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**EXAMINATION OF DYNAMICS
OF FREE MINERAL ACIDS CONTENT
DURING MANUFACTURING PROCESS
OF PAPR-TYPE FERTLIZERS**

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WOLNYCH KWASÓW MINERALNYCH
W CZASIE CYKLU PRODUKCYJNEGO NAWOZÓW TYPU PAPR**

Abstract: Partially acidulated phosphate rock (PAPR) constitute the separate group of phosphate fertilizers. Fertilizers of the PAPR type are produced as a result of the reaction of phosphate rocks with non-stoichiometric, in account of the reaction of the decomposition of fluorapatite contained in phosphate rock, amount of mineral acids. The aim of the investigations was the examination of dynamics of free mineral acids content in preparations of the PAPR type produced under laboratory scale, in respect of their application in commercial products available on the Polish market. The variable production parameters being under investigations were: the type of mineral acid and its concentration, the degree of the PAPR stoichiometric norm (η_{PAPR}), fineness of the phosphate rock applied for the production. Examinations were consisted in determination of the amount of free mineral acids in the product both directly after the acidulation process and during curing of fertilizer after time 2, 4, 7, 10 and 14 days, respectively.

Keywords: partially acidulated phosphate rocks (PAPR), mineral acids, phosphate fertilizers, available phosphate

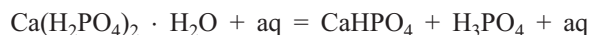
Recently, the importance of fertilizers containing partially acidulated phosphate rock has been increasing significantly. This is due to very high (reaching up to 1000 %) rises in prices of raw materials for phosphates manufacturing between the second half of 2007 to early 2009 [1]. The reason for this state is the fact that the annual world consumption of phosphates is about 35 million Mg (tons) while simultaneously the amount of extractable phosphate rock deposits, rich in P_2O_5 are being reduced. The largest deposits of phosphate rocks are located in Morocco, China and USA. These countries are the largest manufacturers of phosphate rocks. Poland, one of the producers of fertilizers (1.5 % of world production) is of no importance in the extraction of

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phosphate raw materials. It is also important that Poland is included among 10 EU countries of the largest (100–150 kg/ha of agricultural land) mineral fertilizers consumption [2]. The majority of Polish manufacturers of phosphate fertilizers declare the use of partially acidulated phosphate rock for production of phosphate fertilizers. The interest in the PAPR-type fertilizers (*partially acidulated phosphate rocks*) taking into consideration their application in industry appeared as a result of their versatility because phosphate rock of P₂O₅ content even below 20 % by weight can be used for their production whereas for the production of superphosphates content of about 30 % by weight is recommended [3–8]. Economic factors (low mineral acid consumption during the manufacturing process and reduced raw material costs due to the possibility of using low grade deposits) supporting use of the PAPR-type fertilizer are hard to ignore.

Fertilizers of the PAPR-type are produced as a result of the reaction of phosphate rocks with non-stoichiometric amount of mineral acids (usually H₂SO₄ or H₃PO₄) [3]. The product obtained by this method contains phosphorus in the form of water or neutral ammonium citrate-soluble (these are the forms available for plants), and soluble in mineral acids. Forms of phosphorus soluble only in mineral acids are released as a result of metabolic processes of the soil microflora [9, 10]. In the PAPR-type fertilizers the content of water-soluble forms of phosphorus should be at least 40 % of the declared content of P₂O₅ and for superphosphates this ratio should be at least 93 % [11]. Partially acidulated phosphate rocks contain depending on the degree of PAPR stoichiometric norm different content of available phosphates.

Free acids constitute phosphoric acid, which is formed during the following reaction:



Free phosphoric acid is essential in curing process, which consist in an enrichment of the product in available forms of phosphorus after the reaction in a reactor. Curing is a process which takes several weeks, but it is the most dynamic during the first several hours after the end of the process that runs in the reactor. Key elements of the manufacturing process that affect the content of free acids in the fertilizer product is an appropriate selection of the degree of PAPR stoichiometric norm and the time of the reaction in the reactor [3].

