

RESEARCH OF THE PROCESS OF SYNTHESIS OF DIAMMONIUM PHOSPHATE FROM EXTRACTIVE PHOSPHORIC ACID FROM BALANCED PHOSPHATE- SILICON SHAPES OF THE KARATAU BASIN

**K.T Zhantasov¹, A.A. Kadirbayeva¹, N.D. Torebay², G.S. Shaimerdenova^{1,✉},
Z.A. Makhanova¹, K.U. Nyshanbayeva¹, A.B. Seitkhanova¹
and E.B. Mussirepova¹**

¹M. Auezov South Kazakhstan University, Tauke Khan av.5, 160001, Shymkent, Kazakhstan

²Miras University, Sapak Datka St.2, 160000, Shymkent, Kazkhstan

✉Corresponding authors: g.shaimerdenova@bk.ru

ABSTRACT

The article describes the process of obtaining extraction of phosphoric acid from phosphate-siliceous phosphorite shales of the Zhanatas deposit, by the sulfuric acid extraction method of obtaining EPA for use in the production of diammonium phosphate. Extraction decomposition of phosphorite by sulfuric acid proceeds with the formation of phosphogypsum and with fluorine released into the gas phase in the form of HF and SiF₄ and processed into H₂SiF₆. The studies were carried out using circulating solutions of EPA with a concentration of 3.80-18.91% P₂O₅, phosphorite with a content of, (wt. %) P₂O₅ - 18.14; MgO - 13.43; Al₂O₃ -1.01; CaO - 25.1; F - 0.58; CO₂ - 19.55, etc., sulfuric acid concentration of 92.5% was diluted to 50%. The norm of sulfuric acid is 100% of stoichiometry for CaO and MgO. The impurities Fe₂O₃ and Al₂O₃ present in phosphorite by 82-91% are extracted into the phosphogypsum precipitate in the form of medium phosphates. Fluorine introduced with phosphate raw materials into the extraction stage passes into the production acid by 60-70%, 10-20% – into phosphogypsum, and in a small amount 8-12% is released into the gas phase. The resulting EPA product can be used in the production of diammonium phosphate

Keywords: Extraction Phosphoric Acid, Phosphorite, Decomposition, Extraction, Evaporation, Processing Of Phosphate Raw Materials.

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INTRODUCTION

Kazakhstan is one of the largest regions in the world, which has significant reserves of mineral raw materials and prospects for expanding their use in various branches of the chemical industry. One of the promising directions of chemical processing of phosphorite is its decomposition with sulfuric acid by the dihydrate method to obtain phosphoric acid. Acid processing of phosphate raw materials is the main method of obtaining phosphoric fertilizers, where sulfuric, nitric and phosphoric acids, and to a small extent hydrochloric acid, is used most widely in technological cycles for these purposes. The production of highly concentrated fertilizers from phosphorites of the Karatau basin of the Republic of Kazakhstan requires deeper enrichment, with the production of concentrates containing more than 30% P₂O₅ and MgO less than 1%, or additional purification of extraction phosphoric acid from impurities and especially from magnesium and fluorine since iron and sulfur can play the role of micronutrients.¹ Phosphorus and its compounds are of exceptional importance for the processes of vital activity, being irreplaceable components of nerve and brain tissues of bones, and other protein compounds. Plants absorb a significant amount of phosphorus from the soil, which is replenished by introducing phosphorus-containing fertilizers such as amorphous, superphosphate, precipitate, etc. The global demand for fertilizers increases in proportion to the growth of the population. By the end of the first decade of the XXI century, the annual consumption of phosphate raw materials reached 166 million tons.² The consequence of this is the aggravation of the unclosed phosphorus cycle.³ Despite the fact that the world's reserves of phosphate ores are huge, they belong to exhaustible resources since the natural return of phosphorus to the natural

