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Phosphor-Calcium Fertilizers on the basis of Phosphate Raw Material of the Central Kyzylkum

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ABSTRACT. The results of the study of incomplete decomposition of off-balance phosphorite ore of Central Kyzylkum with hydrochloric acid are presented and discussed in this work. A phosphoric calcium fertilizer with a different content of assimilable forms of phosphorus and calcium can be obtained.

KEYWORDS: Phosphate raw materials, hydrochloric acid, decomposition, digestible form, fertilizer.

I. INTRODUCTION

In Uzbekistan, the phosphorites of the Central Kyzylkum are the main phosphate raw material for obtaining phosphorus-containing fertilizers. It is a phosphorus-poor raw material, which also contains a large amount of undesirable impurities, in particular, carbonates and chlorine [1]. Such raw materials are not suitable for direct production of highly concentrated phosphorus-containing fertilizers, i.e. it must first be enriched. Therefore, a multi-stage enrichment was carried out at the KyzylkumPhosphorite Plant (KFP): crushing, dry enrichment to obtain ordinary phosphorite flour, washing away from chlorine, roasting to remove CO_2 [2-4].

At present, KFP produces three types of phosphate raw materials: washed burned concentrate (P_2O_5 -27-29%, C1 <0.04%) in the volume of 400 thousand tons per year; washed dried concentrate (P_2O_5 - 18-19%) in the amount of 200 thousand tons per year; ordinary phosphorite flour (P_2O_5- 16-18%) in the amount of 200 thousand tons per year.

It should be noted that when enriching the phosphorites of the Central Kyzylkum, carried out at the KFP, a large amount of waste is produced (off-balance ore). As a result, the sorting of phosphorite ore with a P_2O_5 content of less than 12-15%, performed directly in the process of extraction, a large amount of it is stored as a waste, unsuitable for fertilizer production. To date, the volume of this waste is more than 5 million tons, and the number of such unused substandard phosphorites is growing from year to year. These wastes are stored up to future times, i.e. until the time when an acceptable technology for their processing is found.

II. METHODS and EXPERIEMNTS

In this regard, we considered it legitimate to conduct studies on the decomposition of off-balance ores of Kyzylkumphosphorites with an incomplete rate of hydrochloric acid. We know that in recent years, the equivalence in efficiency of partially decomposed phosphates and standard traditional fertilizers, ammophos and simple superphosphate, has been proved in agricultural practice both in Russia and abroad [5-6].

To carry out laboratory experiments, we took the phosphate raw material of Tashkura from Jeroy-Sardara deposit, having the following composition, mass%: P_2O_5-12.98; CaO-39.95; Al_2O_3 - 1.17; Fe_2O_3 - 1.37; MgO = 0.53; F, -1.85;

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CO_2 - 12,01 and 32% hydrochloric acid. The norm of hydrochloric acid was varied in the range 10-50% of the stoichiometry for CaO [7].

The decomposition of phosphorite with hydrochloric acid was carried out on a laboratory unit consisting of a tubular glass reactor equipped with a stirrer with an electric drive and placed in an aqueous thermostat. The speed of rotation of the stirrer was regulated by a rheostatic device and measured with a TM-3M tachometer using a D-1MM sensor [8-9]. The temperature in the thermostat was maintained using a TK-300I thermometer and an RT-230U electronic relay. In all experiments it was constant and equal to 400 °C.

After cessation of the reaction, a certain amount of water was added to the resulting dough-like mass in order to obtain a normally flowing pulp. Preliminary experiments have shown that decomposition products having a pH of less than 3.5 due to high acidity are poorly dried [10]. Therefore, the resulting acidic pulps were ammoniated with gaseous ammonia to pH values of 3.42-4.10. Ammonized pulps have good rheological properties, which allow their drying and granulation in such active industrial units as a drum granulator-dryer. Then the ammoniated pulps were dried at a temperature of 95-100 °C, and the resulting fertilizers were analyzed for the content of the main components by standard methods [11].