Materials and methods

The aim of this study was to analyze the dynamics of fluctuations of free acids content in obtained PAPR-type preparations in relation to other commercial products available on the Polish market. Variable production parameters were as follows:

- the type of acid used in the experiment and its concentration (sulfuric acid conc. 65 % w/w and 75 % w/w; phosphoric acid conc. 62 % w/w and 69 % w/w *ie* 45 % w/w and 50 % w/w of P₂O₅, respectively);
- degree of PAPR stoichiometric norm ($\eta_{\text{PAPR}} = 0,3; 0,5; 0,7; 1$) where η is the ratio of the actual amount of mineral acid used for dissolution of raw material to the theoretical amount of acid required for complete dissolution of the phosphate rock;

– fineness of phosphate rock used for the production process (fractions: 125–160 μm and 250–500 μm).

Tunisian phosphate rock samples with P_2O_5 content of 28.5 % w/w were taken into investigation procedure. The study consisted of the determination of amount of free acids in the product immediately after the acidulation process and during curing of fertilizer after 2, 4, 7, 10 and 14 days, respectively. Preparations manufacturing process was carried out in a Atlas Syrris batch reactor equipped with an Teflon reaction vessel with aluminum coating. The reactor provided ability to automatically control the process parameters such as temperature, stirring rate and reaction time. Weight of phosphate rock sample used for the production of each fertilizer preparation was 80 g and the amount of mineral acid introduced into the reactor, which was preliminary heated up to a temperature of 85 $^{\circ}\text{C}$, was dependent on the assumed degree of PAPR stoichiometric norm. The lower acid temperature than 110 $^{\circ}\text{C}$, recommended for the production of superphosphate, was decided by economic reasons [12]. Reactor operating time was 5 min. After this time the batch was unloaded and subjected to chemical analysis. Determination of the composition of obtained fertilizer products was performed using a modified “acetone method” [13]. Product sample of approximately 1 g was being weighed for appropriate test. The sample was shaken subsequently for 1 h in 25 cm^3 of organic solvents mixture, composed from acetone and 1,4-dioxane mixed in a volume ratio of 1 : 1. The sample was then filtered off using qualitative filter and washed on the filter with acetone. The filtrate was titrated with 0.1 M sodium hydroxide standard solution. Titration was performed in two stages, the first step against methyl red as indicator in order to determine the content of sulfuric acid and the first stage of dissociation of phosphoric acid, the second step of the titration was performed against phenolphthalein to determine the second stage of dissociation of phosphoric acid. As a reference point for investigated fertilizer preparations, a sample produced by using degree of stoichiometric PAPR norm $\eta_{\text{PAPR}} = 1$ was used.

Obtained preparations were evaluated for their suitability in manufacturing of fertilizer products available on the market. Commercial products of one of the Polish manufacturers were used as comparative samples. The analyzed preparations were characterized by the following contents of particular forms of phosphorus declared by the manufacturer:

- Commercial Product 1 (CP1) – 13 % w/w P_2O_5 soluble in mineral acids, 8 % w/w P_2O_5 water-soluble;
- CP2 – 10 % w/w P_2O_5 soluble in mineral acids, 8 % w/w P_2O_5 water-soluble;
- CP3 and CP4 – 10 % w/w P_2O_5 soluble in mineral acids, 2.5 % w/w P_2O_5 water-soluble. These formulations differed in the percentage of other nutrients and their use.

Results and discussion

Characteristics of the main process parameters were presented in Tables 1, 3 and 5. The free phosphoric acid (% w/w) content fluctuations during curing process of PAPR-type preparations obtained by the reaction with H_2SO_4 are shown in Tables 2, 4 and 6. Phosphate rock fineness was 125–160 μm .

Table 1

Characteristics of the main parameters of the production process of PAPR-type preparations: P1, P2, P3

	P1	P2	P3
Acid type	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄
Conc. H ₂ SO ₄ [% w/w]	75	75	75
η_{PAPR}	0.7	0.5	0.3

Table 2

Free H₃PO₄ content during curing process of PAPR-type preparations: P1, P2, P3

t [days]	P1 [% w/w]	P2 [% w/w]	P3 [% w/w]
0	8.83	4.64	3.45
2	7.36	0.69	0.40
4	2.70	0.69	0.46
7	2.00	0.69	0.41
10	1.74	0.72	0.39
14	1.52	0.67	0.40

An analysis of the results of investigations suggest that the degree of PAPR stoichiometric norm is the main factor determining the content of free acids. The smaller it is, the less content of free acids in obtained preparations can be observed. In addition, time required for curing of the product is being reduced with decreasing values of the degree of PAPR stoichiometric norm.

