Abstract: Unstable situation on fertilizer raw material market emerges the need to find substitute for superphosphate fertilizers. PAPR-type phosphate fertilizers (partially acidulated phosphate rock) constitute the most relevant alternative. PAPR-type fertilizers are formed by reaction of phosphate rock with nonstoichiometric, in relation to reaction during superphosphate production process, portion of mineral acid. The resulting product contains an available (soluble in water and/or in neutral ammonium citrate) and less available (soluble in mineral acids) forms of phosphorus. Possibility of using low-grade phosphate rock represents a great advantage of PAPR-type over superphosphatic manufacturing process, where applying phosphate rock of high P_2O_5 at low impurities content is highly recommended. Granulation process is an essential stage of PAPR-type fertilizers production. Granulation significantly reduces the dust emissions during the fertilizers application furthermore limits the regression of fertilizers in soil to unavailable forms (so-called the aging processes of fertilizers). Optimization of process parameters is very important for economic and ecological reasons because this process is one of the most energy consuming in whole cycle of PAPR-type fertilizers production. PAPR-type fertilizer preparations obtained under laboratory conditions were subjected to examinations. Products were characterized by a variable humidity, which was achieved by altering the concentration of mineral acid used for investigations. The second variable factor was the type of liquid used for granulation. Both, the sieve analysis and determination of resistance were carried out for classification of obtained granules.

Keywords: fertilizers, granulation, partially acidulated phosphate rock

Phosphorus, next to nitrogen and potassium, is one of the plant essential macronutrients, that is why phosphate fertilizers are an indispensable part of agriculture, and
their consumption in Poland in the 2009/2010 season amounted to about 35 million tons [1]. The main product of phosphate fertilizers industry branch is superphosphate, applied as a straight primary nutrient fertilizer or as an intermediate used in the production of compound primary nutrient fertilizers. Phosphate rock constitutes a basic raw material used for the production of superphosphate. For several years there has been considerable fluctuations in phosphorus commodity prices. Currently, the price of phosphate rock is twice higher than as about 5 years ago and reaches approximately 180 USD per ton [2]. The primary requirement for phosphate raw materials destined to produce superphosphate is high $P_2O_5$ with low impurities content at the same time [3, 4]. Deposits of phosphate rock with high content of $P_2O_5$ are available only in deposits located in a few countries in the world. The greatest resources are in Morocco, China, USA and Russia [1]. Poland has only a few small low-grade deposits, however their extraction is economically unreasonable due to too low concentration of phosphate rock in relation to the entire deposit [5]. Therefore Polish industry of phosphate fertilizers is based on imported raw materials. Possibility of increasing the independence of the phosphorus raw material is one of the main reasons for finding alternatives for conventional superphosphate fertilizers. Poland in 2008 was placed on the 5th place in the EU in terms of consumption of mineral fertilizers (100–150 kg/ha). Moreover Poland was also their significant producer (approximately 1.5 % of world production) [1]. This is another significant reason for becoming the issues, connected with development of technology designed for production of phosphate fertilizers based on low-grade phosphate rock, a priority for Polish phosphate fertilizers industry.

One of the existing alternatives for the production of conventional superphosphate fertilizers is based on partial acidulation of phosphate rocks, so called PAPR-type fertilizers (partially acidulated phosphate rock). The main advantage of PAPR-type fertilizer is economics of the manufacturing process by taking into consideration the fact that their production can be performed using phosphate rock with $P_2O_5$ content below 20 % w/w [4]. The amount of deposits of low-grade and low-quality phosphate rocks is considerably higher worldwide as reserves of high-grade and high-quality phosphate rock are being depleted. It may cause a significant reduction in the cost of raw material required for fertilizer manufacturing processes. PAPR-type fertilizers are produced as a consequence of the following total reaction (1) [6]:

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 7H_2SO_4 \longrightarrow 7CaSO_4 + 3Ca(H_2PO_4)_2 + 2HF$$  \hspace{1cm} (1)

Superphosphate manufacturing process is based on the same reaction, however the PAPR-type fertilizer process involve less amount of mineral acid than it results from the stoichiometry of the process, which is furthermore important taking into consideration environmental aspects. As a consequence of reduced amount of mineral acid, obtained fertilizer formulation contains both forms of phosphorus: water-soluble and soluble in neutral ammonium citrate (ie forms easily absorbed by plants) as well as the forms of phosphorus soluble in mineral acids (forms rather insoluble and thus unavailable to plants). The insoluble forms of phosphorus constitute a phosphorus stock in the soil, which can be transformed in the available form by the microbial metabolic processes occurring in the soil [7].
Granulation is an unit operation by means of fertilizer product alter its form and significantly improves its mechanical properties. The granular form cause increase in bulk density what both reduces the space required for storage and transportation costs. Moreover it significantly facilitates the regular fertilizer dosing on agricultural land [8, 9]. The use of granules reduces dust during packaging and application of fertilizers, which significantly reduces the harmful effects of the production process and applications on the environment. In the case of phosphate fertilizers very important advantage of using granular form is the limitation of precipitation processes which cause reversible transformation from the available phosphorus forms to mineral forms which are insoluble for plants (so-called aging of fertilizers), because of the fact that these processes occur only on the surface of the granules whereas available forms of phosphorus are being regularly released from within the granule (reaction 2–4) [10].

