

Thermal Activation of Phosphate Raw Materials in the Presence of Alkaline Salts

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Abstract: The thermal-alkaline method of phosphate processing makes it possible to involve in industrial production not only ordinary phosphorite flour, but also production wastes, with the subsequent production of high-quality fertilizers with a high content of digestible forms of phosphorus, potassium, calcium, magnesium and other components. Thus, both the problems of rational use of mineral raw materials and many environmental problems, the creation of new technologies for processing waste from mining and chemical industries and reserves of refractory phosphates are solved.

An important indicator of the produced fertilizers is their cost. It should be born in mind that one should not strive for a 100% production of mineral fertilizers in concentrated and complex forms, which are relatively expensive, since this would contradict questions about the economic efficiency of the use of mineral resources. In this respect, a relatively cheap method based on the thermal alkaline activation of phosphate raw materials deserves some attention. The main part of phosphorus and calcium in thermo-alkaline fertilizers is in a lemon-soluble form, that is, the latter has a prolonged effect. According to leading agrochemists, agriculture can get a significant effect from the use of long-acting fertilizers, which are practically not washed out and are not lost in the soil. In such fertilizers, phosphorus can be used by plants for several years. In this regard, the development of acid-free methods for processing phosphate raw materials, including raw materials poor in phosphorus content, is currently relevant.

Keywords: Thermophosphates, thermo-alkaline fertilizers, prolonged effect, heat treatment, sintering, thermogravimetry, IR-spectra, solubility.

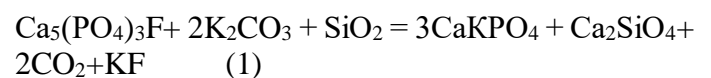
Introduction Thermal-alkaline phosphates (thermophosphates) are obtained by sintering crushed natural phosphates with alkaline salts and minerals (soda, potash, sodium and potassium sulfates and bisulfates, soda slags after desulfurization of cast iron, nepheline, leucite, etc.). Thermophosphates usually have different trade names (Röchling phosphate, renania phosphate, supertomasin, palatia, phosphal, etc.).

The main advantages of the thermochemical method for processing phosphorites, in comparison with the traditional acidic method, are the simplicity of technological design, the non-use of scarce acids, as well as the possibility of processing almost any phosphate raw material and waste of its production.

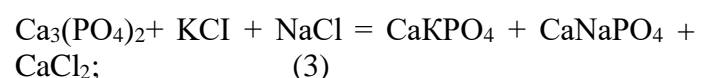
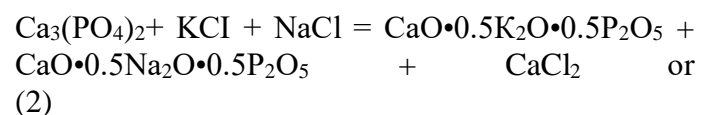
Material and methods. The objective of this study was to study the basic laws of the process of thermal activation of natural phosphates in the presence of various salts and to create an effective technology for obtaining a thermophosphate fertilizer.

The main reaction of the interaction of the components of the charge, consisting of phosphorites and potash or sylvinites, can be represented by the equations:

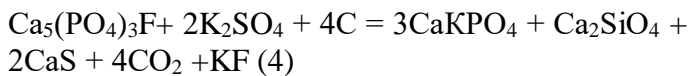
when using potash:



when using sylvinite:



when using potassium sulfates as a reducing agent, carbon-containing materials are used:



The consumption rate of alkali metal salts and silicon oxide was calculated according to the following equation per 100 units of phosphate raw materials:

with the amount of alkaline salts per 100 g of phosphate raw materials:

$$m_{\text{salt}} = a \cdot 2 M_{\text{salt}} / 213 \cdot c_{\text{salt}}$$

where: a - P₂O₅ content in phosphate raw materials;

M_{sal} - the molecular weight of carbonate or sulfate alkaline salts when using chlorides, the molecular weight of the salt is multiplied by 4.

c salt - the content of the main component in alkaline salts

When calculating the amount of silicon oxide, the formula was used:

$$m_{\text{SiO}_2} = a \cdot 60 \cdot b / 213 \cdot 1.315 \cdot c_{\text{SiO}_2}$$

where: a - P₂O₅ content in phosphate raw materials;

b - calcium module of phosphate raw materials;

c - SiO₂ content in quartz sand.

