Thermochimica Acta 488 (2009) 10–16

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Synthesis and thermal behavior of double copper and potassium pyrophosphate

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ARTICLE INFO

Article history:
Received 11 July 2008
Received in revised form 8 January 2009
Accepted 11 January 2009
Available online 20 January 2009

Keywords:
Complex mineral fertilizer
PK fertilizer
Double copper and potassium pyrophosphate
Thermal behavior
X-ray diffractometry
Energy dispersive X-ray spectroscopy
Scanning electron microscopy

ABSTRACT

This paper presents the synthesis and thermal behavior of double copper and potassium pyrophosphate, which can be used as a PK fertilizer containing copper as micronutrient. In order to find the conditions for the synthesis of this compound from copper sulphate and potassium pyrophosphate, various $Cu^{2+}:P_2O_7{}^{4-}$ molar ratios (0:1–2:1), various molar concentrations of the solutions (0.075; 0.1; 0.15 and 0.2 mol L^{-1}) and various temperatures (25, 50, 75 and 100 °C) have been used. The solid product synthesized in optimum conditions for the separation of micronutrient copper from the reaction mass ($Cu^{2+}:P_2O_7{}^{4-}$ molar ratio 1:1, concentration 0.1 mol L^{-1}) was subjected to a complex study: chemical analysis, thermal analysis, energy dispersive X-ray spectroscopy, scanning electron microscopy and X-ray diffractometry. During heating up to 1000 °C, $K_2Cu_3(P_2O_7)_2\cdot 3H_2O$ loses the crystallization water; several transformations of the phosphates also take place: the decomposition of pyrophosphates to ortho-phosphates; the transformation of ortho-phosphates; the polymerization of a fraction of ortho-phosphates to amorphous phosphates with longer chains; the reorganization of ortho-phosphates and poly-phosphates to pyrophosphates and their crystallization. The decomposition mechanism was confirmed when using the X-ray diffraction patterns of the compound, thermally treated at several temperatures.

1. Introduction

The explosive growth of world population imposes as a priority to find new and efficient methods, which can ensure the necessary nourishment, adequate from qualitative and quantitative view point. One of these methods which proved its efficiency is the use of fertilizers with micronutrients. These fertilizers supply the plant with the needed nutritive substances, which do not exist or are insufficient in soil [1–6].

The double pyrophosphate of copper and potassium can be used as a component of copper plating solutions and as a pigment. Although obtaining it is rather expensive, we suggest its use as PK fertilizer with the micronutrient copper in small amounts (4–10 kg/ha) in the areas where there is a shortage of copper. It could also be used with other fertilizers, in small proportions, as a source of copper microelement. This type of fertilizer has the advantage that it is available in the soil so as to be assimilated by plants for a longer period, caused by the hydrolysis of pyrophosphate to phosphate. This way one can avoid the direct genesis of some insoluble phosphates in the soil.

Complex mineral fertilizers of PK type supply the plants with two important primary macronutrients: potassium and phosphorus. Potassium has an important role in maintaining the acid–base equilibrium in cells. A good supplying of the plant with potassium decreases the water consumption and improves the absorption of luminous energy. Phosphorus is a component of DNA and RNA and an essential element for all living cells. The organic compounds of phosphorus play a very important role in the chemical reactions taking place during photosynthesis. They also take part in the growing and development process, as an energy accumulator and carrier.

Although the plants use micronutrients in very small quantities, they are very important for the growth and development of plants. Micronutrients protect the plants from diseases and improve the assimilation of other nutritive elements. Copper is an essential micronutrient for field crops. Copper increases plants resistance at drought and diseases caused by fungii. In cooperation with manganese, zinc and magnesium, copper increases plants resistance to freezing. Copper is also very important for chlorophyll synthesis and it is contained in the enzymes responsible for seed and fruit formation [2,6].

The purpose of the researches presented in this paper is to find out the optimum conditions for the synthesis of double copper and potassium pyrophosphate, from copper sulphate and potassium pyrophosphate. The studies on the thermal behavior and stability of the product are significant for obtaining this type of fertilizer in industrial processes.

The suggested method of obtaining double copper and potassium pyrophosphate has the advantage that there are no wastes

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doi:10.1016/j.tca.2009.01.011

produced alongside the main product. The solution resulting after the precipitate separation may be used as a liquid fertilizer (on the plant leaves, or soil). The method may also be used for the advanced separation of copper out of residual solutions, in view of turning it into account.

2. Experimental

The synthesis has been carried out by adding the copper sulphate (Sigma–Aldrich) solution (containing 0.035 mol L^{-1} H_2SO_4) to the potassium pyrophosphate (Sigma–Aldrich) solution, under continuous stirring with 600 rpm. An “IKA RCT basic” magnetic stirrer which heats was used. The suspension was filtered immediately at room temperature and the precipitate was dried in open air.

