

Article

Influence of the Process Parameters on the Synthesis of Urea Phosphate and the Properties of the Obtained Product

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Abstract: The ever-increasing food demand associated with the growing human population poses similar challenges to both farmers and fertilizer producers. In view of climate change and the increasing area of infertile land, it is very important to use correctly balanced and highly effective fertilizers in agriculture. Water-soluble fertilizers are becoming more and more popular. It is convenient to use them together with irrigation water because this reduces the negative effects of droughts and accelerates the assimilation of nutrients needed by plants. The aim of this work was to synthesize urea phosphate (UP) (water-soluble complex nitrogen–phosphorus fertilizers NPF) through the reaction of phosphoric acid and urea. The most important moment of the work is that the synthesis was carried out using a purified wet-process phosphoric acid (PWPA) and urea by varying the stoichiometric ratio and the duration time of crystallization. Based on the results of the experiment, it was found that, in the presence of excess acid, the concentration of phosphorus pentoxide (P_2O_5) is too high, the concentration of amide nitrogen (N_{amide}) is too low, and vice versa. The best ratio of P_2O_5 and N_{amide} was determined when both reactants were used in a ratio of 1.0:1.0. Crystallization was carried out at 20 °C with different reaction times: 30, 60, 90 and 120 min. Analysis of the chemical composition of the synthesized urea phosphate and determination of the main components, i.e., N_{amide} and P_2O_5 concentrations, were performed using standard fertilizer analysis methods. Using the optical emission spectroscopy, the concentrations of chemical elements (sulphur, aluminium, iron, calcium, magnesium, silicon, etc.) were also determined in the synthesized product. During the experiment, not only the chemical composition of the product, but also the resulting crystals of the product, and their size and shape—properties that are highly dependent on the duration of crystallization—were analysed. The thermal stability of UP crystals was investigated using simultaneous thermal analysis; the crystallinity of UP was determined using X-ray diffraction analysis; the identification of groups of chemical elements was carried out using Fourier Transform Infrared spectroscopy analysis; the shape and size of crystals were investigated using scan electron microscopy and optical microscope techniques.



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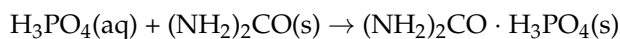
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1. Introduction

Fertilizers with certain plant nutrients are selected depending on the type of plant, season, soil, and climate conditions. Simple fertilizers, which contain only one of the main nutrients, i.e., only nitrogen, only phosphorus or only potassium, are still popular because they have a high concentration of this active substance [1,2]. However, compound fertilizers, which contain at least two and often all three basic nutrients, are more popular and more efficient [3,4]. Nitrogen–phosphorus fertilizers (NPF) are one such compound fertilizer. Complex fertilizers can be obtained when the chemical reaction product is in liquid or solid form. One such chemically produced compound fertilizer is urea phosphate (UP). Urea phosphate fertilizer has advantages when compared with fertilizers such as monoammonium phosphate (MAP) or diammonium phosphate (DAP), which contain

phosphorus, because it contains urea nitrogen and phosphorus in the water-soluble form [5]. The production of UP from pure phosphoric acid involves a reaction of the solid crystalline urea with pure orthophosphoric acid (concentrated phosphoric acid, containing more than 90% of H_3PO_4 by weight) in an essentially anhydrous form. The synthesis of these products occurs according to the following chemical reaction [6]:



Phosphoric acid is heated to a temperature of 60–90 °C to induce a spontaneous reaction with crystalline urea. After orthophosphoric acid is mixed with urea, the mixture must be actively cooled because of the exothermic reaction. The reaction takes place after a few seconds and in this mass of suspension, monocrystalline crystals of urea phosphates are suddenly formed. The resulting product is crystalline urea phosphate containing only 0.4% water [6]. In this case (pure $\text{H}_3\text{PO}_4 \cdot \text{CO}(\text{NH}_2)_2 = 1:1$), the theoretical values of concentrations of nitrogen and phosphorus in urea phosphate are N—17.7%, P_2O_5 —44.9%.

Long B. et al. state that the contents of phosphorus (based on phosphorus pentoxide) and nitrogen in the urea phosphate product are $(44.75 \pm 0.11)\%$ and $(17.27 \pm 0.18)\%$ (mass percent). Therefore, the mass ratios of N:P and N: P_2O_5 are 0.884 and 0.386, respectively. The water content was determined to be $(0.042 \pm 0.005)\%$ [7]. UP is acidic (pH 2.75 of 0.05% solution) and very soluble in water (960 g/L at 20 °C) [6,8]. In the production of urea phosphate, the wet-process phosphoric acid (WPA) can be used, but there are problems with product yield and impurities. This is because the so-called wet-process phosphoric acid (WPA) is usually produced from apatite and phosphorites, which contain a lot of impurities, such as fluorine, arsenic, calcium, iron, aluminium, lead and other metals; therefore, the use of the resulting acid is very limited [9]. It goes without saying that the quality of the final product greatly depends on the quality of the raw materials used. For this reason, WPA produced by conventional sulfuric acid wet-process methods, is used primarily in the manufacture of fertilizer materials in which purity is not a primary consideration. However, with the development of technology, such incompletely pure acid can be purified, and sufficient purity can be obtained to completely suit the production of urea phosphate.

Mubarak Y. A. [8] also states that UP can be produced from WPA through a modified procedure. A liquid mixture of urea and phosphoric acid cannot be obtained without additional heating, as the urea must dissolve. The optimum reaction temperature is around 45 °C; below this temperature, the recovery is slightly reduced, and the resulting crystal size is smaller. The solid content of urea remaining in the mixture is a very important step in the production of crystalline urea phosphate. After a certain time, the mixture is transferred from the reactor to a 15 °C temperature-controlled crystallizer. The reaction and crystallization time vary from 2 to 3 h. The modified procedure involves the addition of a certain percentage of mother liquor to the urea and untreated wet-process phosphoric acid in the reaction vessel. An intermediate product, crystalline urea phosphate, is produced from urea and merchant-grade (54% P_2O_5) wet-process phosphoric acid in the production of a high-quality urea-ammonium polyphosphate base solution. However, the urea phosphate crystals contain from 15% to 20% of the objectionable impurities (iron, aluminium, and magnesium) originally contained in the feed wet-process acid [10]. The process of producing UP comprises the bringing together of the mother liquor from which solid urea phosphate has been separated and urea in such amounts and proportions that there is a concentration of at least 55% of H_3PO_4 by weight, and from about 1 mol of urea to 1 mol of phosphoric acid are present. If desired, urea can be added as a solution [11].

Alternatively, a two-stage continuous crystallization process to produce UP by reaction of impure WPA and urea can be carried out. At the same time, an acidifying agent of choice (H_2SO_4 , HCl or H_3PO_4) is added to clarified mother liquor, which is used as a remnant in the process. Adding the acidifying agent lowers the pH during the crystallization process, increasing the solubility of the contaminated water-insoluble iron phosphate–urea salt. These changes improve the purity of the crystalline UP product and extend the service life

of the recycled mother liquor. UP contains 17.7% N and 19.6% P (equivalent to 44.9% P_2O_5), the pH of 1% solution is 1.8, and the specific gravity is $1.759 \text{ kg}\cdot\text{m}^{-3}$ [12].

