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Thermal Activation of Phosphate Raw Materials from Aznek Ores

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Abstract: The essense of this study is to investigate the microstructure and mechanical properties of Aznek phosphorites mixed alkali metal salts such as sodium and potassium at different compositions. This a low grade raw material on phosphorus and rich in carbonate and chlorine is not suitable for acid processing. To obtain high-quality phosphate fertilizers from raw materials, it must be pre-enriched. In the phosphate plant carried multistage enrichment: crushing, dry dressing, washing from chlorine, sintering to remove carbon dioxide. One of the perspective directions of the processing such type phosphate raw material is a thermal treatment, which based in destruction of unassimilable by plants the crystalline structure of mineral under thermal activation.

Keywords: thermophosphate, salts of alkali metals, sintering, mineral fertilizers, enrichment, phosphoric anhydride , assimilability.

INTRODUCTION

A study of phosphorites from the Aznek deposits during heating carried out using thermoderivatography and IR-spectroscopy methods up to 1000°C, as well as physicochemical analysis of solid heat treatment products made it possible to describe some of the processes occurring during this processes. A significant difference was noted in the behavior of these phosphorites, associated with different genesis and chemical and mineralogical composition of these deposits. The fundamental possibility of using thermogravimetry for a qualitative description of the processes occurring during heat treatment of phosphorites and accompanied by mass loss is observed.

Table 1.
Chemical composition of raw material from Aznek ores.

№	Compound name	Content of elements,

		%
1	P_2O_5	27-28
2	Al_2O_3	1,5-2,0
3	SiO_2	6,0-8,0
4	CaO	48-49
5	MgO	2-3
6	Fe_2O_3	0,6-0,8
7	SO_3	2,8-3,0
8	CO_2	12-15
9	Fluorine	1-2
10	SO_3	2,5- 3,5
11	U	0,003-0,008
12	REE	0,06-0,1
13	H_2O	1,0
14	Insoluble part	3,0-3,2

Experiments shows the possibility thermal activation of Aznek ores phosphates with alkali metal salts in destination to obtain thermal-phosphate fertilizers.

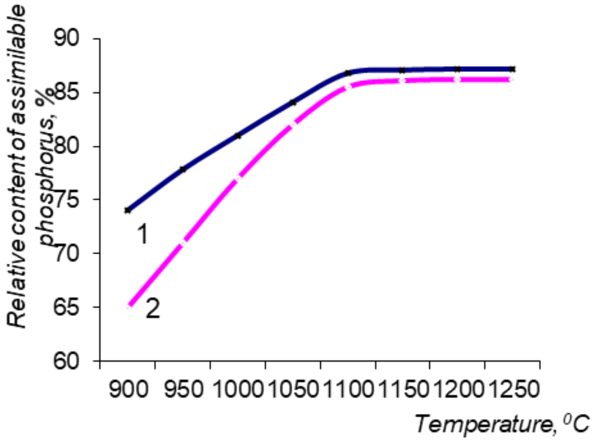
Thermal-alkaline phosphates (thermophosphates) are obtained by sintering crushed natural phosphates with alkaline salts and minerals (soda, potash, sodium and potassium sulfates and bisulfates, soda slags after desulfurization of cast iron, nepheline, leucite, etc.).

The phosphate substance of most thermophosphates is represented by renanite $Na_2O \cdot 2CaO \cdot P_2O_5$ or $CaNaPO_4$, which is highly soluble in 2% citric acid, as well as calcium orthosilicate, which gives solid solutions with calcium sodium phosphate. Fluorine binds as sodium fluoride. 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 mineral acids, as well as the possibility of processing almost any phosphate raw material and waste of its production.

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. The production of thermophosphate, carried out on an industrial scale at a number of enterprises, consists in sintering a mixture of crushed natural phosphate and soda in rotary kilns at 1100-1250^{0}C and subsequent cooling, crushing and grinding of the resulting clinker to nanoparticles.

