this acid may be increasingly used in the production of food and beverages with different reagents. In metalworking, phosphoric acid is used to remove rust without damaging the iron surface, even when used directly. Liquid acid can be used, but acid gel is most commonly used. It can be used as a flux in the soldering process, anodizing processes. In medicine, phosphoric acid is used in dentistry and orthodontics as a corrosive solution to clean and soften the tooth surface. It is also a component of over-the-counter anti-nausea medications. This acid is also used in many teeth whiteners. In agriculture, phosphoric acid is used as a pH regulator in irrigation water, and at the same time as a source of phosphorus. Carbohydrates obtained from fresh banana peel through hydrothermal carbonization catalysed by phosphoric acid have been found to be excellent adsorbents for the removal of lead in the aqueous environment [9]. However, very pure phosphoric acid is used here. Thus, in the production of phosphoric acid, it is necessary to obtain an acid with as few impurities as possible in order to shorten its purification process and at the same time reduce its cost. In summary, H_3PO_4 acid is an integral part of consumer lives.

2.1. Production methods

H_3PO_4 acid is produced in industry by extraction, where natural phosphates are treated with sulfuric acid or by thermal reduction of natural phosphates to phosphorus followed by combustion with excess air or oxygen, followed by dissolution of the phosphorus oxide P_2O_4 in water. Phosphoric acid is produced by thermal or wet process. However, about 96 % of phosphoric acid is produced by the wet method [10]. Thermally produced phosphoric acid is usually produced for chemical reagents, where a product of higher concentration and purity is required. Thus, the production method is chosen according to the intended use of the product.

Hydration and solidification of hemihydrate phosphogypsum are mainly hindered by acidic solutions accumulated in the defects and voids and capillaries of the extraction hemihydrate gypsum crystals, which do not leach out during the filtration of phosphogypsum during the phosphoric acid extraction process by washing in a carousel filter [11]. Extract hemihydrate gypsum retains their apatite decomposition reaction products with dissolved impurities. The main reaction of the process is as follows:



where: $Ca(PO_4)_3F$ is the calcium phosphate fluoride; H_2SO_4 is the sulfur acid; H_2O is the water molecular (n - respectively 0.5 – HH, 2 – DH process); H_3PO_4 is the phosphoric acid; $CaSO_4$ is the calcium sulfate (phosphogypsum); HF is the hydrofluoric acid and Q is the heat released.

2.2. Wet process phosphoric acid process types

Depending on the acid used to produce phosphoric acid in the wet method, there is sub-treatments of nitric acid, hydrochloric acid, and sulphuric acid of which sulphuric acid is most commonly used. According to the condition of the phosphogypsum produced, there are three groups of sulphuric acid process: anhydrite, hemihydrate and dihydrate. Depending on the concentration of phosphoric acid, the purity of the phosphogypsum, and the condition of the phosphogypsum produced, the production process is as follows:

- Dihydrate (DH).
- Hemihydrate (HH).
- Di-Hemihydrate process (DH-HH).
- Hemi-Dihydrate process (HH-DH). It could be single or double stages.

Depending on the concentration of acid required, the most suitable process temperature is selected. Figure 3 shows that in order to achieve 50 % phosphoric acid, the production process must be hemihydrate and low temperature or anhydrite with temperature above 120 °C. The dihydrate method can be used to produce 48 % concentration phosphoric acid at temperatures below 100 °C.

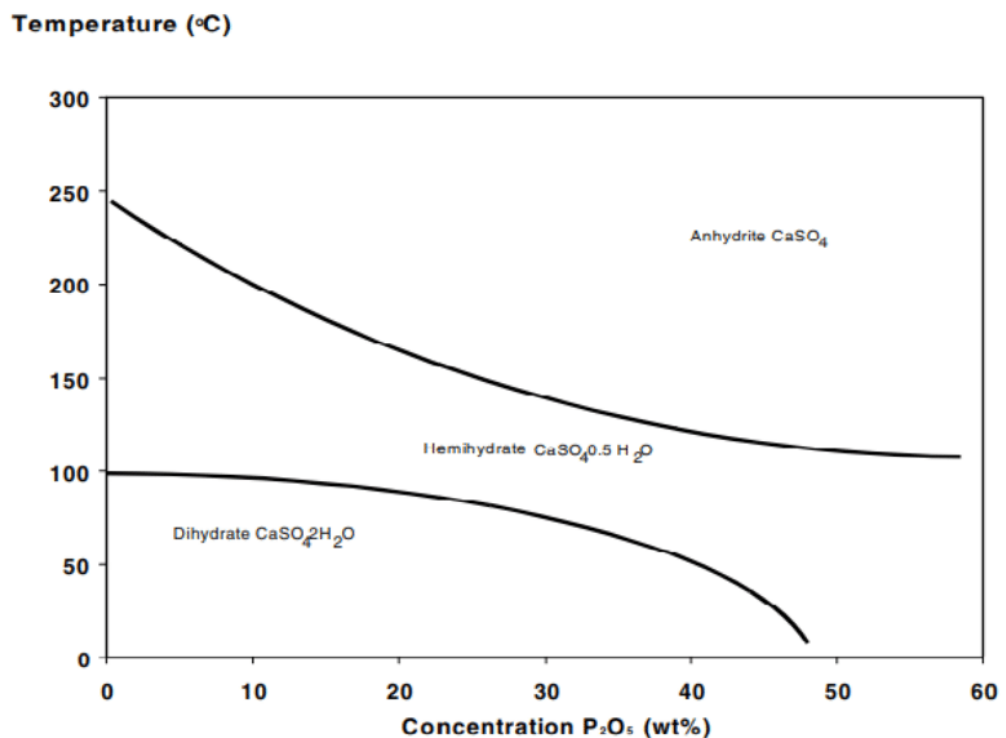


Fig. 3. Dependence CaSO₄ hydrate crystallisation on temperature and P₂O₅ [12]

Therefore, the production process may have two stages instead of one. The choice of process is influenced by the desired result: concentrated acid, lower emissions, acidity of phosphogypsum (lower or higher concentration of phosphoric acid in phosphogypsum) and availability of various raw materials. When phosphogypsum is cleaner, its recyclability is higher. However, only 15 % of phosphogypsum is recycled [13]. The remaining phosphogypsum is stockpiled in planned and prepared areas. This puts the environment at risk and prevents the land from being used for more

appropriate purposes. Phosphogypsum obtained from a single-stage process (hemihydrate or dihydrate) has a higher content of impurities, making recrystallization processes more common. In the first stage, the phosphogypsum produced during the production of phosphoric acid is filtered and washed. The phosphogypsum then is fed to the next stage where the phosphogypsum crystals are transformed [14]. These processes are HH-DH and DH-HH. In summary, the choice of production process depends on the company's desired impact on nature and the ecosystem.

2.2.1. Hemihydrate production technology

Hemihydrate production technology is most widely used in world. Figure 4 shows a simplified schematic of the HH process technology, showing that the process starts in the reactor with a reaction between sulphuric acid and phosphate feedstock. The sequence is then continued with filtration of the solution with a carousel vacuum filter, concentration and storage. In addition to the filtration step, the gases evolved during the reaction are absorbed and purified to release clean gases into the atmosphere.

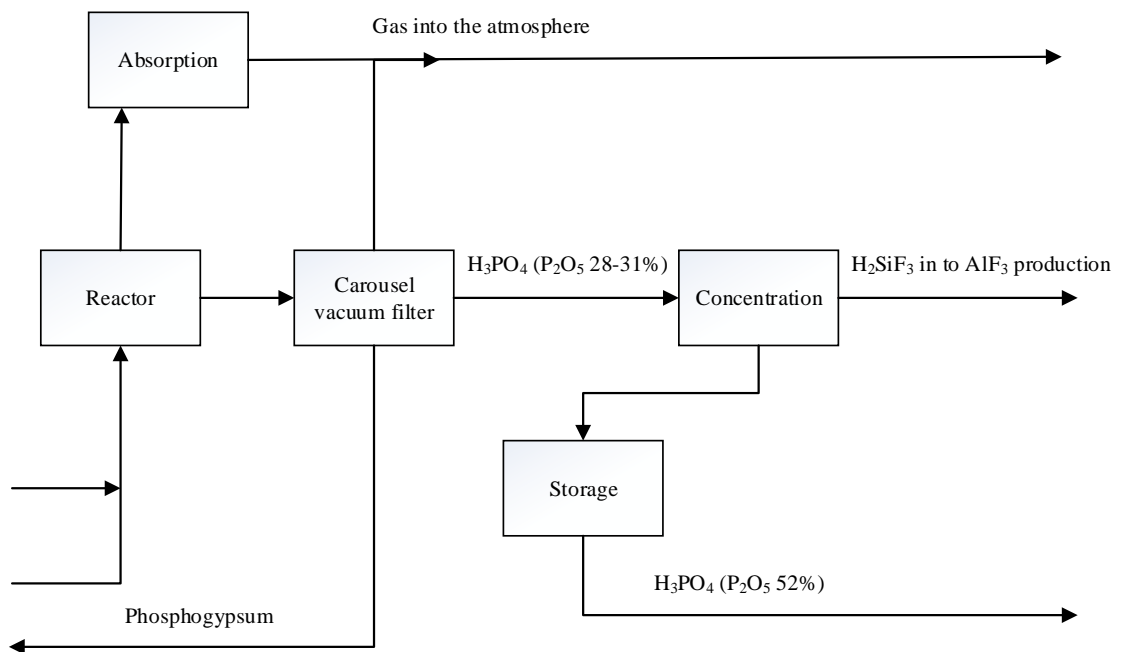


Fig. 4. Phosphoric acid HH production process scheme

The detailed manufacturing process is more complex. Phosphoric acid is obtained in reactors by decomposition of phosphate raw materials (apatites) by sulfuric acid by the hemihydrate method. Phosphate raw materials is delivered in special closed type wagons, which are unloaded and stored in two warehouses. In warehouses, phosphate raw materials are unloaded from wagons into underground bunkers, from which they are transported to warehouses or delivered to production by conveyors and elevators. Dust can be released into the working environment during the unloading, storage and especially during the transfer of raw materials from one facility to another. To improve the sanitary condition of the workplace, 20 cassette air cleaning filters are operating in the phosphate raw material warehouses. The coarse-grained phosphate feedstock is crushed in a ball mill before being placed in storage. Mill capacity is 85 t/h. The phosphate feed mill is equipped with one air pollutant treatment plant.

Part of the dusty air from the mill pneumatic system is directed to the bag filter to clean it of fine particles. The sleeve dust filter consists of 405 sleeves, the total filtration surface is 628 m². Heated air is supplied to the filter to prevent moisture condensation on the sleeves. Dusty air passes through the fabric of the sleeve and is expelled by fan into the atmosphere.

The phosphate raw materials, that the company uses in the production of phosphoric acid are the most ecological in the world, volcanic, which contains 1-2 % F, P₂O₅ - about 39 %. With the introduction of automatic control of the technological process in the workshop, downtime and the production capacity of the phosphoric acid workshop has increased to 480.0 thousand tons of P₂O₅ per year.

The flowability of the pulp is adjusted by maintaining a liquid to solid phase ratio of 2.0-2.8: 1. To maintain the phase ratio, the pulp is mixed with filtrate II (reverse phosphoric acid) obtained by washing the phosphogypsum with water. Therefore, in practice, the phosphate feedstock is degraded by sulfuric and phosphoric acids. The temperature of the pulp is maintained by the heat released during the reaction and is regulated by air cooling in the pulp coolers. During the hemihydrate process, the pulp temperature is maintained in the range of 87 °C – 98 °C and phosphogypsum is formed in the form of CaSO₄·0.5 H₂O. The pulp remains in the reactor for 3-4 hours. The pulp formed in the reactors is pumped to tilt-pan (carousel) vacuum filters (Fig. 5 (a)), in which phosphoric acid with a P₂O₅ content of at least 32 % is filtered off and the phosphogypsum is separated off and washed away (Fig. 5 (c)). The leachate is then returned to the reactor for diluting the sulfuric acid.