UP is also used as a main component in the process of obtaining solid binary NPF. In this case, the action of urea phosphate ammonisation and condensation is used. Because of the way it is formed, this compound allows for the separation of wet-process orthophosphoric acid impurities, such as iron, aluminium, calcium, magnesium, and fluorine, which remain in mother solutions during the centrifugation of urea phosphate crystals. In this way, the chemical reactions between phosphoric acid, urea and ammonia are combined in such a way that the overall thermal balance is in excess, thus making it possible to operate under autothermal conditions [13]. Due to the large quantity of impurities in the WEP, it is not easy to produce large crystals of urea phosphate. They are usually very fine, and the final product is oily or sticky. Crystals are very difficult to dry even at high air temperatures or for long drying times [8].

Having evaluated all the possibilities of producing UP and the challenges that arise during this process, the aim of this work was to synthesize pure UP (water-soluble complex nitrogen–phosphorus fertilizers (NPF)) through the reaction of phosphoric acid and urea in optimal condition. The novelty of the work is that the UP synthesis was carried out using a purified wet-process phosphoric acid (PWPA) and technical urea by varying the stoichiometric ratio of raw materials and the duration time of crystallization. The use of PWPA and technical urea made it possible to synthesize a sufficiently pure UP without imposing special conditions on the purity of the raw materials and without making the final product more expensive.

2. Materials and Methods

The following WPA and urea were used in the experiment: phosphoric acid (H_3PO_4) was produced by AB Lifosa, by applying the wet method with a density of $1.64 \text{ g}\cdot\text{cm}^{-3}$ at 20°C ; the product had a P_2O_5 concentration of 53.6% [14]; industrial urea (IU) produced by AB Achema with N_{amide} concentration of 46.5% [15]. The synthesis was carried out for 1 h by mixing urea and wet-process phosphoric acid in the ratios of 1.5:1.0; 1.0:1.0; 1.0:1.5 at a temperature of 45°C and using a High Torque Lab Stirrer Package (speed 140 rpm) (Mixer Direct, Jeffersonville, IN, USA). Then, the product of synthesis was crystallized using a Werke HBR 4 cold water bath (IKA-Werke GmbH, Staufen, Germany) with ice and mixing speed 100 rpm (Mixer Direct, Jeffersonville, IN, USA). The crystallization time was 30, 60, 90 and 120 min at a temperature of 20°C . After crystallization, the obtained urea phosphate crystals were filtered with a Buchner filter, dried for 6 h at a temperature of 40°C and then analysed.

The concentration of P_2O_5 was determined by applying a colorimetric method based on the measurement of yellow phosphorus vanadium molybdenum complex ($P_2O_5\cdot V_2O_5\cdot 22MoO_3\cdot nH_2O$) compared to a P_2O_5 solution of known concentration at a wavelength of 440 nm. Using a standard solution of potassium dihydrogen phosphate, a graduation graph was made [16]. Light absorption was measured using a photo colorimeter (T70/T80 UV-VIS, PG Instruments Limited, Luttermouth, UK).

Nitrogen was mineralized in the Gerhardt Kjeldatherm KB/KBL mineralizer (Gerhardt GmbH & Co. KG, Koenigswinter, Germany) with sulfuric acid, using a copper sulphate and potassium sulphate catalyst, until ammonia nitrogen was obtained. Ammonia nitrogen concentration was determined by applying the Kjeldahl method [17] using a Vapodest 45s.

Determination of chemical elements (sulphur, aluminium, iron, calcium, magnesium, silicon, etc.) was carried out with an atomic absorption spectrometer (PerkinElmer, Fullerton, CA, USA) using optical emission spectroscopy—Fully Simultaneous analysis (ICP–OES). Chemical elements were broken down and extracted by boiling the sample in concentrated acids. The obtained sample was sprayed into the plasma, which was heated by gas (argon). Highly ionized argon plasma can reach temperatures as high as 10,000 K, allowing for complete atomization of the compounds within a sample and minimizing the potential for chemical interferences [18]. Temperature stability $\pm 0.5^\circ\text{C}$. The radiation

emission of the atoms of the element under investigation was measured. Perkin Elmer standard solutions were used to prepare the calibration solution. The calibration curve was drawn, and the results were calculated in the computer program of the device [19]. Thus, the concentration of chemical elements in urea phosphate crystals was determined using an induced plasma optical emission spectrometer Perkin Elmer ICP–OES 8000 Optima (PerkinElmer, Fullerton, CA, USA).

Fourier Transform Infrared spectroscopy (FTIR) analysis was performed with a spectrometer system SPECTRUM GX 2000 (PerkinElmer, Waltham, MA, USA) and transmission was measured in the wavenumber range 4000–400 cm^{-1} . Sample tablets were formed using KBr [20].

The crystallinity of solid phase was determined by the X-ray diffraction (XRD) analysis using the diffractometer “DRON–6” for $\text{CuK}\alpha$ radiation (Malvern Panalytical Ltd., Malvern, UK). The following settings were used: nickel filter; 0.02° movement step of detector; 0.5 s duration of intensity measurement in the step; 30 kV voltage; angle from 3° to 70° ; rotation angle 2θ . The substances were identified by a computer using the “SearchMatch Version 2,1,1,1” database.

A simultaneous thermal analysis (STA) test was performed with a LINSEIS STA PT–1000 thermal analyser (Linseis Messgeraete GmbH, Selb, Germany). DSC-TG parameters were as follows: the heating rate was $10^\circ\text{C}/\text{min}$, the temperature ranged from 30 to 300°C , standard Al (99.99% purity) was crucible, the atmosphere in the furnace was nitrogen N_2 ($20\text{ cm}^3/\text{min}$). The accuracy of measurements was $\pm 3^\circ\text{C}$ [21].

To scan electron microscopy (SEM), the FEI Quanta 200 FEG electronic microscope (FEI Company, Hillsboro, OR, USA) was used at magnification rates of 5000 and electron acceleration voltage of 5 kV. A secondary electron detector was used to produce a topographic SEM image and Electron source—pre-centred cartridge type tungsten hairpin filament. Before SEM analysis, the product was dried to a constant mass (moisture content less than 1 percent) [22].

Crystal images were obtained using a Leica DM500 biological optical compound microscope (Leica Microsystems, Mannheim, Germany). One drop of crystals was placed on a glass plate and a drop of glycerol was added. After adjusting the lighting and brightness, the crystals were photographed with the help of a computer program and a photo obtained was enlarged 200 times. The photos were processed with the Leica Application Suite V4 computer program [23].

The material was dissolved in water and the turbidity of the fertilizer solution was directly measured with the Turb 550/Turb 550 IR turbidity measuring device (WTW GmbH, Weilheim, Germany). The result was a number measured directly by the device in Nephelometric Turbidity Units (NTU), i.e., the unit used to measure the turbidity of a fluid or the presence of suspended particles in water [24].

The results were expressed as the arithmetic mean of no less than three measurements \pm standard deviation (SD). The results were calculated with 95% probability. In all cases, the significance level was $p \leq 0.05$. One-way analysis of variance (ANOVA) was used to evaluate the differences in the means between groups. Depending on the accuracy of the method, the investigation of the properties of the same sample was performed 3–5 times; the arithmetic mean of the determined values is presented in this study [25].