When calculating the amount of carbonaceous materials:

$$m_c = m_{\text{Salt}} \cdot 48 / 2 M_{\text{salt}} \cdot C_c$$

where: C_c is the carbon content in the carbon-containing material.

For the experiments, we used ordinary phosphorite flour of the Central Kyzyl Kum of the following composition (wt.%): 16.53 P₂O₅; 46.65 CaO; 13% CO₂ and soda ash produced by UE "Kungrad Soda Plant", as well as chemically pure SiO₂xH₂O.

Results and discussion. The experiments were carried out as follows. Initially, the initial substances were weighed in a certain amount on a laboratory balance with an accuracy of 0.01 g. The weighed components were thoroughly mixed in a porcelain mortar and sieved on a No. 1 sieve. From the obtained components, a charge was prepared, from which tablets with a diameter of 50 mm and a height of 10-15 mm were formed on a hydraulic laboratory press at a

pressing pressure of 35-40 kgf / cm². The molded laboratory samples were naturally dried at room temperature 25-30°C during the day. Then the samples were dried in a drying oven at a temperature of 105-110°C for 2 h.

To do this, the hot samples were removed from the oven using tongs and sharply lowered into a metal vessel with cold water. After the abrupt cooling process, the samples were subjected to crushing and grinding to particles with a size of 0.15 mm. Heat-treated samples were analyzed according to standard methods for the content of various forms of phosphorus and calcium.

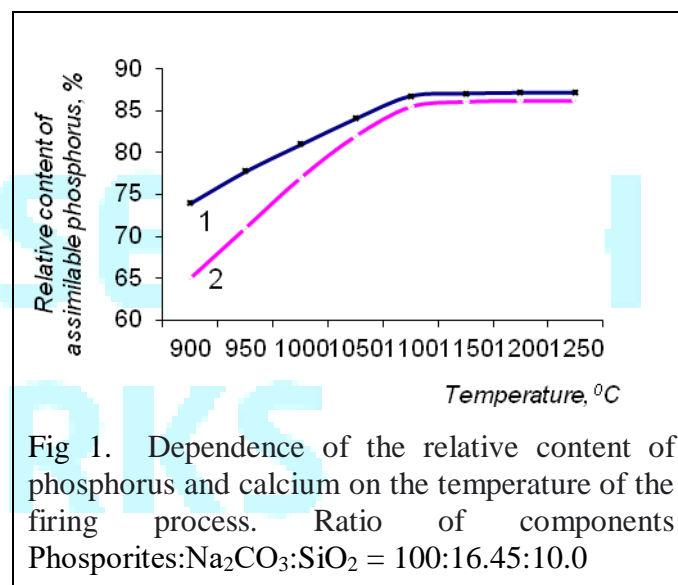


Fig 1. Dependence of the relative content of phosphorus and calcium on the temperature of the firing process. Ratio of components Phosphorites:Na₂CO₃:SiO₂ = 100:16.45:10.0

The results are shown in Figure 1, as well as in Tables 1 and 2.

It follows from the data presented that as a result of firing a mixture of components (phosphorite, Na₂CO₃ and SiO₂xH₂O) at a temperature of 900°C, the activation (conversion of indigestible P₂O₅ forms into plant-assimilable forms) of phosphate raw material occurs (Table 1). In this case, a product is obtained with a content of 17.06-17.80% P₂O₅total, 48-49.84% CaOtotal, of which the relative content of the assimilable form of P₂O₅ and CaO is 50.76-72.45% and 70.70 -801%, respectively.

