Abstract: Use of phosphate fertilizers in the world constantly decreases in the last few years. The reason is increase of a unit prices of nutritious components what results in automatic growth of phosphate fertilizers prices. It is a well-known fact that phosphorus in a fertilizer causes not only growth but also a stabilization of plant production. That’s why economic aspects exacted a necessity of searching cheaper resolutions for plant fertilization. Fertilizers containing partially acidulated phosphate rock like PAPR show long-lasting activity thanks to content of phosphorus with different solubility extent. Therefore, they can be an alternative for present sources of phosphorus like superphosphate. Very important is an optimization of PAPR composition. Content of macro- and microelements like zinc, manganese, copper, iron determine usefulness of definite preparation for fertilization goals. Knowledge of heavy metals concentration in given fertilizer may turn out fundamental if we are talking about ecological and healthy aspects of using partially acidulated phosphate rocks. Products type PAPR were made in laboratory by dissolving phosphate rocks with non-stoichiometric quantity of sulphuric acid. Next mineralization of appropriate fertilizer weighted amount was conducted in the aim of determine heavy metal concentration. Lead content in fertilizers type PAPR was studied in Autolab device using differential pulse voltammetry method.

Keywords: partially acidulated phosphate rock, heavy metals, lead, voltammetry

Introduction

Poland is an important producer of mineral fertilizers not only in Europe but also in the world. National industry brings about 1.5 % of world production of nitric fertilizers and about 1.6 % of phosphate fertilizers [1]. Poland is a second producer (after Russia) of phosphate fertilizers in an European scale [2]. The observed trend of increasing
nutrient unit prices meant that at the turn of 2007/2008 was reached record prices of mineral fertilizers, which resulted in large instability of fertilizer sector in Poland and worldwide. In the second half of 2008, as a result of drastically deteriorating relations between fertilizers prices to grain prices and also expected weakening of demand for food due to financial crisis, there has been a clear breakdown in the fertilizers market. Then, for the first time in several years, wasn’t observed the increasing tendency for the global use of mineral fertilizers, and the main reason was the sharply reduce their purchases in the second half of 2008 [3]. The food production is inseparably connected with using fertilizers in agriculture, so the aspect of economic production of phosphate fertilizers as well as modification of existing technologies for their manufacture should be taken into consideration.

Partially acidulated phosphate rocks

In recent years PAPR-type fertilizers (partially acidulated phosphate rocks) have become a prospective alternative to existing sources of phosphorus, such as superphosphates. phosphate, have recently become a PAPR fertilizers (partially acidulated phosphate rocks). They are formed by partial acidulation of phosphate rock through the use of nonstoichiometric amount of sulfuric or phosphoric acid (or their solution in the appropriate ratio – optionally).

Reactions of receiving the PAPR fertilizers can be divided into stages and described using chemical reactions [4].

Stage I: The reaction takes place on the surface of ground phosphate rock grains. Using in the initial stage of reaction the excess of sulfuric acid, we receive phosphoric acid in the first place:

$$\text{Ca}_5\text{F} (\text{PO}_4)_3 + 5\text{H}_2\text{SO}_4 + aq = 5\text{CaSO}_4 - 0.5\text{H}_2\text{O} + 3\text{H}_3\text{PO}_4 + aq + \text{HF} \quad (1)$$

Stage II: In this stage phosphoric acid reacts with undecomposed to this point fluoroapatite:

$$\text{Ca}_5\text{F} (\text{PO}_4)_3 + 7\text{H}_3\text{PO}_4 + aq = 5\text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + aq + \text{HF} \quad (2)$$

Degree of PAPR stoichiometric norm is a parameter expressing the proportion of the quantity of mineral acid used in the process to the quantity of acid, which results from the stoichiometric reaction of PR dissolution. This factor can be expressed by the formula [5]:

$$\eta_{\text{PAPR}} = \frac{\eta^r_{\text{PAPR}}}{\eta^s_{\text{PAPR}}} \quad (3)$$

where: $\eta_{\text{PAPR}}$ – degree of PAPR stoichiometric norm,
$\eta^r_{\text{PAPR}}$ – actual quantity of mineral acid used in the process,
$\eta^s_{\text{PAPR}}$ – quantity of acid results from the stoichiometric reaction.
Degree of PAPR stoichiometric norm is typically less than one, and for the stoichiometric reaction with complete PR dissolution takes a value equal one; this coefficient is dimensionless.