Table 3

Characteristics of the main parameters of the production process of PAPR-type preparations: P4, P5, P6

	P4	P5	P6
Acid type	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄
Conc. H ₂ SO ₄ [% w/w]	65	65	65
η_{PAPR}	0.7	0.5	0.3

Table 4

Free H₃PO₄ content during curing process of PAPR-type preparations: P4, P5, P6

t [days]	P4 [% w/w]	P5 [% w/w]	P6 [% w/w]
0	4.33	2.48	1.67
2	2.06	0.91	0.41
4	1.96	0.89	0.37
7	2.05	0.76	0.34
10	1.96	0.84	0.33
14	2.06	0.74	0.30

Similar dependence between value of the PAPR stoichiometric norm and dynamics of changes in free acids content occurred by using lower concentrations of sulfuric acid. In addition, the initial content of free acids was decreased for the preparations obtained by acidulation of phosphate rock with H_2SO_4 of lower concentrations.

Table 5

Characteristics of the main parameters of the production process of PAPR-type preparations: P29, P30

	P29	P30
Acid type	H_2SO_4	H_2SO_4
Conc. H_2SO_4 [% w/w]	75	65
η_{PAPR}	1	1

Table 6

Free H_3PO_4 content during curing process of PAPR-type preparations: P29, P30

t [days]	P29 [% w/w]	P30 [% w/w]
0	4.71	4.85
2	1.54	2.43
4	1.24	2.42
7	1.23	2.34
10	1.20	2.27
14	1.18	2.25

Sample of PAPR product of $\eta_{PAPR} = 1$ does not indicate dependence between the concentration of H_2SO_4 used for manufacturing process and the initial amount of free acids in the product.

Tables 7, 9 and 11 present characteristics of the main process parameters. The free phosphoric acid [% w/w] content fluctuations during curing process of PAPR-type preparations obtained by the reaction with H_2SO_4 are shown in Tables 8, 10 and 12. Phosphate rock fineness was 250–500 μm .

Table 7

Characteristics of the main parameters of the production process of PAPR-type preparations: P7, P8, P9

	P7	P8	P9
Acid type	H_2SO_4	H_2SO_4	H_2SO_4
Conc. H_2SO_4 [% w/w]	75	75	75
η_{PAPR}	0.7	0.5	0.3

Table 8

Free H₃PO₄ content during curing process of PAPR-type preparations: P7, P8, P9

t [days]	P7 [% w/w]	P8 [% w/w]	P9 [% w/w]
0	9.51	2.09	3.79
2	1.18	0.60	0.52
4	0.95	0.62	0.50
7	0.80	0.64	0.40
10	0.76	0.70	0.37
14	0.64	0.59	0.36

Alteration of the fineness of raw material had no influence on the trends observed previously. The only difference in comparison with finer size fraction is more dynamic curing process, particularly in its early stages.

Table 9

Characteristics of the main parameters of the production process of PAPR-type preparations: P10, P11, P12

	P10	P11	P12
Acid type	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄
Conc. H ₂ SO ₄ [% w/w]	65	65	65
η_{PAPR}	0.7	0.5	0.3

Table 10

Free H₃PO₄ content during curing process of PAPR-type preparations: P10, P11, P12

t [days]	P10 [% w/w]	P11 [% w/w]	P12 [% w/w]
0	2.50	1.85	1.30
2	1.13	0.95	0.60
4	0.89	0.73	0.55
7	1.02	0.76	0.49
10	0.98	0.78	0.43
14	1.08	0.74	0.37

For reduced concentration of applied H₂SO₄ the initial content of free acids is lower than in preparations produced in reaction with the acid of higher concentration. It was found that finer size fraction of the raw material increase the efficiency of the curing process in the initial stage.

Table 11

Characteristics of the main parameters of the production process of PAPR-type preparations: P31, P32

	P31	P32
Acid type	H ₂ SO ₄	H ₂ SO ₄
Conc. H ₂ SO ₄ [% w/w]	75	65
η_{PAPR}	1	1

Table 12

Free H₃PO₄ content during curing process of PAPR-type preparations: P31, P32

t [days]	P31 [% w/w]	P32 [% w/w]
0	3.58	6.59
2	1.81	3.05
4	1.56	2.57
7	1.52	2.08
10	1.47	2.00
14	1.46	1.95

Alteration in fineness of raw material in case of PAPR of $\eta_{\text{PAPR}} = 1$ does not affect dynamics of free acids content fluctuations in obtained preparations. It was observed that increasing concentration of sulfuric acid used in acidulation process caused increase of initial content of free H₃PO₄ in obtained PAPR-type fertilizer preparations. In further stages of curing process the amount of free H₃PO₄ stabilizes at a similar level, regardless of the concentration of acid used in the production process. This dependence determines effectiveness of the curing process. This dependence was not observed for $\eta_{\text{PAPR}} = 1$. In addition, fineness of raw materials used in manufacturing process had also influence on curing of the products. More dynamic curing process in its initial phase was observed for larger fractions.

