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# THE CONTENT OF SELECTED PHOSPHORUS FORMS IN PARTIALLY ACIDULATED PHOSPHATE ROCKS ENRICHED WITH SULFUR

## BADANIE ZAWARTOŚCI WYBRANYCH FORM FOSFORU W FOSFORYTACH CZĘŚCIOWO ROZŁOŻONYCH WZBOGACONYCH W SIARKĘ

**Abstract:** Sulfur enrichment becomes emerging issue in fertilizer production as levels of available compounds decrease over the years. Companies are in need of exact parameters and methods of enrichment. In this group PAPR-type fertilizers with this element are interesting solution. Specific technology of PAPRs production consists of phosphate rock acidulation with non-stoichiometric, in relation to production of superphosphates, amount of mineral acid (mainly orthophosphoric or sulfuric acids). Additional function of S after applying fertilizer to soil can be used in this. S in product made that way can be, after the process of mineralization, used by plants as a nutrient in form of sulfate ion $SO_4^{2-}$, additionally it can act as an increasing factor in the phosphorus availability from PAPRs. In an optimal conditions (pH ~6.0–6.8) $SO_4^{2-}$ ions can activate conversion of undissolved part of fluorapatite ($Ca_5(PO_4)_3F$), contained in phosphate rock, to available $H_2PO_4^-$ and $HPO_4^{2-}$ phosphate ions. The aim of this research was the evaluation of contents of selected phosphorus forms in PAPR-type fertilizer enriched with S depending on a various methods of enrichment. The obtained products were characterized by constant ratio of S : $P_2O_5$ (1 : 1 w/w), value of degree of PAPR stoichiometric norm ($\eta_{PAPR}$ = 0.5), constant amount of surfactant (5 $cm^3$) and variable humidity, which was achieved by different amounts of water introduced into the system (0, 15, 35 % w/w). Method with less additional $H_2O$ (~15 % m/m) and surfactant added to slurry was selected for further studies. Although the best solution for industrial manufacturing might be the method with melted S, where usage of this medium and temperatures of 140 °C are easily achievable and facilitates production without adding dispensable water, which has a negative influence on granulation process. Next step was to study sulfur effect on PAPRs based on phosphoric acid enriched with sulfur using chosen method. Results revealed that $\eta_{PAPR}$ = 0.5 is unaffected by addition of sulfur and might be best for mixing with sulfur-based fertilizers. Furthermore $\eta_{PAPR}$ = 0.7 indicated decreases in P forms with addition of excessive amounts of elemental sulfur.

**Keywords:** phosphate fertilizers, partially acidulated phosphate rocks (PAPR), elemental sulfur, available phosphorus

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## Introduction

Poland after joining the EU was obliged to fulfill standards in field of environmental protection. From base year 1988 total emission of sulfur dioxide ($SO_2$) to the atmosphere was reduced to 861 thousand Mg in year 2009, where years 2000–2009 noted 43 % reduction [1]. Reduced flow of $SO_2$ from main sources *ie* stationary, power engineering, industrial power engineering (correspondingly: 39.3; 37.5; 20.7 %) with simultaneously restricted use of fertilizers containing this element, caused, in late 90's of last century, degradation of available sulfur supply in soil and in plants [2].