Partially acidulated phosphate rocks, sulphuric or phosphoric acid are mostly cheaper counting the total phosphorus than other phosphate fertilizers. It is caused by the less use of acids during obtaining the product, additionally PAPR fertilizers usually contain more phosphorus than single superphosphate. Another advantage of using partially acidulated phosphate rocks is the fact that they have a higher tolerance for lower quality rock phosphate, which can not be used for the production of superphosphate [4]. Using this type of fertilizers is economically more profitable and also phosphorus from the PAPR type fertilizer remains longer in soil as a dicalcium phosphate, which is better absorbed by plants [6].

Heavy metals

Soil contamination with heavy metals constitutes nowadays a serious problem of developed countries [7]. High concentration of heavy metals in soils may cause not only the risks to ecosystems, but also for the people. The total natural content of heavy metals in soil depends primarily on the type of parent rock and special soil factors. The content of individual elements in the soil is determined by the impact anthropogenic and climatic factors [8]. Cultivated soil and fertilizers are known to contain some amounts of heavy metals such as cadmium, copper, lead, mercury, derived mainly from anthropogenic sources. Average content of heavy metals in phosphate fertilizers can be presented in the following order: Cd < Cu < Pb < Ni < Zn. Although we should remember about a great variety of heavy metals level concentrations depending on the type of fertilizer, in addition various is the degree of solubility and availability of heavy metals in plants in phosphate fertilizers [8]. Due to negative impact of these compounds on human health, it is recommend to reduce their level in fertilizers using appropriate monitoring of the concentration in raw materials and also in manufactured fertilizers [7, 9].

Lead in soil and fertilizers

Lead, one of the well-explored heavy metals, constitutes a major threat to human health [10]. Average natural content of lead for Polish soils is 18 ppm, and it is assumed that the natural content of this metal for most soils should not exceed 20 ppm [11]. In a result of weak lead migration, its natural distribution in soil profile reflects its content in parent rocks. However, the availability of lead in the surface soil layers is mainly connected with the influence of anthropogenic factors and is generally overestimated in relation to its natural content. In general, lead isn’t mobile in soils. This metal rarely occurs in the form of cation Pb^{2+}, but he creates the ions complex, such as Pb(OH)^+ and Pb(OH)_{2}^{2+}, which mostly regulate the sorption and desorption processes. In acid soils dominate the organic forms of lead, which can both decrease or increase its migration. Mobile forms of lead in acid soils occur mainly as Pb^{2+} and PbHCO_{3}^{+} or organic
complexes. In alkaline soils dominate: Pb(OH)\(^+\) and Pb(CO\(_3\))\(_2\)^{2-}\. Lead is strongly immobilized by most soil components: loamy minerals, Fe and Al hydroxides, and organic substance. Lead precipitation to carbonates and phosphates is an important process, which decides of its immobilization in soils at pH > 6.5. The increase of lead content in the surface soil layers unfavorably influences the microflora and microfauna, because higher concentration of this metal inhibits the decomposition of organic matter, which ultimately causes the degradation of the soil. This metal is particularly decomposed in phosphate raw minerals, which can accumulate up to a content of approximately 30 \% w/w of PbO. The content of this element in phosphate rocks used to produce phosphate fertilizers determines its concentration in the manufactured fertilizer materials. That is why important is not only the economic aspect of using different solutions in the production of phosphate fertilizers, but also the guarantee that the received fertilizer brings the smallest potential threat to ecosystems and human health. It should be remembered that even a small amount of lead put into the human body with food can cause the nervous system disorders, and chronic lead poisoning leads to brain damage, coma or even death [12]. Lead in soils and the control of its content in applied fertilizers is a subject of many researches, which basic goal is to define its bioavailability, the migration to ground waters, toxicity to organisms and the degree of incorporation into the food chain [11].

**Materials and methods**

The aim of the studies was to investigate the lead content in a PAPR-type fertilizer formulations using differential pulse voltammetry method in accordance with Polish Standard PN-92, C-87070/05. The method consisted in wet digestion of lead compounds found in the sample of the fertilizer solution using perchloric acid, and then receiving the metal peak by voltammetry method through analysis and interpretation of the graph [13, 14]. To produce PAPR fertilizer we used samples of 50 g phosphate rock ZIN, which was dissolved with a stoichiometric amount of sulfuric acid to give products of varying degrees of PAPR stoichiometric norm \(n_{\text{PAPR}} = 0.1, 0.2, 0.3, 0.4 \) and 0.5.

Fertilizer formulations were produced in a laboratory reactor Syrris Atlas, which allow to control the temperature and process time, pH and mixing rate. After the reaction the fertilizer preparation was dried at room temperature for approximately 24 h before the mineralization.