cycle is not compensated by its quantitative consumption. Acid processing of phosphate raw materials is the main method for obtaining phosphorus fertilizers, where sulfuric, nitric and phosphoric acids are used most widely in technological cycles for these purposes, and to a small extent hydrochloric acid. A number of data on industrial acid processing of poor phosphorites are presented in the literature, mainly in the form of developments. However, global trends indicate a desire to reduce the involvement of high-grade phosphate raw materials in industrial production by replacing them with lower-grade ones during processing. It should be noted that low-grade raw materials are used not as an independent component, but as an additive to high-grade raw materials.^{6,7} Processing of natural phosphate raw materials by sulfuric acid extraction is mainly in various variants and has been studied most fully.^{4,5} Depending on the type of precipitated calcium sulfate, there are 3 methods for obtaining extraction of phosphoric acid: decomposing natural phosphorites with sulfuric acid, dihydrate, hemihydrate (semi-hydrate), and anhydrite. In addition, there are combined methods of dihydrate-hemihydrate, and hemihydrate-dihydrate. However, the dihydrate method is widely used and the semi-hydrate method is less common. The anhydrite method is not yet used on an industrial scale.⁴ There is information in the literature on the production of EPA (extractive phosphoric acid) from phosphate-siliceous shales of the Zhanatas deposit by the dihydrate-semihydrate method.⁸

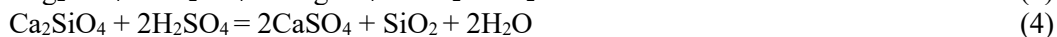
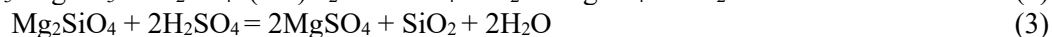
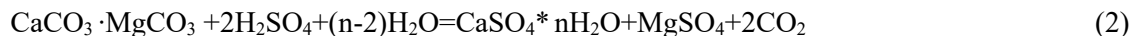
EXPERIMENTAL

We have studied the process of obtaining extraction of phosphoric acid from off-balance phosphorite of the Zhanatas deposit, by the sulfuric acid extraction method of obtaining EPA for use in the production of diammonium phosphate. For the production of concentrated phosphoric and complex fertilizers, phosphoric acid containing 37-55% P₂O₅ or more is required, and for the production of ammonium polyphosphates and concentrated liquid fertilizers, an acid containing 72-83% P₂O₅ is required. Therefore, in many cases, the extraction of phosphoric acid is subjected to concentration by evaporation.⁴ The essence of the method is the processing of natural crushed phosphate raw materials with an excess of sulfuric acid, followed by filtration of the resulting suspension to separate the phosphoric acid from the precipitated calcium sulfate. After the filtration stage, part of the obtained main filtrate and the washing waters obtained during the first washing of the sediment on the filter is returned to the extraction process (dilution solution) to ensure good mobility of the pulp during its mixing and transportation. The dilution solution is a mixture of the main filtrate and washing water obtained after the first washing of the sediment gypsum. The mass ratio between the liquid and solid phases is maintained in the range W: T = 2:1 to 3.5:1.^{4,5}

During the decomposition of natural phosphate, the extraction process is carried out by a mixture of aqueous solutions of sulfuric and phosphoric acid according to the total reaction equation:



The phosphoric acid solution obtained after the separation of phosphogypsum is contaminated with impurities that have passed into the solution: silica, sulfates, and phosphates of iron, aluminum, magnesium, etc. Simultaneously with the phosphate, other impurities that are part of the raw material are decomposed. For example, when decomposing dolomite and magnesium silicates, magnesium sulfate passes into the solution:



Depending on the decomposition conditions, 5-30% of the fluorine contained in the raw material passes into the gas phase, the rest remains in the pulp, where it is in the form of H₂SiF₆ and partially interacts with sodium, potassium, and calcium salts to form poorly soluble Na₂SiF₆, K₂SiF₆, CaSiF₆, and others.

Phosphate raw materials containing a lot of iron and aluminum oxides are unsuitable for the production of EPA. Especially harmful is the admixture of iron Fe₂O₃: P₂O₅ = (8÷10): 1, because, during the extraction process, supersaturated solutions are first formed, from which iron phosphates are gradually released into

the precipitate, which leads to losses of P_2O_5 with the precipitate. Thus, the impurities contained in the phosphate raw materials complicate the extraction process, worsen its performance, and reduce the quality of the products obtained:

- The consumption increases H_2SO_4 ,
- The released CO_2 forms a persistent foam in the extractors,
- Soluble phosphates of magnesium, iron and aluminum reduce the activity of phosphoric acid,
- the precipitation of phosphate hydrates from supersaturated solutions of one-and-a-half oxides

reduces the yield of P_2O_5 in phosphoric acid, impurities in the production waste are calcium sulfates, making their further use difficult. The basis for choosing the technological parameters of phosphate extraction processes is the isolation of calcium sulfate in the form of sufficiently large, easily separated, and well-washed crystals from phosphoric acid. Under production conditions, the resulting precipitate is contaminated with P_4O_{10} impurities in the form of undecomposed phosphates, unwashed H_3PO_4 , etc. Therefore, the resulting calcium sulfates are called phosphogypsum, phosphohemihydrate, and phosphoanhydrite, respectively.