Tables 7, 13 and 15 present characteristics of the main process parameters. The free phosphoric acid [% w/w] content fluctuations during curing process of PAPR-type preparations obtained by the reaction with H₃PO₄ are shown in tables 8, 10 and 12. Phosphate rock fineness was 125–160 μm .

Table 13

Characteristics of the main parameters of the production process of PAPR-type preparations: P13, P14, P15

	P13	P14	P15
Acid type	H ₃ PO ₄	H ₃ PO ₄	H ₃ PO ₄
Conc. H ₃ PO ₄ [% w/w]	69	69	69
η_{PAPR}	0.7	0.5	0.3

Table 14

Free H₃PO₄ content during curing process of PAPR-type preparations: P13, P14, P15

t [days]	P13 [% w/w]	P14 [% w/w]	P15 [% w/w]
0	2.72	2.16	1.71
2	1.95	1.63	1.04
4	1.85	1.53	0.90
7	1.81	1.48	0.72
10	1.77	1.44	0.65
14	1.50	1.34	0.55

Studies on preparations obtained by the reaction with phosphoric acid indicate that the main factor influencing the dynamics of free acids content fluctuations was the degree of PAPR stoichiometric norm. The content of free acids in preparations was reduced together with decreasing η_{PAPR} value.

Table 15

Characteristics of the main parameters of the production process of PAPR-type preparations: P16, P17, P18

	P16	P17	P18
Acid type	H ₃ PO ₄	H ₃ PO ₄	H ₃ PO ₄
Conc. H ₃ PO ₄ [% w/w]	62	62	62
η_{PAPR}	0.7	0.5	0.3

Table 16

Free H₃PO₄ content during curing process of PAPR-type preparations: P16, P17, P18

t [days]	P16 [% w/w]	P17 [% w/w]	P18 [% w/w]
0	3.46	3.14	1.89
2	2.67	2.46	1.40
4	2.48	2.35	1.19
7	2.41	2.16	1.27
10	2.32	2.13	1.07
14	2.13	1.95	1.02

Reduction of applied phosphoric acid concentration increased concentration of free acids in obtained products. In addition, the final content of free acids was higher which effects in curing process elongation.

Table 17

Characteristics of the main parameters of the production process of PAPR-type preparations: P25, P26

	P25	P26
Acid type	H ₃ PO ₄	H ₃ PO ₄
Conc. H ₃ PO ₄ [% w/w]	69	62
η_{PAPR}	1	1

Table 18

Free H₃PO₄ content during curing process of PAPR-type preparations: P25, P26

t [days]	P25 [% w/w]	P26 [% w/w]
0	3.09	5.20
2	2.16	4.21
4	2.03	4.12
7	1.84	3.82
10	1.73	3.74
14	1.70	3.71

Sample of PAPR product of $\eta_{\text{PAPR}} = 1$ represented the same dependence as the products of lower values of PAPR stoichiometric norm.

Tables 19, 21 and 23 present characteristics of the main process parameters. The free phosphoric acid [% w/w] content fluctuations during curing process of PAPR-type preparations obtained by the reaction with H₃PO₄ are shown in Tables 20, 22 and 24. Phosphate rock fineness was 250–500 μm .

Table 19

Characteristics of the main parameters of the production process of PAPR-type preparations: P19, P20, P21

	P19	P20	P21
Acid type	H ₃ PO ₄	H ₃ PO ₄	H ₃ PO ₄
Conc. H ₃ PO ₄ [% w/w]	69	69	69
η_{PAPR}	0.7	0.5	0.3

Table 20

Free H₃PO₄ content during curing process of PAPR-type preparations: P19, P20, P21

t [days]	P19 [% w/w]	P20 [% w/w]	P21 [% w/w]
0	3.19	1.69	1.18
2	2.26	1.55	1.00
4	1.88	1.47	0.85
7	1.86	1.48	0.93
10	1.75	1.43	0.83
14	1.71	1.33	0.73

Fineness alteration, unlike in the case of production using H_2SO_4 , did not affect the content of free acids in the product. The dependence between degree of PAPR stoichiometric norm and dynamics of free acids content fluctuation corresponded with products manufactured from the raw material of a finer size fractions.