In order to prepare phosphate fertilizers samples for voltammetric researches, approximately 3 g of the fertilizer was weighted, 10 cm\(^3\) of perchloric acid was added, and the contents of the beaker was heated to boiling until a clear brightening solution was given. Then the 5 cm\(^3\) of distilled water was added to the beaker, again heated to boiling, and after cooling, the contents of the beaker were transferred quantitatively to a volumetric flask and made up 100 cm\(^3\) with distilled water. The prepared solution was mixed and filtered again, and from the filtrate samples were taken for further analysis. Determination of lead content were performed in flasks with a capacity of 50 cm\(^3\), to which were entered: 25 cm\(^3\) of a basic electrolyte (78 g sodium chloride and 53 g sodium hypophosphite dissolved in a volumetric flask of capacity 1 dm\(^3\)), 1 cm\(^3\) of
0.1 % w/w gelatin solution in order to minimize electric noises, and 4, 6, 8 or 10 cm³ of earlier prepared solution of fertilizer samples. Lead concentration in PAPR type fertilizers was studied in Autolab device using differential pulse voltammetry method. Lead peaks were recorded in the potentials from –0.2 to –0.7 V, gaining the most pronounced peaks of lead at the half-wave around –0.38 V.

Additionally, in manufactured PAPR fertilizers were made an extraction of water-soluble phosphorus and total phosphorus extraction with a mixture of hydrochloric and nitric acid according to Polish Norm PN-88, C-87015 [15, 16].

**Water soluble phosphorus**

Approximately 1 g of fertilizer sample was added to the 500 cm³ flask, then 400 cm³ of water was poured and the flask was placed into the rotational set where it was shaken for 0.5 h at 45 rpm. Then a flask was filled up with distilled water and carefully mixed. After the residue precipitate the solution was filtered through the dry filter into dry vessel. Phosphorus concentration was measured in the water phase.

**Total phosphorus**

Fertilizer sample 1 g was added to 400 cm³ beaker. Then 50 cm³ of the nitric and hydrochloric acid mixture at 3:1 ratio (v/v) was poured into the beaker. The solution was heated to boiling for 0.5 h. After this time 100 cm³ of water was added and boiled again for 15 minutes. When the mixture was cooled it was transferred quantitatively to the 500 cm³ flask, carefully mixed and filtered to the dry vessel rejecting about 50 cm³ of the first part of the filtrate.

**Spectrophotometric analysis**

Samples of 1 cm³ from the received filtrate was added to the 100 cm³ flask. Next the 20 cm³ of the vanadate-molybdate complex and the distilled water were poured to the flask. Solutions were left for 15 minutes at room temperature. After this time absorbance was measured at 430 nm wave-length using spectrophotometer of the JASCO company. Phosphorus content in the analyzed fertilizers samples was found from the calibration curve which was prepared in earlier investigations.

**Results and discussion**

Table 1 describes the average concentration of lead for varying degree of PAPR stoichiometric norm, calculated in accordance with the formula in the Polish Norm PN-92/C-87070/05.

Additionally the content of lead in phosphate rock ZIN was measured, the preparing procedure was the same as for the PAPR type fertilizer samples [PN-92/C-87070/05]. For the phosphorous material concentration of lead was equal to: 1.00375 µg/g.
Table 1

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( \eta_{\text{PAPR}} )</th>
<th>Lead content [( \mu g/g )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.364</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.368</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.375</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.487</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.948</td>
</tr>
</tbody>
</table>

The investigations revealed that increased values of lead content in obtained fertilizer samples were followed by raising the \( \eta_{\text{PAPR}} \) value. The lead content in ZIN phosphate rock is higher in comparison with the PAPR-type formulations.

\[ \text{Fig. 1. Comparison of the content ratio of lead to phosphorus soluble in water [} \alpha = \frac{\text{Pb}}{\text{P}_2\text{O}_5} (\mu g/g)/(mg/100 \text{ cm}^3)] \text{ in relation to various degree of PAPR stoichiometric norm} \]

The lead content in obtained PAPR-type fertilizers were compared with a \( \text{P}_2\text{O}_5 \) content by calculating the \( \alpha \) coefficient. Coefficient \( \alpha \) was obtained by dividing the concentration of lead (Table 1) by the content of water soluble phosphorus or total phosphorus (Table 2) in a PAPR-type fertilizers:

\[ \alpha = \frac{\text{Pb}}{\text{P}_2\text{O}_5} \frac{\mu g}{g} \frac{mg}{100 \text{ cm}^3} \]

where: \( \text{Pb} \) – concentration of lead in a sample of PAPR-type fertilizers [\( \mu g/g \)],

\( \text{P}_2\text{O}_5 \) – content of water-soluble or total phosphorus in PAPR – type fertilizers [\( mg/100 \text{ cm}^3 \)].
Content of P₂O₅ soluble in water and a mixture of HNO₃ + HCl (3:1 v/v) in phosphate PAPR-type fertilizers