III. RESULTS

Analysis of the square diagram of the CaO-P_2O_5-HCl-H_2O [($Ca_3(PO_4)2$ -$CaCl_2$ -6HCl-$H_6(PO_4)_2$-H_2O)] system shows that when the phosphate raw material is decomposed with the calcium modulus equal to 3.08 32% an acid taken in an amount of 10 and 50% of the stoichiometric norm, the figurative point of the system is outside the square of the system. The liquid phase of the system consists of a solution of $CaCl_2$, and a solid phase of tricalcium phosphate under-decomposed phosphorite. The hydrochloric acid formed during decomposition of the mineralized mass has a pH range of 3.5-5.5.

Table

Chemical composition of dried products

The rate of hydrochloric acid, %	P_2O_{5tot}, %	P_2O_{5assim} by citric, %	$P_2O_{5assim.}$ by EDTA, %	CaO_{tot}, %	$CaO_{assim.}$by citric, %	CaO_{water}, %	pH 2% suspension
10	12,55	2,40	2,01	38,24	20,93	3,07	5,8
15	12,37	3,12	2,23	37,87	21,65	3,67	5,5
20	12,10	3,67	2,40	37,25	23,31	4,33	5,4
25	12,00	4,49	2,73	36,82	24,51	5,01	5,1
30	11,70	5,13	3,02	36,05	25,46	5,63	4,9
35	11,61	5,72	3,38	35,61	25,66	6,52	3,8
40	11,48	6,23	3,81	35,41	26,10	7,11	3,5
45	11,33	6,61	4,03	35,12	26,37	8,39	3,5
50	11,29	7,26	4,20	34,80	26,51	9,20	3,1

The results of determining the composition of fertilizers are given in the table. From the data it can be seen that the content of the assimilated form of P_2O_5 significantly depends on the norm of hydrochloric acid. An increase in the rate of hydrochloric acid from 10 to 50% leads to an increase in $P_2O_{5assim.}$in citric acid and EDTA from 2.4 to 7.26% and from 2.01 to 4.20%, respectively. At the same time, the degree of decarbonization of the initial phosphorite is from 25.12 to 82.23% (Figure 1). The content of total phosphorus and calcium in the fertilizers obtained, depending on the experimental conditions, is 11.29-12.55% and 34.8 - 38.24%, respectively.

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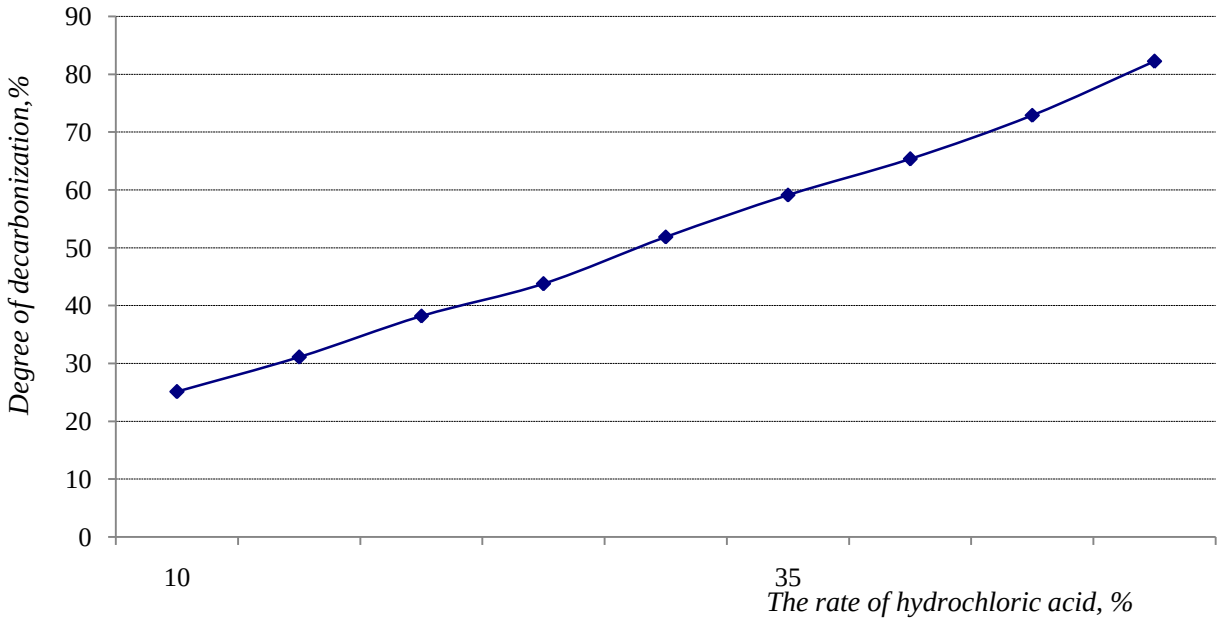