To obtain extraction of phosphoric acid (Figure 1), it includes a reactor-beaker 1 with a capacity of 400-500 ml with one or two agitators 5 driven by electric motors 4. Through a hole in the lid of the beaker, the initial materials are loaded and pulp samples are taken. The reactor is placed in a water thermostat 9, equipped with an electric heater 6, adjusted to a certain temperature. The set temperature is maintained by means of a relay 8 connected to heater 6 and a contact thermometer 7. To prevent water evaporation during the extraction process, the reactor is equipped with a reverse refrigerator 3.

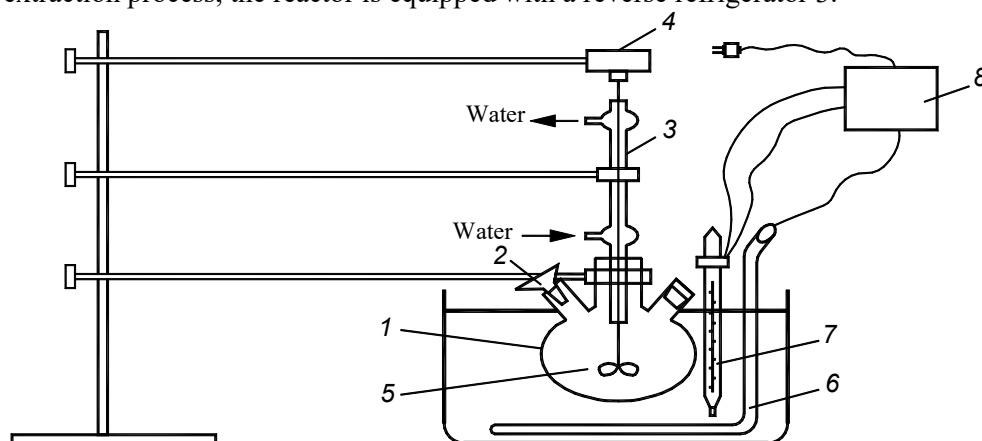


Fig.-1: - Installation Diagram for Obtaining EPA:

1-flask, 2-funnel, 3-reverse refrigerator, 4-motor, 5-agitator, 6-heater, 7-contact thermometer, 8-relay, 9-thermostat

The calculated amount of dilution solution and sulfuric acid is poured into the reactor intended for the production of phosphoric acid, the reactor is placed in a water thermostat heated to a temperature of $80^{\circ}C$, depending on the extraction mode, and a stirrer is turned on. After warming up the mixture of solutions for 30 minutes, a predetermined amount of crushed phosphate raw materials is gradually poured into the reactor with the agitator running and the reaction start time is noted. In agreement with the teacher, the initial materials can be loaded into the reactor in the following sequence: dilution solution - phosphate raw materials - sulfuric acid. The reaction start time, in this case, is noted from the moment of mixing the phosphate raw material with the dilution solution. The decomposition of phosphate raw materials is carried out within 2-4 hours.⁹ At the end of the experiment, the extraction pulp is filtered on the Buchner funnel, creating a vacuum in the Bunsen flask. Previously, a filter is placed in the funnel and the vacuum is set on the filter unit. To do this, turn on the vacuum pump and when the tap is closed, a vacuum of 0.04 - 0.05 MPa, measured by a vacuum meter, is set using the tap. Then the extraction pulp is transferred to the funnel, and at the same time the tap is opened and the start time of filtration is recorded by a stopwatch. Note the time during which the sediment surface on the filter is released from the liquid (the so-called "rough suction" time or the time of "clarification" of the sediment surface). Then continue filtering and mark the time of complete cessation of liquid droplets from the funnel (the time of "drying

the sediment”). Then the filtrate is poured into a pre-weighted measuring beaker, and the volume of the filtrate and its mass is determined. The sediment on the funnel is washed 2-3 times with distilled water heated to 60-70°C, each time, pouring enough water so that it covers the surface of the sediment by 0.5-1 cm. The washing waters are collected separately from the filtrate, and their volume and mass are determined. The precipitate (phosphogypsum) is carefully removed from the funnel, placed in a porcelain cup, and dried at a temperature of 100-105°C to a constant mass. In the filtrate and washing waters, the content is determined P_2O_5 by the photocolorimetric method, in phosphogypsum-the content of P_2O_5 , P_2O_5 , P_2O_5 .