\[ \text{Ca(H}_2\text{PO}_4\text{)}_2 + 2\text{Al(OH)}_3 \rightarrow 2\text{Al(OH)}_2 \cdot \text{H}_2\text{PO}_4 + \text{Ca(OH)}_2 \] (2)

\[ \text{Ca(H}_2\text{PO}_4\text{)}_2 + \text{Ca(HCO}_3\text{)}_2 \rightarrow \text{CaHPO}_4 + 2\text{H}_2\text{CO}_3 \] (3)

\[ 2\text{CaHPO}_4 + \text{Ca(HCO}_3\text{)}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{CO}_3 \] (4)

As a result of the granulation process the product is characterized by homogeneous composition which allows regular supply of macro- and micronutrients into the soil [9]. The most relevant disadvantage of granulation process constitutes significant increase in production costs, it may be as high as 30 % [8, 9]. Granulation can be carried out using diversified methods, however the pug-mill, drum and pan granulators are selected for the most part by phosphate fertilizer manufacturers [9]. The required size of the granules for phosphate fertilizers is 1–6 mm [8, 11].

Materials and methods

The aim of the experiment was to determine dependence of the type of granulating liquid and the moisture content of samples on the quality of resulting granules. Production parameters subjected to modifications were:

- the type of granulating liquid (water and sulfuric acid (H\(_2\)SO\(_4\)) 5 % w/w solution);
- moisture content of the fertilizer formulation (2.5 %, 5.0 %, 7.5 % and 10 % w/w H\(_2\)O);
- the degree of PAPR stoichiometric norm (\(\eta_{\text{PAPR}} = 0.3; 0.5; 0.7\); where \(\eta_{\text{PAPR}}\) defines the proportion of the quantity of mineral acid used in the process to the quantity of acid, which results from the stoichiometric reaction of phosphate rock acidulation).

Phosphate rock used in this investigation was provided from the phosphate deposits located in west part of the Nagev desert in Israel. The study consisted in granules formulation in laboratory conditions, sieve analysis of the obtained product and performing the test of mechanical strength of granules. Acidulation process for fertilizer products was conducted in modular batch reactor Atlas (Syrris Ltd.) equipped with a reaction vessel made from teflon introduced into an aluminum heating jacket,
possessing the ability to control the process parameters such as temperature, stirring intensity and reaction time automatically from the main panel. In order to obtain the fertilizer product, each time a weighed portion of phosphate rock (50 g) was stirred with the amount of acid suitable in accordance with the assumed values of PAPR stoichiometric norms as well as established moisture content of the sample. After completion of the acidulation reaction in the reactor 15 g of the PAPR product was subsequently subjected to granulation process. Granulation was carried out in a laboratory-scale granulator using elements of the drum and pan granulators. Granulator is made of tube containing two rings, which serve as mechanical barriers for granular material, which facilitated the agglomeration of particles of the fertilizer. However, in contrast to the standard drum granulators is opened only on one side, causing further agglomeration of particles at the bottom of the granulator, which is a feature of the pan granulation. The resulting granules were subjected to drying at 105°C for 6 hours. After the drying process and adjusting temperature to room conditions granules were then sieved and analyzed in scope of separation of the desired fraction (1–6 mm). Then, the desired fraction was tested for crushing strength of granules using the ERWEKA® device in order to evaluate the mechanical strength. The obtained granules were compared with granules based on powder superphosphate fertilizer provided by one of the leading manufacturers of phosphate fertilizers. In addition results of the strength of lab-derived PAPR-type fertilizers granules were related to the strength of granulated fertilizers available on the Polish market.

**Results**

Figure 1 shows the results of sieve analysis for a PAPR-type product of $\eta_{\text{PAPR}} = 0.5$ where water was used as a granulating liquid. Figure 2 shows the mechanical strength test results of granules obtained for the same product.

![Fig. 1. The results of sieve analysis of a sample granulated by H$_2$O ($\eta_{\text{PAPR}} = 0.5$)](image)

Granule size distribution for all levels of moisture contents in the examined samples was identified by the highest values for medium-mesh sieve which means that the size distribution is close to normal distribution.
The highest compressive strength was achieved for moisture content equal to 5.0 % w/w of H₂O. It should be noted that the sample of the following moisture content was characterized by the highest share of granules with a diameter greater than 4 mm, which can cause increase in the value of the granules mechanical strength.

Figure 3 shows the results of sieve analysis for a PAPR-type product of $\eta_{\text{PAPR}} = 0.3$ where $\text{H}_2\text{SO}_4$ 5.0 % w/w solution was used as a granulating liquid. Figure 4 shows the mechanical strength test results of granules obtained for the same product.
Granule size distribution for the following moisture contents 7.5 % w/w H₂O and 10.0 % w/w H₂O in obtained samples revealed a trend for smaller mesh sizes which turns this distribution to the left-oblique approach. However, for the moisture content of 5.0 % w/w H₂O granule size distribution is slightly shifted to the right.