In soil sulfur occurs in organic forms (amino acids: cysteine and methionine, deciding on biological properties of proteins), in turn direct sources of S available are only inorganic sulfates [3, 4]. Organic P must be converted to inorganic P through a relatively slow mineralization process before it becomes available, organic fertilizers may not meet plants' early P requirements often resulting in lower crop yield [5, 6]. In order to supplement deficiency of $SO_4^{2-}$ ions in soil, the mineral fertilizers enriched with S are used preferably. These are mainly sulfate fertilizers which are main source of this component: ammonium sulfate, single superphosphate, potassium sulfate or gypsum [7]. Unlike conventional N fertilizers which are all water soluble, P fertilizers vary widely in solubility that can influence the initial and residual P effects. For this and other reasons, inorganic P fertilizers remain the major sources of P application used by farmers in both developed and developing countries [5, 8]. Interesting product in this group are PAPR-type (*Partially Acidulated Phosphate Rock*) fertilizers enriched with S. Specific production technology of PAPR-type fertilizers is based on dissolution of phosphate raw materials (mainly phosphate rocks) by non-stoichiometric amount of mineral acids (mainly sulfuric acid, ortophosphoric or mixture of those). It enables tapping additional function of sulfur after applying fertilizer product to soil [9]. In PAPR technology, beside water soluble $Ca(H_2PO_4)_2$, calcium sulfate is created (source of $SO_4^{2-}$) – important source of S, which is supplemented by elementary sulfur [10]. Elementary sulfur in this fertilizer system, after mineralization process (optimal conditions: pH ~6.0–7,0; humidity ~60 %, temp. 20–30 $^{o}$C) can be used by plants as nutrient in form of $SO_4^{2-}$ ion. Additionally intensifying phosphorus solubility from PAPR-type fertilizer. In optimal conditions (pH ~6.0–6.8) $SO_4^{2-}$ ions can activate conversion of undissolved fraction of $Ca_5(PO_4)_3F$ from phosphate rock to available phosphate ions $H_2PO_4^-$ and $HPO_4^{2-}$ [11–13].

Important factor in industrial methods of sulfur enrichment is optimization of process parameters to intermediate product by economic and ecological reasons. Significant problem of sulfur is flammable dusts emission which occurs during grinding process in order to obtain fine particles. Another factor is the water added in slurry with sulfur, making granulation process more expensive due to increased humidity. Mineralization process comes with lower pH of the soil. Soil's pH, fertilized by the product is one of the main reasons deciding on heavy metals availability to plants. Lowering pH to acidic increases mobility of the available heavy metals forms concentration and increases their accumulation in plants. It is caused by increased solubility and lower absorption on soil colloids.

## Materials and methods

The purpose of the research was to determine impact of methods of adding sulfur to fertilizer products on selected P forms in PAPR-type fertilizers obtained in laboratory scale. Parameters which were modified were as follows:
– method of adding sulfur: in slurry with water; melted sulfur,
– percentage of water added to the reactor (0 – none, 15, 35 % w/w),
– percentage of surfactant added to the reactor (0 – none, 2.3, 3.0, 3.5 % w/w).

Table 1

Matrix of the experiment

| Fertilizer PAPR product | ZIN weighed portion [g] | S : $P_2O_5$ ratio [w/w] | $H_2O$ added to the reactor [% w/w] | Surfactant added to the reactor [% w/w] | Method of adding sulfur |
|---|---|---|---|---|---|
| 1 | 100 | 1 : 1 | 35 | 2.3 (5 $cm^3$) | Sulfur water slurry<br>Surfactant added to slurry |
| 2 | | | 15 | 3.0 (5 $cm^3$) | Sulfur water slurry<br>Surfactant added to slurry |
| 3 | | | 35 | 0 | Sulfur water slurry |
| 4 | | | 0 | 0 | Melted sulfur |
| 5 | | | 0 | 3.5 (5 $cm^3$) | Melted sulfur<br>Surfactant added to slurry |
| 6 | | | 0 | 0 | Control sample: PAPR 0.5 without sulfur |

Israeli “ZIN” phosphate rock was used in the research for which constant degree of PAPR stoichiometric norm $\eta_{PAPR}$ = 0.5 was applied. Rate of S : $P_2O_5$ was established at 1:1 (w/w) with constant value throughout the investigations. Selected forms of P were analyzed using methods in the Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers, and Polish standard PN-88C-87015 – Mineral Fertilizers, Methods of phosphate content determination [10, 14]. PAPRs were obtained in modular ATLAS batch reactor (Syrris Ltd.) using overhead stirrer RW 28 basic (IKA®-Werke GmbH&Co. KG) to ensure efficient homogenization taking into account the resistance of pulp solidifying in the reactor. The apparatus applied during investigations allowed the batch type production process. To ensure sufficient sulfur diffusion “Superplasticizer CA40 FF” (Liquid solution of calcium naphthalenesulphonates condensed with formaldehyde) was used provided by PCC Rokita S.A. In second method sulfur was introduced to the reactor and then heated up to 140 $^oC$ and mixed at 50 rpm. After the process product was dried on air and analyzed.