RESULTS AND DISCUSSION

The studies were carried out on a laboratory installation using recycled solutions of EPA concentration 3,80-18,91% P_2O_5 , phosphorite with content, (wt.%) P_2O_5 – 18,14; MgO – 13,43; Al_2O_3 – 1,01; CaO – 25,1; F – 0,58; CO_2 – 19,55 and others, sulfuric acid concentration 92,5% they were diluted to 50%. The norm of sulfuric acid is 100% of the stoichiometry for CaO and MgO. The results of the study are shown in Table-1.

Fig.-2. During the study on the «Avatar 370 CsI» IR-Fourier spectrometer, the spectra were obtained in the spectral range of 4000-300 cm^{-1} , when using preparations in the form of a tablet prepared by pressing 2 mg of the sample and 200 mg of KBr. Prefix for the experiment: Transmission E. S. P. When studying the phosphate-siliceous raw materials of the Zhanatas deposit, it was found that it contains in its composition:

- $Ca_5(PO_4)_3F$ – 1094, 1045, 965, 603, 577, 570, 471 cm^{-1} .
- SiO_2 – 798, 779, 694, 521, 471, 396 cm^{-1} .
- $CaMg[CO_3]_2$ – 1454, 880, 729 cm^{-1} .
- $CaM[CO_3]_2$ – 1432, 880, 729 cm^{-1} .

In addition, as shown in Figure 2, during the X-analysis, the possibility of the presence of:

- $CaCO_3$ – 1432, 714 cm^{-1} .
- $FeCO_3$ – 1432, 865 cm^{-1} .

Table-1 presents the results of studies on the production of EPA from phosphate-siliceous shales at a temperature of 80 °C and the extraction process time of 4 hours (240 min).

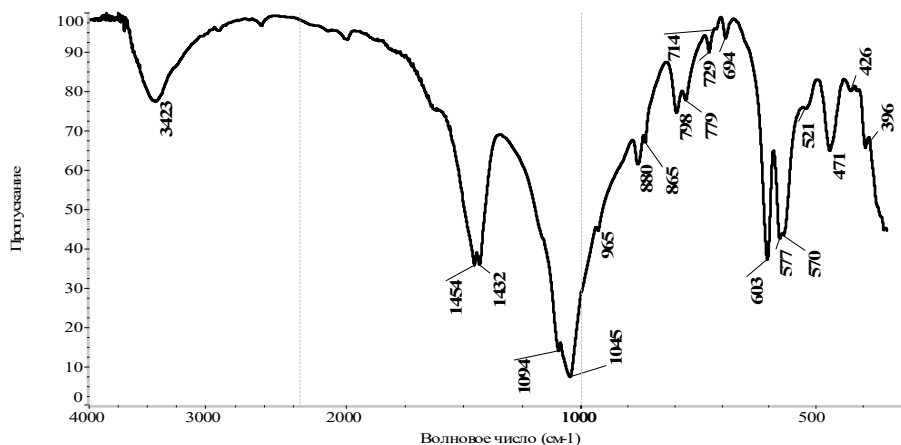


Fig.-2: X-analysis of Phosphate-Siliceous Shales of the Zhanatas Deposit

The analysis of Table-1 shows that when treated with 50% sulfuric acid, there is abundant foaming, while after 15 minutes the degree of decarbonization is 45.4% and a foam mass is formed. In the case of processing this mass at the second stage, there is almost the same abundant foaming as in the first.

In the case of treatment of phosphorite with 90% sulfuric acid diluted with recycled EPA, the degree of decarbonization practically reaches more than 85%, and at the second stage, when processing the remaining recycled EPA or circulating pulp, foaming is practically not observed, and the decomposition coefficient can reach 92-94% or more, depending on the ratio of W: T in the system, the concentration of P_2O_5 in the solution and the duration of extraction. However, the filtration rate, the washing coefficient,

and the output coefficient of P_2O_5 are reduced. Therefore, the extraction process was further studied after decarbonization using 50% sulfuric acid.