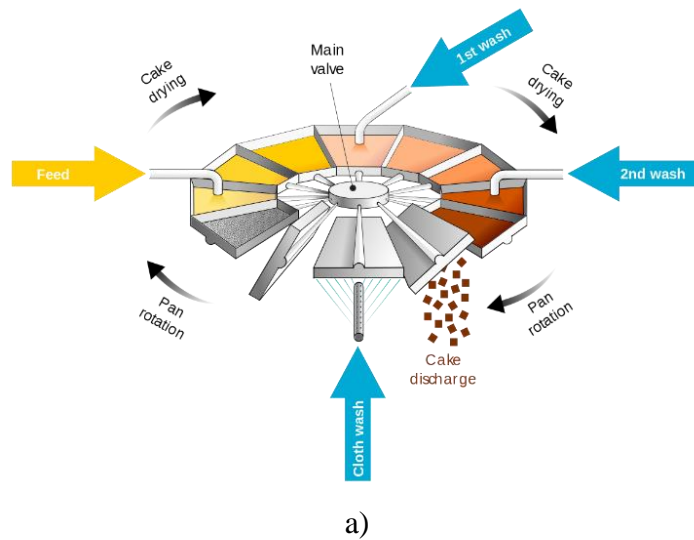


Fig. 5. Cake tilt-pan vacuum filter: (a) principal scheme of phosphoric acid pulp filtration [15]; (b) phosphogypsum filtration/drying stage; (c) phosphogypsum discharging stage

The production of phosphoric acid produces foam that interfere with efficient production. This problem can be solved by adding antifoam to the reactors, which reduces the amount of foam and makes the process less affected. However, various studies are being carried out to investigate and discover effective solutions to this problem. Foaming is influenced by the composition of the phosphate material, more specifically the impurities, the particle size of the phosphate feedstock, the temperature of the reaction, and the intensity of mixing [16]. The production of highly concentrated, pure phosphoric acid avoids foaming by slower mixing. However, when the scale of production is large and the phosphoric acid has to be obtained as quickly as possible with minimal energy loss, antifoaming and other methods are used. Sulphated fatty acids, fatty acids [17], tall oil [18] are used as antifoaming agents. Therefore, efficient production requires not only carefully and properly selected raw materials, but also additional liquids to keep the production process on track.

The filtered phosphoric acid is concentrated on an evaporator using steam at a pressure of 6 bar and a temperature of 133 °C. The steam circulates the acid in the evaporation circuit to a temperature of not more than 98 °C. In evaporators, at a vacuum 0.8-0.9 bar and a temperature of 88-98 °C, gases and vapour are intensively evolved in the condensers. Condensation creates a vacuum in the evaporation system. Water from the fertilizer production cycle is supplied to the condenser tubes. Concentrated to a concentration of 52-58 % P₂O₅, phosphoric acid is supplied from the evaporation circuit to the storage facilities. The gas-vapor mixture from the evaporators enters the spray traps and two-stage absorption systems that absorb fluorine to obtain silicofluoric acid with a concentration of at least 15 %, which is transferred to an aluminium fluoride production plant. Thus, the waste generated during the process is used in other production processes as a raw material.

The air polluted with fluorine compounds No. 1 from the reactor is fed to a series-connected jet absorber and two series-connected absorbers for purification. The irrigation liquid is sprayed through nozzles installed in the pipeline from the reactor and in the pipeline between the absorbers. The absorbers do not have nozzles, they work as a splash traps. The absorption fluid, which passes sequentially through all absorption systems and increases to a concentration of 5-12 % H₂SiF₆, is fed to the reactor for dilution of H₂SO₄. The cleaned gas-vapor mixture is blown through the chimney into the atmosphere by a fan.

The air from the carousel vacuum filter cover, from the maturators and from the tanks is interrupted by a sanitary fan. The gases in the vapor environment in the pipelines are partially absorbed and released into the atmosphere through a common chimney. The condensate is returned to production. The capacity of the circulating system is 6400 m³/h. The water of the circulation system is used for cooling the gas - steam mixture in surface condensers, a small amount of water is used in the technological process. Relatively clean cleaning water is discharged from the water circulation system to the TV-2.

Contaminated water generated during production is used in the technological production process:

1. The water collected in the non-hazardous waste (phosphogypsum) landfill pond T-6 is supplied to the absorption compartment and used for the capture of fluorine gas.
2. After the absorption compartment, the contaminated water is directed to the pond T-13 for clarification and cooling of the liquid, then fed to the reactor for dilution of acids.
3. Contaminated water used to cool the gas-vapor mixture in the barometric condensers of the evaporation unit No. 2 of the phosphoric acid section No. 2 is directed to the pond T-11, then clarified

and cooled in the ponds T-3, T-4, T-5 and returned for use in gas-vapor cooling. Part of the water is used in the phosphoric acid section No.1 in the technological process for the leaching of phosphogypsum and production of phosphoric acid.

Phosphogypsum is produced during the production of phosphoric acid. Phosphogypsum is a hemihydrate calcium sulphate ($\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$) containing residues of undegraded phosphate, phosphoric acid, clay minerals and other impurities. Sulfuric acid and phosphate feedstocks are metered into a reactor to produce a pulp of liquid phosphoric acid and crystalline calcium sulphate (phosphogypsum). The resulting pulp is filtered through a carousel vacuum filter. Separated from the filtrate the productive phosphoric acid and calcium sulphate, washed and dried up to 35 % moisture, are transported by conveyor belts with small amount of phosphorus compounds to the phosphogypsum loading station, and from there to a specially equipped non-hazardous waste (phosphogypsum) landfill. 4.7-4.8 tons of phosphogypsum are formed in order to produce 1 ton of phosphoric acid. Phosphogypsum should be stored in a specially equipped landfill. Storage conditions must be ensured in such a way that groundwater is not damaged.

Disadvantages of the hemihydrate process [12]:

- Not all types of phosphate feedstock can be used.
- Phosphogypsum has more impurities.
- Process control is more complex.
- Production yield is lower.
- Larger filter surface is required.

To summarise, the advantages of the hemihydrate process are:

- Single-stage filtration, resulting in a shorter production process.
- The acid is stronger, reaching a concentration of 40-48 % P_2O_5 .
- Phosphate feedstocks of various particle sizes may be used, not necessarily the smallest fractions
- Maintenance of production processes is easier.

2.2.2. Dihydrate production technology

The production of phosphoric acid in the reactor at a temperature of 70-80 °C and an acid concentration of less than 50 % leads to a production of dihydrated phosphogypsum waste. Depending on the temperature in the reactor during phosphoric acid production and the acid concentration, it is possible to determine which type of phosphogypsum will be produced in the reaction.

As in all phosphoric acid production methods, phosphate feedstock, water and concentrated sulphuric acid react in the reactor (Fig. 6). Sometimes multi-vessel reaction systems are used instead of single reactors. The mixture is then fed to the maturers. It is then transferred to a vacuum filter and the phosphogypsum is washed with water. The final products are dihydrate phosphogypsum and weak 26-32 % P_2O_5 phosphoric acid.

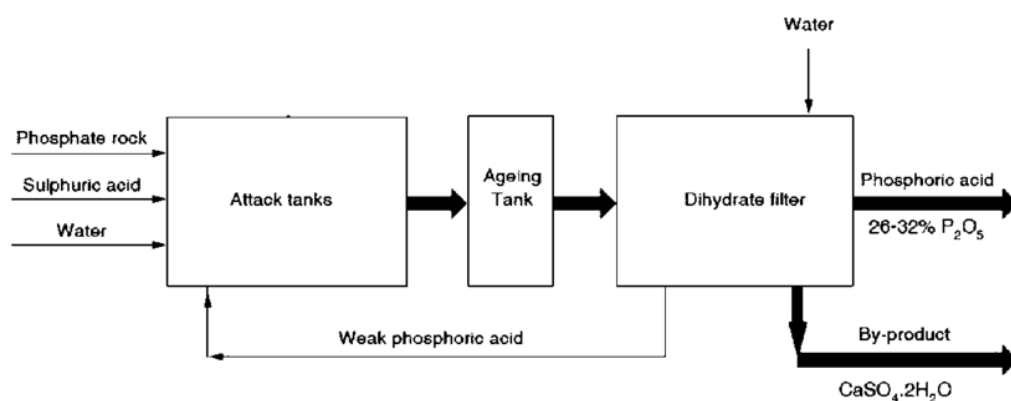


Fig. 6. Phosphogypsum dihydrate production process scheme [19]

Research is carried out to select the optimal production parameters to save time and reduce costs, without conducting practical experiments. The relative error of the tests carried out is below 3.5 % [20]. It can therefore be said that it is practical, time-saving and financially advantageous to evaluate production processes in this way. Research is also being carried out to solve the two biggest problems with the dihydrate process: fouling and cleaning of heat exchangers. Contamination concentration, surface temperature and liquid velocity were found to have the greatest influence on the precipitation process in heat exchangers [21]. As the settling velocity increases, the heat transfer coefficient decreases faster with increasing fouling concentration and surface temperature. Thus, there are many problems in the production of phosphoric acid that need to be investigated and solutions found.

2.2.3. Di-Hemihydrate production technology

This type of production process consists of two stages. In the first stage, the reaction of phosphate feedstocks with H_2SO_4 in aqueous media at 70 °C to 90 °C produces DH phosphogypsum and H_3PO_4 acid with P_2O_5 up to 38 % and less than 0.5 % free SO_3 [22] (Fig. 7). This is followed by a recrystallization step at temperature above 90 °C to produce HH phosphogypsum. The hemihydrate phosphogypsum obtained from the two stages has fewer impurities and is therefore more suitable for processing. When DH is converted to HH phosphogypsum, H_3PO_4 acid P_2O_5 is 33-35 %. It has been found that it is possible to achieve recrystallization of HH into DH phosphogypsum where the P_2O_5 of H_3PO_4 acid increases to 42-52 % [23]. A study in Belgium has found that phosphogypsum produced by the di-hemihydrate process is cleaner and achieves an efficiency of 98 % in P_2O_5 [24]. However, this production involves additional oxidation, defluorination and purification steps. Thus, the improvement of the DH-HH process achieves similar results as in the HH-DH process.

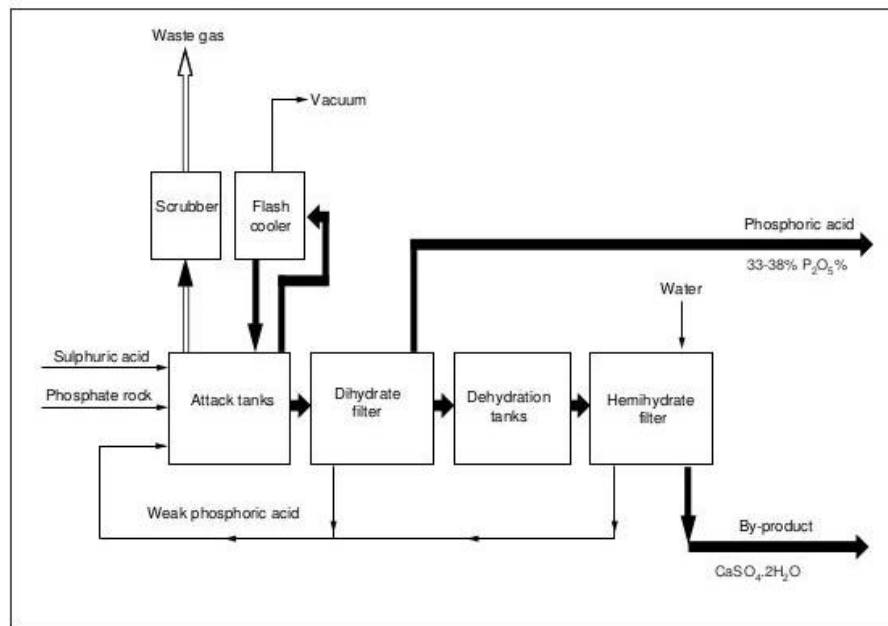


Fig. 7. Phosphogypsum DH-HH production process scheme [12]

This technology does not achieve a high yield of P_2O_5 in the production of phosphoric acid, but phosphogypsum can be used directly for the production of plasterboard, a cement retarder, after addition of natural rehydration [12]. Many factories still operate by using this process because it is easy and simple. In summary, the main advantages of this process are flexibility and reliability [25].

