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STUDY OF THE SOLUBILITY OF FERTILIZERS OBTAINED FROM LOW-GRADE PHOSPHORITES BY HEAT TREATMENT

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ABSTRACT:

The conducted studies have shown the possibility of thermo-alkaline processing of phosphorites of the Central Kyzylkum for phosphorus-containing fertilizers such as thermophosphate. X-ray studies showed that with an increase in the firing temperature, the mass of the compounds decreased and the digestibility of P_2O_5 increased. The transition of phosphorus to an assimilable form is due to the fact that, with an increase in temperature, the solubility increases.

Keywords: Phosphorene's, alkaline salts, thermal treatment, phosphorous V anhydride, solubility, assimilability, citrate acid.

INTRODUCTION:

In the world practice of beneficiation of phosphate ores, thermal roasting has also become quite widespread. It is mainly used for upgrading phosphate ores in the USA, Algeria, Morocco and Israel. After roasting, the product contains 31% P_2O_5 and more, the yield of phosphorus in the concentrate is about 90%. Ores are fired at 680-980^{0}C, then treated with water or saline solutions (sea water can also be used) and dicalcium phosphate is separated. It should be noted that concentrates containing at least 33% P_2O_5 are sold on the world market.

In the Republic of Uzbekistan, the production of phosphorus-containing fertilizers is limited by the quality of the phosphorite we have at the Central Kyzylkum deposit. This raw material is poor in phosphorus, and also contains a large amount of undesirable impurities, in particular, carbonates and chlorine. Such raw materials are not suitable for obtaining highly concentrated phosphorus-containing fertilizers from it, i.e. not suitable for nitric acid, sulfuric acid and hydrochloric acid processing of it into concentrated phosphorus-containing fertilizers. In this case, a large amount of acid will be spent not on the decomposition of fluorapatite, but on interaction with calcium carbonate, giving large-tonnage production wastes such as nitrate, sulfate or calcium chloride. Acid processing of such highly carbonized raw materials is accompanied by abundant foaming, which significantly disrupts the entire technological process and reduces equipment productivity.

METHODS AND MATERIALS:

One of the real ways to increase the production of phosphate fertilizers, in our opinion, is the thermochemical processing of low-grade highly carbonized phosphorites of the Central Kyzylkum with the addition of potassium and sodium alkali metal salts. In this case, products are obtained, the so-called thermophosphates - with a high content of assimilable phosphorus, potassium and calcium of prolonged action. With this approach to solving the problem, deficient sulfuric acid is not consumed for the processing of phosphate raw materials, large-tonnage wastes such as phosphogypsum are not formed, and due to the involvement of low-grade phosphorites in the technology, the production of phosphorus-containing

fertilizers increases by at least 20-25%. It follows that the development of alternative acid-free methods for processing low-grade phosphorites of the Central Kyzylkum, allowing them to be processed into phosphorus-containing fertilizers, is a very urgent task facing science and the chemical industry, and this project is dedicated specifically to solving this problem.[2]

For the experiments, ordinary phosphorite flour of the Central Kyzylkum was used with the following composition (wt., %): 16.53 P_2O_5 ; 46.65 with; 15.3% CO_2 and soda ash produced by the UE Kungrad soda plant, as well as SiO_2 x H_2O chemically pure.

Dried laboratory samples were subjected to heat treatment in a laboratory oven with exposure for 2 hours at various temperatures (from 900 to 1250 ^{0}C). After exposure, the heat -treated samples were subjected to rapid cooling and dried at a temperature of 60-80 ^{0}C in a thermostat.

RESULTS:

The results of the experiments are shown in tables 1 and 2.

Table 1. Heat treatment of Kyzylkum phosphorites in the presence of Na_2CO_3 and SiO_2xH_2O at different temperatures

№	t, ^{0}C	Chemical composition of the sintered product, %							
		P_2O_5 total.	P_2O_5 assim on citrate acid	P_2O_5 assim on EDTA	CaO total.	CaO assim.	$\frac{P_2O_5 \text{ assim}}{P_2O_5 \text{ total}}$ on citrate acid	$\frac{P_2O_5 \text{ assim}}{P_2O_5 \text{ total}}$ on EDTA	$\frac{Ca \text{ assim.}}{Ca \text{ total.}}$
1	900	17.88	11.78	10.52	48.09	33.06	65.89	58.85	68.75
2	1000	17.92	12.24	10.81	48.20	34.63	68.29	60.31	71.84
3	1100	18.45	11.54	11.54	49.63	36.54	72.76	62.57	73.62
4	1200	18.59	11.93	11.93	50.0	38.27	76.28	64.18	76.54
5	1250	18.94	12.51	12.51	50.95	40.33	78.86	66.03	79.16