Further research was made to determine impact of sulfur on PAPR-type fertilizers based on phosphoric acid. Method of enrichment was based on adding elemental sulfur as slurry with water as described above (Product No. 2). Constant S : $H_2O$ ratio was established at 1 : 1 (w/w). Analysis was made on the day of production and consecutively week and two later. Parameters which were modified were:

– Degree of PAPR stoichiometric norm ($\eta_{PAPR}$ = 0.3, 0.5, 0.7),
– S : $P_2O_5$ ratio (w/w) (1:2; 1:3; 1:4; 1:6).

Table 2

Matrix of the experiment

| Fertilizer PAPR product | ZIN weighed portion [g] | PAPR norm | S : $P_2O_5$ ratio | $H_2O$ added to reactor [% w/w] | Surfactant added to reactor [% w/w] |
|---|---|---|---|---|---|
| D1 | 100 | 0.3 | 1:2 | 8.88 | 3.51 |
| D2 | | | 1:3 | 6.29 | 3.73 |
| D3 | | | 1:4 | 4.87 | 3.86 |
| D4 | | | 1:6 | 3.35 | 3.99 |
| E1 | | 0.5 | 1:2 | 7.82 | 3.10 |
| E2 | | | 1:3 | 5.51 | 3.27 |
| E3 | | | 1:4 | 4.24 | 3.36 |
| E4 | | | 1:6 | 2.91 | 3.46 |
| F1 | | 0.7 | 1:2 | 7.00 | 2.77 |
| F2 | | | 1:3 | 4.89 | 2.90 |
| F3 | | | 1:4 | 3.76 | 2.98 |
| F4 | | | 1:6 | 2.57 | 3.05 |

## Results and discussion

Results of the selected phosphorus forms in PAPR-type fertilizers enriched with sulfur analysis are shown in the Table 3.

Table 3

Results of various forms of P analysis in the investigated products expressed as % $P_2O_5$ (w/w)

| Product | P soluble in mineral acids [% w/w] | P soluble in citric acid 2 % [% w/w] | P soluble in neutral ammonium citrate [% w/w] | P soluble in formic acid 2 % [% w/w] | Water-soluble P [% w/w] |
|---|---|---|---|---|---|
| 1 | 18.68 | 13.21 | 9.98 | 12.98 | 6.76 |
| 2 | 19.20 | 10.71 | 10.15 | 11.03 | 5.98 |
| 3 | 25.07 | 13.25 | 9.26 | 13.00 | 8.13 |
| 4 | 19.79 | 6.50 | 7.01 | 5.78 | 3.87 |
| 5 | 21.19 | 9.21 | 7.09 | 7.79 | 6.13 |
| Control sample PAPR 0.5 without sulfur | 24.15 | 11.83 | 9.92 | 11.99 | 8.36 |

Product No. 3 revealed the highest amount of available phosphorus forms (P soluble in $H_2O$ : 8.13 %), however in this case, the applied method did not assure sufficient diffusion of sulfur in fertilizer product and requires adding additional amount of water which has adverse influence on granulation process. Fertilizer products obtained by methods with melted sulfur contained least amounts of soluble phosphorus forms (correspondingly 3.87 and 6.13 % for water-soluble P). This might be connected to high temperature of the process which degrades soluble forms into insoluble. In the laboratory research method according to product No. 2 was selected for further studies, where humidity is lower and diffusion sufficient. Worth noting is that better for industrial manufacturing might be method based on melting sulfur because temperature of 140 $^{o}$C is easily achievable and sulfur handling is relatively safe without the need of adding dispensable water.

Results of further research were shown in Table 4.

Table 4

Results of various forms of P analysis in the PAPRs enriched with sulfur expressed as % $P_2O_5$ (w/w)