3. Results and Discussions

3.1. Characteristics of the Phosphoric Acid Used for the Synthesis of UP

As mentioned, the literature sources [26] state that, compared to pure phosphoric acid, WPA used in industry contains a large number of various impurities that affect the quality of the resulting fertilizer. Therefore, wet-process phosphoric acid, which had been defluorinated, desulfurized and passed through precipitators, was used in this study. These stages of WPA purification resulted in lower relative density ($1.5\text{ g}/\text{cm}^3$) and reduced impurity concentration compared to the initial WPA (Table 1).

Table 1. Concentrations of P₂O₅ and other elements in WPA.

Elements	Units	Concentration	Elements	Units	Concentration	Elements	Units	Concentration
P ₂ O ₅	%	44.18	Bi	mg/kg	<3	Ni	mg/kg	6.4
S	%	0.04	Co	mg/kg	5.0	Se	mg/kg	<3
Al	%	0.16	Cr	mg/kg	11.2	Sr	mg/kg	21.8
Fe	%	0.50	Cu	mg/kg	11.5	Ti	mg/kg	200.5
Ca	%	0.75	Ga	mg/kg	16.9	Tl	mg/kg	<1
Mg	%	1.34	In	mg/kg	1.3	V	mg/kg	23.9
Si	%	0.004	K	mg/kg	448.6	Zn	mg/kg	10.4
Ag	mg/kg	<467	Li	mg/kg	2.3	As	mg/kg	<2
B	mg/kg	<11	Mn	mg/kg	348.4	Pb	mg/kg	<1
Be	mg/kg	2.0	Mo	mg/kg	1.0	Cd	mg/kg	<1.6
Ba	mg/kg	<5	Na	mg/kg	984.4	F	%	0.13

It was determined that the concentration of P₂O₅ in purified WPA (PWPA) was 44.18%. ICP–OES results showed that most of the impurities in the PWPA did not exceed 1%, except for magnesium, which was 1.34%. Certain concentrations of other chemical elements, such as potassium—448.6 mg/kg, sodium—984.4 mg/kg, manganese—348.4 mg/kg, which are not found in pure phosphoric acid, were found. This means that the purification process was effective, but the PWPA is not completely pure, and the impurities can affect the synthesis of UP. However, after evaluating the economic aspects, i.e., the prices of pure (thermal process phosphoric acid) and purified PWPA, the latter phosphoric acid was chosen as the raw material for the production of UP.

3.2. The Influence of the Crystallization Conditions on the Chemical Composition of the Obtained Product

When urea interacts with phosphoric acid at different stoichiometric ratios of initial substances, the final product is also different. The duration of synthesis and crystallization also has an influence on the properties of the final product. On the other hand, the cost-effectiveness also depends on the duration of crystallization, so it was necessary to determine the conditions under which the most economical and high-quality product, i.e., UP, can be produced.

The synthesis was performed by changing the stoichiometric ratio of phosphoric acid and urea (1.5:1.0; 1.0:1.0; 1.0:1.5) and the duration of crystallization (30, 60, 90, and 120 min). The concentration of P₂O₅ and N_{amide} was chosen as the main criteria of optimal conditions for the synthesis–crystallization reaction, because these two substances are the main indicators for the production of high-quality urea phosphate that is suitable for production [27]. Concentrations of sulphur, aluminium, iron, calcium, magnesium, silicon were also monitored in the final product because their content in PWPA was the highest (%). The concentration of P₂O₅, N_{amide}, Al, Fe, Ca, Mg, S, and Si elements, moisture content and NTU were determined in the product obtained through reaction with stoichiometric ratio PWPA:IU = 1.5:1.0. The results obtained with different crystallization times are presented in Figure 1a and Table 2.

It was found that, in this case, the required concentration of P₂O₅ and N was not reached (Figure 1a). The concentration of P₂O₅ in UP was 45.1–45.3% (±0.15–±0.21), which means it was slightly higher than required (theoretically calculated concentration of 44.9% P₂O₅), and the nitrogen concentration (N_{amide}) concentration was 16.3–16.8% (±0.02–±0.06), which is lower than the theoretically calculated concentration of 17.7%.

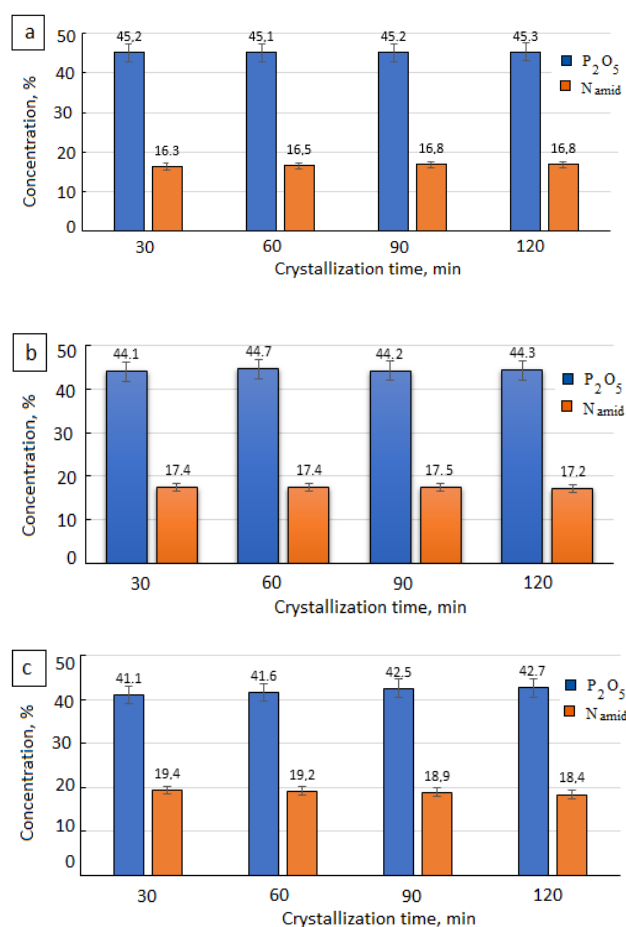


Figure 1. Dependence of the concentration of N_{amid} and P₂O₅, on the duration of crystallization when UP is made from PWPA and IU at a stoichiometric ratio: (a)—1.5:1.0; (b)—1.0:1.0; (c)—1.0:1.5.

Table 2. Chemical composition, NTU and moisture content of UP produced with different crystallization times at a stoichiometric ratio PWPA:IU = 1.5:1.0.