Various Cu^{2+}:$P_2O_7{}^{4-}$ molar ratios (0:1–2:1), various molar concentrations of the solutions (0.075; 0.1; 0.15 and 0.2 mol L^{-1}) and various temperatures (25, 50, 75 and 100 °C) have been used. The solid product obtained in optimum conditions for the separation of copper from the reaction mass, was subjected to a complex study: chemical analysis, thermal analysis, energy dispersive X-ray spectroscopy, scanning electron microscopy and X-ray diffractometry. We have also analyzed and registered the patterns of the products resulting after its treatment, at several temperatures corresponding to the changes shown on TG and DTG curves. The samples were heated in a “Nabertherm B 150” oven with 10 °C min^{-1} up to desired temperature which was maintained for 1 h. The patterns were recorded after cooling at room temperature.

The pH of the reaction mass has been measured using a “Denver Instrument 250” pH-meter/conductivity-meter“.

The copper and potassium contents of the precipitates and solutions have been determined by means of atomic absorption spectrometry [7] using a “Varian Spectr AA 110 spectrophotometer”.

The pyrophosphate ion has been hydrolyzed to phosphate by boiling the solution containing ~0.1 mol L^{-1} H_2SO_4 (Merck) for 45 min [7]. The phosphorus content has been spectrophotometrically determined, using the molybdovanadophosphate method [7]. The absorbance of the solutions was measured using a “Cary 50 spectrophotometer” at 460 nm.

The X-Ray powder diffraction patterns were recorded on a “Bruker D8 Advance automated powder diffractometer” in Bragg–Brentano geometry, fitted with a NaI(Tl) scintillation detector and a graphite monochromator on the diffracted beam for the Cu K_α radiation (λ = 1.5418 Å). The diffractometer was operated in constant scan mode over the range $5^\circ < 2\theta < 60^\circ$ with zero point determined from an external quartz standard. Step scanning was performed with a step size of 0.02° 2θ and a scanspeed of 7 s $step^{-1}$.

The TG, DTG and DTA curves have been registered using a “PerkinElmer Diamond TG/DTA Analyzer” in an Al_2O_3 crucible, with a linear heating rate of 10 °C min^{-1}, in dynamic atmosphere (air, 100 mL min^{-1}), Al_2O_3 as DTA reference, on a sample of ~7 mg.

The SEM images of the sample were taken and the energy dispersive X-ray spectroscopy was performed using an “Inspect S” scanning electron microscope.

3. Results and discussion

In order to find out the optimum conditions for the synthesis of double copper and potassium pyrophosphate, the following influences were studied – the influence of Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio, the concentration of the reactants and temperature, on the final pH of the reaction mass, and on the separation degree of copper from solutions, respectively.

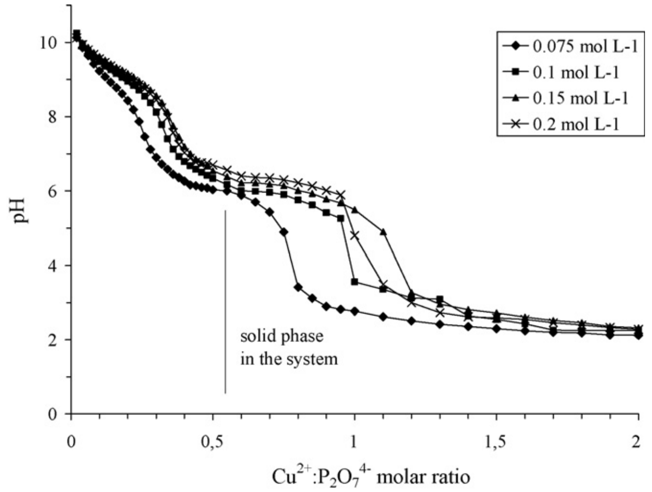

Fig. 1. Dependence of the pH of the reaction mass on the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio, at various concentrations of the reactants and 25 °C.

The experimental data regarding the dependence of the pH of the reaction mass on the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio, using solutions of various molar concentrations (0.075; 0.1; 0.15 and 0.2 mol L^{-1}) at the temperature of 25 °C, are presented in Fig. 1. One may notice that there is a well defined dependence between the pH of the reaction mass and the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio; the shape of the curves being similar for all studied concentrations. In the beginning, before adding the $CuSO_4$ solution, the $K_4P_2O_7$ solution has an ~10 pH value, owing to the alkaline hydrolysis of this salt (pyrophosphate anion is a weak base). As we add $CuSO_4$ solution, $P_2O_7{}^{4-}$ binds Cu^{2+} and the concentration of $P_2O_7{}^{4-}$ unbound in the solution decreases, which leads to its pH value diminishing.