In particular, the effect of the P_2O_5 content in recycled phosphoric acid on the techno-analytical parameters of the extraction process was studied.¹⁰ The chemical analysis given in Table-1 of EPA and phosphogypsum obtained by decomposition of reverse phosphorite with a content of 3.80-13.91% P_2O_5 showed that the decomposition process takes place almost completely, quite easily, and quickly without excess sulfuric acid at 80-85°C in 2 hours. At the same time, there is no intensive foaming. This makes it possible to effectively use the reaction volume of extractors.

Table-1: Chemical Composition of EPA and Phosphogypsum from Phosphate-Siliceous Shales of the Zhanatas Deposit. The Temperature is 80°C, The Duration is 4 Hours.

No. Experiments	Content P_2O_5 in the reverse EPA, %	Content of the components in the extraction of phosphoric acid, %						Content of components in phosphogypsum, %			K_{output} , %
		P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	F	P_2O_5	P_2O_5	P_2O_5	
1	0	18,80	0,58	0,10	0,15	0,07	0,15	0,92	0,17	0,20	92,80
2	3,80	19,98	0,45	0,11	0,17	0,12	0,13	0,81	0,21	0,28	93,66
3	6,98	16,84	0,47	0,18	0,150	0,14	0,10	0,65	0,24	0,30	94,91
4	12,89	18,95	0,50	0,26	0,16	0,18	0,19	0,60	0,27	0,36	95,31
5	18,95	19,91	0,50	0,30	0,21	0,29	0,18	0,80	0,25	0,38	93,74

The optimal temperature, W: T in the system, the norm of sulfuric acid, the total duration of the process, and the dosage time of sulfuric acid are selected 75-80°C, 3:1, 100%, 4 hours, respectively. The table shows that when using a circulating EPA with a concentration of 12.89-18.95%, an EPA with a content of 18.95-19.91% P_2O_5 is obtained with the achievement of K_{output} and K_{interm} 91.47 and 96.7%, respectively. Based on the results of the study, a principal technological scheme for obtaining EPA from phosphate-siliceous shales of the Zhanatas deposit was developed, shown in Fig.-3.

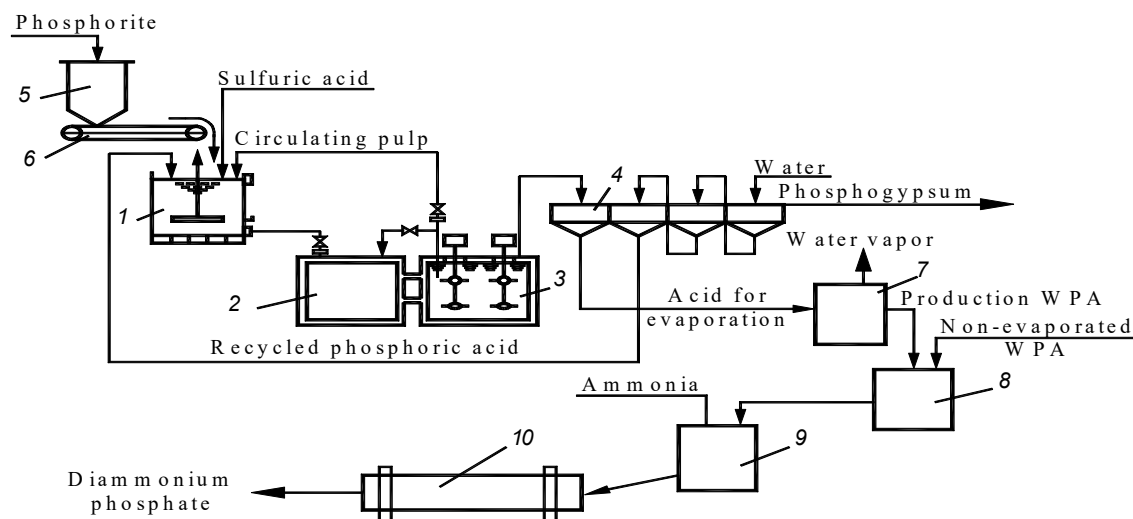


Fig.-3: Basic Technological Scheme for Obtaining DAP from Extraction Phosphoric Acid Obtained from Phosphate-Siliceous Shales of The Zhanatas Deposit
1-reactor, 2,3-extractor, 4-filter, 5-hopper, 6-dispenser, 7-acid evaporation apparatus, 9-neutralizer, 10-drum granulator-dryer