Crystallization Time, min	pH	NTU	Moisture Content, %	Concentration of Chemical Elements, %					
				Si	S	Al	Fe	Ca	Mg
30	2.65	3	1.45	<0.003 ±0.001	0.017 ±0.01	0.04 ±0.02	0.14 ±0.07	0.14 ±0.05	0.39 ±0.21
60	2.64	3	1.28	<0.003 ±0.002	0.014 ±0.01	0.03 ±0.01	0.12 ±0.05	0.14 ±0.08	0.31 ±0.22
90	2.63	2	1.03	<0.003 ±0.002	0.011 ±0.01	0.03 ±0.02	0.11 ±0.06	0.13 ±0.06	0.29 ±0.21
120	2.60	4	0.90	<0.003 ±0.001	0.010 ±0.01	0.03 ±0.01	0.09 ±0.07	0.14 ±0.06	0.28 ±0.23

The moisture content of the product is not high and, as the crystallization time increases, the moisture content in the product decreases from 1.45% to 0.90%. However, it was found that the product obtained under such conditions is sticky and oily like honey or resin. From the data presented in Table 2, it can be seen that the concentrations of sulphur, aluminium, iron, calcium, magnesium were highest in the UP whose crystallization time was only 30 min. It can be seen that sulphur, iron and magnesium concentrations decreased with increasing crystallization time: concentrations of sulphur decreased from 0.017% to 0.01%, concentrations of iron decreased from 0.14% to 0.09%, and concentrations of magnesium decreased from 0.39% to 0.28%. the concentration of other elements did not change. NTU ranged between

2 and 4 and no clear dependence on the duration of crystallization could be determined. The pH values of UP varied from 2.65 to 2.60. Because UP is an acidic fertilizer, it facilitates the absorption of other nutrients by the plants and also has positive effects on the pH value of water used for watering. UP dissolves bicarbonate in water and prevents blockages in watering pipes and nozzles [5]. Since the biggest changes occur within the first 60 min of crystallization, the UP produced during this time was further analysed.

After evaluating the results obtained by us and the data presented in the literature [10], a synthesis of PWPA and IU at a stoichiometric ratio of 1.0:1.0 was also carried out by changing the crystallization time: 30, 60, 90, and 120 min. The results obtained from this study are presented in Table 3 and Figure 1b.

Table 3. Chemical composition, NTU and moisture content of UP for different crystallization times at a stoichiometric ratio PWPA:IU = 1.0:1.0.

Crystallization Time, min	pH	NTU	Moisture Content, %	Concentration of Chemical Elements, %					
				Si	S	Al	Fe	Ca	Mg
30	2.65	5	0.53	<0.003 ±0.001	0.009 ±0.003	0.03 ±0.01	0.11 ±0.07	0.13 ±0.09	0.33 ±0.21
60	2.64	2	0.48	<0.003 ±0.001	0.008 ±0.002	0.02 ±0.01	0.08 ±0.03	0.08 ±0.04	0.22 ±0.18
90	2.63	5	0.47	<0.003 ±0.002	0.009 ±0.003	0.03 ±0.02	0.11 ±0.08	0.13 ±0.10	0.33 ±0.25
120	2.60	2	0.46	<0.003 ±0.001	0.009 ±0.004	0.02 ±0.01	0.08 ±0.05	0.07 ±0.04	0.21 ±0.17

The concentration of P_2O_5 and N_{amide} depends little on the duration of crystallization and 60 min of crystallization is a sufficient time. As the crystallization time increases, the moisture content in the product decreases from 0.53% to 0.48% during 60 min of crystallization and, after two hours of crystallization, it drops to 0.47%. Similar results were obtained for other chemical elements present in urea phosphate crystals when evaluating the duration of crystallization (Table 3). When the reaction time was 30 min and 90 min, contents of 0.03% aluminium, 0.11% iron, 0.13% calcium, 0.33% magnesium were obtained, and when it was 60 min and 120 min, 0.02% aluminium, 0.08% iron, and calcium, were obtained, where magnesium differs only by 0.01%. It can be concluded that the UP produced in this stoichiometric ratio (PWPA:IU = 1.0:1.0) after crystallization for 60 min or 120 min has slightly fewer impurities. NTU values range from 2 to 5 and vary similarly to those of aluminium, iron, calcium, magnesium concentrations. The pH values of UP slightly vary, from 2.65 to 2.60.

Figure 1b shows that the concentration of P_2O_5 and N_{amide} corresponds well enough to the theoretically calculated concentration in urea phosphate, which is 44.1–44.7% (± 0.15 – ± 0.21) and 17.2–17.5% (± 0.02 – ± 0.04), respectively. Compared with the theoretical ratio ($N: P_2O_5 = 0.394$), our result is very close $N: P_2O_5 = 0.389$. In addition, the concentration of nutrients (nitrogen and phosphorus together) is 99.2% of the theoretical value.

The synthesis and crystallization of PWPA and IU was also carried out at a stoichiometric ratio of 1.0:1.5, changing the duration time of crystallization to 30, 60, 90, and 120 min. The concentrations of P_2O_5 and N_{amide} are presented in Figure 1c. Under these conditions, the ratio of P_2O_5 and N_{amide} and their concentration in produced UP do not correspond to the theoretical values. The concentration of P_2O_5 , depending on the crystallization time, is 41.1–42.7% (± 0.15 – ± 0.35), but in all cases is less than 44%. Nitrogen concentration in the product was 18.4–19.4% (± 0.01 – ± 0.06), i.e., much too high. In general, it can be seen from the graph that, as the crystallization time increases, the concentration of phosphorus increases and the concentration of nitrogen decreases, but the time of

120 min is too short to reach the theoretical values. Therefore, such a stoichiometric ratio is completely inappropriate.

The concentration of sulphur, aluminium, iron, calcium, magnesium, silicon and other properties of UP produced under these crystallization conditions are presented in Table 4. As the crystallization time increases, the moisture content in the product decreases slightly, i.e., from 0.57% to 0.50%. the concentration of sulphur, aluminium, iron, calcium, magnesium also decreases, but the concentration of silicon remains the same. As in other cases, the greatest change in parameters is observed within 60 min of the start of crystallization, for example, in 60 min, the concentration of Mg decreases from 0.33% to 0.24%, and then only from 0.24% to 0.23%. The change in NTU, in this case, is minimal, and the pH values, like in other cases, slightly decrease from 2.70 to 2.56 as the crystallization time increases.

Table 4. Dependence of the chemical composition (NTU and moisture content) of urea phosphate obtained at a ratio of extractable phosphoric acid and industrial urea of 1.0:1.5 on the duration of crystallization.

Crystallization Time, min	pH	NTU	Moisture Content, %	Concentration of Chemical Elements, %					
				Si	S	Al	Fe	Ca	Mg
30	2.70	3	0.57	<0.003 ±0.001	0.012 ±0.011	0.05 ±0.03	0.15 ±0.13	0.14 ±0.12	0.33 ±0.11
60	2.69	4	0.53	<0.003 ±0.002	0.008 ±0.003	0.04 ±0.01	0.11 ±0.07	0.09 ±0.05	0.24 ±0.11
90	2.67	4	0.52	<0.003 ±0.001	0.007 ±0.002	0.03 ±0.02	0.09 ±0.04	0.09 ±0.05	0.23 ±0.13
120	2.56	4	0.50	<0.003 ±0.002	0.008 ±0.004	0.03 ±0.01	0.09 ±0.04	0.11 ±0.08	0.23 ±0.11

3.3. The Influence of the Crystallization Conditions on the FTIR Spectrum of the Obtained Product

The obtained urea phosphate was also identified by the FTIR method. Figure 2a presents the IR spectrum of UP produced from PWPA and IU (PWPA:IU = 1.5:1.0) with a crystallization time of 60 min.