Fig. 1.Dependence of the degree of decarbonization of phosphate raw materials on the norm of hydrochloric acid.

IV. DISCUSSION

The dependence of the change in the assimilable forms of P_2O_5 on EDTA and the 2% solution of citric acid is shown in Fig. 2 and 3. The figures clearly show changes in the relative content of assimilable forms of phosphorus from the initial rate of hydrochloric acid. An increase in the rate of hydrochloric acid in CaO from stoichiometry from 10 to 50% contributes to an increase in the relative content of the assimilated form of phosphorus in EDTA and a 2% solution of citric acid from 16.01 to 37.20 and from 19.12 to 64.30%. The relative content of assimilable calcium fluctuates within the range 54.73-76.18% (Fig. 4).

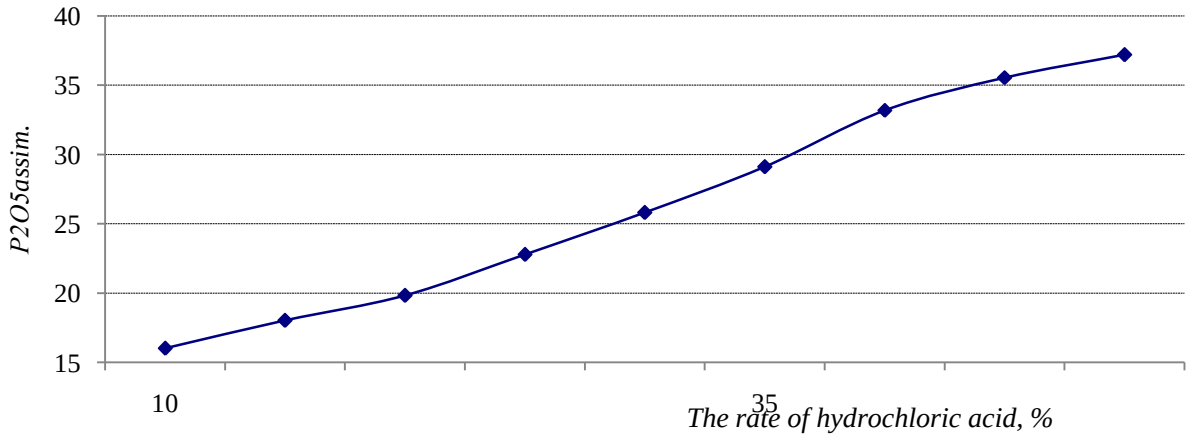

Fig. 2.Dependence of the relative content of assimilable forms of phosphorus on EDTA on the norm of hydrochloric acid.