In the developed technological scheme, phosphate-siliceous shale phosphorite is subjected to preliminary decarbonization and decomposition with a mixture of sulfuric and recycled phosphoric acids before dosing into the extractor. As a result of leaching, a pulp is formed in the reactor (pos. 1), which is sent to the extractor (pos. 2), where it is treated with the remaining recycled EPA and circulating pulp. The production extraction of sulfuric acid pulp after the extractor (pos. 3) is fed to the filtration stage into the

filtration unit (pos. 4). The filtrate obtained at the filtration is fed to the evaporation stage to increase the concentration of the production acid. The remaining filtrates are used as recycled phosphoric acid.¹¹⁻¹² The process of evaporation of the acid is carried out at a temperature of 80-90°C until an EPA concentration of 50% H₃PO₄ is obtained. The evaporated acid is mixed with the production EFC in the ratio in the mixer (pos.8) and acid with a concentration of 65% H₃PO₄ is obtained, which is sent to the neutralization, drying, and granulation stage in the granulator-dryer drum. The stage of neutralization of the mixture of evaporated and not evaporated is performed using ammonia according to the traditional scheme.

CONCLUSION

As the results of the analysis of EPA and phosphogypsum for the content of various components show (Table. 1), the magnesium content varies over the entire range, P₂O₅ in the circulating EPA almost completely passes into the liquid phase and the concentration of MdO in the EPA samples is proportional to the content of P₂O₅. The impurities of Fe₂O₃ and Al₂O₃ present in phosphorite by 82-91% are extracted into the phosphogypsum precipitate in the form of medium phosphates. Fluorine introduced with phosphate raw materials into the extraction stage passes into the production acid by 60-70%, 10-20% – into phosphogypsum, and in a small amount of 8-12% is released into the gas phase. The resulting EPA product is evaporated and it can be used in the production of diammonium phosphate.

REFERENCES

1. R. al Rawashdeh and P. Maxwell, *Mineral Economics*, **24**, 15(2011), <https://doi.org/10.1007/s13563-011-0003-8>
2. G. Shaimerdenova, K. Zhantasov, A. Kadirbayeva, G. Shaimerdenova, G. Jussupbekova, Zh. Iztayev and B. Tastanbekova, *Rasayan Journal of Chemistry*, **14(4)**, 2273(2021), <http://doi.org/10.31788/RJC.2021.1446472>
3. G. T. Austin(1984), Shrieve's Chemical Process Industries, McGraw Hill, New York, USA.
4. Official Website of Kazphosphate LLP, <http://www.kpp.kz/products/index.php> (Available on 08.08.2021)
5. P.V.Klassen, S.V.Sushchev and D.K. Klados, *Chemical Industry Today*, **2**, 24(2010).
6. N.A. Doniyarov and I.A.Tagayev, *Materials and Geoenvironment*, **65(3)**, 157(2018), <http://doi.org/10.2478/rmzmag-2018-0016>
7. K.T. Zhantasov, A. M. Kozhakhmetova, O.B. Dormeshkin, N. K.Sarypbekova, M.K. Zhantasov, O.P. Baiysbay and A. M. Dosbayeva, *Rasayan Journal of Chemistry*, **14(2)**, 1208(2021), <http://dx.doi.org/10.31788/RJC.2021.1426344>
8. K.T. Zhantasov1, G.S. Shaimerdenova, Zh.K. Dzhanmuldaeva , A.A. Kadirbayeva, E.B. Mussirepova, *News of the Academy of sciences of the Republic of Kazakhstan*, **4(442)**, 44(2020), <https://doi.org/10.32014/2020.2518-1491.63>
9. K. Zhantasov, T. Bazhirov, A. Kadirbayeva, G. Jussupbekova, Zh. Iztayev, Z. Makhanova, *Revista de Chimie*, **71(12)**, 85(2020), <https://doi.org/10.37358/RC.20.12.8389>
10. M. Gargouri, C. Chtara, P. Charrock, Ange Nzihou, H. El Feki, *American Chemical Society*, **50(11)**, 6580(2011), <https://doi.org/10.1021/ie102237>
11. M. Gargouri, C. Chtara, P. Charrock\$, A. Nzihou, and H. El Feki, *Industrial & Engineering Chemistry Research*, **50(11)**, 6580(2011), <https://doi.org/10.1021/ie102237n>
12. B.V. Salas, M.S. Wiener and J.R.S. Martinez, *Phosphoric Acid Industry: Problems and Solutions*, *Phosphoric Acid Industry - Problems and Solutions*, IntechOpen Limited, London, UK, p.168 (2017).
[RJC-6800/2021]