Vibrations of the valence –OH group in the region 3650–3200 cm⁻¹ can be seen, which confirms the presence of water in the crystal structure of urea phosphate. On the other hand, the double peaks at 3300–3500 cm⁻¹ are characteristic of NH₂ [28]. An intense band at 1668.04 cm⁻¹, visible in the IR spectrum, is attributed to the NH₂ group [28] or P=O stretch [6] because it falls into the vibrational region (1600–1740 cm⁻¹). Vibrations of the CO group are visible in the region 1260–1000 cm⁻¹. Vibrations of the PO₄³⁻ group visible in the region 1100–950 cm⁻¹ correspond to the 994 cm⁻¹ band, and the deformed vibrations of the PO₄³⁻ group correspond to the 480 cm⁻¹ band [29]. Vibrations visible in the region 875–710 cm⁻¹ are characteristic of the CO₂ group and probably represent CO₂ absorption from the environment [21].

The FTIR spectrum of the sample (PWPA:IU = 1.0:1.0) is displayed in Figure 2b. This clearly shows that all characteristic bands corresponding to urea phosphate are present, as stated by Abou-Okeil and El-Shafie [30]. According to Ilczyszko et al. [31], the characteristic bands of the urea phosphate can be attributed to three types of vibrations: urea vibration (NH₂, C=O and CN₂ species), phosphate vibration (PO₄³⁻ group) and hydrogen bond vibrations (O–H–O bond) [32]. Valence vibrations of the –OH group are visible in the frequency range of 3650–3200 cm⁻¹. An intense band (3459 cm⁻¹) is seen here, which describes the vibrations of the valence –OH group in the urea phosphate crystal structure. An intense 1667 cm⁻¹ band is visible in the 1680–630 cm⁻¹ region of NH₂ vibrations of the valence urea amide group. Also, in the vibrational region, 1100–950 cm⁻¹ band 992 cm⁻¹ is visible, which corresponds to the PO₄³⁻ group and the strained vibrations of the PO₄³⁻ group are seen in the 480 cm⁻¹ band. Vibrations of CO₂ groups in the region 875–710 cm⁻¹ (band 776 cm⁻¹) are also visible.

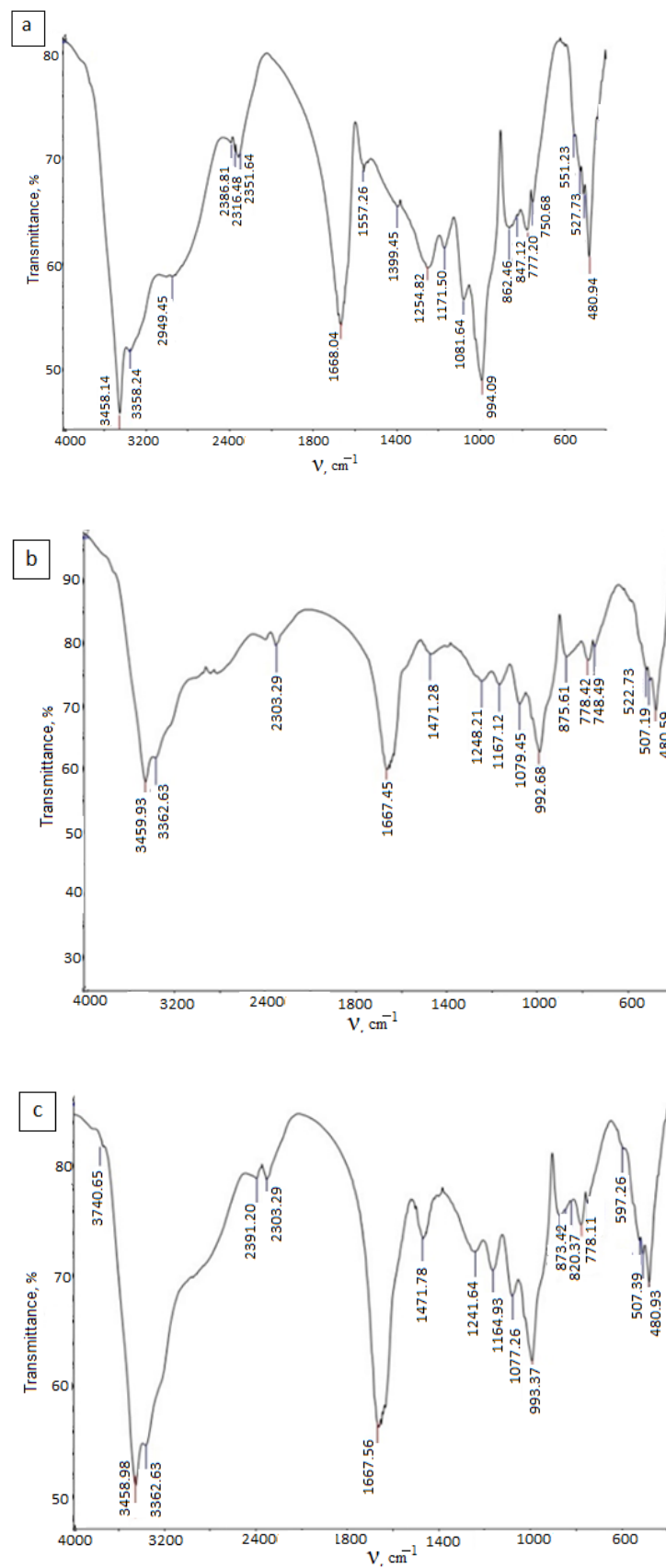


Figure 2. FTIR spectrum of UP produced with a different stoichiometric ratio PWPA:IU, when crystallization time is 60 min: (a)—1.5:1.0; (b)—1.0:1.0; (c)—1.0:1.5.

In the FTIR spectrum (Figure 2c) of UP produced from purified wet = process phosphoric acid and industrial urea (PWPA:IU = 1.0:1.5), with a crystallization time of 60 min, like in other cases, valence vibrations of the –OH group in the region 3650–3200 cm^{-1} are visible. There is an intense band 3458 cm^{-1} , describing the valence vibrations of –OH groups in the structure of urea phosphate crystals or those of NH_2 [28]. The band in the frequency range of 1667 cm^{-1} reflects the amide –NH₂ band, respectively [33]. In our opinion, vibrations in the spectrum part at 993 cm^{-1} and 480 cm^{-1} can be attributed to the PO_4^{3-} group, which corresponds to the data in the publication of Long B. et al. in the scientific literature [7]. The peaks related to the vibrations of CO_2 are also identified at 873 and 778 cm^{-1} , respectively.

3.4. The Influence of the Crystallization Conditions on the XRD of the Obtained Product

In order to confirm the results obtained above, an XRD analysis was performed. On the basis of the data acquired by performing the X-ray analysis (Figure 3a), it would be safe to claim that some of the diffractogram peaks are characteristic of pure UP ($d = 5.7230$; 4.3694; 3.8082 et al. Å), in accordance with the data in the SearchMach database. However, a very intense peak at 10.8091 Å, which is not attributed to urea phosphate, changes the overall characteristic spectrum of UP.

A curve (Figure 3b) was obtained by the XRD analysis, which confirmed the data of the chemical analysis. The material obtained under mentioned conditions is almost pure UP. All the visible peaks, except insignificant peaks with an interplanar d -spacing of 2.8494, 2.6019, 2.1053, and 1.6191 Å (which were not assigned to UP but could be assigned to urea), are characteristic of crystal urea phosphate.