2.2.4. Hemi-Dihydrate production technology

A diagram of the HH-DH production process is shown in Fig. 8, which shows that the essence of this technology is the production of strong phosphoric acid and the recrystallized of HH phosphogypsum crystals to DH, increasing the P_2O_5 yield. This technology achieves a higher yield by producing a more concentrated phosphoric acid. The final phosphogypsum is also cleaner, as P_2O_5 is collected in the second stage of acid production. A small amount of sulphuric acid is added to the DH reactor to allow the co-crystallised P_2O_5 to precipitate out and enter solution [26], as sulphuric acid is used to form dihydrate crystals.

Table 2. Key differences between HH and HH-DH processes [26]

Feature	HH process	HH-DH process
Typical P_2O_5 recovery	94 %	98 %
By-product phosphogypsum	With impurities	With less impurities
Investment cost	Low	Similar to DH process
Energy efficiency	40 % lower than DH process	Similar to DH process
Water consumption	Lowest	Lower than DH process

When comparing the HH and HH-DH processes in terms of efficient utilisation of P_2O_5 phosphate feedstock, the HH-DH process is more preferable. The data presented in Table 2 summarize that the HH-DH process has the following advantages over the HH process: P_2O_5 recovery is higher, less impurities in the phosphogypsum, lower energy consumption. However, water consumption and investment are higher. Thus, the HH-DH process is more suitable for higher P_2O_5 yields.

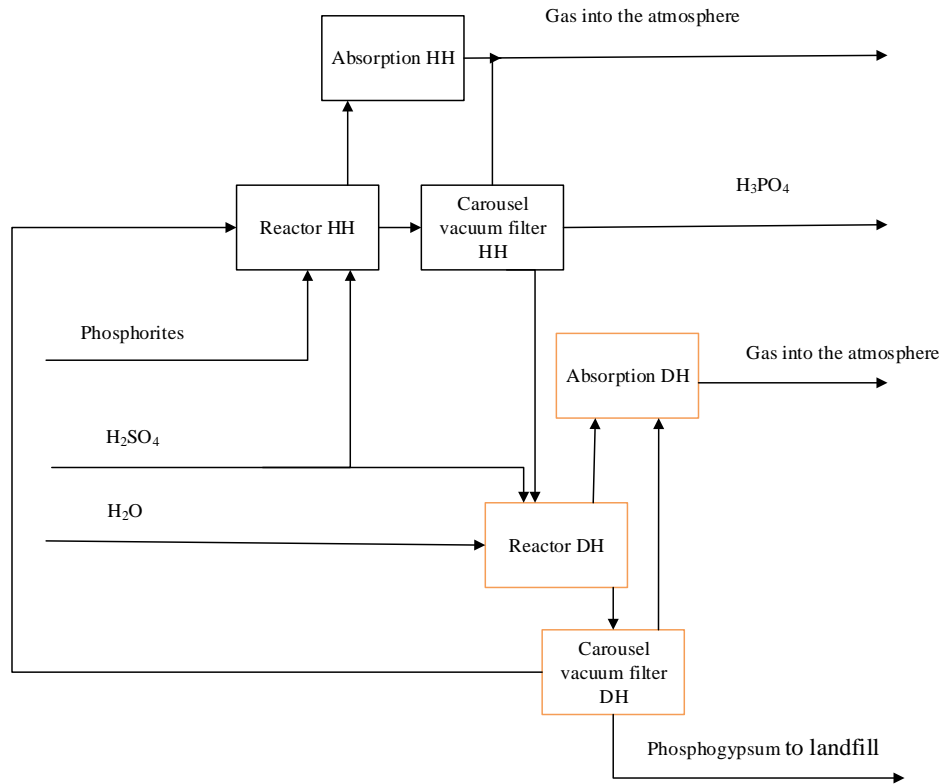


Fig. 8. Phosphogypsum HH-DH production process scheme

The most important requirements for this process are that phosphoric acid and phosphogypsum has to be cleaner, have the highest P_2O_5 yield, and produce phosphoric acid with 42-50 % P_2O_5 . Due to these advantages, this project proposes to upgrade the HH production process to the HH-DH process. The HH-DH process consumes more electricity but reduces the amount of steam required. Replacing steam with electricity significantly changes the amount of energy needed, and the end result is a reduction in the total amount of energy required. As steam is a by-product of another process in the company it can be used for other processes such as space heating, thus reducing emissions from solid fuel boiler plants.

3. Analysis of phosphorus raw materials and phosphogypsum

The price of phosphate rock is projected to increase from \$120 per tonne to \$130 between 2021 and 2035 (Fig. 9). Political relations between Russia and Ukraine could accelerate price increases. Some sources of raw materials will be "unavailable", at least temporarily, as Europe and other countries refuse to buy and sell with Russia. As price increase is projected, there is a need for more efficient use of the raw material in order to increase profits from the same reagents and quantities. This section will not examine the price differences between phosphate feedstocks, but rather the composition of the feedstock and the composition of the resulting product, phosphogypsum.

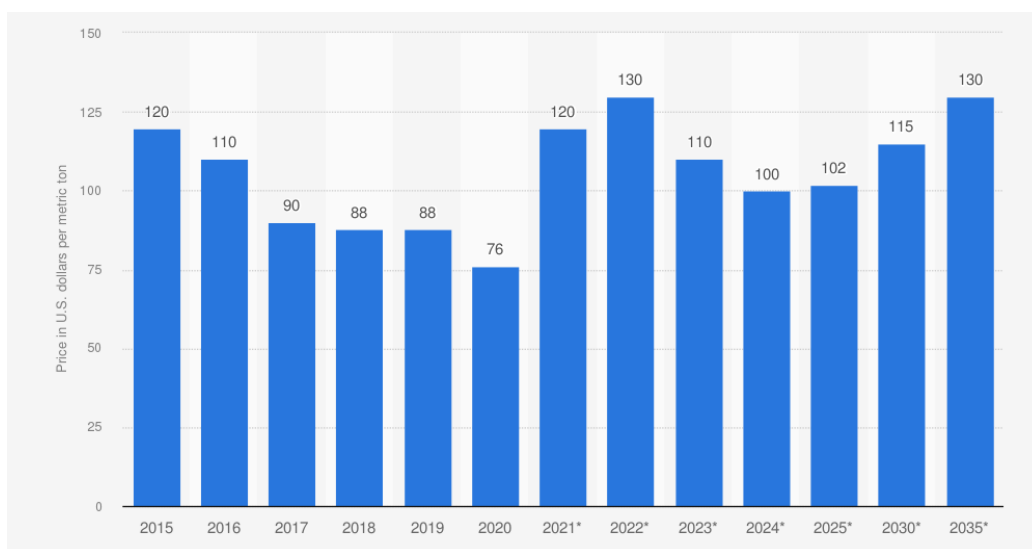


Fig. 9. Price for phosphate rock from 2015 to 2020 with a forecast for 2021 to 2035 [27]

The main raw materials for the production of phosphoric acid are phosphate raw feedstocks, also known as apatite, and sulfuric acid. As the phosphate raw material is a depleting resource, it is necessary to use it very purposefully so that it can be processed into the final product with the highest production yield. Of course, because the sources are not renewable, various apatites are used in the production process, as their supply is volatile and with limited resources. Thus, four samples of apatite were examined in the study: Kirov, Covdor, Morocco-Casablanca and South Africa Republic. The names of these phosphate rocks are commercial names and will be referred to by these names throughout this paper. The composition of the by-product depends on the apatite chosen for production of phosphoric acid, so phosphogypsum samples were also analysed.

3.1. Descriptions of the research methodology

Nowadays, there is a wide range of equipment to determine not only the physical composition of materials, but also the chemical composition. The quality control department is responsible for the selection of equipment and method for determining the composition of samples. In conclusion, the best methods for determining the physical and chemical composition of phosphate rock and phosphogypsum have been identified on the basis of the studies carried out at Company X.

3.1.1. Determination of mass fraction of water, organic matter, carbon dioxide in phosphate raw materials

The method is based on heating the sample at different temperatures and determining the difference in weight. The water content (moisture) is determined at 100 °C to 110 °C, the organic matter at 520 °C ± 10 °C and the carbon dioxide at 975 °C ± 25 °C.

Laboratory equipment, accessories: analytical balance, oven, muffle furnace, desiccator filled with silica gel, crucibles.

3.1.1.1. Water, organic matter, carbon dioxide in phosphate raw materials determination procedure

- Weigh, to the nearest 0.0001 g, about 1 g of the mixed raw material into a crucible previously weighed and calcined.
- Heat in an oven at 105 °C to 110 °C to constant weight for 1 hour, then cool in a desiccator and weigh in analytical balance.
- Then heat the sample in a muffle furnace at 520 °C ± 10 °C for 2 hours, cool in a desiccator and weigh.
- Then burn the sample in a muffle furnace at 975 °C ± 25 °C for 1 hour, cool in a desiccator and weigh.

Formulas to calculate the mass fraction % of water (H₂O), organic matter (O.M.), carbon dioxide (CO₂):

$$H_2O = \frac{(m-m_1) \times 100}{m}, \quad (2)$$

$$O.M. = \frac{(m_1-m_2) \times 100}{m}, \quad (3)$$

$$CO_2 = \frac{(m_2-m_3) \times 100}{m}, \quad (4)$$

where: m is the initial mass of the sample (g), m_1 is the mass after drying at 105 °C to 110 °C (g), m_2 is the mass of the sample after drying at 520 °C ± 10 °C (g), and m_3 is the mass of the sample after drying at 975 °C ± 25 °C (g).

Table 3 data represents H₂O, O.M. and CO₂ results of compositions of phosphate raw materials analysed obtained by using the methodology described above.

Table 3. Results of H₂O, O.M. and CO₂ of phosphate raw materials

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
H ₂ O	%	1.50	2.00	2.80	1.20
O.M.	%	0.11	0.17	2.02	0.33
CO ₂	%	0.30	2.30	5.70	3.40

Humidity in Morocco-Casablanca (2.8 %) is 2.3 times higher than Covdor's apatite (1.2 %). South Africa Republic humidity is 2.0 %, while Kirov is 1.5 %. The highest number of organic matters 2.02 % is in Morocco-Casablanca raw material, while in others samples the organic materials are less than

0.33 %. The Morocco-Casablanca phosphate raw material also has the highest CaO content of 5.7 %, while Covdor has 3.4 %, South Africa 2.3 % and Kirov only 0.3 %. Thus, it can be observed that the Moroccan-Casablanca sample has the highest levels of H₂O, organic materials and CaO.

3.1.2. Determination of the mass fraction of chlorides in phosphate raw materials and phosphogypsum

The method is based on potentiometric measurement of chlorine ion concentration with a silver electrode.

Chemicals, mixtures and solutions that are required:

- Concentrated nitric acid.
- 1: 2 solution of nitric acid.
- 0.02 N solution of silver nitrate (AgNO₃). Preparation of the solution: dissolve 3.3978 g of silver nitrate, dry for 2 hours at 105 °C, in a small quantity of distilled water and then dilute to 1 l.
- Standard chloride solution 9999 mg Cl⁻/l.

Laboratory equipment, supplies: pestle, oven, desiccator with silica gel, analytical balance, titrator with silver electrode for chlorine, heating plate, shaker, magnetic stirrer, standard laboratory glassware.