| Product | Fertilizer growth [days] | P soluble in mineral acids [% w/w] | P soluble in citric acid [% w/w] | P soluble in formic acid 2 % [% w/w] |
|---|---|---|---|---|
| D1 | 0 | 32.84 | 18.62 | 20.07 |
| | 7 | 29.69 | 17.19 | 17.71 |
| | 14 | 32.12 | 19.36 | 19.36 |
| D2 | 0 | 28.29 | 17.09 | 19.83 |
| | 7 | 31.69 | 16.26 | 17.37 |
| | 14 | 32.92 | 17.44 | 18.89 |
| D3 | 0 | 30.49 | 16.48 | 18.22 |
| | 7 | 31.37 | 15.60 | 16.29 |
| | 14 | 33.26 | 15.70 | 16.37 |
| D4 | 0 | 31.49 | 16.77 | 19.24 |
| | 7 | 31.64 | 17.05 | 17.60 |
| | 14 | 34.52 | 18.46 | 17.79 |
| E1 | 0 | 32.78 | 26.18 | 23.14 |
| | 7 | 32.13 | 22.34 | 23.39 |
| | 14 | 34.84 | 23.90 | 24.46 |
| E2 | 0 | 34.62 | 22.39 | 23.87 |
| | 7 | 32.24 | 22.59 | 22.87 |
| | 14 | 36.89 | 24.35 | 23.32 |
| E3 | 0 | 36.19 | 24.68 | 25.32 |
| | 7 | 33.73 | 23.40 | 24.25 |
| | 14 | 34.65 | 23.73 | 23.71 |
| E4 | 0 | 37.44 | 25.16 | 26.41 |
| | 7 | 34.04 | 22.94 | 23.47 |
| | 14 | 35.52 | 23.61 | 24.01 |

Table 4 contd.

| Product | Fertilizer growth [days] | P soluble in mineral acids [% w/w] | P soluble in citric acid [% w/w] | P soluble in formic acid 2 % [% w/w] |
|---|---|---|---|---|
| F1 | 0 | 35.25 | 26.31 | 28.43 |
| | 7 | 34.70 | 26.36 | 26.66 |
| | 14 | 33.77 | 26.12 | 26.43 |
| F2 | 0 | 35.45 | 28.22 | 29.25 |
| | 7 | 34.32 | 27.23 | 27.11 |
| | 14 | 34.69 | 28.18 | 28.43 |
| F3 | 0 | 37.34 | 32.67 | 32.46 |
| | 7 | 37.45 | 25.23 | 29.60 |
| | 14 | 35.55 | 30.70 | 31.86 |
| F4 | 0 | 38.11 | 32.56 | 31.77 |
| | 7 | 37.94 | 30.87 | 30.91 |
| | 14 | 38.44 | 31.45 | 32.29 |

Fertilizer products of the degree of PAPR stoichiometric norm at 0.3 (D series products) were characterized by increased contents in selected phosphorus forms along with increasing amount of sulfur (difference being 1 % w/w for water-soluble P). This might be accounted for further dissolution of phosphate rock by sulfuric acid obtained from oxidized elemental sulfur. In turn products of the degree of PAPR stoichiometric norm at 0.3 (F series products) noted inversed correlation. Increase of S to enriched PAPR-type fertilizers resulted in decrease of contents of selected P forms (difference about 6 % w/w for water-soluble P). This might be due to high amount of phosphoric acid which favors elemental sulfur form rather than oxidized. Degree of PAPR

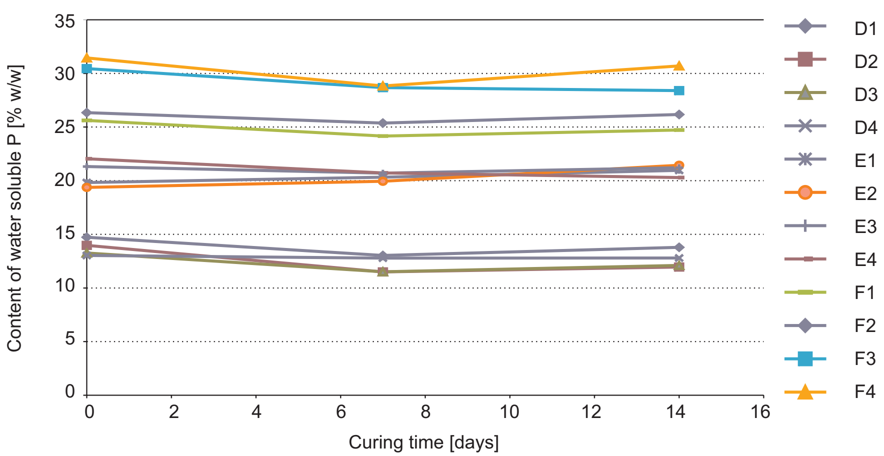


Fig. 1. Results of water soluble forms of P analysis in PAPR-type fertilizer products enriched with sulfur expressed as % $P_2O_5$ [w/w]