The pH of the reaction mass strongly decreases from ~10 to ~6.5 as the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio increases up to ~0.5:1, presenting an inflexion for a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of ~0.3:1. When the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio increases from 0.5:1 to 0.7–0.9:1 (depending on the concentration of the reactants) the pH of the reaction mass decreases very slowly. In the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio range 0.7:1–1.2:1, the pH of the reaction mass strongly decreases from ~6 to ~3, with a second inflexion for a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of ~1:1. As the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio further increases, in the range 1.2:1–2:1, the pH of the reaction mass remains practically unchanged. The solid phase resulted in the reaction mass when the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio reached the value of ~0.55:1 and the pH was ~6. The resulting suspensions lead to precipitates easy to settle, filtrate and wash.

For values of the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio lower than 0.5:1 (and pH >6.5) soluble complex combinations copper(II)–pyrophosphate are present in the liquid reaction mass, which may be used as liquid fertilizer [8]. In order to synthesize double copper and potassium pyrophosphate, a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio higher than 0.5:1 (and pH < 6) should be used. This result is consistent with other data in the literature which are reporting the synthesis of double zinc and potassium pyrophosphate in the pH range 2–6 [9]. One can conclude that the pH of the reaction mass represents an important control parameter for the synthesis of double copper and potassium pyrophosphate.

In order to establish the optimum conditions for the synthesis, we studied the dependence of copper separation degree on the process parameters: Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio, initial concentration of the reactants and temperature. We consider as optimum, the conditions which ensure a maximum separation degree of micronutrient copper from the reaction mass.

Copper separation degree was calculated using the relation:

$$\alpha = \frac{n_\mathrm{i} - n_\mathrm{f}}{n_\mathrm{i}} \times 100 \tag{1}$$

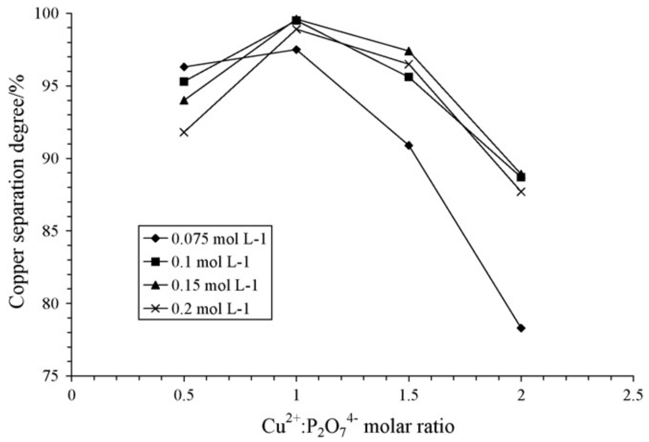

Fig. 2. Dependence of copper separation degree on the Cu^{2+}: $P_2O_7{}^{4-}$ molar ratio using various molar concentrations, at 25 °C.

where n_i is the amount of copper added to the reaction mass and n_f represents the amount of copper remained in the solution resulted after the separation of the precipitate.

Fig. 2 illustrates the dependence of copper separation degree on the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio for the initial concentrations of the reactants we have studied, for a temperature of 25 °C.

From Fig. 2 one may notice that the maximum copper separation degree ($\alpha = 99.5\%$) was reached for a value of Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of 1:1 and for concentrations of 0.1 and 0.15 mol L^{-1}. For the other two concentrations the values are close but somehow lower. We consider as optimum the concentration of 0.1 M as the constitution of crystalline precipitates to obtain some bigger crystals, easy to filtrate and wash, it is recommended that the precipitation be performed in diluted solutions.

Our research has started from the idea of identifying a new method for removing as efficient as possible the copper from certain waste solutions. We have also considered obtaining some products which may be turned into account. For the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio for which the separation degree of copper is maximum, we would expect to get a compound under the form of $K_2Cu(P_2O_7)_2$. From the X-ray diffractometry studies which will be presented later in this paper we have concluded that in fact we obtained $K_2Cu_3(P_2O_7)_2 \cdot xH_2O$, generated as a consequence to the reaction described by the following equation:

$$3CuSO_4 + 2K_4P_2O_7 + xH_2O \rightarrow K_2Cu_3(P_2O_7)_2 \cdot xH_2O + 3K_2SO_4 \quad (2)$$

The case of this precipitate is that in which the pyrophosphate anion which forms the precipitate works as a ligand for Cu^{2+}. Considering the solubility equilibrium:

$$K_2Cu_3(P_2O_7)_2 \rightleftharpoons 2K^+ + 3Cu^{2+} + 2P_2O_7{}^{4-} \quad (3)$$

on the increase of pyrophosphate amount (the decrease of the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio – in Fig. 1 to the left of the x axis) the solubility Eq. (3) is gliding to the left (Le Châtelier's Principle). Consequently the solubility of the precipitate decreases (common ion effect) and the separation degree of copper increases. The precipitate solubility decreases to a certain value – in Fig. 2 one can notice that the separation degree of copper increases from the ratio 2:1 up to 1:1, copper being bound in the precipitate. On a progressive increase of pyrophosphate amount (the decrease of the Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio) the solubility of the precipitate begins to increase owing to the formation of soluble complex combinations copper(II)–pyrophosphate (the solubility equilibrium (3) glides to the right – complexation effect). The result is that part of the copper enters the solution and its separation degree decreases. For a lower molar ratio than 0.5:1 there is no precipitate genesis and the whole copper amount is to be found as soluble complex combinations copper(II)–pyrophosphate.

