INNOVATIVE AND CLEANER INORGANIC TECHNOLOGIES
Module supervisor: dr hab. inz. Marcin Banach
Laboratory Instruction No 5
PHOSPHORIC ACID PRODUCTION BY CLEANER TECHNOLOGY

REPORT:
ONE WEEK AFTER THE END OF THE CLASS

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Projekt „Międzynarodowy program kształcenia Innowacyjne Technologie Chemiczne”
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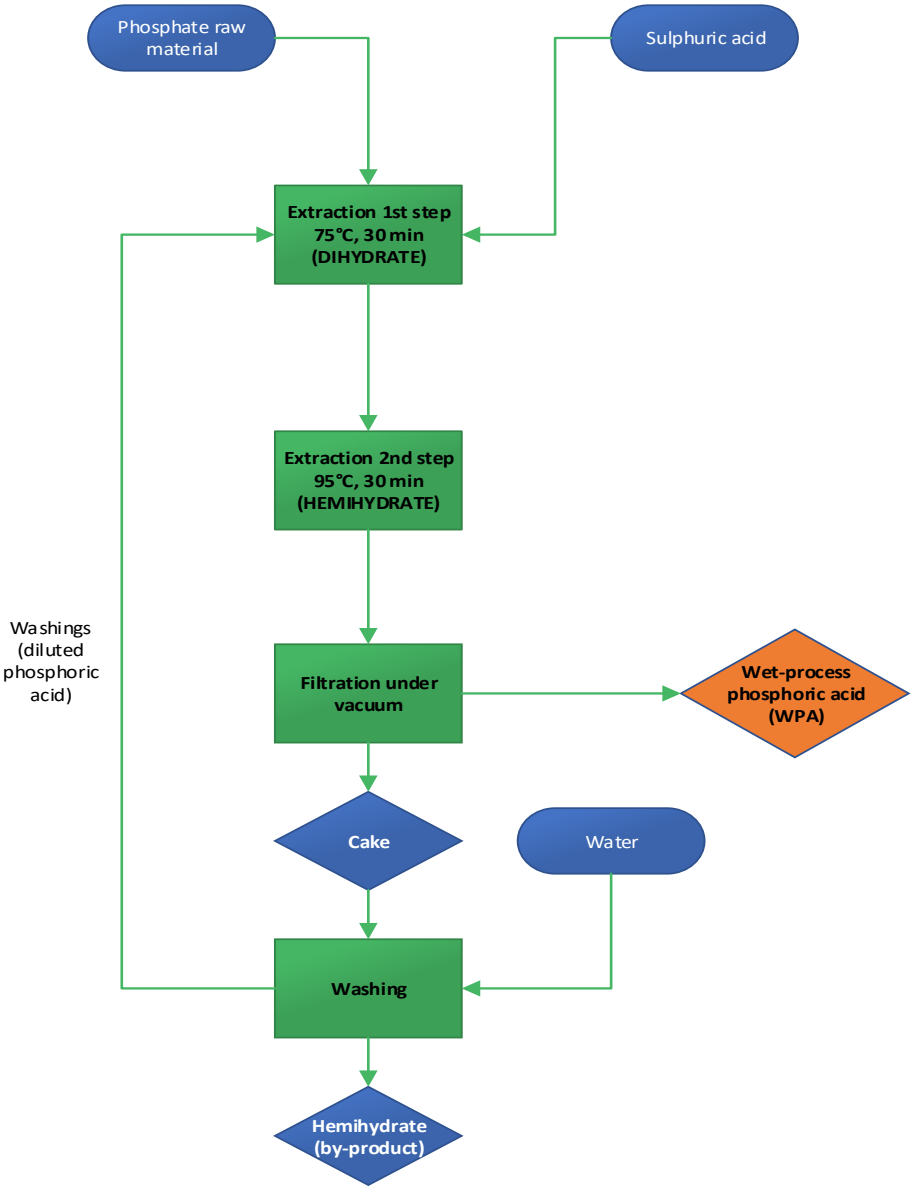

Figure 1. Scheme of the wet-process phosphoric acid production using dihydrate-hemihydrate method

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1. Subject of the exercise

The main goal of the exercise is to obtain phosphoric acid using wet-process method. The proposed method is a dihydrate-hemihydrate process which allows obtaining hemihydrate as a by-product which can be used as a substitute for natural gypsum in building industry. The assumptions were taken from the Patent of the Prayon Technologies Company[1] and Handbook of R. Gilmour[2].

2. Equipment

- Polypropylene reactor
- thermostat
- kit for the filtration under lowered pressure (Büchner funnel, suction flask, vacuum pump)
- moisture analyzer

3. Chemical reagents

- Phosphoric acid, concentrated (p.a., pure or technical grade)
- Sulphuric acid, concentrated (p.a., pure)
- Raw materials: phosphate rock (apatite or phosphorite)

4. Description of the process

The extraction process is conducted in a polypropylene reactor with mechanical stirrer, placed in the thermostat. First stage of the extraction is conducted at 75°C for 30 min and subsequently the temperature is raised to 95°C. The process is carried on for further 30 min (Fig. 1).