In Figure 3c, the urea phosphate peaks are clearly visible. There are also many peaks not assigned to UP, but some of them could be assigned to urea. It is likely that the appearance of these peaks in the XRD spectrum is caused by a higher concentration of urea in the mixture of raw materials.

3.5. The Influence of the Crystallization Conditions on the STA of the Obtained Product

After performing a simultaneous thermal analysis (Figure 4a), it was found that, during the exothermic process (temperature range of 119–170 °C), the mass loss of the sample was initially 17.64%, then 5.94%, and then 16.71%. The total mass loss was about 41.13%. This means that, at a higher temperature of 119 °C, the substance is thermally unstable. The product loses the interlayering (crystalline) of chemically combined water and decomposes to release carbon monoxide or dioxide. In the temperature range of 178–190 °C, an insignificant endothermic effect takes place.

After STA, it was found that, during the exothermic process (at a temperature of 121–164 °C), the mass loss of the sample is 21.99%. Total mass loss is about 40.07% (Figure 4b).

After performing an STA (Figure 4c), it was found that, in the beginning, two endothermic processes take place, one after another. The first effect occurs at 64–81 °C with a mass loss of 0.02%, and the second one occurs at 86–103 °C with a mass loss of 0.54%. This is usually attributed to the removal of free water. An exothermic process follows at 116–168 °C; the mass loss is initially 17.9% and later reaches 24.66%. Total mass loss is 43.61%. A total of 88.48% of the product remains in the mixture; the other part is a part of the CO_2 released during the UP decomposition.

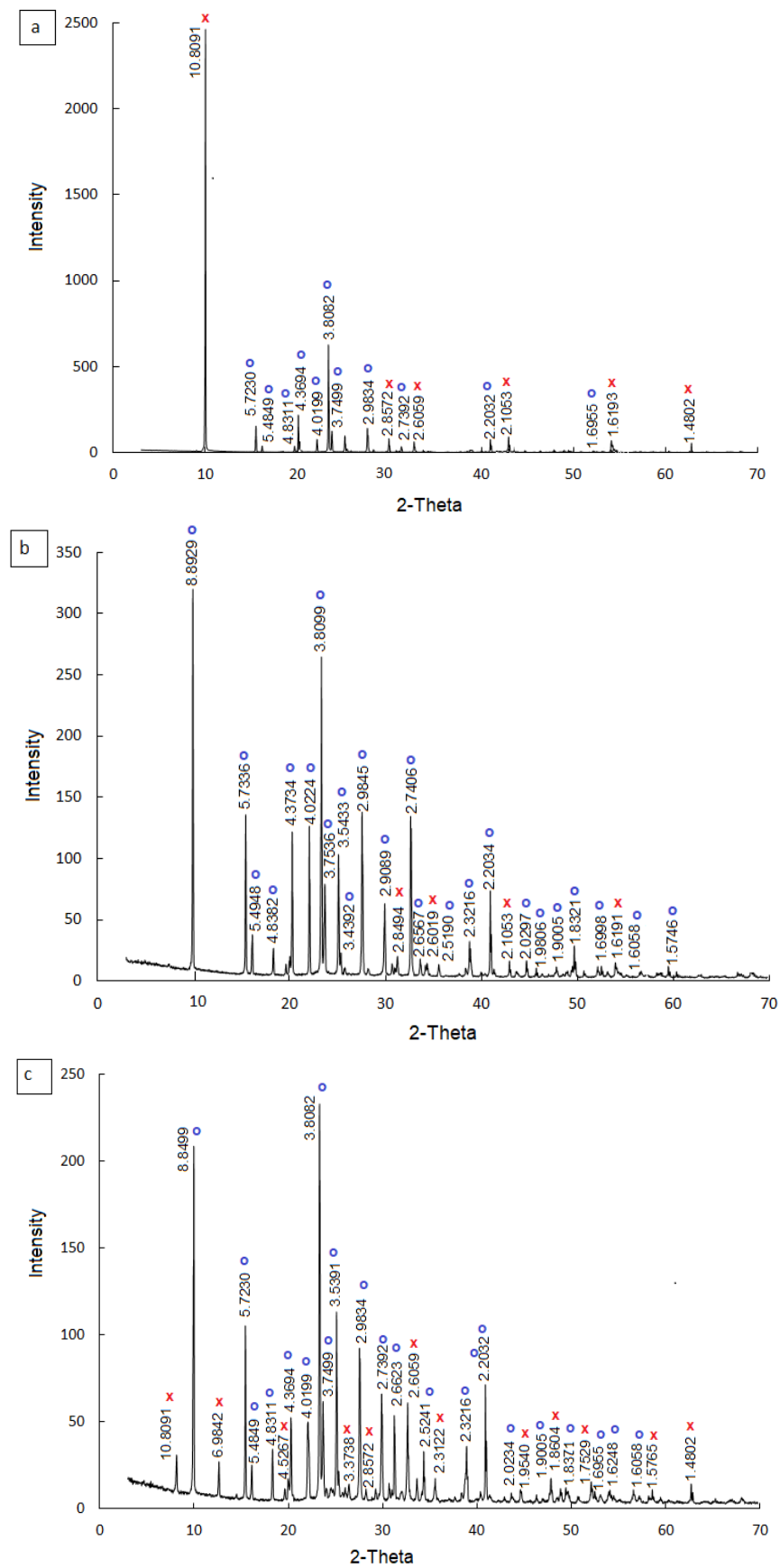


Figure 3. XRD curve of UP produced with a different stoichiometric ratio PWWA:IU, when crystallization time 60 min: (a)—1.5:1.0; (b)—1.0:1.0; (c)—1.0:1.5; x—unidentified, o—urea phosphate.