Table 1
Dependence of copper separation degree on temperature.

Temperature (°C)	25	50	75	100
Copper separation degree (%)	99.5	98.1	97.0	97.1

The Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of 1.5:1 is equal to the stoichiometric composition of the precipitate $K_2Cu_3(P_2O_7)_2$. For a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of 2:1, copper is in excess in comparison with the stoichiometric composition and remains unreacted in the solution, leading to a smaller separation degree. For a molar ratio 1:1 pyrophosphate is in excess vs. the stoichiometric composition and the separation degree is higher than in the case of 1.5:1 ratio. If a higher separation of copper out the solution is desired, the 1:1 molar ratio is recommended.

The experimental data regarding the dependence of copper separation degree on temperature are presented in Table 1. The influence of temperature was studied for a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of 1:1 and an initial concentration of the reactants of 0.1 mol L^{-1}.

One can notice that the copper separation degree slightly decreases as the temperature of the reaction mass increases, due to the fact that the solubility of the precipitates increases with the temperature. Although this decrease is not significant, the synthesis of double pyrophosphate at 25 °C is also beneficial from the economic point of view. If the product is synthesized in view of using it as a fertilizer, to avoid an increase in expenses this temperature is recommended for operation. Moreover, washing the precipitate in view of purification is not necessary, considering that the remaining solution in the precipitate contains compounds which may be used as fertilizers.

The product synthesized in optimum conditions (Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio 1:1, concentrations of copper sulphate and potassium pyrophosphate 0.1 mol L^{-1}) has been submitted to a complex study: chemical analysis, X-ray diffractometry, energy dispersive X-ray spectroscopy, scanning electron microscopy and thermal analysis. Although the optimum temperature for the separation of copper is 25 °C, the X-ray diffraction pattern of the product synthesized at this temperature showed that the double pyrophosphate also contains another crystalline phase. The product synthesized at 75 °C, no longer contained this phase, it was better crystallized and its diffraction lines were stronger.

To obtain a product as pure as possible to be characterized, it has been synthesized under controlled conditions. The copper sulphate solution has been added to the one of potassium pyrophosphate at a constant flow of 1 mL min^{-1}, up to a Cu^{2+}:$P_2O_7{}^{4-}$ molar ratio of 1:1. During the synthesis the evaporated water was added and the temperature was maintained to 75 ± 1 °C. The suspension has been left for 24 h at 75 °C for ageing, then the precipitate has been washed at room temperature with distilled water until negative reaction for the sulphate. The precipitate was filtered and dried for 48 h in a dessicator.

Figs. 3 and 4 present the X-ray diffraction patterns of the precipitate and the products resulted after its thermal treatment at various temperatures.

The X-ray diffraction pattern of the initial product shows the presence of a crystalline phase (Fig. 3a). The phase could not be identified; in the available database we did not find any X-ray diffractometry data for the double copper and potassium pyrophosphate. Working in similar conditions, we synthesized double cobalt and potassium pyrophosphate [10] and double zinc and potassium pyrophosphate, respectively [11,12]. As the shape of the pattern of our product is very similar to the patterns of other two double pyrophosphates and the positions of the corresponding diffraction lines are very close, we concluded that the product we syn-