For the experiments, we used ordinary phosphorite flour of the Central Kyzyl Kum of the following composition (wt.%): 16.53 P_2O_5; 46.65 CaO; 13% CO_2 and soda ash produced by UE "Kungrad Soda Plant", as well as chemically pure SiO_2xH_2O [1].



Pic 1. Dependence of the relative content of phosphorus and calcium on the temperature of the firing process. Ratio of components Phosporites:Na_2CO_3:SiO_2 = 100:16.45:10.0

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 №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/cm^2. The molded laboratory samples were naturally dried at room temperature 25-30^{0}C during the day. Then the samples were dried in a drying oven at a temperature of 105-110^{0}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 [2].

It follows from the data presented that as a result of firing a mixture of components (phosphorite, Na_2CO_3 and SiO_2xH_2O) at a temperature of 900^{0}C, the activation (conversion of indigestible P_2O_5 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% P_2O_{5total}, 48-49.84% CaO_{total}, of which the relative content of the assimilable form of P_2O_5 and CaO is 50.76-72.45% and 70.70 -801%, respectively [3].

An increase in the firing temperature from 900 to 1250^{0}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^{0}C the relative phosphorus content in the finished product reaches 658% in a 2% citric acid solution, then at a temperature of 1250^{0}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 [4].

From the data presented in Table 1, it follows that, as a result of firing a mixture of components (phosphorite, K_2CO_3 and SiO_2) at a temperature of 900 ^{0}C, the activation (conversion of indigestible P_2O_5 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% P_2O_{5total}, 48.09-50.95% CaO_{total}, of which the relative content of the assimilable form of P_2O_5 in 2% citric acid and 0.2M Trilone 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% [5].

As can be seen from the data presented, an increase in the firing temperature from 900 to 1250 ^0C contributes to a significant increase in the assimilable forms of phosphorus and calcium For example, if at a firing temperature of 900^0C 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 [6].

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.

The study was carried out using a LABSYSEVOSTA derivatograph (SETARAMEVOLUTION, France) in the temperature range $30\text{-}1100^0C$. 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 P_2O_5, 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 740^0C and above. The derivatogram of the mixture phosphorite: potassium chloride: sand revealed additional endothermic effects associated with the melting of potassium chloride (770 and 800^0C) and the formation of potassium calcium and calcium silicate phosphates (above 102^0C).

The study of the charge, consisting of phosphorite and potassium sulfate, showed, as in the previous cases, at 110^0C there is an endothermic effect caused by the removal of hygroscopic moisture.

Endothermic effects in the temperature range $110\text{-}180\text{-}315^0C$ indicate dehydration of the present mineral salts at $410\text{-}770^0C$ - melting of potassium sulfate, dissociation of carbonate rocks, i.e. complete decomposition of calcite and other carbonate-containing minerals. At temperatures above 1000^0C, 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 CO_2, HF, SiF_4. 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.

Table 2

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

Temperature interval, °C	Loss of mass		Loss of mass
30-125			Removal of hygroscopic moisture
125-200			Dehydration of minerals Removal of crystalline moisture
200-565			Dissociation of siderite, polymorphic transformation of SiO_2, beginning of dissociation of magnesite
565-740			Dissociation of magnesite minerals present, dehydration of halloysite
740-940			The beginning of the dissociation of calcite
940-1020			Dissociation of calcite
above 1020			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			

The resulting compounds are determined by the structure of the sections of the $CaO-K_2O-Na_2O-MgO-$ $(Al, Fe)_2O_3-P_2O_5-SiO_2$ system. The main crystalline phases are represented by lemon-soluble phosphates $CaKPO_4$, $MgKPO_4$, 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 one doublet and one triple endothermic effect is observed at 115, 205 and 720, 840, 860^0C, 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 330^0C [7].

In these ranges of temperature fluctuations, practical weight loss is not observed without taking into account 1.052 ppm at 330^0C, 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 $850\text{-}950^0$C.

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.

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