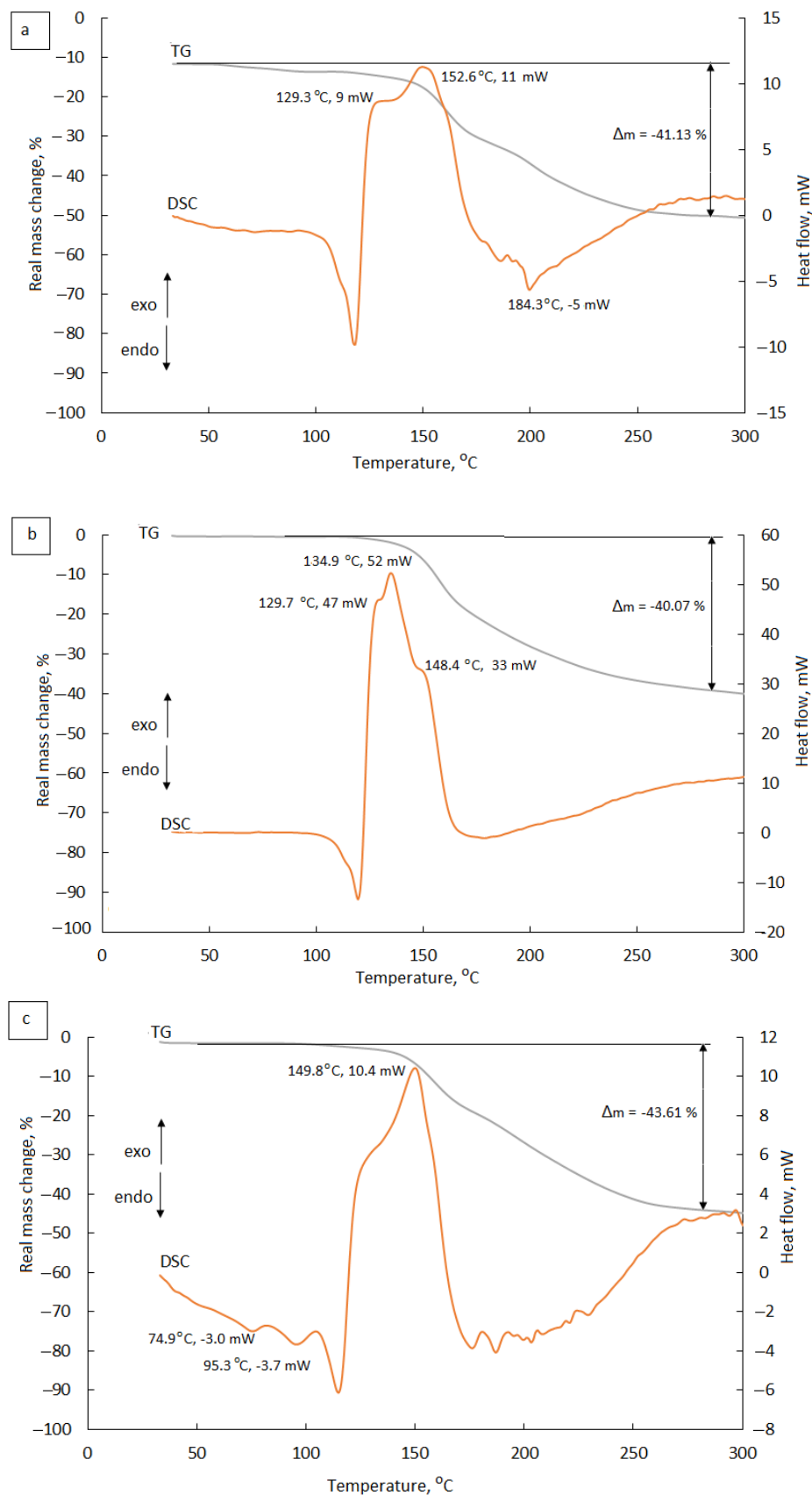


Figure 4. STA curves of the UP produced with a different stoichiometric ratio PWWA:IU, when crystallization time is 60 min: (a)—1.5:1.0; (b)—1.0:1.0; (c)—1.0:1.5.

3.6. The Influence of the Crystallization Conditions on the Crystal of the Obtained Product

Figure 5 presents the microscope photographs of the UP crystals formed during crystallization (at the beginning, and after 30 min and 60 min) at a 1.5:1.0 stoichiometric ratio of extractable phosphoric acid and industrial urea. The image of the UP crystals shows that they are colourless transparent prismatic crystals that have a typical orthorhombic shape and a wide range of diameters (200–500 μm). It has a parallel layered structure, and the layers are connected by hydrogen bonds, which belongs to orthorhombic crystal system. According to Long B. et al. [7], crystals have the same shape, but the average crystal size is about 836 μm , and this confirms the statement that the crystal size depends on the conditions of crystallization. It could be maintained that, in correspondence with the data presented in Table 2 (the greatest concentration of impurities is observed within 30 min from the start of crystallization and decreases as crystallization continues), crystallization is also a purification method, and increases in time are corroborated by crystal growth, as observed in Figure 5.

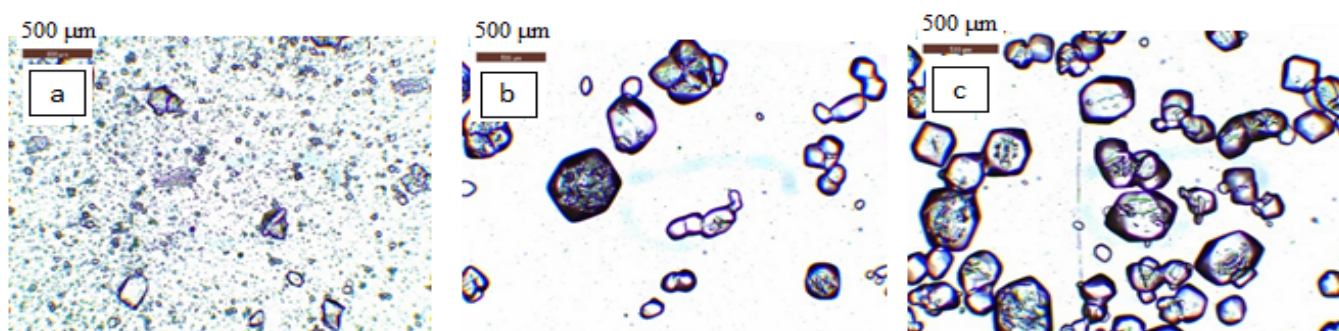


Figure 5. Microscope photographs of UP crystals obtained at a stoichiometric ratio PWPA:IU = 1.5:1.0 and a different crystallization time: (a)—at the beginning of crystallization; (b)—after 30 min; (c)—after 60 min.

Photographs of the crystals formed during crystallization at a stoichiometric ratio PWPA:IU = 1.0:1.0, obtained at different times of crystallization, are presented in Figure 6.

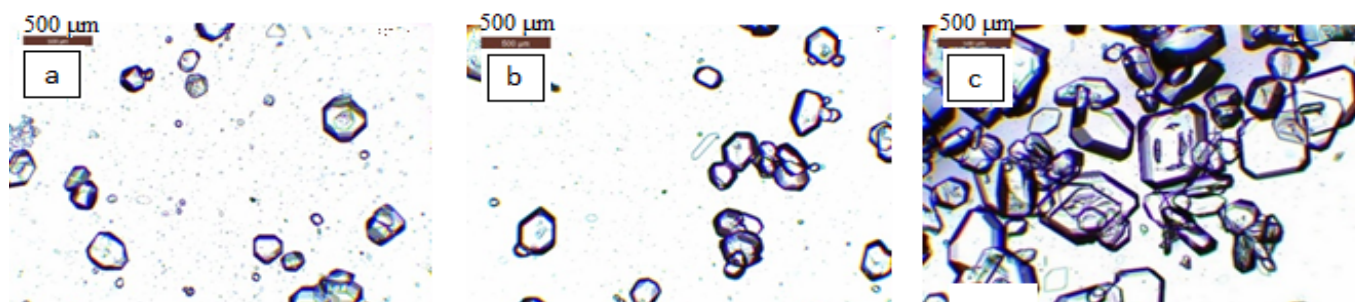


Figure 6. Microscope photographs of UP crystals obtained at a stoichiometric ratio PWPA:IU = 1.0:1.0 and a crystallization time: (a)—at the beginning of crystallization; (b)—after 30 min; (c)—after 60 min.