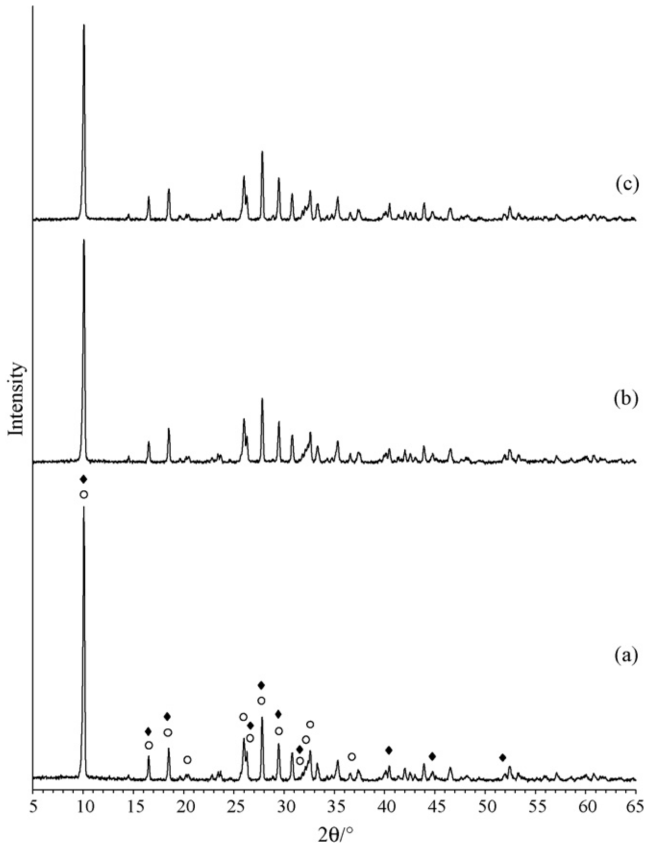

Fig. 3. X-ray diffraction patterns of the initial sample (a) treated at 150°C (b) and 250 °C (c) (○) $K_2Co_3(P_2O_7)_2·2H_2O$ (♦) – $K_2Zn_3(P_2O_7)_2·3H_2O$.

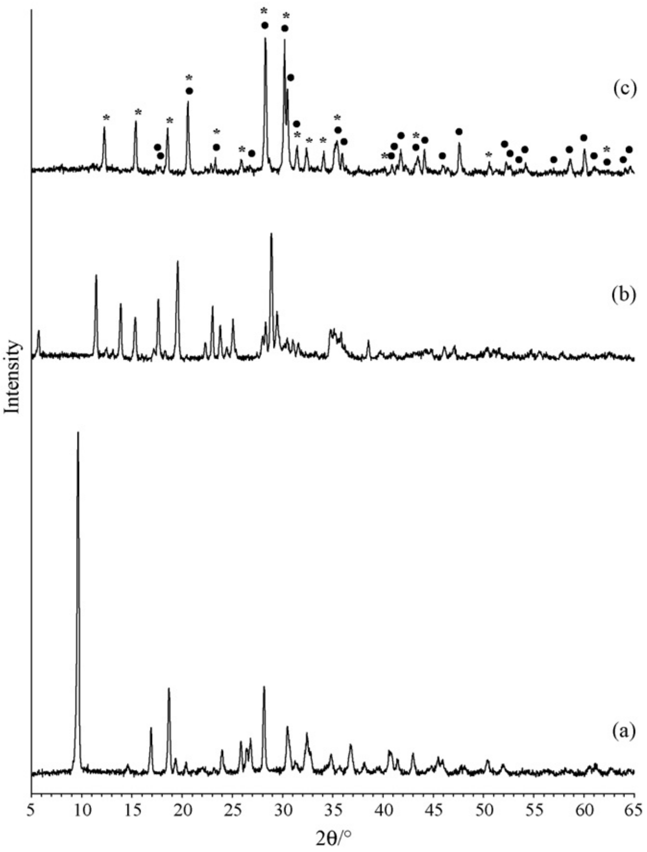

Fig. 4. X-ray diffraction patterns of the sample treated at 350 °C (a) 500 °C (b) and 800 °C (c) (●) $Cu_2P_2O_7$ (*) $K_2CuP_2O_7$.

thesized is in fact $K_2Cu_3(P_2O_7)_2·xH_2O$. For comparison purposes, in Fig. 3a the lines of $K_2Co_3(P_2O_7)_2·2H_2O$ (monoclinic) [13] and $K_2Zn_3(P_2O_7)_2·3H_2O$ [14] are indicated.

From the X-ray diffraction data for line broadening β at half the maximum intensity (FWHM – the full width at half-maximum), the mean crystallite dimension was calculated. The crystallite size was obtained from the β values using the Williamson–Hall method [15] (shape factor $K = 1$; X-ray wavelength $\lambda = 1.5418$ Å). By using the data for five diffraction lines, the dimension of crystallites was obtained ~60 nm.

The powder X-ray diffraction pattern of double copper and potassium pyrophosphate was indexed using the program EXPO2004 [16] on the basis of 34 observable reflections, leading to the lattice parameters (monoclinic crystal family): $a = 9.178$, $b = 8.476$ and $c = 8.921$ Å, respectively, $\beta = 100.108°$. Systematic absences are consistent with space group $P2_1/a$ (space group number 14). The space group is the same and the lattice parameters are close to those obtained previously [13] from powder X-ray diffraction data for $K_2Co_3(P_2O_7)_2·2H_2O$ ($a = 9.229$, $b = 8.11(1)$ and $c = 9.122$ Å, $\beta = 99.310°$). The unit cell volume of double copper and potassium pyrophosphate is 683.14 Å^3, consistent with the assignment of two molecules per unit cell. Data concerning the refinement of the parameters defining the unit cell and the atomic position in the unit cell will be published elsewhere.