The substrates for the process are:

- Phosphate raw material
- Sulphuric acid for raw material decomposition
- Washings/filtrate – diluted phosphoric acid recycled for the process after filtration of the phosphogypsum

5. Basic assumption for the process - calculations

As a prerequisite for the exercise some basic calculation of the amount and/or concentration of the reagents must be done. Thus, the following values must be calculated:

- Weight of the concentrated sulphuric acid
- Weight of the washings (diluted phosphoric acid)

[1] Patent US 9255006 B2,Method for producing phosphoric acid, Prayon Technologies

[2] R. Gilmour, Phosphoric acid. Purification, uses, technology and economics. Animal feed phosphates, CRC Press, 2014:

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- Concentration of the washings – how much water and concentrated H_3PO_4 must be taken to the process?

The main assumptions were listed below:

1) The calculation should be conducted for 100 g of phosphate rock (the raw material is selected and provided by the tutor)
2) The amount of H_2SO_4 should be used in stoichiometric amount, according to the calcium content in the raw material and following reaction (Eq.1):

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 2{,}5\ H_2O = 3\ H_3PO_4 + HF + 5\ CaSO_4 \cdot ½\ H_2O \quad (1)$$

3) The final product (phosphoric acid) contain 95% of the phosphorus present in the substrate (phosphate rock) – the efficiency of the extraction process.
4) The phosphate recycle to the process with washings is:

$$\frac{P_2O_{5\ recycled}}{P_2O_{5\ product}} = 1.43$$

5) The washings amount is tripled weight of the raw material.

In table 1 the chemical composition of the selected raw materials were presented.

Table 1. Elemental analysis of the selected phosphate rocks

Phosphate rock	$\%P_2O_5$	$\%Fe_2O_3$	%Ca	% Substances insoluble in acid
Florida phosphorite	31.5	0.77	32.4	**4.4**
Morocco phosphorite	29.8	0.56	33.1	**4.2**
Kola apatite	**29.5**	**0.87**	**33.2**	**3.4**

The whole calculations must be checked and approved by the tutor.

6. Exercise contents

Extraction

1) Set a thermostat at 75°C (it must be placed under the fume hood).
2) Weight on technical balance previously calculated amounts of the substrates.
3) Place PP reactor in the thermostat and mount stirring rod made of Teflon. Check proper fixation of the equipment.
4) Pour all liquid substrates into the reactor, turn on the stirring.

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5) Gently and slowly start adding phosphate rock into the reactor in small portions.
6) Increase stirring speed if necessary.
7) When dosing is completed, leave the mixture for 30 min in the thermostat.
8) Afterwards, change the thermostat settings at 95°C and leave for further 30-40 min.

Filtration

1) Turn off the stirring and the thermostat.
2) Remove gently the reactor from the hot water bath.
3) Mount the kit for filtration under vacuum.
4) Separate and collect the product – wet-process phosphoric acid.
5) Wash the cake with distilled water (ca. 100 mL) and collect washings separately.
6) Take sample of the phosphogypsum and dry it on moisture analyzer (105°C). Leave the dried sample for the XRD analysis in double plastic bag in desiccator.
7) Leave the by-product (hemihydrate) for drying o.n. (overnight) for further analysis.

Density determination

In order to calculate the phosphorus mass balance, the density of the solutions (phosphoric acid and washings solution) must be determined as follows:

Using the automatic pipette at volume range 100-1000µL weight on the analytical balance 1.00 mL of the solution in a weight bottle. The final value should be the arithmetic mean of 3 repeating.

Mass balance

In table 2 the value necessary for the mass and phosphorus balance were collected. The phosphorus determination in the products will be conducted on the next laboratory classes **(Ex. 2).**

Table 2. Values for the mass balance

	Mass, g	Density, g/cm^3	Phosphorus content, %P_2O_5 or g P_2O_5/dm^3	Mass of phosphorus, calculated as P_2O_5, g
Substrates				
Phosphate rock				
Washings solution				
Sulphuric acid				
Products				
Phosphoric acid (WPA)				
Washings solution				
Phosphogypsum (hemihydrate)				

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7. Report requirements

The final report should summarize Exercise 1a and 1b and comprise:

- Initial Calculations
- Descriptions of the experimental part
- Results of the products analysis with analytical methods description
- Mass balance for materials and phosphorus (calculated as P_2O_5)
- Comment about the result of the XRD analysis of the solid by-product
- Conclusions, reference to the cleaner production

Appendix 1

Brochure, Prayon Process for phosphoric acid production, 2012

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