An increase in the firing temperature from 900 to 1250°C also contributes to a significant increase in the

assimilable forms of phosphorus and calcium (Table 1. and Figure 1). For example, if at a firing temperature of 900°C the relative phosphorus content in the finished product reaches 658% in a 2% citric acid solution, then at a temperature of 1250°C this indicator increases to 86.94%

A similar pattern is observed for the relative phosphorus content of 0.2 M trilon B and calcium. The products obtained by the above method contain 17.2-18.84% total phosphoric anhydride and 48.49-49.99% total calcium oxide, of which 11.28-16.38% phosphorus and 36.21-43.89% calcium, respectively, are in digestible forms.

Based on the above, the temperature range of varying the temperature of the process of thermal alkaline treatment of low-grade CK phosphorites was determined. The experiments were carried out as follows. Initially, the initial substances (phosphorite flour of the Central Kyzyl Kum desert, potassium carbonate, and quartz sand) were weighed in a certain amount using a laboratory balance with an accuracy of 0.01 g. [4]

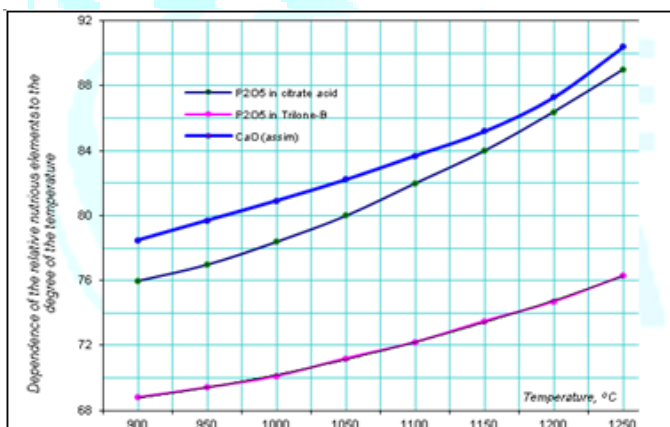


Fig. 2. Dependence of the relative phosphorus content in 2% citric acid, Trilon-B and CaO absorption on the applied temperature of the firing process

Charges were prepared from the components obtained. Further, from the prepared mixtures, tablets with a diameter of 50 mm and a height of 10-15 mm were formed in a hydraulic laboratory press at a pressing pressure of 35-40 kgf / cm².

The molded laboratory samples were naturally dried at room temperature 25-300C for a day. Then the samples were dried in a drying oven at a temperature of 105-110°C for 2 h.[7]