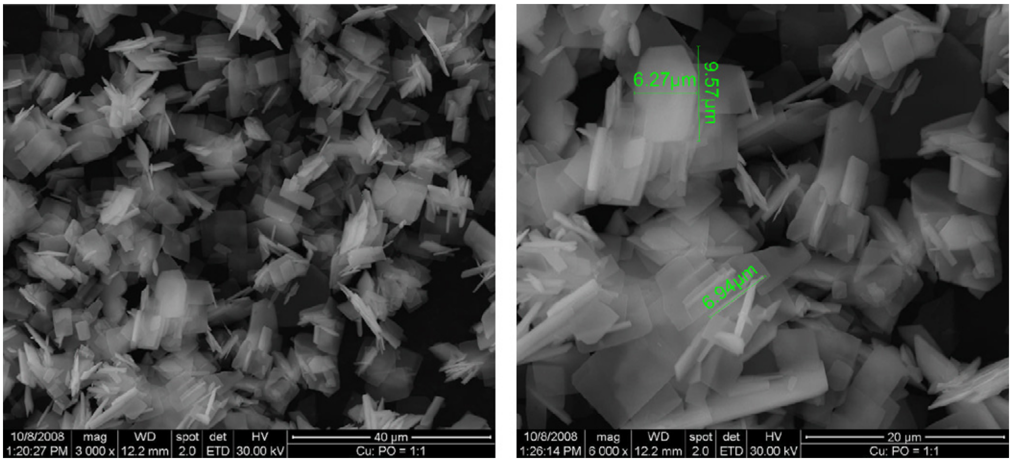

Fig. 5. SEM images of the double copper and potassium pyrophosphate.

Table 2
Chemical composition and product aspect.

	Product					Aspect
	K%	Cu%	P%	O%	H%	
Initial						
Theoretic						Very light green powder
$x=3$	11.7	28.4	18.5	40.5	0.9	
$x=2$	12.0	29.2	19.0	39.2	0.6	
Chemical analysis	11.5	27.6	18.4	42.5*		
EDX	9.5	22.2	18.6	49.7	–	
Treated at 150 °C	11.2	26.5	18.6	43.7*		Very light green powder
Treated at 250 °C	11.9	26.9	18.5	42.7*		Very light green powder
Treated at 350 °C	11.7	29.5	20.3	38.5*		Greenish powder
Treated at 500 °C	11.8	29.6	22.5	36.1*		Greenish, partially melted
Treated at 800 °C	11.1	28.3	18.6	42.0*		Melted, green glassy mass

* Values resulting by difference up to 100%.

SEM images of the initial product are shown in Fig. 5. One can notice tabular crystals of ~10 μm.

The chemical composition and the aspect of the initial sample and of the products obtained by thermal treatment is shown in Table 2.

Out of the data presented in Table 2, one can notice that the values obtained through the chemical analysis for the composition of the initial product are closer to the theoretical values calculated for $K_2Cu_3(P_2O_7)_2{\cdot}3H_2O$ than to the ones calculated for $K_2Cu_3(P_2O_7)_2{\cdot}2H_2O$. One can also see that the composition of the products obtained through thermal treatment at various temperatures is similar, which is in agreement with our supposition that during the thermal decomposition of the sample, only the crystallization water is lost.

The thermal behavior of double copper and potassium pyrophosphate is illustrated in Fig. 6. During heating at a constant heating rate of $10\,^{\circ}C\,min^{-1}$ up to 1000 °C, a decomposition process with mass loss takes place in the sample: up to 220 °C the sample slowly loses 0.6%; between 220 and 370 °C, the sample loses 6.1% with maximum rate at 295 °C, and endo-thermal effect at 305 °C; between 370 and 800 °C, the sample slowly loses 1.0%; at 800 °C another process with mass loss begins and at 1000 °C the residue was of 90.6%. DTA curve shows an exo-thermal effect at 535 °C and another endo-thermal effect at 660 °C.

The theoretical mass loss corresponding to the loss of two moles of crystallization water is of 5.5%; for the loss of three moles of crystallization water is of 8.1%. The TG curve presented in Fig. 6, shows that the mass loss up to 900 °C is of ~8%; one may conclude that the double copper and potassium pyrophosphate crystallizes with three moles of water.

Out of the data obtained through the chemical and thermal analysis, we consider that the product synthesized by us is $K_2Cu_3(P_2O_7)_2{\cdot}3H_2O$. By considering reaction (2) of obtaining $K_2Cu_3(P_2O_7)_2{\cdot}3H_2O$, the product was obtained at a yield of 68,8% (calculated for the limitative $CuSO_4$ reactant, after washing and drying the precipitate).

According to the data in the literature, when the di-phosphate (pyrophosphate) of potassium and zinc is heated, it decomposes to ortho-phosphates below 150 °C. In the range of temperature 150–400 °C, polymerization of ortho-phosphates to phosphates with longer chains takes place, giving amorphous phosphates. At a temperature over 400 °C the reorganization of poly-phosphates to di-phosphates takes place [9].