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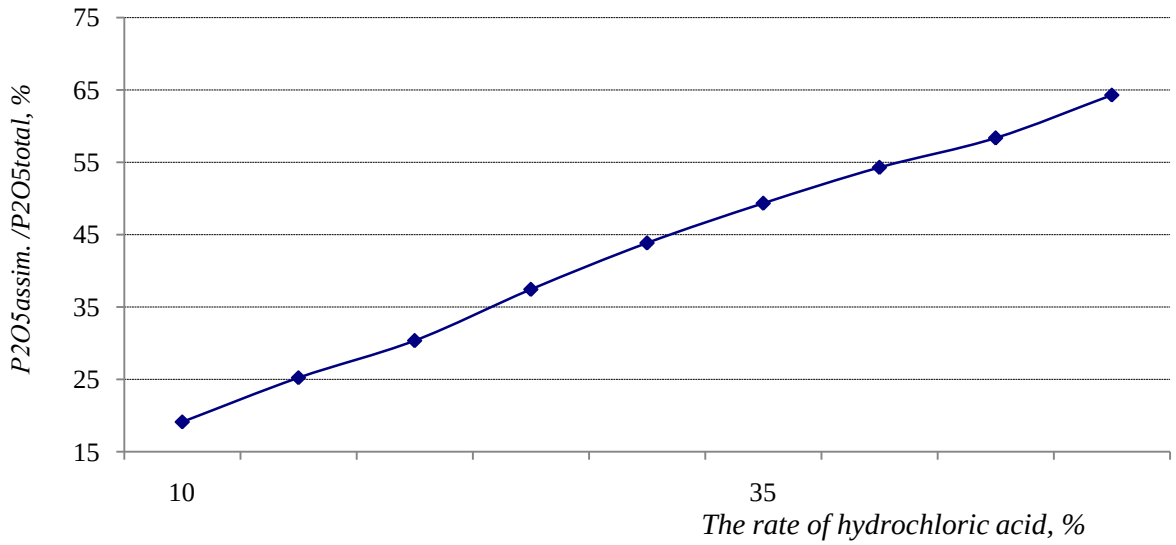

Fig. 3.Dependence of the relative content of assimilable forms of phosphorus on citric acid on the norm of hydrochloric acid.

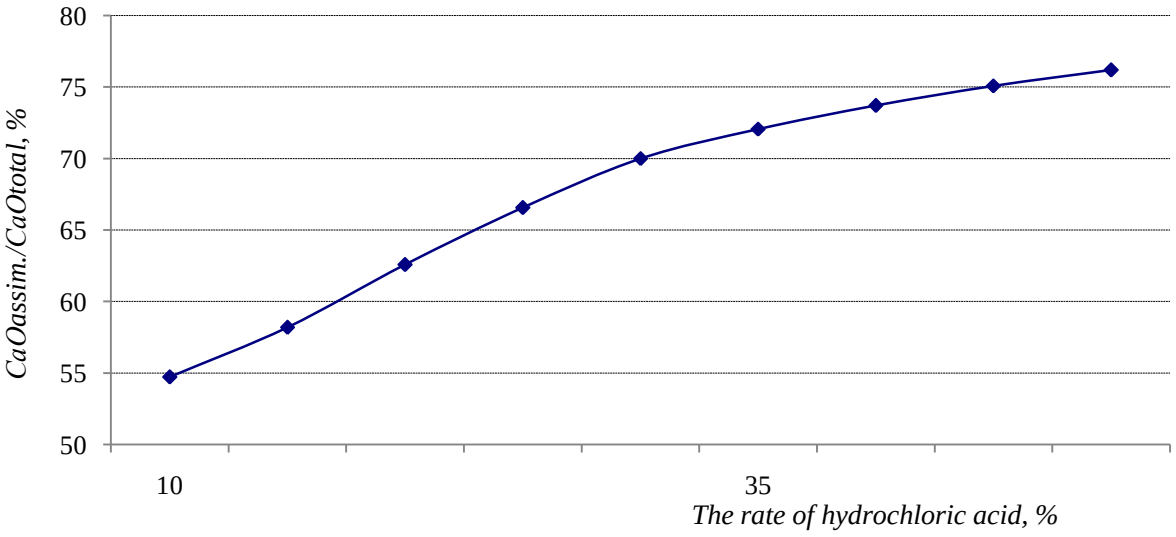

Fig. 4.Dependence of the relative content of assimilated forms of calcium on the norm of hydrochloric acid.

V. CONCLUSION

Thus, the resulted results of laboratory researches testify that by carrying out the process of decomposition of off-balance ore of Kyzylkumphosphorites with an incomplete norm of hydrochloric acid, there is a principal possibility of obtaining phosphoric calcium fertilizers with different content of assimilable forms of phosphorus and calcium.

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