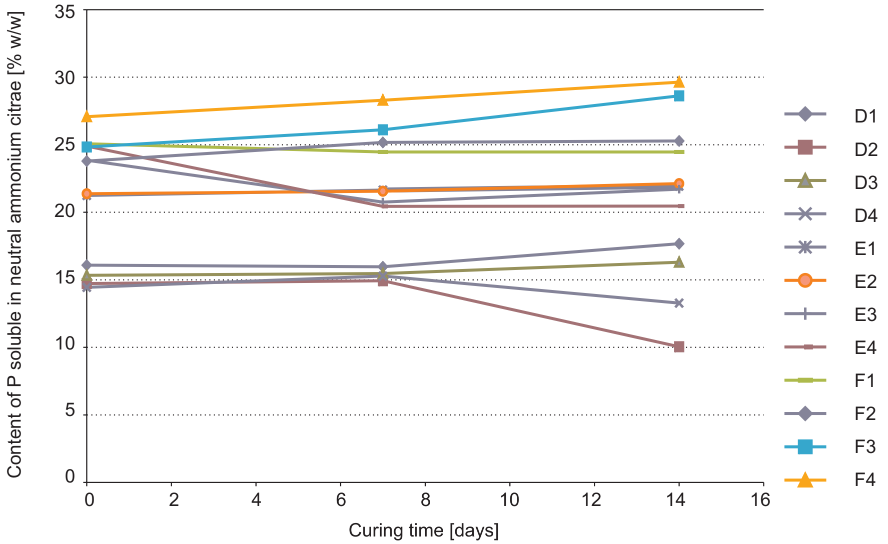


Fig. 2. Results of neutral ammonium citrate soluble forms of P analysis in PAPR-type fertilizer products enriched with sulfur expressed as % $P_2O_5$ [w/w]

stoichiometric norm at 0.5 (E series products) indicates similarity to 0.3 value in higher S : $P_2O_5$ ratios (1 : 2; 1 : 3), corresponding to 0.7 when considering lower ratios (1 : 4; 1 : 6). This would confirm the authenticity of previous trends and speculations of what causes them.

## Conclusions

The best method of enrichment is adding sulfur in slurry with water and surfactant. It ensures sufficient diffusion and allows usage of decreased amount of water (15 instead of 35 % w/w) which has negative influence on granulation process. Addition of water is important factor in decreasing the soluble forms, but surplus increases insoluble forms. Usage of slurry greatly reduces dangers of working with sulfur and makes handling easier. The content of phosphorus forms soluble in water and/or neutral ammonium citrate is satisfactory. Worth noting is that better for industrial production might be method based on melting sulfur (product No. 5) where handling this medium is easy and no dispensable water is used in manufacturing process. However this method reduces content of phosphorus forms soluble in water and/or neutral ammonium citrate. Addition of sulfur in PAPR-type fertilizers based on phosphoric acid is most effective in case of degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.3$, where higher amounts of sulfur in product boosts content of phosphorus, especially in the available forms (4 % increase for neutral ammonium citrate and 1 % increase for water-soluble forms). Lower ratios are more effective for the degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.7$ (5 % increase for neutral ammonium citrate and 6 % for water-soluble forms). For the degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.5$ results imply that sulfur has no effect on P forms. It allows mixing with sulfur-based or sulfur enriched fertilizers without decrease in P content. Taking into consideration industrial conditions, where superphosphate constitutes the primary product (degree of PAPR stoichiometric norm at $\eta_{PAPR} = 1.0$) we can predict lower ratios being most effective (phosphorus content-wise). This also influences lower humidity (decreased amount of dispensable water added from 7.00 to 2.57 %) which makes it more economical than higher ratios, at least when using slurry method.

## Acknowledgements

Work financed by grants from the Ministry of Science and Higher Education for the statutory activities of the Faculty of Chemistry, Wroclaw University of Technology.