In the case of our sample, probably the following overlapping processes take place:

- Loss of the most of the crystallization water between 220 and 370 °C; the X-ray patterns of the sample treated at 150 and 250 °C (Fig. 3b and c) show the presence of the same crystalline com-

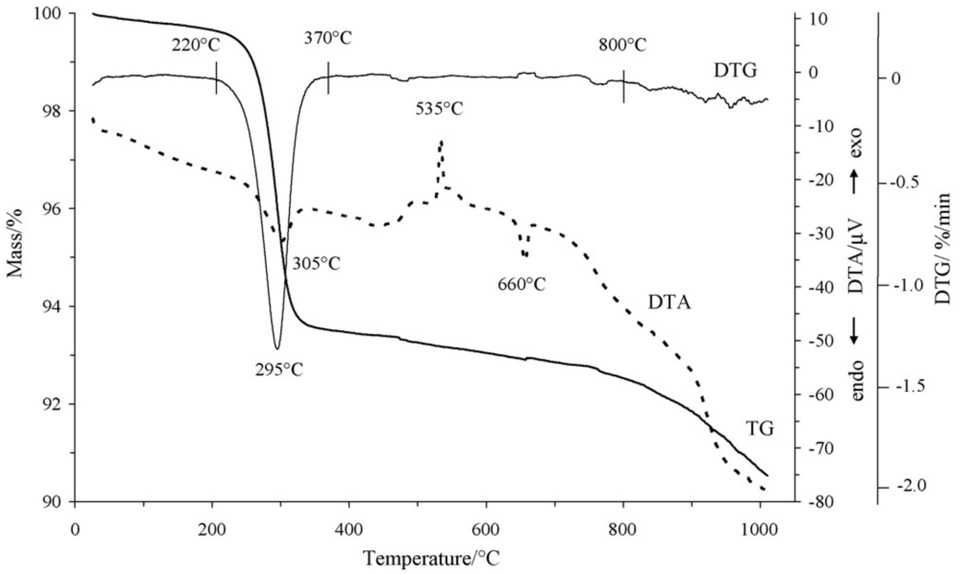

Fig. 6. TG, DTG and DTA curves of the double copper and potassium pyrophosphate.

pound as the pattern of the initial sample, consistent with the fact that up to 220 °C the thermal curves show no transformation. The intensity of the diffraction lines slowly decreases as the temperature increases probably due to the fact that the sample begins to lose slowly the crystallization water. At 250 °C only a fraction of $K_2Cu_3(P_2O_7)_2 \cdot 3H_2O$ dehydrated and the lines of this compound are still present in the pattern. There are no new lines in the pattern so one can conclude that the dehydration products such as intermediary hydrates or anhydrous $K_2Cu_3(P_2O_7)_2$ are amorphous. The pattern of the product of the thermal treatment at 350 °C is totally different (Fig. 4a) and shows that the product is crystalline. The sample treated at this temperature, besides intermediary hydrates or anhydrous double copper and potassium pyrophosphate, may also contain other compounds resulting from the decomposition of $K_2Cu_3(P_2O_7)_2$ according to Eq. (4) presented below. Unfortunately, since the available data base does not contain any diffraction data for intermediary hydrates or anhydrous double copper and potassium pyrophosphate, the crystalline phases present in the sample could not be identified.

- Besides the elimination of crystallization water, several transformations of the phosphates take place [9], according to the Eqs. (4)–(7), where M represents K and/or 1/2Cu:

○ the decomposition of pyrophosphates to ortho-phosphates, using a fraction of the crystallization water:

$$(n+1)M_4P_2O_7 + (n+1)H_2O \rightarrow 2(n+1)M_2HPO_4 \qquad (4)$$

○ followed by the transformation of ortho-phosphates according to the equation:

$$2nM_2HPO_4 \rightarrow nM_3PO_4 + nMH_2PO_4 \qquad (5)$$

○ and the polymerization of ortho-phosphates to amorphous phosphates with longer chains; in the process is given out the water used in reaction (4):

$$2M_2HPO_4 + nMH_2PO_4 \rightarrow M_2PO_4{-}[MPO_3]_n - PO_3M_2 + (n+1)H_2O \qquad (6)$$

The products resulting from the thermal treatment of the sample at 350 °C (Fig. 4a) and 500 °C (Fig. 4b) are crystalline and contain completely different phases. These products may contain mixtures resulting from reactions (4)–(6). Diffraction lines of some compounds such as $KCuPO_4$, $K_3Cu_2[(P_2O_7)H(P_2O_7)]$, KH_2PO_4, $Cu_3(PO_4)_2$ are present in the patterns, but they could not be identified with certainty. Similarly, according to the suggested mechanism, a lot of other mixtures for which there are no diffraction data in the available data base may result.