The sample of phosphate raw material is mixed, then 300 g to 400 g of the sample is transferred to a porcelain pestle, heated in an oven at 105 °C for 3 hours and cooled in a desiccator. A sample of phosphogypsum is prepared by crushing phosphogypsum in a porcelain mortar. The sample mass required for the determination of the different phosphate raw materials and phosphogypsum are given in the Table 4. The samples from Kirov and Covdor are in the same group, as these phosphate rock fractions are finer than those from Morocco-Casablanca and South Africa.

Table 4. For chloride determination required mass of samples from Covdor, Kirov, South Africa Republic, Morocco-Casablanca, phosphogypsum, volumes of 1:2 HNO₃ acid and water

Sample	Mass, g	HNO ₃ 1:2, ml	H ₂ O, ml
Covdor, Kirov	4	20	25
South Africa Republic, Morocco-Casablanca	2.5	20	25
Phosphogypsum	10	20	25

3.1.2.1. Determination of the mass fraction of chlorides procedure

- Weigh the required sample weight according to the data in the Table 4.
- Transfer the reagents and sample to a 100 ml flask.
- Place the flask on a hot plate. Bring the solution to the boil. Remove the flask from the hot plate after the solution has started to boil.
- Place the flask in an electric shaker and shake for 30 minutes.
- Then cool to room temperature and dilute to the mark with distilled water.
- Pour the prepared sample into a measuring beaker and immerse the electrode.
- Titrate the samples with 0.02 N AgNO₃ solution.

Formula to calculate the mass fraction of chlorine in mg/kg:

$$Cl = \frac{v \times N \times 35.45 \times 1000}{m}, \quad (5)$$

where: m is the mass of the sample (g), v is the quantity of $AgNO_3$ used for chlorination (ml), N is the normality of the silver nitrate.

Table 5. Results of Cl determination of phosphate raw materials

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
Cl	mg/kg	62	484	209	144

The raw material from South Africa Republic contains 484 mg/kg of Cl element, while from Morocco-Casablanca 209 mg/kg, Covdor 144 mg/kg and Kirov 62 mg/kg.

3.1.3. Determination of the total mass fraction of silica (SiO_2) in phosphate raw materials and phosphogypsum

The essence of the method is that the sample is melted with sodium carbonate to convert the silica to a soluble form.

Chemicals, mixtures and solutions that are required:

- Sodium carbonate anhydrous (Na_2CO_3).
- Concentrated HCl.
- $AgNO_3$ 1 % solution.

Laboratory equipment, supplies: pestle, analytical balance, drying oven, desiccator with silica gel, evaporating dishes and crucibles, water bath, filters with white strip, standard laboratory glassware.

3.1.3.1. Determination of the total mass fraction of SiO_2 procedure

Sample preparation starts with the mixing of the phosphate sample, then 300 g to 400 g of the sample is transferred to a porcelain pestle, heated in an oven at 105 °C for 3 hours and cooled in a desiccator. Meanwhile, a sample of phosphogypsum is prepared by grinding the sample in a porcelain grater.

- Weigh, to the nearest 0.0001 g, about 0.5 g of the sample and mix with 3 g of sodium carbonate in an evaporating crucible.
- Cover with a lid and place in an unheated muffle furnace.
- After gradually raising the temperature to 1000 °C to 1050 °C, keep in the oven for 15 to 20 minutes until the sample is completely thawed and CO_2 bubbles are evolved.
- Remove the crucible from the muffle furnace, carefully spread the alloy on the sides of the crucible, allow to cool slightly and immerse in cold distilled water, taking care not to allow water to enter the crucible.
- After cooling, wash the alloy with 25-30 ml of hot distilled water and place in an evaporating dish.
- Rinse the lid and crucible with distilled water and place in the same evaporating dish.
- Carefully acidify with concentrated hydrochloric acid until no more CO_2 is released, add a further 10 ml of concentrated hydrochloric acid and evaporate on the water bath until the odor of hydrochloric acid disappears.

- Then add 5-8 ml of concentrated hydrochloric acid dropwise to the plate, cover with a watch glass and hold for 10 minutes.
- Add 80 ml of boiling distilled water and filter with white strip to a 250 ml conical flask.
- Wash the dish with hot distilled water and place everything on the filter. Wash the precipitate with hot distilled water until no chlorine ions remain.
- Place the filter with the precipitate in a weighed and calcined crucible, dry and incinerate in a muffle furnace at 1000 °C to 1100 °C for 20 minutes, cool in a desiccator and weigh.

Formula to calculate the total SiO₂ mass:

$$SiO_2 = \frac{s_1 \times 100}{s}, \quad (6)$$

where: *s* is the initial mass of the sample (g), *s₁* is the mass of burned sediment.

Table 6. Results of SiO₂ determination of phosphate raw materials

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
SiO ₂	%	1.3	2.4	1.7	1.4

As with Cl, raw material from South Africa Republic has the highest content 2.4 % of SiO₂ compared to other raw materials. From Morocco-Casablanca has 1.7 %, Covdor 1.4 % and Kirov 1.3 % of SiO₂.

3.1.4. Determination of the mass fraction of calcium oxide CaO in phosphate feedstock and phosphogypsum by gravimetric method

The mass fraction of calcium oxide CaO is determined by observing the change in weight of the sample.

Chemicals, mixtures, and solutions that are required:

- HCl 1:1 solution.
- H₂SO₄ 1:1 solution.
- ethyl alcohol (C₂H₅OH)

Laboratory equipment, supplies: analytical balance, oven, silica gel desiccator, crucibles, hot plate, filters with blue and white stripe, standard laboratory glassware.

3.1.4.1. Determination of the mass fraction of CaO procedure

- Mix the sample, place 300 g to 400 g of the sample in a porcelain plate and heat for 3 hours in an oven at 105 °C, cool in a desiccator.
- Weigh, to the nearest 0.0001 g, about 1 g of the sample into a beaker, add 50 ml of 1: 1 hydrochloric acid solution and cook for 15 minutes.
- Cool the solution, transfer to a 100 ml volumetric flask, make up to the mark with distilled water, mix and filter through a white strip.
- Transfer 50 ml of the filtrate to a 400 ml beaker, add 10 ml of a 1: 1 solution of H₂SO₄ and 200 ml of C₂H₅OH. Leave to stand for 30 minutes, stirring occasionally.

- Filter the solution through a blue stripe filter. Wash the filter with the residue 6-8 times with C₂H₅OH.
- Dry the filter with the precipitate, place in a crucible which has been heated to constant weight and weighed at 600 °C to 700 °C for 20 to 25 minutes.
- Cool the crucible in the desiccator and weigh.

Formula to calculate the total CaO mass:

$$CaO = \frac{c_1 \times 0.4119 \times 2 \times 100}{c}, \quad (7)$$

where: c_1 is the mass of calcium sulphate precipitate (g), c is the mass of the sample (g), 0.4119 is the conversion factor from CaSO₄ to CaO.

Table 7. Results of CaO determination of phosphate raw materials

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
CaO	%	52.9	53.7	49.7	51.5

The highest level of 53.7 % Cao was found in the raw material from South Africa. However, the next highest grade was found in the raw material from Kirov, where the previous SiO₂ and Cl results for this raw material were among the lowest. The lowest CaO was found in the Morocco-Casablanca sample at 49.7 %.

3.1.5. Determination of chemical elements by atomic absorption spectrometry (ICP-OES)

The essence of the method is the emission of radiation from atoms of different elements. The chemical elements are decomposed and extracted by boiling the sample in concentrated acid. The resulting sample is sprayed into a plasma heated with argon gas. At a temperature of 10 000 °C, the material decomposes into atoms. The nuclear emission is then measured.

Chemicals, mixtures and solutions that are required:

- Concentrated HCl 1:1 solution.
- Concentrated HNO₃ solution.
- HNO₃ 5 % solution.
- Standard (buffer) solutions: PerkinElmer pure IV, silicon, sulphur, beryllium, molybdenum, selenium, titanium, vanadium, arsenic, mercury, phosphorus, potassium (concentrations of all solutions 1000 mg/l).

Laboratory equipment, supplies: crusher, grinder, drying cabinet, desiccator with silica gel, analytical balance, ICP-OES iCAP 7000 spectrometer, hotplate, standard laboratory vessels.

3.1.5.1. Determination of chemical elements procedure

Sample preparation. Stir the sample of phosphate raw materials. Pour 50 g of the sample into the grinder and grind for 10-15 seconds. Dry 5 g of the ground sample at 105 °C in a drying cabinet and pour the prepared sample into a glass burette. Crush the phosphogypsum sample.

Table 8. Quantities of solutions required for the method for the determination of chemical elements in samples

Sample	Mass, g	HNO ₃ 5%, ml	conc. HNO ₃ , ml	conc. HCl, ml
Covdor, Kirov	5	60	-	-
South Africa Republic, Morocco-Casablanca phosphorites	5	-	7	21
Phosphogypsum	5	60	-	-

- Weigh the samples to the nearest 0.0001 g into 250 ml volumetric flasks according to the data in the Table 8. Samples of phosphorites from South Africa Republic and Morocco-Casablanca require concentrated HNO₃ and HCl acids as these samples have a coarser fraction.
- To all samples add 20 ml of bi-distilled water and the required quantity of acids to the flasks.
- Place vertical refrigerators on the flasks and boil the samples for 90 minutes.
- Cool to 20 °C, dilute to the mark with bi-distilled water and filter through a blue tape filter, discarding the first portions of the filtrate.
- Pour the samples into beakers and place them in the apparatus ready for measurement.

The analysis result of the chemical compositions of the phosphate raw material (apatites) in Table 9 shows that the components of the apatites are similar but the parts by weight and mass are different.

Table 9. Results of chemical elements of phosphate raw materials by (ICP-OES)

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
P ₂ O ₅	%	38.80	36.50	32.30	36.60
Fe ₂ O ₃	%	0.24	0.22	0.35	0.28
MgO	%	0.19	0.92	0.53	1.71
F %	%	2.90	2.00	4.30	1.20
Al ₂ O ₃	%	0.50	0.21	0.47	0.19
S	%	0.03	0.01	-	-
Pb	mg/kg	<1	<1	<1	<1
As	mg/kg	<2.60	<3	9.10	<2.60
Cd	mg/kg	<0.60	<0.60	14.70	<0.60
Hg	mg/kg	<0.02	<0.02	0.03	<0.02
Ag	mg/kg	<467	<467	<467	<11
B	mg/kg	14.10	15.60	407.20	<10
Be	mg/kg	1.50	<0.30	1.40	<0.30
Ba	mg/kg	399	252	85	140
Bi	mg/kg	<3	<3	<3	1.00
Co	mg/kg	0.80	1.50	0.30	3.00
Cr	mg/kg	4.40	6.00	200.90	3.50
Cu	mg/kg	24.50	15.50	36.80	22.90
Ga	mg/kg	97.50	51.10	8.60	30.20
In	mg/kg	<1	<1	<1	<0.70
K	mg/kg	1872	1922	689	765
Li	mg/kg	3.10	2.00	65.50	1.00

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
Mn	mg/kg	134	51	9	223
Mo	mg/kg	<0.30	<0.40	2.20	<0.40
Na	mg/kg	2541	283	5081	1281
Ni	mg/kg	<0.20	4.60	25.50	2.10
Se	mg/kg	<3	<3	<3	<2
Sr	mg/kg	370	1145	950	1818
Ti	mg/kg	253	74	19	67
Tl	mg/kg	<1	<1	<1	<1
V	mg/kg	28.80	<0.50	152.90	7.60
Zn	mg/kg	<2	1.30	183.60	5.10

Phosphate raw material from Kirov, compared to others, has the highest P_2O_5 content. It stands at 38.8 %, compared to 36.6 % in Covdor, 36.5 % in South Africa Republic and 32.3 % in Morocco-Casablanca. Thus, raw material from Kirov has the highest amount of the most important element- P_2O_5 , which is the main indicator in phosphorus acid production. The Morocco-Casablanca raw material contains more iron (III) oxide (Fe_2O_3). The data in Table 9 shows that the phosphate rock of South Africa Republic and Covdor have the lowest levels of impurities and Morocco-Casablanca the highest. The Morocco-Casablanca sample contained 4.3 % fluorine, which promotes corrosion by reacting with various surfaces. According to the experiments performed, the electrochemical parameters of the anodic polarization diagram reveal anodic dissolution due to the addition of HF to phosphoric acid and the passive behavior in the presence of H_2SiF_6 [28]. The basis of the study was the mass change during the electrochemical reactions. Thus, a higher mass fraction of fluoride in the apatite indicates a tendency to more active corrosion of phosphoric acid. Less than 1 mg/kg of lead was detected in all samples. The arsenic content in the Morocco-Casablanca sample is 3 times higher than that of all others at 3 mg/kg. Similarly, the cadmium content is 24.5 times higher than that in all others. Silver, barium, potassium, sodium and strontium were detected at levels above 100 mg/kg. In a sample from Morocco-Casablanca 5081 mg/kg of sodium was detected, while the second highest, Kirov, is only half of that. Looking at the results for the remaining metals, there is a tendency for many of the highest concentrations to be present in the sample from Morocco-Casablanca. Raw material from Covdor and South Africa Republic have the lowest number of metals elements. Covdor phosphate rock has a higher mass fraction of P_2O_5 and has more advantages compared to South Africa Republic phosphate rock. In conclusion, Covdor apatite is the purest and most suitable for the cleaner production of phosphoric acid.