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>ηₚ₆₉</th>
<th>P₂O₅ soluble in water [mg/100 cm³]</th>
<th>P₂O₅ soluble in HNO₃ + HCl [mg/100 cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.318</td>
<td>3.031</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.678</td>
<td>2.782</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>1.035</td>
<td>2.788</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>1.346</td>
<td>2.651</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1.645</td>
<td>2.409</td>
</tr>
</tbody>
</table>

Water soluble phosphorus was measured using spectrophotometry method with vanadate-molybdate complex in water phase, while the total phosphorus was determined through the initial mineralization of fertilizer preparations using a mixture of nitric and hydrochloric acids in a volume ratio of 3:1, and then by spectrophotometry method [15, 16]. The resulting coefficients were related to varying degrees of PAPR stoichiometric norm.

Fig. 2. Comparison of the content ratio of lead to phosphorus soluble in mixture of mineral acids HNO₃ + HCl (3:1 v/v) \( \alpha = \frac{\text{Pb/P₂O₅ (µg/g)/(mg/100 cm³)}}{\text{P₂O₅ soluble in HNO₃ + HCl [mg/100 cm³]}} \) in relation to various degree of PAPR stoichiometric norm

The coefficient based on the analysis of content ratio of lead to phosphorus soluble in mixture of mineral acids HNO₃ + HCl (3:1 v/v) (Fig. 2) represent the raising trend with increased ηₚ₆₉ values and lead concentration contained in the PAPR-type fertilizers. Lead comes in this case mainly from phosphoric raw material, phosphate rock ZIN. The small contamination of samples with used reagents is also observed, these are vestigial amounts of lead inserted with the reagent. For coefficient based on the analysis of content ratio of lead to phosphorus soluble in water, the reverse trend is observed comparing to the total phosphorus. It is related with a fact that with increasing degree of PAPR stoichiometric norm the content of water soluble phosphorus also increases, that
is phosphorus compounds available to plants and living organisms, but in the other hand the total content of phosphate decreases.

Conclusions

The results indicated that the highest lead content was found in an unprocessed ZIN (Israeli) phosphate rock which is caused by the ability of phosphate minerals to absorb this heavy metal. However, phosphate rock ZIN shows a very low content of lead compared to those from other regions of the world, such as phosphate rock from Pakistan with an average lead content of 89 μg/g or phosphate located in the South Africa-35 μg/g [17].

Partial acidulation of phosphate raw material by using less than stoichiometric amount of sulfuric acid allowed to obtain PAPR-type fertilizer formulations with lower lead content than the phosphate rock. Use of sulphuric acid in the analysis caused the transformation of organic lead compounds in the hard-absorbable sulphureous forms. In addition, the polarographic analysis has shown that with increasing degree of stoichiometric norm slightly increases the lead content in the investigated samples in relation to the quantity of total phosphorus.

The most preferred, due to the limited content of heavy metal toxicity, is the application of the lower $\eta_{\text{PAPR}}$ values and using phosphate rocks with the smallest content of this heavy metal. The lead content in produced PAPR-type fertilizers is so low that when we use them for fertilization in temperate climate zone, for example for corn, which shows the greatest response to phosphorus fertilization, the content of lead per 1 ha of crop would be only 9.61 mg of Pb (using $\eta_{\text{PAPR}} = 0.1$) [18]. Therefore, fertilizers containing partially acidulated phosphate rocks are relatively competitive to other phosphate fertilizers. Their application may contribute to decrease in the level of lead content in agricultural soils, which has a beneficial effect on the microflora, microfauna, and reduce the potential risk to human health.

References

Abstrakt: Nawozy zawierające częściowo rozłożony fosforyt, czyli nawozy typu PAPR (z ang. partially acidulated phosphate rock) wykazują długotrwałe działanie dzięki zawartości fosforu o różnym stopniu rozpuszczalności. Ważna jest optymalizacja składu nawozów typu PAPR. Znajomość poziomu stężenia metali ciężkich w danym nawozie może się okazać kluczowa, jeśli chodzi o ekologiczne i zdrowotne aspekty wykorzystywania nawozów fosforowych częściowo rozłożonych. W badaniach zastosowano produkty typu PAPR otrzymane w warunkach laboratoryjnych poprzez roztwarzanie fosforytów z niestechochemiczną ilością kwasu siarkowego. Następnie przeprowadzono mineralizację uzyskanych nawozów w celu oznaczenia stężenia ołowiu. Zawartość ołowiu w nawozach typu PAPR badano za pomocą urządzenia Autolab metodą woltamperometrii pulsuwej różnicowej.

Słowa kluczowe: fosforyty częściowo rozłożone, metale ciężkie, ołów, woltamperometria