The highest compressive strength was achieved for moisture content equal to 5.0 % w/w of H₂O despite the fact that part of the granules with a diameter greater than 4 mm for this sample was the lowest among the tested samples.

Figure 5 summarizes the results of mechanical strength analysis for all formulations obtained during the investigations.

The results indicates clearly that the sample of moisture content at 7.5 % w/w H₂O is characterized by the highest mechanical strength. It is relevant to point out that for the majority of applied values of degree of PAPR stoichiometric norms the lowest values of mechanical strength were found for samples of moisture content at 5.0 % w/w H₂O. The optimum moisture content for granular samples comprises between 7.5 and 10.0 % w/w H₂O. The results of analysis presented in this paper does not allow to select certain granulating liquid, which could improve mechanical properties of the granules in a significant degree.

Figure 6 depicts the comparison of results of mechanical strength analysis for selected products obtained during the investigations commercial products available on the market.

For the majority of applied values of degree of PAPR stoichiometric norms the highest strength was recorded for samples of moisture content at 7.5 % w/w H₂O. It was also verified that the highest mechanical strength of granules occurs for samples in which the size distribution of granules during sieve analysis is shifted to the right, towards the larger diameter of the granules. However, these results in increase in the amount of oversized particles which in turn generates the necessity to transfer oversized...
granules into crushing unit and turning them back to the process. The best properties are achieved when granules size distribution is close as possible to normally distributed (sufficient strength and a small amount of undersized and oversized granules). Commercial products were characterized by a higher mechanical strength of granules, however it is worth noting that industrial granulators have a much larger diameter resulting in a much larger forces that affect the particles during the granulation process. This was confirmed by the result of single superphosphate granulation by method used to obtain investigated PAPR formulations. The mechanical strength of the superphosphate granules was similar to the strength of the other granules obtained on the basis of PAPR fertilizers.

Conclusions

The research indicated the possibility to obtain a ready PAPR product of proper quality at reduced influence of the curing process, which may reduce the time required for fertilizer manufacturing and unit production costs. The most promising results were obtained for the PAPR-type formulations of a moisture content at 7.5 % w/w. Further studies on this issue should be conducted for a sample with a moisture content at 7.5 % w/w or close to this value. Any significant difference in the quality of the PAPR fertilizer products obtained on the basis of different granulating liquid was found, what allows to draw a conclusion that there is no need for a specific granulating liquid that could raise production costs. Further investigations on this issue should focus on determining the quality of granules depending on such factors as the angle of the granulator, the number of rate per minute and feeding conditions of granulating liquid.
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References


Wpływ czynnika granulującego przy zmiennej wilgotności na granulację fosforytów częściowo rozłożonych

Instytut Technologii Nieorganicznej i Nawozów Mineralnych
Politechnika Wrocławska

Abstrakt: Niestabilna sytuacja na rynku surowców nawozowych stwarza konieczność znalezienia substytutu dla nawozów superfosforatowych. Najważniejszą alternatywą wydają się być nawozy fosforowe typu PAPR (partially acidulated phosphate rock). Nawozy typu PAPR powstają w wyniku reakcji fosforytów z niesztatetycznoścą, względem reakcji produkcji superfosfatów, ilością kwasu. Tak powstały produkt zawiera formy fosforu zarówno łatwo przyswajalne (rozpuszczalne w wodzie i/lub w obojętnym cytrynianie amonu), jak i nieprzyswajalne (rozpuszczalne tylko w kwasach mineralnych) przez rośliny. Zależną tego rodzaju nawozów jest fakt, że do ich produkcji można wykorzystać fosforuty o znacznie mniejszej zawartości P2O5 niż jest to wymagane dla procesu produkcji nawozów superfosforatowych. Proces granulacji jest niezbędnym elementem procesu otrzymywania nawozów typu PAPR ponieważ znaczną zmniejsza emisję pylów w czasie stosowania nawozów, dodatkowo granulacja nawozów fosforowych znacznie ogranicza uwstępnianie się nawozów do form nieprzyswajalnych (tzw. procesy starzenia się nawozów) w glebie. Optymalizacja parametrów procesu granulacji jest bardzo istotna ze względów ekonomicznych oraz ekologicznych, ponieważ proces ten jest jednym z najbardziej energochłonnych w całym cyklu produkcji nawozów. Do badań wykorzystano preparaty nawozów fosforowych typu PAPR otrzymane w laboratorium. Otrzymane preparaty charakteryzowały się zmienią wilgotnością, co osiągnięto poprzez zmianę stężenia kwasu użytego do reakcji. Drugim zmiennym czynnikiem był rodzaj cieczy użytej do procesu granulacji nawozów typu PAPR. W celu klasyfikacji otrzymanych granulatów przeprowadzono analizę sitową oraz oznaczone wytrzymałość otrzymanych preparatów.

Słowa kluczowe: nawozy, granulacja, częściowo rozłożone fosforyty