3.1.6. Determination of the distribution of particles in phosphate rock

Weight 100 g of phosphate rock into a dish using an electronic balance. Pour the sample into an electromagnetic sieve “Fritsch” shaker containing sieves with holes of 0.2 mm, 0.5 mm and 1.0 mm and a lower vessel to collect the rest of the sample finer than 0.2 mm (Fig. 10).



Fig. 10. “Fritsch” sieve shaker [29]

- Shake phosphate rock sample for thirty minutes.
- Collect the remaining sample from each sieve. Weigh with an electronic laboratory balance.
- Calculate the percentage weight on each sieve. The bulk of the sample is concentrated in the lowest vessel.

It has been mentioned before that in the case of larger particles, the apatite is prepared and crushed in mills before being fed to the reactor. So, if apatite is a small fraction it does not need the use of an additional step-shredding. The data in Table 10 shows that the particle sizes of the apatites varied. It can be seen that the Morocco-Casablanca sample has the largest percentage of particles in the 1.0 mm fraction (4.3 %), while the Covdor sample has only 12.3 % of the larger particles than 0.2 mm and smaller than 0.5 mm.

Table 10. Results of the particle size distribution of phosphate compounds

Element	Units	Phosphate raw material			
		Kirov	South Africa Republic	Morocco-Casablanca	Covdor
Material on a sieve 0.2 mm	%	27.7	30.9	49.7	12.3
Material on a sieve 0.5 mm	%	0.4	0.4	2.8	0.0
Material on a sieve 1.0 mm	%	0.0	0.1	4.3	0.0

Thus, Morocco-Casablanca apatite particles larger than 0.2 mm sample account for 56.8 %, South Africa for 31.4 %, Kirov for 28.1 %, and Covdor for only 12.3 %. According to a research conducted by Nora Kybartiene, the amount of sulphuric acid and impurities in the apatite, rather than the size of the apatite particles, has a greater influence on the rate of decomposition of Kirov apatite [30]. It can be concluded that Covdor apatite would be the most appropriate in terms of particle distribution results and its composition with the lowest amount of chemical impurities.

3.1.7. Results of the analyses of the samples of phosphogypsum

The composition of the phosphogypsum is very important for the choice of phosphoric acid production processes, as the aim is to keep the by-product (phosphogypsum) as clean as possible, with the lowest residual acid content. Table 11 shows the phosphogypsum composition data for the

different raw materials used for the acid production. Table 11 data were obtained by using the methods described above: determination of the mass fraction of CaO, determination of the mass fraction of H₂O and determination of chemical elements by atomic absorption spectrometry. Raw material dosages are based on experiments carried out by Company X. The dosage of Moroccan-Casablanca sample must not exceed 50 % of the composition of the blend for stable production in order to achieve the specified phosphoric acid quality. This phosphate rock is a coarse fraction, it contains the highest amount of impurities, which prolongs the production process and increases the amount of various sediments and elements present in the produced acid.

It can be seen that the phosphogypsum with the highest moisture content of 27.6 % was obtained by using 1:1 Kirov and Moroccan-Casablanca raw materials. This gypsum is not as strong as the one with lower moisture content, because the strength and hardness of recycled phosphogypsum deteriorate with increasing moisture content. Covdor raw material has a moisture content of 17.6 %. The CaO content suggests that the most suitable sample for the processing of phosphogypsum into hydroxyapatite is the sample that contains only Covdor phosphate rock. Various studies have been conducted on the recycle and use of phosphogypsum: for wastewater treatment to remove unwanted copper, lead ions or dispersed paint residues, for the removal of fluoride ions from drinking water [31], for medical dental prosthetics and the coating of bone implants.

Table 11. The results of the analysis of phosphogypsum samples obtained by using different proportions of raw materials

Phosphate raw material (%)	H ₂ O	Fe	Mg	Al	Si	CaO	F
	%	%	%	%	%	%	%
Kirov 50+Morocco-Casablanca 50	27.6	0.003	0.008	0.058	0.42	28.7	0.4
Covdor 100	17.6	0.007	0.011	0.03	0.55	32.8	0.2
South Africa Republic 50+Morocco-Casablanca 50	26.5	0.003	0.013	0.04	0.56	29.0	0.3
South Africa Republic 100	19.8	0.004	0.019	0.023	0.59	31.6	0.2

Covdor 100 and South Africa Republic 100 phosphogypsum also contains the lowest fluoride content by mass. The percentage of iron, magnesium, aluminium, silicon, and fluorine analysed by mass is the highest in the phosphogypsum of the South Africa Republic 50+Morocco-Casablanca 50 raw materials mix (0.916 %) and the lowest in the phosphogypsum of Covdor phosphate raw material (0.798 %). It can be concluded that the production process using Covdor phosphate raw material is the most suitable for obtaining reusable phosphogypsum.

3.1.8. Determination of the total and water soluble P₂O₅ mass in phosphogypsum by photometric method

The essence of the method is based on the formation of a yellow phosphorus-vanadium molybdate complex in a solution, the colour intensity which depends on the concentration of P₂O₅ in it.

Chemicals, mixtures and solutions that are required:

- 20 % solution of hydrochloric acid HCl.
- Phosphate reagent. For preparation it needs these reagents: solution A - 1: 2 solution of nitric acid HNO₃, solution B – 0.25 % solution of ammonium metavanadate NH₄VO₃ (dissolve 2.5 g of ammonium metavanadate in 500 ml of water at 60 °C to 90 °C, add 20 ml of concentrated nitric

acid HNO₃ diluted to 1 l and then filtered); and solution C - ammonium molybdate (NH₄)₆Mo₇O₂₄ * 4H₂O 5 % solution (dissolve 50 g of ammonium molybdate in 500 ml of water at 50 °C and dilute to 1 l, filter). Combine solutions A, B and C in equal parts and in the order indicated, filter the solution and store in a dark glass vessel.

- Standard solution. Dry potassium dihydrogen phosphate KH₂PO₄ at 105 °C to constant weight (for at least 2 hours) and cool in a desiccator. Dilute sulfuric acid H₂SO₄ to 1 l. Check the solution after 3 days. Use a calibration graph prepared with an old standard solution for the test. Add 2.0 ml of the new standard solution to a 100 ml volumetric flask, dilute to 30 ml with distilled water, make up to the mark with 25 ml of phosphate reagent and mix, then mix it after 15 minutes, measure the optical density with a spectrophotometer and determine the P₂O₅ concentration according to the old calibration graph.

Laboratory equipment, supplies: porcelain pestle, analytical balances, GENESYS 180 UV-Vis spectrophotometer, filter white bar, heating tile, shaker, standard laboratory vessels (flasks, pipettes).

Calibration curve preparation is the first step in the analysis. Add successively to four 100 ml volumetric flasks: 0, 1, 2, 3 ml of standard solution corresponding to 0, 1, 2, 3 mg of P₂O₅, each diluted in 30 ml distilled water, then add 25 ml of phosphate reagent at room temperature and mix it well. Measure the optical density of the solutions after 15 minutes. Plot a calibration graph. The P₂O₅ content of the solution is plotted on the abscissa axis and the measured optical density is plotted on the ordinate axis. This density is compared with a solution containing 25 ml of phosphate reagent and 75 ml of distilled water. Measurements are made at a wavelength of 440 nm using 10 mm cells.

3.1.8.1. Total P₂O₅ determination procedure

- Weigh, to the nearest 0.0001 g, about 5 g of phosphogypsum crushed in a porcelain pestle.
- Transfer the phosphogypsum to a 250 ml beaker and add 75 ml of 20 % hydrochloric acid.
- Cover the beaker with a watch glass and boil for 30-40 minutes.
- Dilute the solution in the beaker twice with distilled water and transfer to a 250 ml graduated flask.
- Thoroughly wash the glass walls with water. Cool the solution, dilute to the mark with distilled water then stir and filter through a dry filter with a white band, discarding the first portions of the filtrate.
- Pipette 10 ml of the filtrate into a 100 ml graduated flask, make up to 30 ml with distilled water and 25 ml of phosphate reagent.
- Dilute further to the mark with distilled water. Mix well and measure the optical density after 15 minutes. Make the measurements at a wavelength of 440 nm using 10 mm cells.

Formula to calculate the total P₂O₅ mass:

$$P_2O_5(t.) = \frac{a \times V_f \times 100 \times 100}{m \times V_s \times 1000 \times (100 - B)}, \quad (8)$$

where: *a*- P₂O₅ quantity, determined according to the calibration graph (mg); *V_f* is the volume of the graduated flask used for dilution (ml); *V_s* is the volume of the solution taken from the optical density measurements (ml); *m* is the mass of the sample (g); *B* - moisture of phosphogypsum (%).

3.1.8.2. Water soluble P₂O₅ determination procedure

- Weigh, to the nearest 0.0001 g, about 10 g of the phosphogypsum crushed in a porcelain pestle.
- Transfer to a 500 ml volumetric flask.
- Add 400 ml of distilled water to the sample and mix it immediately to avoid lumps. Stopper the flask, place in a shaker and shake for 30 minutes at 300 rpm.
- Then dilute the solution in the flask to the mark with distilled water and mix it well for a few minutes.
- After settling, filter the solution into a dry container, discarding the first portions of the filtrate.
- Pipette 25 ml of the filtrate obtained and place in a 100 ml graduated flask, diluting to 30 ml with distilled water.
- Then add 25 ml of phosphate reagent, make up to the mark with distilled water, mix well and measure the optical density of this solution after 15 minutes. The reference solution consists of 25 ml of phosphate reagent and 75 ml of distilled water. Measure optical density at a wavelength of 440 nm using 10 mm cells. Water soluble phosphates are converted to P₂O₅ (w.s.) and calculated according to the same formula as for total P₂O₅ calculation.

Table 12. Results of total and water soluble P₂O₅ mass in phosphogypsum and P₂O₅ mass in phosphate raw material

Phosphate raw material (%)	P ₂ O ₅ (t.)	P ₂ O ₅ (w.s.)	P ₂ O ₅ (apatite)
	%	%	%
Kirov 50+Morocco-Casablanca 50	0.79	0.51	32.3
Covdor 100	0.93	0.32	36.5
South Africa Republic 50+Morocco-Casablanca 50	1.70	0.74	36.6
South Africa Republic 100	0.88	0.18	38.8

The data in Table 12 represents that the P₂O₅ mass of all phosphogypsum samples exceeds 0.79 %. This indicates that all of the samples contain phosphoric acid, which means that the resulting phosphogypsum has acidic properties and is impure. Impure phosphogypsum is more difficult to recycle and reuse. According to Ruiquan Jia [32], phosphogypsum can be used to replace natural gypsum to produce hemihydrate gypsum. However, the phosphogypsum should not contain more than 0.1 % of phosphoric acid as it reduces the dry strength. This is due to the fact that the phosphoric acid on the surface of the dihydrate gypsum converts the short-range electrostatic attraction between the crystals of the dihydrate gypsum into hydrogen bonds. Therefore, it is useful to find solutions that makes phosphogypsum by-product in the production phosphoric acid as clean as possible, as this would reduce the amount of phosphogypsum going to landfill.