Table 2. Influence of additions of Na_2SO_4 and SiO_2xH_2O on the heat treatment of Kyzylkum phosphorites at a temperature of 900 ^{0} C

№	t, ^{0}C	Chemical composition of the sintered product, %							
		P_2O_5 total.	P_2O_5 assim on citrate acid	P_2O_5 assim on EDTA	CaO total.	CaO assim.	$\frac{P_2O_5 \text{ assim}}{P_2O_5 \text{ total}}$ on citrate acid	$\frac{P_2O_5 \text{ assim}}{P_2O_5 \text{ total}}$ on EDTA	$\frac{Ca \text{ assim.}}{Ca \text{ total.}}$
1	900	18.82	12.40	11.56	49.91	32.45	65.88	61.42	65.02
2	1000	18.90	12.52	11.67	49.97	33.30	66.24	61.75	66.64
3	1100	18.91	12.64	11.89	49.98	35.65	67.55	62.88	71.33
4	1200	18.92	12.78	11.97	50.20	37.0	67.55	63.27	73.71
5	1250	18.92	12.77	12.68	50.93	38.73	67.50	67.0	76.05

From the presented data, it follows 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, activation (transfer of indigestible forms of P_2O_5 into forms assimilable by plants) of phosphate raw materials occurs (Table 1). This results in a product of 17.88-18.94% $P_2O_{5tot.}$, 48.09-

50.95% C aO tot ., of which the relative content of the digestible form P_2O_5 and CaO is 50.76-72.45% and 70.7-85.0%, respectively. And 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 2). For example, if at a firing temperature of 900 ^{0}C the relative content of phosphorus in the finished product reaches up to 65.58% in a 2% solution of citric acid, and at a temperature of 1250 ^{0} C this value reaches 86.94%. Similar patterns are repeated when observing the relative content of phosphorus according to 0.2 M EDTA and calcium oxide.

The conducted studies have shown the possibility of thermo-alkaline processing of phosphorites of the Central Kyzylkum for phosphorus-containing fertilizers such as thermophosphate. Fertilizers are not hygroscopic, do not caked.

The process of obtaining thermophosphate fertilizers based on phosphorites of the Central Kyzylkum, potassium salts and quartz sand was studied. The experiments were carried out as follows: the initial substances were weighed in a certain amount (phosphorite flour of the Central Kyzylkum, potassium carbonate and quartz sand) and mixtures were prepared. The samples were dried in an oven at a temperature of 105-110 ^{0}C for and 2 hours.

Dried laboratory samples were subjected to heat treatment in a laboratory oven for 2 hours at various temperatures (from 900 to 1250 ^{0}C). After exposure , the heat - treated samples were subjected to rapid cooling. To do this, samples with a temperature were taken out of the furnace with tongs and abruptly lowered into a metal vessel with cold water. After the process of rapid cooling, the samples were dried at a temperature of 60-80 ^{0}C in a thermostat.

From the presented data, 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 , activation (transfer of indigestible forms P_2O_5 into forms assimilable by plants) of phosphate raw materials occurs (table 3). This results in a product of 17.88-18.94% $P_2O_{5tot.}$, 48.09-50.95% CaO tot, of which the relative content of the digestible form P_2O_5 for 2% citric acid and 0.2 M EDTA is 75.89-88.86% and 68.85-76.03%, respectively. At the same time, the relative content of digestible calcium oxide ranges from 78.75-89.16%.