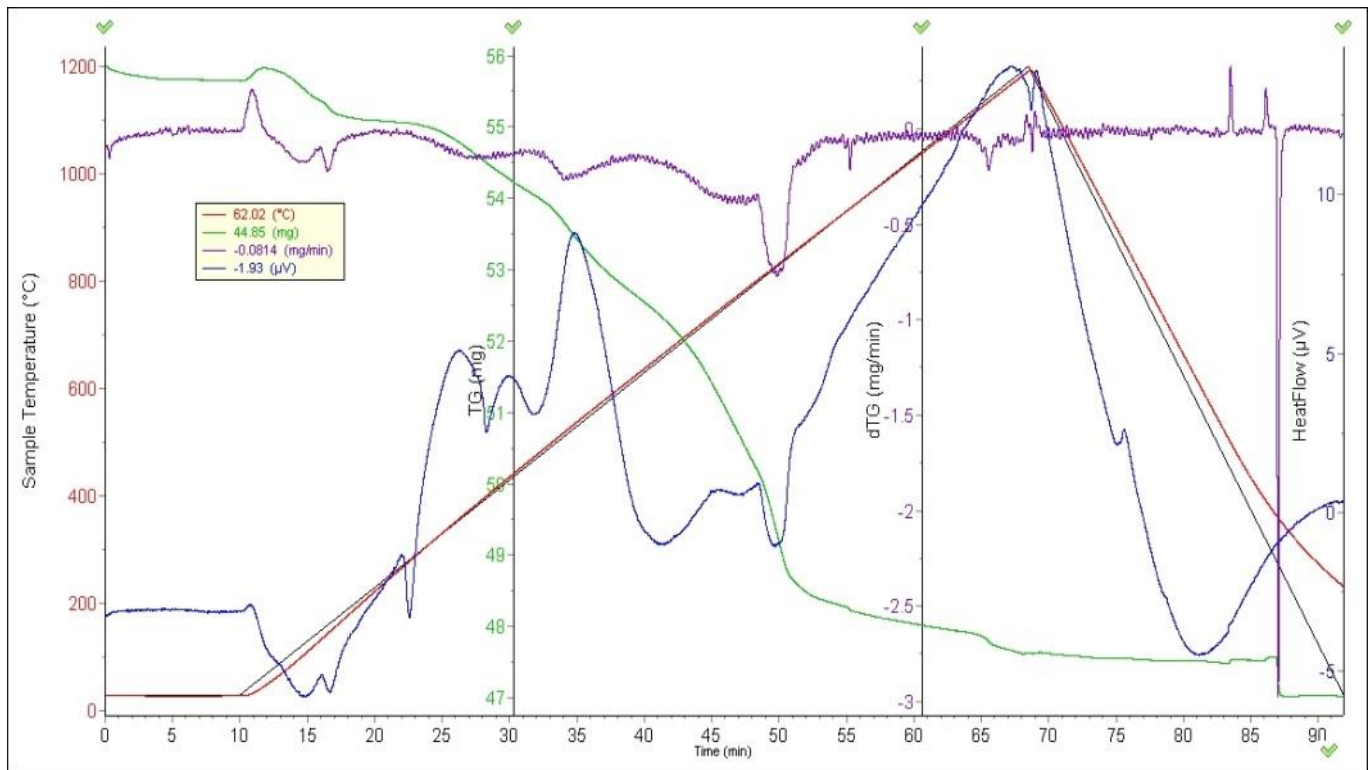
The dried laboratory samples were heat treated in a laboratory oven with a holding time of 2 hours at various temperatures (from 900 to 1250°C). After holding, the heat-treated samples were subjected to sharp cooling. To do this, the hot samples were taken out of the oven and drastically lowered into a metal vessel with cold water. After the quenching process, the samples were crushed and analyzed according to a known technique for various forms of phosphorus and calcium. The results are shown in Figure 2.

In this case, a product is obtained with a content of 17.88-18.94% P₂O_{5total}, 48.09-50.95% CaO_{total}, of which the relative content of the assimilable form of P₂O₅ in 2% citric acid and 0.2M Trilon-B is 75, 89-88.86% and 68.85-76.03%, respectively, and the relative content of assimilable calcium ranges from 78.75-89.16%. [8]

As can be seen from the data presented, an increase in the firing temperature from 900 to 1250 °C contributes to a significant increase in the assimilable forms of phosphorus and calcium (Fig. 2). For example, if at a firing temperature of 900°C the relative content of assimilable phosphorus in the finished product reaches 789% in a 2% citric acid solution, then at a temperature of 1250 ° C this value reaches 88.86%. Similar patterns are observed in the relative phosphorus content of 0.2 M Trilon B and calcium. The products obtained by the above method contain 17.88-18.94% total phosphoric anhydride and 48.09-50.5% total calcium oxide. Of these, 13.57-16.83% of phosphorus and 37.87-443% of calcium, respectively, are in the assimilable form.

To elucidate the mechanism of formation of thermophosphates, samples of a charge composed of phosphorite from the Dzheroy-Sardarinsky deposit, potassium chloride and quartz sand, as well as a charge consisting of phosphorite, potassium sulfate and quartz sand were studied.