3.1.9. P₂O₅ yield calculation of phosphogypsum

The calculation of phosphate yields requires the total and water-soluble P₂O₅ mass fraction in phosphogypsum and the P₂O₅ mass fraction in phosphate raw materials.

Formulas to calculate P₂O₅ yield:

$$K_{yield} = \frac{K_S * K_W}{100}, \quad (9)$$

$$K_s = 100 - \frac{[P_2O_5(t.) - P_2O_5(w.s.)] * G * 100}{P_2O_5(apatite)}, \quad (10)$$

$$K_w = 100 - \frac{P_2O_5(w.s.) * G * 100 * 100}{P_2O_5(apatite) * K_s}, \quad (11)$$

where: $P_2O_5(t.)$ is phosphogypsum total phosphates mass (%), $P_2O_5(w.s.)$ is phosphogypsum water soluble phosphates mass (%), $P_2O_5(apatite)$ is the mass of phosphate of the phosphate feedstock used to produce the acid (%), G is gyps number equal to 1.4, K_s is coefficient of sulphuric acid decomposition of phosphate rock concentrate (%), K_w is phosphogypsum leaching coefficient (%), K_{yield} is yield coefficient (%).

This formula is used to calculate the practical production yield. The theoretical yield is calculated from the reaction equation and the number of substances involved in moles. It is usually higher than the practical yield because unforeseen reactions often occur, and the substances are not fully adjusted. Higher practical production yield means better use of raw materials, lower production losses, more efficient and productive production process. K_s coefficient is defined as the percentage of P_2O_5 that enters from the phosphate rock into the produced phosphoric acid. K_w is defined as the percentage of water-soluble P_2O_5 that passes from the phosphogypsum suspension into the produced phosphoric acid during washing of phosphogypsum.

Yield is the most important indicator of phosphoric acid production. The most important compound in the production of phosphoric acid is P_2O_5 , because of this the yield is calculated by taking into account its processing into the final product. Table 13 shows the results of the yield calculations and Table 12 presents the data required to obtain them. The yield calculations requires the P_2O_5 content of the phosphate feedstock and the mass fractions of total and water-soluble P_2O_5 in phosphogypsum. When dosing Kirov 50+Morocco-Casablanca 50 mixture the sulphuric acid decomposition coefficient of phosphate rock concentrate is 98.8 %, but the leaching coefficient of phosphogypsum is the lowest - 97.8 %. In contrast, using only Covdor feedstock, the decomposition coefficient is lower - 97.7 %, and the leaching coefficient is higher - 98.7 %. This trend can also be seen for the South Africa Republic 50+Morocco-Casablanca 50 mixture (K_s - 96.3 %, K_w - 97.1 %). However, in the case of the mix of these raw materials, the decomposition coefficient has the lowest value, resulting in the loss of part of the P_2O_5 in the unreacted feedstock form together with phosphogypsum. When dosed with only South Africa Republic feedstock, the decomposition coefficient was 97.5 %, but the leaching coefficient was the highest - 99.3 %. Thus, the results for K_s and K_w fluctuate, there is no tendency for one coefficient to always be higher than the other.

Table 13. Production yield results with different phosphate feedstocks and dosage

Phosphate raw material (%)	K_s (%)	K_w (%)	K_{yield} (%)
Kirov 50+Morocco-Casablanca 50	98.8	97.8	96.6
Covdor 100	97.7	98.7	96.4
South Africa Republic 50+Morocco-Casablanca 50	96.3	97.1	93.5
South Africa Republic 100	97.5	99.3	96.8

Regarding the results, it can be stated that the lowest yield of 93.5 % was achieved using the South Africa Republic 50+Morocco-Casablanca 50 blend, while the results for all other blends were quite similar, ranging from 96.4 % to 96.8 %. Previously established, that fine fraction and low amount of impurities of Covdor phosphate rock are most appropriate to produce cleaner and concentrated phosphoric acid. The P_2O_5 yield results are affected by the amount of impurities in the phosphate

rock. Phosphate rock impurities (CaO, O.M., Si, etc.) are involved in the main reaction. Impurities promote side reactions, so interfere with the main reaction. This leads to the formation of various precipitates in phosphoric acid and increases the reaction time. The lower impurity content of phosphate rock means that its most important constituent, P_2O_5 , will react efficiently to form phosphoric acid rather than various precipitates. More specifically, the production yield will be higher. So, the Covdor phosphate rock is the most suitable rock for the production of phosphoric acid due to its fine fraction, low impurity content and good production yields. Therefore, Covdor raw material will be named as the main raw material for further research and use it to calculate the payback of the project.

4. Technological description of the process and proposal of improvement

The aim of this work is to connect DH process equipment to the existing production process equipment, which would be a continuation of the existing HH phosphoric acid production process. Figure 11 shows a proposed scheme for the HH-DH production of phosphoric acid. All the equipment for DH technology production process is installed in the new premises. These premises are 40x100 m in size and are connected to the existing phosphoric acid plant. Some of HH technology equipment is also being replaced. It is planned to replace a larger 450 m³ HH process reactor with stirrers, new water supply, absorption, and condensing systems. A renewal of the filtration system is also planned. To implement the project, the search for equipment would be carried out by sending out requests for quotations on the best options available. Reactors, tanks, pipes must be suitable for acid storage. The surface area of the No.1 filter is planned to be 180 m², while the surface area of the No.2 filter is 240 m². It is not necessary to completely dry the phosphogypsum during the first filtration as it will be fed to the HH-DH reactor for further reaction. Meanwhile the No.2 filter has a higher load due to the more intensive washing and filtering of the phosphogypsum so it requires more working area. Cost reductions are likely to be made by choosing a single supplier with the most satisfactory equipment offer.

At the start of the HH-DH phosphoric acid production process, 101 t/h of phosphate rock feedstock, 91.3 t/h of sulphuric acid and 50 t/h of water are dosed into three 450 m³-1 reactors (Fig.11). The stirrers in the reactors ensure that the resulting pulp is stirred continuously, and that the reaction takes place throughout the volume. During the hemi-hydrate process, the pulp temperature is maintained above 90 °C. From the 450 m³ reactors, the pulp is piped to two smaller 210 m³ reactors, where the reaction lifetime is extended. Air contaminated with gaseous fluorine compounds from the reactors is fed via sanitary ventilator -5 to absorbers - 4 for cleaning. Formed condensate is returned onto the vacuum filter No 1. The “mature” pulp is fed onto vacuum filter No 1. - 2. At the beginning of this process step, the vacuum equipment separates the hemihydrate phosphogypsum and 90.8 t/h of the phosphoric acid containing 40 % P₂O₅. The acid is fed into two pulp tanks - 6, where it is stored. At the same time, the phosphogypsum is washed with water and fed into the DH 440 m³ reactor. The effluent is returned to the HH process reactors to dilute the sulphuric acid. The DH reactors keep the pulp temperature below 50 °C. This reactor is fed with 7.7 t/h sulphuric acid, as well as effluent water. Four 440 m³ reactors are used for the recrystallization of hemihydrate phosphogypsum to dihydrate. As for the HH process, steam condensation is also performed, but with separate units. The pulp is fed onto vacuum filter No. 2 - 3. This vacuum filter has a work surface of 240 m². The washing process requires more water than the one which uses No. 1 filter. Since phosphogypsum is fed from the No. 2 vacuum filter to the landfill by conveyor belt - 8, it must have a minimal concentration of H₃PO₄. The filtered acid is stronger and is stored in storage tanks – 6 and the phosphogypsum is dihydrate.

The project requires a new 400 m² building with a height of 25 m. The units are installed in a staged manner, the reactor at the highest level compared to the pulp tanks, and a filtration system that facilitates the movement of pulp, leachate and acid through the pipes, resulting in less strain on the pumps. Table 14 shows the estimates, not only for the equipment, but also for the construction of the building. It also includes the cost of training and familiarizing employees with new technology. The final amount of EUR 11 520 is included. 24 employees would be trained during their working hours and the additional training costs are 48 hours with an hourly rate of EUR 10. Additional staff will not be hired as the production processes are computer-controlled. Overtime would be arranged for additional maintenance or major works.

Table 14. Funding required for the project

Cost centres for the project		Price, EUR
Cost of construction, installation of production facilities	Pipes 101.6D 500 m	11 300
	Pipes 219.1D 500 m	25 800
	Sanitary ventilator, 3 pcs	43 065
	Condensate system, 3 pcs	26 900
	Pulp tank, 6 pcs	150 000
	Belt conveyor, 96 m	45 000
	Filtration system, 2 pcs	5 200 000
	Reactor with mixers, 5 pcs	2 000 000
	Exhaust stack, 1 pcs	300 000
	Absorption system, 5 pcs	4 000 000
	Water supply system	2 000 000
Construction, installation	Materials	2 000 000
	Installation	2 000 000
Total:		17 802 065

The cost of the equipment is EUR 13.8 million and EUR 4 million is needed for the construction of the building. The indicative prices for the equipment are based on data currently available from online sources [33][34][35], as well as on the prices of previous acquisitions of equipment by company X. Therefore, the total cost of the project is EUR 17.8 million.