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## BADANIE ZAWARTOŚCI WYBRANYCH FORM FOSFORU W FOSFORYTACH CZĘŚCIOWO ROZŁOŻONYCH WZBOGACONYCH W SIARKĘ

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**Abstrakt:** Wzbogacanie nawozów mineralnych siarką elementarną staje się coraz bardziej widocznym problemem dla przemysłu nawozowego. Zakłady produkcyjne potrzebują specyficznych metod i parametrów procesu dodawania siarki. W tej grupie interesującym produktem są nawozy typu PAPR (*Partially Acidulated Phosphate Rock*). Specyficzna technologia produkcji nawozów PAPR polegająca na rozkładzie surowców fosforowych (głównie fosforytów) niestechiometryczną, względem reakcji wytwarzania superfosfatów, ilością kwasów mineralnych (głównie siarkowym lub fosforowym) pozwala na wykorzystanie dodatkowej funkcji siarki po aplikacji nawozu do gleby. S w tak przygotowanym układzie nawozowym może po uprzednim procesie mineralizacji (warunki optymalne: pH ~6,0–7,0; wilgotność ~60 %, temp. 20–30 $^{o}$C) zostać wykorzystana przez rośliny jako składnik odżywczy w postaci jonu siarczanowego $SO_4^{2-}$, a dodatkowo działać jako czynnik intensyfikujący przyswajalność fosforu z nawozu PAPR. W optymalnych warunkach (pH ~6,0 – 6,8) jony $SO_4^{2-}$ mogą aktywować konwersję nierozłożonej frakcji fluoroapatytu ($Ca_5(PO_4)_3F$) zawartego w surowcu fosforowym do przyswajalnych jonów fosforanowych w formie $H_2PO_4^-$ i $HPO_4^{2-}$. Celem niniejszych badań była ocena zawartości poszczególnych form fosforu nawozów PAPR wzbogaconych w siarkę, uwzględniając różne metody wzbogacania. Analizy zawartości poszczególnych form P przeprowadzono metodyką analityczną zgodną z dyrektywą Wspólnoty Europejskiej w sprawie nawozów oraz z procedurami zawartymi w polskich normach. Otrzymane preparaty charakteryzujące się stałym stosunkiem S : $P_2O_5$ (1 : 1 m/m), wartością stopnia normy stechiometrycznej PAPR ($\eta_{PAPR}$ = 0,5), oraz zmienną wilgotnością, co osiągnięto poprzez zmienne ilości wody wprowadzanej do układu (0, 15, 35 % m/m), uzyskiwały najwyższe zawartości przyswajalnych form P (P rozpuszczalny w wodzie: 8,13 % $P_2O_5$ m/m, P rozpuszczalny w obojętnym cytrynianie amonu: 10,15 % $P_2O_5$ m/m) dla metody dodawania siarki w postaci zawiesiny wodnej bez dodatku surfaktantu ($H_2O$ ~35 % m/m). Do dalszych badań laboratoryjnych wybrano metodę produkcji, gdzie dodatek $H_2O$ jest niższy (~15 % m/m), a surfaktant wprowadzony do zawiesiny wodnej S. Metoda stapiania S może być najlepsza do produkcji przemysłowej, gdzie stosowanie stopionej S lub temperatury rzędu 140 $^{o}$C zostało opanowane w stopniu znacznie ułatwiającym produkcję bez dodawania zbędnej zawartości wody mającej niekorzystny wpływ na proces granulacji. Kolejnym krokiem było określenie wpływu zawartości siarki na produkty nawozowe typu PAPR wytworzone z zastosowaniem kwasu fosforowego wzbogaconego w siarkę elementarną, bazując na wybranej metodzie. Wyniki wykazały, że produkty o $\eta_{PAPR}$ = 0,5 nie są znacząco podatne na wprowadzenie siarki elementarnej do składu nawozu, co może być przydatne podczas komponowania mieszanek nawozów wieloskładnikowych. Ponadto dla produktów nawozowych typu PAPR o $\eta_{PAPR}$ = 0,7 wykazano tendencje spadkowe rozpuszczalnych form P wraz z zastosowaniem wyższych zawartości siarki elementarnej.

**Słowa kluczowe:** nawozy fosforowe, fosforyty częściowo rozłożone (PAPR), siarka elementarna, fosfor przyswajalny