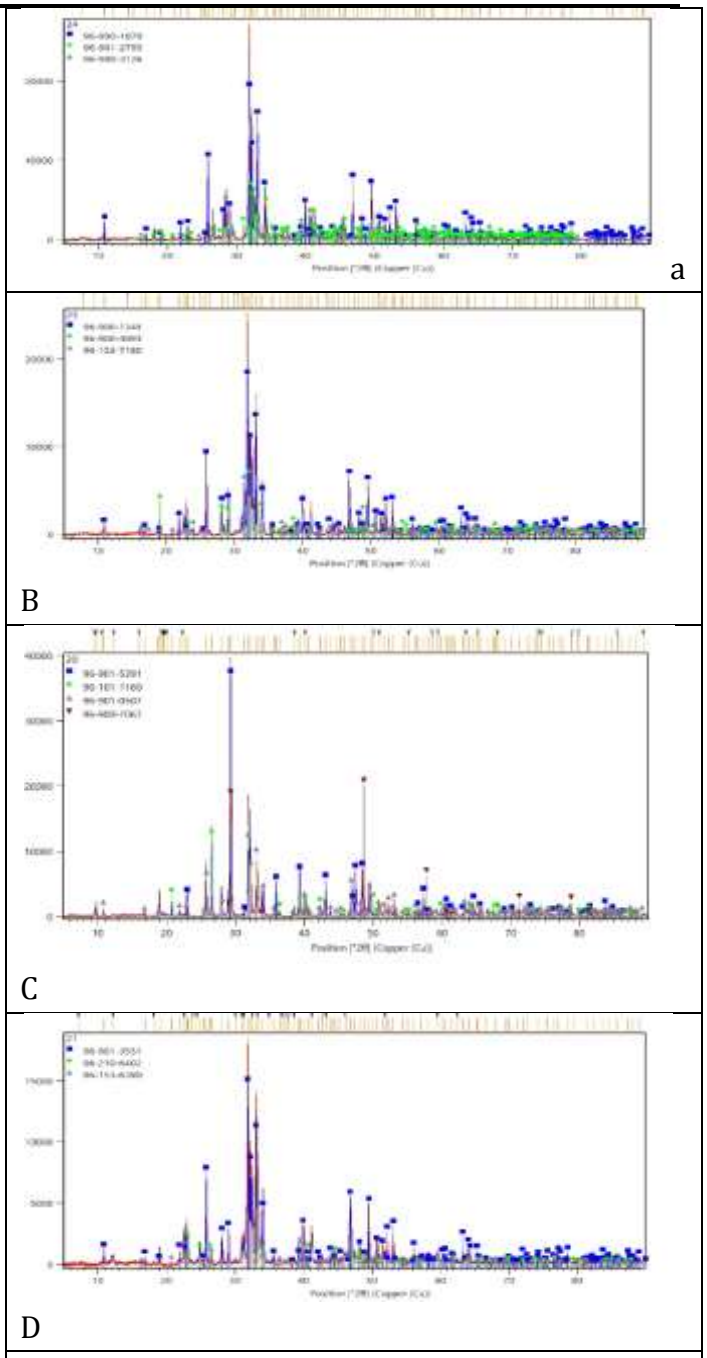
Table 3 Thermal treatment of Kyzylkum phosphorites in the presence of K_2CO_3 and SiO_2 at different temperatures

№	Phosp. weight, g	W-t K_2CO_3, g	W-t of SiO_2, g	t,^{0}C	Chemical composition of the sintered product, %							
					P_2O_5 total.	P_2O_5 assim. on citrate acid	P_2O_5 assim on Trilon B	CaO total	$CaO_{as\,sim}$	P_2O_5 assim P_2O_5 total (Citrate acid.)	P_2O_5 assim P_2O_5 total (EDTA)	$\frac{CaO_{as\,sim}}{CaO_{total}}$
1	100	16,0	10,0	900	17,88	13,57	12,31	48,09	37,87	75,89	68,85	78,75
2	100	16,0	10,0	1000	17,92	14,03	12,60	48,20	39,45	78,29	70,31	81,84
3	100	16,0	10,0	1100	18,45	15,27	13,39	49,63	41,5	82,76	72,57	83,62
4	100	16,0	10,0	1200	18,59	16,04	13,79	50,0	43,27	86,28	74,18	86,54
5	100	16,0	10,0	1250	18,94	16,83	14,4	50,95	45,43	88,86	76,03	89,16

As can be seen from the presented data, an increase in the firing temperature from 900 to 1250 ^{0}C contributes to a significant increase in the assimilable forms of phosphorus and calcium. For example, if at a firing temperature of 900 ^{0} C, the relative content of phosphorus in the finished product reaches up to 75.89% for a 2% solution of citric acid, and at a temperature of 1250 ^{0}C, this value reaches 88.86%. Similar patterns are repeated when observing the relative content of phosphorus according to 0,2 M EDTA and calcium. To carry out physical and chemical analyzes of the obtained products in laboratory conditions, modern methods of analysis were used, such as electron-scanning microscopy, X-ray, mass spectroscopy and thermogravimetry, etc. [3]

We have obtained thermophosphate materials based on potassium and sodium salts, quartz sand, coal and low-grade phosphorites. To begin with, we analyzed the original components and then a laboratory study was carried out pic. 4. shows the results of X-ray analysis of the obtained products.