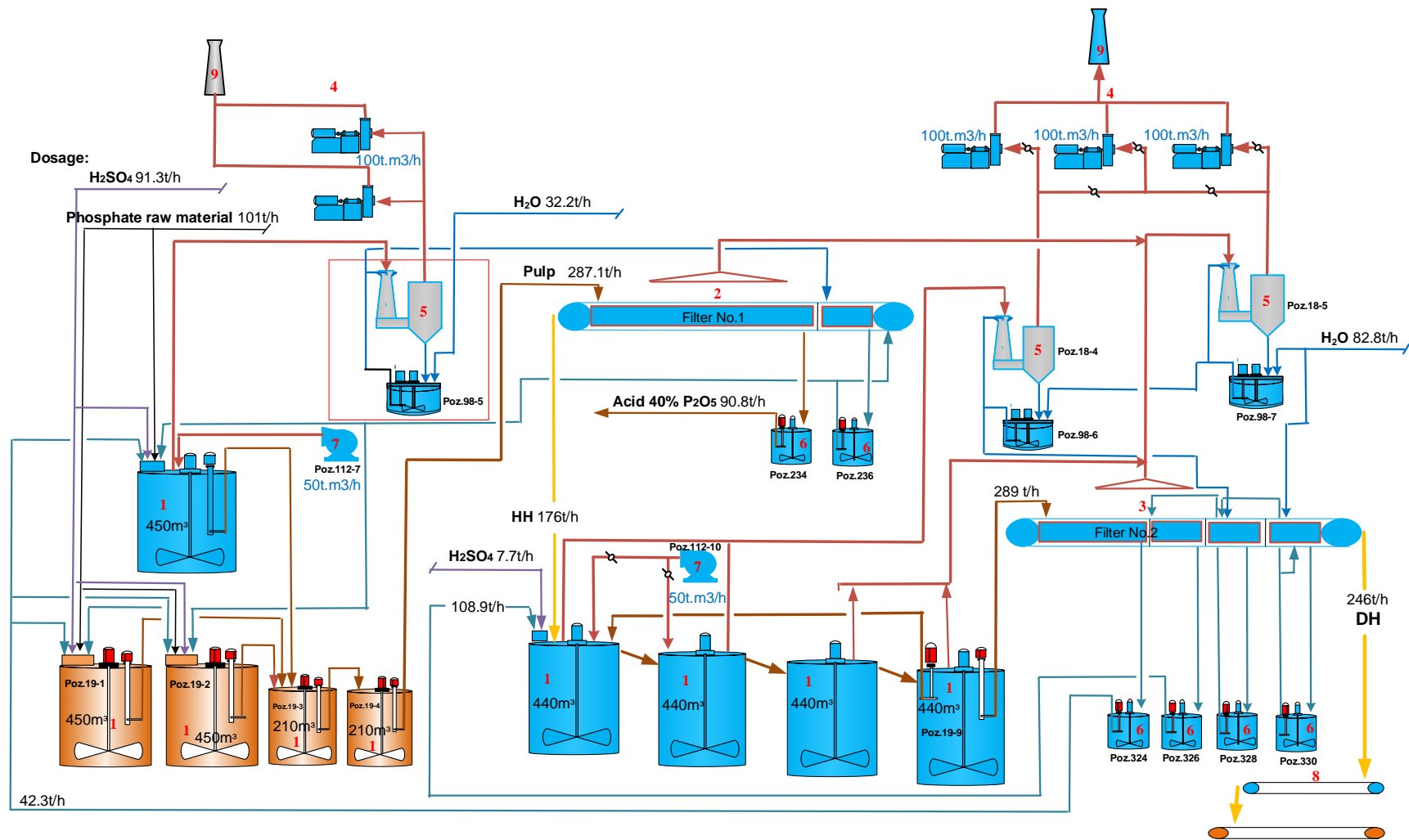


Fig. 11. HH-DH phosphoric acid production schematic drawing (blue devices are the new equipment needed for the project): 1- reactor with mixers; 2-HH phosphogypsum filter No. 1; 3- DH phosphogypsum filter No. 2; 4- absorption system; 5- sanitary ventilator and condensate system; 6- pulp tanks; 7- water dispensers; 8- conveyor belt; 9- the exhaust stack

4.1. The payback of a production process project using raw yield variables

The project is expected to increase the P₂O₅ production yield from 95.8 % to 98.9 %. Variable amounts of impurities in the phosphate feedstock compositions lead to different reaction yields. Calculation of the theoretical mass of phosphate feedstock required to produce 1 t (1 000 000 g) of P₂O₅:

$$M(P_2O_5) = 2 \times M(P) + 5 \times M(O) = 2 \times 31 + 5 \times 16 = 142 \text{ g/mol}; \quad (12)$$

$$M(Ca_5(PO_4)_3F) = 5 \times M(Ca) + 3 \times (M(P) + 4 \times M(O)) + M(F) = 5 \times 40 + 3 \times (31 + 4 \times 16) + 19 = 504 \text{ g/mol}; \quad (13)$$

$$M(H_2SO_4) = 2 \times M(H) + M(S) + 4 \times M(O) = 2 \times 1 + 32 + 4 \times 16 = 98 \text{ g/mol}; \quad (14)$$

$$n(P_2O_5) = \frac{m_t(P_2O_5)}{M(P_2O_5)} = \frac{1\,000\,000 \text{ g}}{142 \text{ g/mol}} = 7\,042.25 \text{ mol}; \quad (15)$$

The reaction of 2 moles of Ca₅(PO₄)₃F produces 3 moles of P₂O₅, thus:

$$n(Ca_5(PO_4)_3F) = \frac{2 \text{ mol} \times n(P_2O_5)}{3 \text{ mol}} = \frac{2 \text{ mol} \times 7042.25 \text{ mol}}{3 \text{ mol}} = 4\,690.14 \text{ mol}; \quad (16)$$

$$m(Ca_5(PO_4)_3F) = n(Ca_5(PO_4)_3F) \times M(Ca_5(PO_4)_3F) = 4\,690.14 \times 504 = 2\,363\,830.99 \text{ g} = 2.3638 \text{ t}; \quad (17)$$

The reaction of 10 moles of H₂SO₄ produces 3 moles of P₂O₅, thus:

$$n(H_2SO_4) = \frac{10 \text{ mol} \times n(P_2O_5)}{3 \text{ mol}} = \frac{10 \times 7042.25 \text{ g}}{3 \text{ mol}} = 23\,474.17 \text{ mol}; \quad (18)$$

$$m(H_2SO_4) = n(H_2SO_4) \times M(H_2SO_4) = 23\,474.17 \times 98 = 2\,300\,468.66 \text{ g} = 2.3005 \text{ t}; \quad (19)$$

A theoretical mass of phosphate feedstock of 2.3638 t and 2.3005 t of H₂SO₄ is required to produce 1 tonne of P₂O₅ in phosphoric acid. The average yield of the 4 phosphogypsum samples tested, using different raw materials, is 95.8 %. This yield is equivalent to the average yield of the current process, therefore the quantity of phosphate feedstock required is recalculated:

$$m_f = \frac{100\% \times m_t}{w_f} = \frac{100\% \times 1\,000\,000 \text{ g}}{95.8\%} = 1\,043\,841 \text{ g} = 1.0438 \text{ t}; \quad (20)$$

$$n(P_2O_5) = \frac{m_f(P_2O_5)}{M(P_2O_5)} = \frac{1\,043\,841 \text{ g}}{142 \text{ g/mol}} = 7\,350.99 \text{ mol}; \quad (21)$$

$$n(Ca_5(PO_4)_3F) = \frac{2 \text{ mol} \times n(P_2O_5)}{3 \text{ mol}} = \frac{2 \text{ mol} \times 7350.99 \text{ mol}}{3 \text{ mol}} = 4\,900.66 \text{ mol}; \quad (22)$$

$$m(Ca_5(PO_4)_3F) = n(Ca_5(PO_4)_3F) \times M(Ca_5(PO_4)_3F) = 4\,900.66 \times 504 = 2\,469\,932.64 \text{ g} = 2.4699 \text{ t}; \quad (23)$$

$$n(H_2SO_4) = \frac{10 \text{ mol} \times n(P_2O_5)}{3 \text{ mol}} = \frac{10 \times 7\,350.99 \text{ g}}{3 \text{ mol}} = 24\,503.3 \text{ mol}; \quad (24)$$

$$m(H_2SO_4) = n(H_2SO_4) \times M(H_2SO_4) = 24\,503.3 \times 98 = 2\,401\,323.4 \text{ g} = 2.4013 \text{ t}; \quad (25)$$

Converting the required masses of raw materials to the 95.8 % production yield, the quantity of phosphate raw material required increases to 2.4699 t and H₂SO₄ to 2.4013 t. Increasing the P₂O₅ production yield to 98.9 % requires adjustments to the theoretically required quantities of P₂O₅ of phosphate feedstock and sulphuric acid.

$$m_f = \frac{100\% \times m_t}{w_f} = \frac{100\% \times 1\,000\,000 \text{ g}}{98.9\%} = 1\,011\,122 \text{ g} = 1.0111 \text{ t}; \quad (26)$$

$$n(P_2O_5) = \frac{m_f(P_2O_5)}{M(P_2O_5)} = \frac{1\,011\,122 \text{ g}}{142 \text{ g/mol}} = 7\,120.58 \text{ mol}; \quad (27)$$

$$n(\text{Ca}_5(\text{PO}_4)_3\text{F}) = \frac{2 \text{ mol} \times n(\text{P}_2\text{O}_5)}{3 \text{ mol}} = \frac{2 \text{ mol} \times 7 \text{ } 120.58 \text{ mol}}{3 \text{ mol}} = 4 \text{ } 747.05 \text{ mol}; \quad (28)$$

$$m(\text{Ca}_5(\text{PO}_4)_3\text{F}) = n(\text{Ca}_5(\text{PO}_4)_3\text{F}) \times M(\text{Ca}_5(\text{PO}_4)_3\text{F}) = 4 \text{ } 747.05 \times 504 = 2 \text{ } 392 \text{ } 513.2 \text{ g} = 2.3925 \text{ t}; \quad (29)$$

$$n(\text{H}_2\text{SO}_4) = \frac{10 \text{ mol} \times n(\text{P}_2\text{O}_5)}{3 \text{ mol}} = \frac{10 \times 7 \text{ } 120.58 \text{ g}}{3 \text{ mol}} = 23 \text{ } 735.3 \text{ mol}; \quad (30)$$

$$m(\text{H}_2\text{SO}_4) = n(\text{H}_2\text{SO}_4) \times M(\text{H}_2\text{SO}_4) = 23 \text{ } 735.3 \times 98 = 2 \text{ } 326 \text{ } 059.4 \text{ g} = 2.326 \text{ t}; \quad (31)$$

Converting the required masses of raw materials to the 98.9 % production yield of P_2O_5 , the quantity of phosphate raw P_2O_5 material required decreases to 2.3925 t and the quantity of H_2SO_4 to 2.326 t. Since the dosing of 101 t/h of phosphate raw material is designed (assume that the phosphate feedstock contains 36.6 % P_2O_5), the conversion results in a theoretical production rate of 15.4 t/h of P_2O_5 (in phosphoric acid).

Impurities in phosphate rock affect the amount of phosphate rock required for production. The apatites of Kirov, Covdor, Morocco-Casablanca and South Africa Republic contain 38.8 %, 36.6 %, 32.3 % and 36.5 % of P_2O_5 , respectively. Based on the results of the previously studied phosphate rock compositions, the Moroccan-Casablanca phosphate rock was found to contain the highest amount impurities. It was experimentally determined that in order to produce 1 t of P_2O_5 in phosphoric acid required 7.95 t of Moroccan-Casablanca raw material. The quantities of phosphate rock mix required to produce phosphoric acid were calculated for P_2O_5 yields of 95.8 % and 98.9 %. Fig. 12 shows that the Kirov has the lowest 0.2 t reduction in phosphate rock and Morocco-Casablanca the highest 0.24 t.

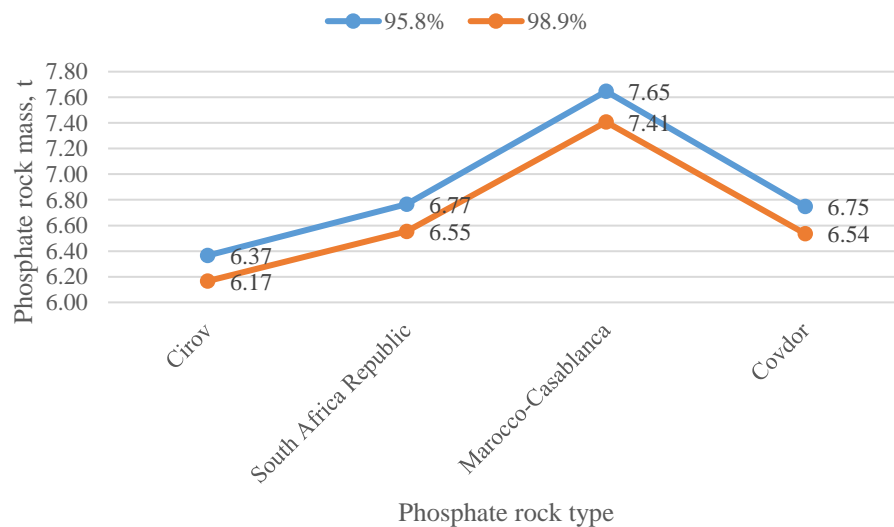


Fig. 12. The quantities of phosphate rock needed to produce 1 tonne of P_2O_5 , using the HH process with production yield 95.8 % and HH-DH process with production yield 98.9 %

The results in Table 15 represents that, in terms of the variation in the required mass of phosphate rock, when the price of all raw materials is defined as EUR 200 per ton, the most cost-effective option would be to use Moroccan-Casablanca raw material. The large particle fraction of Morocco-Casablanca's sample and high content of impurities leads to a higher use of phosphate rock to produce 1 t of phosphoric acid. Therefore, in view of these drawbacks, this raw material was not selected as the most suitable raw material for the upgrade of production.