UP crystals have a parallel layered structure, and the layers are connected by hydrogen bonds, which belong to orthorhombic crystal system and vary widely in size [34]. At the beginning of crystallization, when there are few crystals, their size is about 200–300 μm , and after 60 min, more and larger (400–500 μm) orthorhombic crystals are formed.

Photographs of the crystals formed during crystallization at a stoichiometric ratio PWPA:IU = 1.0:1.5 are presented in Figure 7 at the beginning of crystallization and when crystallization time was 30 min and 60 min.

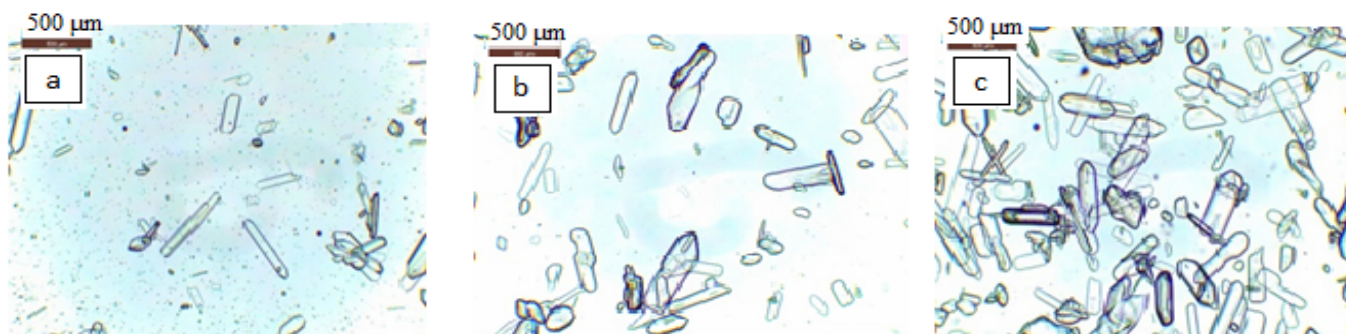


Figure 7. Microscope photographs of UP crystals obtained at a stoichiometric ratio PWPA:IU = 1.0:1.5 and a crystallization time: (a)—at the beginning of crystallization; (b)—after 30 min; (c)—after 60 min.

From the presented photographs, it can be seen that the crystals formed when the ratio of phosphoric acid and urea was 1.0:1.5 have a slightly different shape than those at another mole ratio. In this case, some of the crystal shapes resemble needles, which is characteristic of urea crystals. This is also confirmed by the data of the chemical analysis, according to which the nitrogen concentration in the product obtained under these conditions is higher than it should be (according to theoretical calculations). In summary, it can be said that this stoichiometric ratio (PWPA:IU = 1.0:1.5) is completely inappropriate.

In order to evaluate the surfaces of the crystals and the distribution of elements in the crystals, SEM studies were performed, and an element map was obtained. Only the highest quality UP crystals, obtained at a 1:1 ratio of reactants and a crystallization temperature of 60 min, were selected for this study. Scanning electron microscopy photographs are presented in Figure 8.

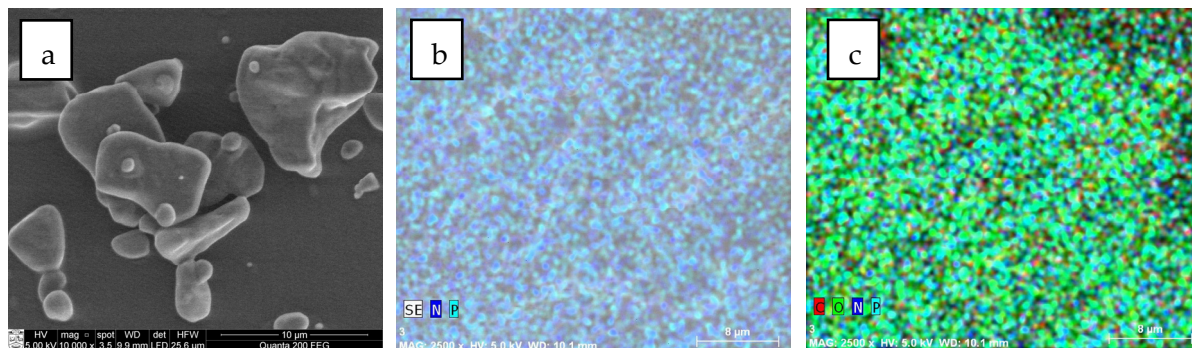


Figure 8. SEM pictures of UP crystals obtained at a stoichiometric ratio PWPA:IU = 1.0:1.0 when a crystallization time is 60 min: (a)—crystal picture magnification 5000× (image dimensions 20 μm); (b)—distribution map of P and N elements; (c)—distribution map of P, N, O and C elements.

The SEM analysis shows that the surface of the crystals is smooth, and only in some places are smaller crystals attached to larger crystals. When analysing the distribution of elements, it can be seen that all elements are evenly distributed and the UP obtained under the described conditions (PWPA:IU = 1.0:1.0 and crystallization time 60 min) is of high quality.

The result of our work is high-purity UP (concentration of nutrients is 99.2% of the theoretical value) from the chemical reaction between technically purified wet-process phosphoric acid and industrial urea at a stoichiometric ratio PWPA:IU = 1.0:1.0 and a reaction time of 60 min. This is a better result compared to Cherrat et al.'s [33] studies, because they used unpurified phosphoric acid, which contains many impurities, and obtained a product with 84% of the mass of P₂O₅ in the form of urea phosphate. Li Zhang et al. [35] also found that the crystallization time of urea phosphate increased with the addition of impurities, and the yield of urea phosphate decreased with increasing

concentrations of Al, Mg, Fe and SO_4^{2-} , except for F. It can be said that our chosen method, which uses purified wet-process phosphonic acid to obtain UP, is superior to others.

4. Conclusions

During the production of urea phosphate from purified wet-process phosphoric acid and industrial urea, high-quality UP was obtained at a stoichiometric ratio PWPA:IU = 1.0:1.0 and crystallization duration of 60 min. The chemical composition of this product is as follows: 44.7% P_2O_5 , 17.4% N_{amide} , 0.02% aluminium, 0.08% iron, 0.08% calcium, 0.22% magnesium, 0.008% sulphur, 0.003% silicon, moisture content of crystals 0.48%, and pH of 2.64. The product is thermally stable up to a temperature of 120 °C. UP crystals have an orthorhombic shape, and their size is about 400–500 μm . The surface of the crystals is smooth, and elements (P, C, N) are evenly distributed. In the case of a stoichiometric ratio PWPA:IU = 1.5:1.0, a compound was obtained whose chemical composition and other properties are similar to UP, but the ratio P_2O_5 : N does not correspond to the theoretical one. Meanwhile in the course of the reaction, when the starting materials were taken at a ratio of 1.0:1.5, high-quality urea phosphate could not be synthesized, because a part of the urea failed to react. After evaluating the obtained experimental results, as well as the technological and economic aspects, it was established that purified wet-process phosphoric acid and industrial urea can be used for the production of high-quality UPF, because the product has the required P_2O_5 : N ratio ($\text{N}:\text{P}_2\text{O}_5 = 0.389$ when the theoretical ratio $\text{N}:\text{P}_2\text{O}_5 = 0.394$), and other properties comply with the requirements for crystalline fertilizers.

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