Fig.3. Thermogravimetric picture of prepared the pattern from phosphorite: potassium chloride: quartz sand



The study was carried out using a LABSYSEVOSTA derivatograph (SETARAMEVOLUTION, France) in the temperature range 30-1100°C. The rate of temperature rise was 10 deg / min, and the weight of the sample was 360 mg. The chemical composition of solid phases, intermediate and end products of the reaction, the content of P₂O₅, was determined by the photocalorimetric method, and Ca⁺², Mg⁺² by the complexometric method.

The experimental data of the thermographic study of the samples showed that there is a fundamental difference from the known processes at 740°C and above. The derivatogram of the mixture phosphorite: potassium chloride: sand revealed additional endothermic effects associated with the melting of potassium chloride (770 and 800°C) and the formation of potassium calcium and calcium silicate phosphates (above 102°C). The study of the charge, consisting of phosphorite and potassium sulfate, showed, as in the previous cases, at 110°C there is an endothermic effect caused by the removal of hygroscopic moisture. Endothermic effects in the temperature range 110-180-315°C indicate dehydration of the present mineral salts at 410-770°C - melting of potassium sulfate, dissociation of carbonate rocks, i.e. complete decomposition of calcite and other carbonate-containing minerals. At temperatures above 1000°C, the phosphorite crystal lattice is rearranged and double potassium phosphates are formed (Table 1).

The loss of mass is explained by the removal of crystallization water, as well as gaseous components CO₂, HF, SiF₄. The study of the reaction products obtained under conditions corresponding to the thermal effects on the derivatograms, as well as the kinetics of the process, made it possible to reveal the features of the mechanism of the main process and the accompanying chemical transformations, as well as the optimal parameters of the process. The processes occurring during the sintering of mixtures of the above ores lead to the formation of a number of compounds, including their numerous impurities, therefore, the mechanism of thermal alkaline decomposition of phosphates can only be assumed.

Table 1
Results of thermogravimetric study of the charge phosphorite: potassium chloride: quartz sand

Temperature interval, °C	Loss of mass		Loss of mass
	mg	%	
30-125	0	8	Removal of hygroscopic moisture
125-200	0	8	Dehydration of minerals Removal of crystalline moisture
200-565	15	18.0	Dissociation of siderite, polymorphic transformation of SiO ₂ , beginning of dissociation of magnesite
565-740	18.0	20.7	Dissociation of magnesite minerals present, dehydration of halloysite
740-940	14.0	16.2	The beginning of the dissociation of calcite
940-1020	19.0	10.3	Dissociation of calcite
above 1020	20.0	23.2	Continuation of the process of decomposition of calcite with the release of CO ₂ into the gas phase, decomposition of fluorapatite with the release of HF and SiF ₄ into the gas phase, the formation of calcium-potassium and silicate phosphates
Total	86.5	100.0	

The resulting compounds are determined by the structure of the sections of the CaO-K₂O-Na₂O-MgO- (Al, Fe)₂O₃-P₂O₅-SiO₂ system. The main crystalline phases are represented by lemon-soluble phosphates CaKPO₄, MgKPO₄, phosphate with a fluorapatite structure (0.1 wt% F in the finished product), as well as, probably, formed solid solutions of phosphates with calcium silicates, aluminosilicates, and calcium chloride. Due to the incomplete decomposition of the feedstock, the finished product contains the original components.

On the derivatogram when using potassium carbonate (Fig.3), one doublet and one triple endothermic effect is observed at 115, 205 and 720, 840, 860°C, which shows two processes occurring in two and three stages, respectively showing the process of dehydration and dissociation of carbonates with the formation potassium renanite. There is also a three-maximum exothermic effect at 330°C.

In these ranges of temperature fluctuations, practical weight loss is not observed without taking into account 1.052 ppm at 330°C, which can be attributed to the combustion of organic matter from the phosphorus component. Based on this, we can conclude that the optimal temperature range for varying potassium carbonate is 850-950°C.