X-ray studies showed that with an increase in the firing temperature, the mass of the compounds decreased and the digestibility of P_2O_5 increased. The transition of phosphorus to an assimilable form is due to the fact that, with an increase in temperature, the solubility increases.



Pic 4 . X-ray images of the obtained products: a) KCl-phosphorite 1200^{0}C, b) NaCl - phosphorite 1200 ^{0}C, c) Na_2SO_4 -phosphorite 1100 ^{0}C, d) Na_2SO_4 - phosphorite 900^{0}C

Using X-ray analysis the distribution of rare earth, alkali, alkaline earth, noble, heavy metals and other elements in decomposition was investigated.

It has been established that the content of rare earth, alkali and alkaline earth elements in the sludge is 7.0-10 and 2-6 times higher, and heavy metals Mn , Zn and U 4; 1.4 and 2.7 times, respectively, less than dicalcium phosphate , which is important in the complex processing of low-grade phosphorites of the Central Committee.

As it seemed in the results of mass-spectral analysis, the content of heavy metals is iron 5400 - 9500 μg/ l and chromium 44-100 μg/l.

On the basis of the research carried out in the project, urgent scientific and technical problems were solved for the development of a technology for obtaining new types of thermophosphate fertilizers based on thermo - alkaline processing of low-grade phosphorites of the Central Kyzylkum .

The main scientific and practical results obtained during the implementation of this research work are the following:

The chemical and mineralogical composition of phosphorite flour of the Central Kyzylkum was studied using physicochemical methods of analysis (X-ray, IR spectroscopic and thermographic). The results of the analysis show that the Kyzylkum phosphate rock consists mainly of fluorocarbonate apatite (≈30-40%) and quartz (≈10%). Dolomite, calcite, iron hydroxides, glauconite, feldspars, etc. are present in a smaller amount. The phosphate component of the raw material is partially (up to 20%) in an assimilable form. The dispersion of phosphorite flour is characterized as follows (wt.%): + 0,315 mm-2.8%; +0.25-0.31 - 3.35%; +0.16-0.25 - 16.2%; +0.1-0.16 - 21.1%; +0.05-0.1 - 33.3%; -0.05-23.2%.

DISCUSSION:

The study of the process of roasting phosphorite flour of the Central Kyzylkum with sodium carbonate and quartz sand in the range of various mass ratios of Phophorite: Na_2CO_3:SiO_2, shows the fundamental possibility of obtaining thermophosphate phosphorus fertilizers with desired composition and properties. The dependence of the change in the assimilable form of phosphorus and calcium on the weight ratio of phosphorite was established: Na_2CO_3:SiO_2 and temperature. [5]

It has been experimentally proven that 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. For example, if at a firing temperature of 900 ^{0}C the relative content of phosphorus in the finished product reaches up to 65.58% in a 2% solution of citric acid, and at a temperature of 1250 ^{0}C this value reaches 86.94%. Similar patterns are repeated when observing the relative content of phosphorus according to 0,2 M EDTA and calcium.

We also studied the process of obtaining thermophosphate fertilizers based on thermo - alkaline activation of low-grade phosphorites of the Central Kyzylkum in the presence of potassium salts. The results obtained show that, as a result of firing a mixture of components (phosphorite, K_2CO_3 and SiO_2) at a temperature of 900 ^{0}C, activation (transfer of indigestible forms of P_2O_5 into forms assimilable by plants) of phosphate raw materials occurs. This results in a product of 17.88-18.94% $P_2O_{5tot.}$, 48.09-50.95% CaO_{total}, of which the relative content of the digestible form P_2O_5 for 2% citric acid and 0.2 M EDTA is 75.89-88.86% and 68.85-76.03%, respectively. At the same time, the relative content of digestible calcium ranges from 78.75-89.16%.[6]

CONCLUSION:

The total content of nutrients in thermophosphate fertilizers is in the range of 57-60% (P_2O_{5tot} +$CaO_{ass.}$). Unlike water-soluble forms, the lemon- soluble form of phosphate components present in the fertilizer increases the use of phosphorus by plants on any soil and is associated with a decrease in the retrogradation process. Being weakly alkaline, thermophosphates simultaneously average soil acidity and can be used both independently and as part of fertilizer mixtures. Thermophosphate fertilizers has been worked out under laboratory conditions and the main technological parameters of the process have been established.

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