○ The DTA curve shows an exo-thermal effect at 535 °C which could be due to the reorganization of ortho- and poly-phosphates to pyrophosphates and their crystallization (processes that take place without any mass loss):

$$M_2PO_4 - [MPO_3]_n - PO_3M_2 + nM_3PO_4 \rightarrow (n+1)M_4P_2O_7 \qquad (7)$$

On temperatures over 700 °C, the transformation of these pyrophosphates in orto-phosphates and poly-phosphates is possible, with endo-thermal effect [9]. In the case of our sample an endo-thermal effect has been observed at 660 °C, but it could also be due to the melting of the sample. It is possible that a small amount of the phosphates has polymerized and the 1.4% mass loss between 900 and 1000 °C is due to the elimination of the resulting water.

The X-ray diffraction pattern of our product treated at 800 °C (Fig. 4c) shows only the presence of the crystalline phases $Cu_2P_2O_7$ [17] and $K_2CuP_2O_7$ [18], which confirms reaction (7). The product of the thermal treatment of the sample at 1000 °C was a green phosphatic glass which could not be taken from the crucible.

The proposed decomposition mechanism suggests the fact that for various temperatures the sample is made up from totally different mixtures. This is confirmed by the fact that the sample treated at 350, 500 and 800 °C is made up from totally different crystalline phases.

The overall reaction for the decomposition of double copper and potassium pyrophosphate may be written as follows:

$$K_2Cu_3(P_2O_7)_2 \cdot 3H_2O \rightarrow Cu_2P_2O_7 + K_2CuP_2O_7 + 3H_2O \qquad (8)$$

The thermal behavior of our product allows us to conclude that if we intend to use it as a fertilizer, in the industrial process, during drying and granulation, the PK fertilizer loses neither the primary macronutrients (potassium and phosphorus), nor the micronutrient (copper). Depending on the temperature of the process, which is usually of 180–200 °C, the fertilizer may lose a fraction of the crystallization water and also a fraction of the double pyrophosphate can decompose to ortho-phosphates.

4. Conclusions

In the paper are presented researches carried out in order to determine the conditions for the synthesis of double copper and potassium pyrophosphate, from copper sulphate and potassium pyrophosphate. The thermal behavior and stability of this compound, which may be used as a PK fertilizer containing copper as micronutrient, was also studied.

In order to find the synthesis conditions, various Cu^{2+}:$P_2O_7{}^{4-}$ molar ratios (0:1–2:1), various molar concentrations of the solutions (0.075; 0.1; 0.15 and 0.2 mol L^{-1}) and various temperatures (25, 50, 75 and 100 °C) have been used. The solid product synthesized in optimum conditions for the separation of micronutrient copper from reaction mass as double pyrophosphate, was subjected to a complex study: chemical analysis, thermal analysis, energy dispersive X-ray spectroscopy, scanning electron microscopy and X-ray diffractometry.

By means of X-ray diffractometry and comparing the pattern of the product with those of $K_2Co_3(P_2O_7)_2 \cdot 2H_2O$ and $K_2Zn_3(P_2O_7)_2 \cdot 3H_2O$ we concluded that the product we synthesized is $K_2Cu_3(P_2O_7)_2 \cdot xH_2O$.

Using the X-ray diffractometry data, were calculated the mean crystallites dimension ~ 60 nm, and the lattice parameters (monoclinic crystal family): $a = 9.178$, $b = 8.476$ and $c = 8.921$ Å, respectively, $\beta = 100.108°$.

The SEM images of the double pyrophosphate of copper and potassium show tabular crystals of ~10 μm.

During the heating up to 1000 °C, the compound undergoes a decomposition process with mass loss. The total mass loss up to 900 °C corresponds to the loss of three moles of crystallization water. The data obtained by chemical analysis confirm that the synthesized product is $K_2Cu_3(P_2O_7)_2 \cdot 3H_2O$. Besides to the removal of crystallization water, several transformations of the phosphates take place: the decomposition of pyrophosphates to ortho-phosphates; the transformation of ortho-phosphates; the polymerization of a fraction of ortho-phosphates to amorphous phosphates with longer chains; the reorganization of ortho-phosphates and poly-phosphates to pyrophosphates and their crystallization. The decomposition mechanism was confirmed using the X-ray diffraction patterns of the compound, thermally treated at 150, 250, 350, 500 and 800 °C.

The thermal behavior of our product leads to the conclusion that in the industrial process, the PK fertilizer loses neither the primary macronutrients (potassium and phosphorus), nor the micronutrient (copper); it may lose a fraction of the crystallization water and also a fraction of the double pyrophosphate can decompose to ortho-phosphates.

The suggested method of obtaining double copper and potassium pyrophosphate has the advantage that there are no wastes produced alongside the main product. The solution resulting after the precipitate separation may be used as a liquid fertilizer (on the plant leaves, or soil). The method may also be used for the advanced separation of copper out of residual solutions, in view of turning it into account.

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