Based on the composition of the raw materials, Covdor was found to be the best raw material. Therefore, by upgrading the production process to HH-DH and achieving a yield of P₂O₅ 98.9 %, it is theoretically estimated that 0.21 t less raw material will be needed to produce 1t P₂O₅, resulting in a saving of EUR 653.04/h. If phosphoric acid is produced 300 days a year due to planned maintenance, the final estimated theoretical amount of money saved is EUR 4,701,888.

Table 15. At 98.9% P₂O₅ production yield, estimated teoretical amount of money to be saved of phosphate rock and amount of money needed to produce 1 t of P₂O₅

Phosphate rock	Phosphate rock mass, t	Estimated amount of money to be saved per production P ₂ O ₅ tone, EUR	Estimated amount of money to be saved per hour, EUR
Kirov	0.20	39.90	653.11
South Africa Republic	0.21	42.41	653.98
Morocco-Casablanca	0.24	47.93	653.23
Covdor	0.21	42.30	653.04

In summary, the payback of the project can be deduced from the increased raw material yields, which will result in more P₂O₅ being produced with the same amount of raw materials. Thus, with an annual theoretical saving of EUR 4,701,888, the project will for itself in 3.8 years.

4.2. The payback of a production process project using raw material and resources

The main raw materials for the production process are phosphate rock and sulphuric acid, while the main energy sources are electricity and steam power. For the use of Covdor, Morocco-Casablanca and South Africa as phosphate rock, the cost of producing 1 tonne of P₂O₅ was determined. Calculations have been carried out by estimating the consumption of phosphate rock, sulphuric acid, electricity and steam energy. The calculations are based on a price of H₂SO₄ of 250 EUR/t, all phosphate rock of 200 EUR/t and electricity of 0.167 EUR/kWh. P₂O₅ and H₂SO₄ dosages for the HH process determined experimentally at plant X during phosphoric acid production. The phosphate feedstock rates (2.6936 t; 3.3194 t; 2.8928 t) are not the same as the theoretical P₂O₅ rate (2.3925 t). This is explained by the different reaction yields due to impurities in the raw materials and the size of the fractions.

The results is given in Table 16. It is clear, that changing the process will increase the electricity consumption per tonne of P₂O₅ produced by 32.8 kWh. Meanwhile, the steam energy required decreases from 0.88 Gcal to 0.7319 Gcal. The steam energy converted into kWh for the HH process is 900.03 kWh, while for the HH-DH process it is 748.56 kWh. Therefore, the total kWh consumption for the HH process is 1023.03 kWh and for the HH-DH 904.36 kWh. This corresponds to EUR 170.85 and EUR 151.03 expences for electricity. This year, the price of electricity per kWh is expected to rise to EUR 0.3. It is therefore important to consider that the total cost of electricity would then increase to EUR 271.31 per 1 t of P₂O₅ produced which is 1.8 times higher expenses for electricity. Process improvements have the greatest impact on the cost of sulphuric acid and phosphate feedstock when Moroccan-Casablanca apatite is used. Production requires 0.0172 t less of apatite and 0.0153 t less of sulphuric acid to produce 1 tonne of P₂O₅.

Table 16. Resource expenses to produce 1 tonne of P₂O₅ by HH and HH-DH processes

	Resource	HH	HH expenses, EUR	HH-DH	HH-DH expenses, EUR
Covdor	P ₂ O ₅ , t	2.6936	1471.91	2.6797	1464.32
	H ₂ SO ₄ acid, t	2.5	625.00	2.4871	621.78
	Electricity, kWh	123.0	20.54	155.8	26.02
	Steam energy, Gcal	0.88	170.80	0.7319	142.06
	Total		2288.25		2254.18
Morocco-Casablanca	P ₂ O ₅ , t	3.3194	2055.36	3.3022	2044.71
	H ₂ SO ₄ acid, t	2.965	741.25	2.9497	737.43
	Electricity, kWh	123	20.54	155.8	26.02
	Steam energy, Gcal	0.88	170.80	0.7319	142.06
	Total		2987.95		2950.22
South Africa Republic	P ₂ O ₅ , t	2.8928	1585.10	2.8778	1576.88
	H ₂ SO ₄ acid, t	2.59	647.50	2.5766	644.15
	Electricity, kWh	123.0	20.54	155.8	26.02
	Steam energy, Gcal	0.88	170.80	0.7319	142.06
	Total		2423.94		2389.11

After the process is changed to HH-DH, the biggest savings are to be made with Morocco-Casablanca (EUR 37.73). Meanwhile, Covdor's savings to produce 1 tonne of P₂O₅ is the lowest EUR 34.08.

Table 17. Practical savings from the production of phosphoric acid in the HH-DH process

Phosphate rock	Savings in raw materials, EUR			
	1 tone	1 hour	1 day	1 year
Covdor	34.08	526.13	12,627.06	3,788,119.46
Morocco-Casablanca	37.73	514.26	12,342.29	3,702,686.47
South Africa Republic	34.83	537.07	12,889.58	3,866,874.67

However, considering that the dosage of materials for continuous production will be 101 t/h, the results vary due to different amounts of P₂O₅ involved in the production reaction during the dosing of different phosphate rocks. This means that the 32.3 % P₂O₅ in Morocco-Casablanca produces less phosphoric acid, resulting in a practical saving of EUR 3,702,686.47 compared to the savings of EUR 3,788,119.46 in Covdor (36.6 % P₂O₅) and the savings of EUR 3,866,874.67 in South Africa (38.8 % P₂O₅). The project would then pay for itself after 8.6 months. It can be concluded that most of the savings are due to reduced energy expenses (19.82 EUR/1t P₂O₅). That is almost half of the savings. Reducing energy consumption reduces emissions to the environment, so the project not only produces a more concentrated acid and cleaner phosphogypsum, but also contributes less to environmental pollution. The results show that Morocco-Casablanca would be the most appropriate choice of raw material in order to save money. However, after taking into account all the criteria investigated, the best raw material for production was found to be the phosphate rock of Covdor. Thus, the project would pay for itself in 4.7 years, with daily savings of EUR 12,627.06 if the proposed upgrade of the production using the Covdor raw material is implemented. The theoretical savings of raw materials without considering the influence of impurities and fraction on the reaction are higher. The practical energy savings and the experimentally determined different doses of feedstock increase the payback

period. Thus, the practical payback period of the investment in the use of Covdor raw material is 4.7 years, with annual savings of EUR 3,788,119.46.

4.3. Investment in the improvement of the Quality Control Department

The Quality Control Department ensures that the raw materials and the final product complies with the specified parameters. This is achieved when laboratory technicians do their job thoroughly and efficiently. This requires analytical equipment and various analytical methods. Of course, funding is needed for quality assurance. However, these expenses must be included in the cost of producing premium quality product. Thus, a higher profit margin is achieved when the final product is of better quality.

After the reconstruction of the phosphoric acid plant, the H_3PO_4 acid will be stronger and will contain fewer impurities. This will affect fertilizer production facilities. Doses of Raw material, possibly temperatures and gases, will change in the production processes. As the production process has to produce diammonium phosphate and mineral fertilisers with a fixed composition of sulphur compounds.

The project is expected to pay for itself in about 5 years, and the changes will continue to generate profit for the company each year. Therefore, this amount could be invested in the improvement of analytical equipment. In a previous study, it was found that Elementar Analysensysteme GmbH produces Vario MAX cube analysers, which reduce the time required to determine total sulphur and nitrogen, and this equipment can work 24/7 [36]. The unit is shown in Fig. 13. The equipment takes up about 1 m². The results are displayed on a computer. Modern equipment is needed for efficient laboratory technician's work. The standard LST EN 15925: 2011 method for analysing a sulphur element takes over 3 hours. Meanwhile, the Vario Max Cube gives the results in 15 minutes and all that is needed to prepare the fertiliser sample is to crush and weigh it.

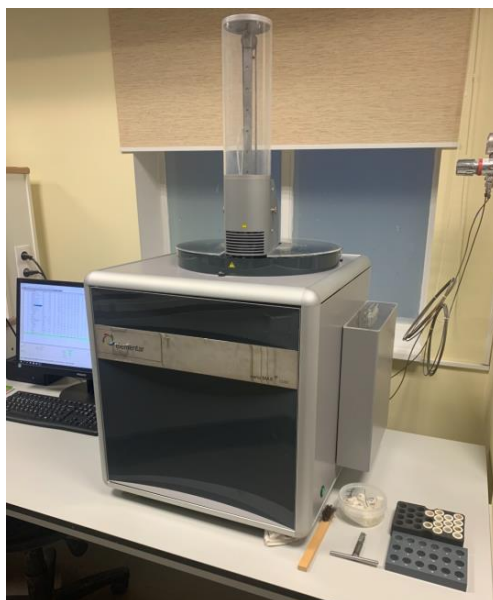


Fig. 13. Vario MAX cube equipment [36]

Part of the projected profits could be prospectively invested in the improvement of the Vario Max Cube equipment. Currently, once the analysis has been carried out, the data is transmitted to the process operator via a telephone call. One of the upgrades could be transmission of sulphur and

nitrogen results directly to the fertiliser operators' control panel, without any intermediaries, calls or messages. This would save time in transmitting and reacting to the results, avoid human error due to mixing up the results or misunderstandings during the conversation.

Table 18. Funding required for improving of the Quality Control Department

Cost centres for the project	Price, EUR
Monitors in control panels, 2 pcs	20 000
Vario Max Cube device	125 000
Helium gas cylinder, 2 pcs	400
Oxygen gas cylinder, 2 pcs	300
Computer for Vario Max Cube	3 000
Reagents for Vario Max Cube equipment for samples for 1-year	4 000
Programme development expenses	10 000
Installation of facilities for gas cylinders	2 000
Expenses of maintenance for 1 year	20 000
Expenses of staff training	10 000
Total:	194 700

The planned cost of this improvement is EUR 194 700. The expenses includes: upgrading of the computer equipment by introducing a new programme, purchase of two monitors for two control panels, installation of the equipment, expenses for testing, purchase of spare parts. Compared to the modernisation of the phosphoric acid plant, this investment is small. However, the end result will be a more efficient use of staff time, the avoidance of human error and a step towards full automation of equipment. Investment brings more than just expenses. It broadens the view of the company's situation, reveals weaknesses that, if improved, lead to better results and higher profits. To sum up, it could be said that improving production processes and searching for various solutions are inseparable from the efficient use of resources, computerisation of equipment, and the overall development of the entire company and its employees.

It has been found that a HH phosphoric acid production process upgrade to the HH-DH production process is required to obtain a higher concentration of acid and to increase the P₂O₅ yield. The analysis of 4 phosphate rock feedstocks: Covdor, Kirov, South Africa Republic and Morocco-Casablanca, showed that Covdor phosphate rock is the most suitable due to its fine fraction and the lowest impurity content. The project cost is EUR 17.8 million. Considering the energy and feedstock changes in the HH-DH process, the project will payback in 4.7 years. In anticipation of rising profits, it is worth investing in the improvement of the quality control department. To determine sulphur element, the Vario Max Cube instrument shortens the analysis time and simplifies the process of analysis. Therefore, continuous improvement and modernisation of processes and equipment is a way to increase profits and expand production capacity.

Conclusions

1. The HH-DH phosphogypsum process is not only the most suitable for the production of concentrated phosphoric acid but also produces cleaner phosphogypsum. Cleaner phosphogypsum is more suitable for secondary use, which reduces the amount of phosphogypsum accumulated in landfills
2. The phosphate rock of Covdor is best suited for the production of cleaner phosphoric acid due to its fine fraction, 36.6 % of P_2O_5 and the lowest impurity content: 0.33 % organic matter, 1.2 % fluorine and 0.19 % Al_2O_3 .
3. The project requires a new 400 m² building and dihydrate phosphogypsum production equipment, bringing the total cost of the project to EUR 17.8 million.
4. The process improvement increases the P_2O_5 production yield to 98.9 %. The payback period of the project is 4.7 years, if reduction in energy costs and experimentally determined dosages of Covdor raw material are taken into consideration.

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