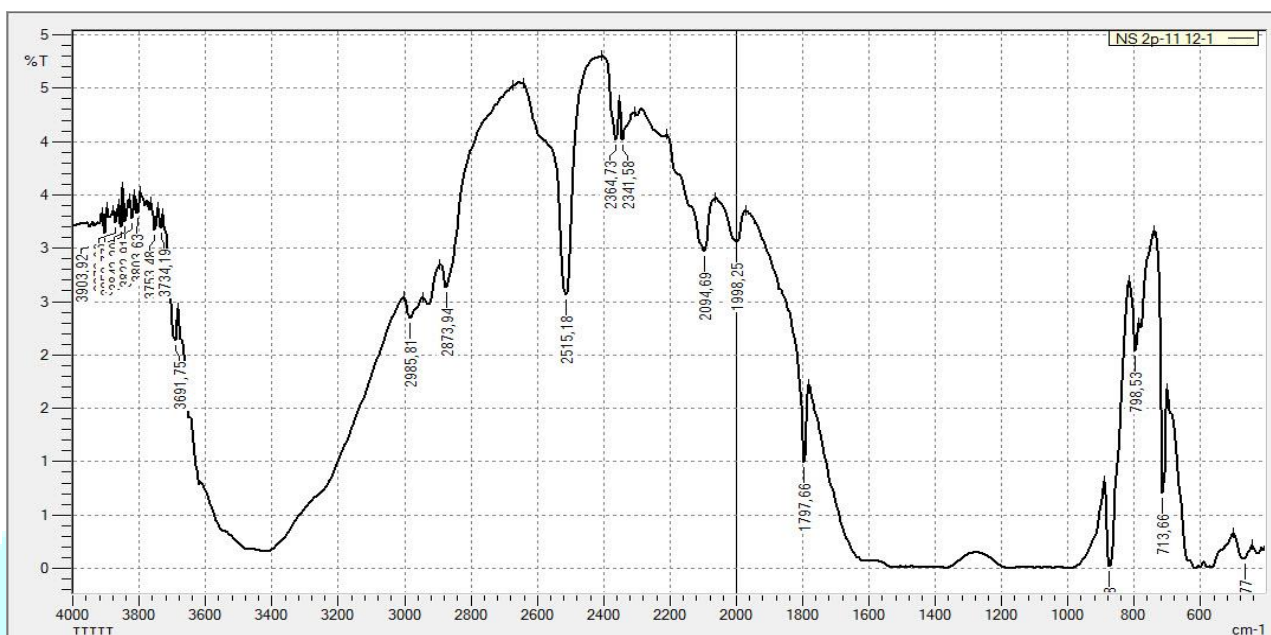
Thermophosphates obtained at different temperatures were investigated by X-ray phase analysis. In fig. 4 shows the diffraction patterns of samples of thermophosphate obtained on the basis of phosphorite, Na₂CO₃ and SiO₂xH₂O at temperatures of 900°C and 1200°C. As can be seen from the figure, the diffractogram exhibits reflections of 3.04 Å, 1.88 Å, 2.29 Å, 2.10 Å, 1.60 Å, 1.93 Å, 1.53 Å, 1.51 Å, which indicate the presence of phosphates - CaNaPO₄ in the sample.

The resulting compounds are determined by the structure of the sections of the CaO-K₂O-Na₂O-MgO- (Al, Fe)₂O₃-P₂O₅-SiO₂ system. The main crystalline phases are represented by lemon-soluble phosphates CaNaPO₄, MgNaPO₄, phosphate with a fluorapatite structure (0.1 wt% F in the finished product), as well as, probably, formed solid solutions of phosphates with calcium silicates, aluminosilicates, and calcium chloride. Due to the incomplete decomposition of the feedstock, the finished product contains the original components.

At the same time, a complex equilibrium is established, which leads to the formation of double calcium-sodium phosphates. The presence of fluorides in the composition of phosphorite (0.4 wt% F) indicates the presence of apatite grains, the crystal lattice of which is destroyed during heat treatment with the release of fluoride gases.