Table 21

Characteristics of the main parameters of the production process of PAPR-type preparations: P22, P23, P24

	P22	P23	P24
Acid type	H_3PO_4	H_3PO_4	H_3PO_4
Conc. H_3PO_4 [% w/w]	62	62	62
η_{PAPR}	0.7	0.5	0.3

Table 22

Free H_3PO_4 content during curing process of PAPR-type preparations: P22, P23, P24

t [days]	P22 [% w/w]	P23 [% w/w]	P24 [% w/w]
0	3.68	3.22	2.28
2	2.98	2.38	1.55
4	2.87	2.29	1.46
7	2.63	2.,24	1.34
10	2.48	2.22	1.39
14	2.43	2.20	1.41

The results of analyzes for products of both 250–500 μm and 160–250 μm fineness revealed correlation between increase in the content of free acids with decrease in concentrations of H_3PO_4 used for the experiment.

Table 23

Characteristics of the main parameters of the production process of PAPR-type preparations: P27, P28

	P27	P28
Acid type	H_3PO_4	H_3PO_4
Conc. H_3PO_4 [% w/w]	69	62
η_{PAPR}	1	1

Table 24

Free H₃PO₄ content during curing process of PAPR-type preparations: P27, P28

t [days]	P27 [% w/w]	P28 [% w/w]
0	5.57	6.20
2	3.55	4.04
4	3.22	3.68
7	2.86	3.37
10	2.56	3.17
14	2.48	3.06

Products acidulated with H₃PO₄ demonstrated opposite dependence than products dissolved with H₂SO₄. Decrease in concentration of acid used for acidulation process caused an increase in free acids content. Unlike products acidulated with H₂SO₄, these preparations are not influenced by fineness of phosphate raw material in relation to dynamics of free acids content fluctuations.

Commercial fertilizer preparations were characterized by the following content of free phosphoric acid: CP1 = 0.18 % w/w; CP2 = 0.16 % w/w; CP3 = 0.22 % w/w; CP4 = 0.17 % w/w. The content of free acids in tested commercial products was much lower than in preparations obtained during the research. Minimal amount of free sulfuric acid in the products acidulated with H₂SO₄ were observed, what can be explained by the accuracy of the analytical method.

Conclusions

The results of tests performed under laboratory conditions indicate that the curing process carried out for production of PAPR-type fertilizers acidulated with H₂SO₄ gives more satisfactory results by using higher acid concentration. Use of lower degree of PAPR stoichiometric norm may cause local acidulation, resulting in an insufficient product homogeneity. Use of efficient stirring during acidulation process could be the possible solution for this problem. The content of free phosphoric acid in laboratory-produced preparations is higher than in tested commercial products, what may cause the physical properties instability. Future research should attempt to correlate the content of various forms of phosphates with free acids content in obtained PAPR-type fertilizer preparations.

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BADANIA DYNAMIKI ZMIAN ZAWARTOŚCI WOLNYCH KWASÓW MINERALNYCH W CZASIE CYKLU PRODUKCYJNEGO NAWOZÓW TYPU PAPR

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Abstrakt: Fosforyty częściowo rozłożone (*partially acidulated phosphate rock* – PAPR) stanowią odrębną grupę nawozów fosforowych. Nawozy typu PAPR powstają w wyniku reakcji fosforytów z niestechiometryczną, względem reakcji rozkładu fluoroapatytu zawartego w fosforycie, ilością kwasu mineralnego. Celem badań była analiza dynamiki zmian zawartości wolnych kwasów w otrzymanych preparatach typu PAPR. Parametrami produkcyjnymi, które ulegały modyfikacji, były: rodzaj stosowanego kwasu i jego stężenie, stopień normy stechiometrycznej PAPR (η_{PAPR}), uziarnienie fosforytu użytego do produkcji. Badania polegały na oznaczeniu ilości wolnych kwasów w produkcie zarówno bezpośrednio po zakończeniu procesu produkcji, jak i podczas dojrzwania nawozu odpowiednio po czasie 2, 4, 7, 10 i 14 dób.

Słowa kluczowe: fosforyty częściowo rozłożone (PAPR), wolne kwasy, nawozy fosforowe, fosforany przyswajalne