Available in the raw material in the form of impurities, carbonates of magnesium, iron and aluminum dissociate into carbon dioxide and oxides, which also participate in the formation of double magnesium-potassium and magnesium-calcium phosphates.

Fig. 4. The IR spectra of the initial low-grade phosphorite of the Central Kyzyl Kum and the products of its sintering with carbonates



Experimental data showed that at 25^oC with a gradual increase in the concentration of carbamide for 60 minutes, the solubility of thermophosphates increases, and after 240 minutes it dissolves within 0.70-0.25% of P₂O₅. A similar pattern is observed at temperatures of 25 and 50^oC in 10, 20, 30 and 40% solutions of ammonium nitrate. The solubility of thermophosphates increases within 0.81-0.47 and 0.84-0.68%, respectively. As the data on the solubility of thermophosphates at 25 and 50^oC in 10, 20, 30, and 40% solutions of potassium chloride and sulfate show, the solubility of thermophosphates increases from 0.45 to 0.56% with increasing fertilizer concentration.

The IR spectra of the initial low-grade phosphorite of the Central Kyzyl Kum and the products of its sintering with carbonates are shown in Fig. 4. The absorption maxima for thermophosphates (curve 3) are mainly observed in the same range of values as for pure p-KCaPO₄ (415, 540, 665 cm⁻¹).

The gentle character of the curves indicates a rather low degree of crystallinity of the products, which determines their higher solubility (hence, digestibility)

in comparison with the original phosphorite. In thermophosphates, the content of the initial phosphate part (1060, 1430 cm⁻¹) is insignificant; the lines characteristic of K₂SO₄ are also practically absent.

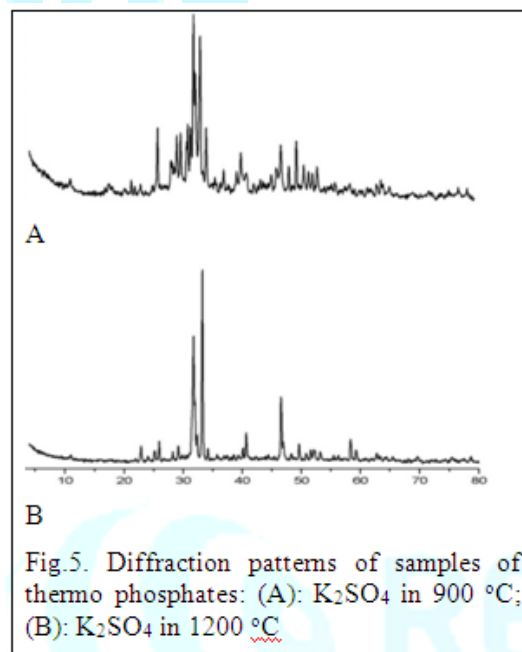


Fig.5. Diffraction patterns of samples of thermo phosphates: (A): K₂SO₄ in 900 °C; (B): K₂SO₄ in 1200 °C

In fig. 5 shows the diffraction patterns of samples of thermophosphates obtained from phosphorite flour of the Central Kyzyl Kum, potassium sulfate and quartz sand at different temperatures and exposures. Reflexes were found in the samples, which may indicate the presence of CaKPO₄ at 900 and 1200^oC.

Conclusion. We have studied the process of obtaining thermophosphate fertilizers based on thermal alkaline activation of low-grade phosphorites of the Central Kyzyl Kum in the presence of potassium salts. The results obtained show that as a result of firing a mixture of components (phosphorite, K₂SO₄) at a temperature of 900^oC, the activation (conversion of indigestible P₂O₅ forms into plant-assimilable forms) of phosphate raw material occurs. In this case, a product is obtained with a content of 17.88-18.94% P₂O_{5 total}, 48.09-50.95% CaO total, of which the relative content of the assimilable form of P₂O₅ in 2% citric acid and 0.2M Trilon B is 75.89-88.86% and 68.85-76.03%, respectively, and the relative content of assimilable calcium ranges from 78.75-89.16%.

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