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Kinetic Characteristics of Decomposition of Central Kyzylkum Phosphorites by Nitric Acid

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Abstract: *Data on the kinetics of decomposition of Central Kyzylkum phosphorites by nitric acid with a concentration of 57%, at a rate of 100% and a temperature of 40, 50 and 60 ° C are given. It is shown that the decomposition of raw phosphate raw materials, washed dried concentrate and washed burnt fosconcentrate proceeds at a high speed – in the first 30 seconds of interaction, 87-90%* P_2O_5 *passes into the solution. The remaining 9-12% is extracted in the next 15-20 minutes. This indicates that the phosphorites of Central Kyzylkum are highly reactive phosphate raw materials.*

Keyword: phosphorites, nitric acid, decomposition, kinetic characteristics, degree of decomposition.

I. INTRODUCTION

For normal growth and development of plants, it is necessary to provide them with a sufficient amount of nutrients. The main nutrients are nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. In addition to plants for the life of the essential trace elements. Nitrogen, phosphorus and potassium are an integral part of the main mineral fertilizers in agriculture [1-3]. Fertilizers containing two or three main components are complex or complex fertilizers[4] .

The production of complex fertilizers has become widespread in the industry, in contrast to the production of one-sided fertilizers, since their production is complex and requires large operating and capital costs. In turn, the simplicity of producing complex fertilizers and obtaining a product in a single technological process that contains several nutritional components simultaneously, and the minimal or almost complete absence of ballast, determines the cost-effectiveness of their transportation and application to the soil [5].

Since the phosphorites of Central Kyzylkum are the only raw phosphate in the Republic, research on the production of complex NPK fertilizers was carried out with this raw material. The most rational way of processing phosphorites into complex fertilizers, which allows to achieve a high degree of raw material utilization, to create a low-waste (or non-waste) technology of complex NP and NPK fertilizers is nitric acid processing of phosphates [6-10].

The nitric acid method for obtaining phosphorus-containing fertilizers is the most progressive and economical method for obtaining fertilizers. In this case, not only the chemical energy of nitric acid is used to open the phosphate cheese, but also the NO_3 anions - in the form of a nutrient companion-remain in the fertilizer. In addition, with the release of potash fertilizers, it is possible to produce full-fledged NPK fertilizers based only on local raw materials.

II. MATERIAL AND METHODS

Based on this, it follows that the development of a rational, waste-free technology for obtaining complex NP and NPK fertilizers with acceptable technical and economic indicators from the phosphorites of Central Kyzylkum is an urgent task[11].
Method of research. To establish the optimal technological parameters of the process of decomposition of phosphorites by nitric acid, data on the kinetics of the process are needed. Kinetic studies of phosphorite decomposition with nitric acid were performed with UN-enriched phosphate raw materials(NFS), washed dried concentrate (MSK) and washed burnt fosconcentrate (MOFC). The chemical composition of the used CC phosphorites is shown in table **1.**

Table 1
Chemical composition of phosphorites of the Central Committee

№	Phosphorite	Chemical composition, mass. %								
		P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	F	CO_2	SO_3	H.O.
1	НФС	16,44	45,76	1,00	1,10	0,80	1,70	17,55	1,84	9,13
2	МСК	20,44	42,16	0,74	0,54	0,59	2,42	8,25	1,26	9,47
3	МОФК	26,25	51,64	0,64	0,84	0,61	2,65	11,46	2,36	1,18

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Research was carried out with nitric acid with a concentration of 55% at a rate of 100%, a temperature of 40, 50 and 60 C and a constant mixing speed.

The decomposition reaction was stopped by introducing isopropyl alcohol (IPS) cooled to minus 10C into the system at a volume ratio of IPS:pulp of 2.5:1. Isopropyl alcohol, extracting nitric and phosphoric acid from the system, leads to the termination of reactions of interaction of components, in addition, due to the low temperature of the alcohol, a sharp cooling of the pulp occurs, which also slows down the reaction [12]. After phase separation, the solid residue on the filter was washed with water to a negative reaction for methyl orange, dried, and analyzed for P_2O_5, Cao, and F.

From the results of the analysis, an indicator of the completeness of the process was calculated – the degree of extraction of P_2O_5 solution by the formula

$$К_{изв} = А_р/А_ф \cdot 100\ \%$$

where Ar - the amount of P_2O_5 transferred to the solution, g; AF-the amount of P_2O_5 in the initial suspension of phosphorite, g.

The chemical composition of the initial, intermediate and final products was carried out by known methods of chemical analysis [13].

Results and discussion. Decomposition of all types of Central Kyzylkum phosphorites proceeds at a high rate – in the first 30 seconds of interaction, 85-90% P_2O_5 passes into the solution. The remaining 10-15 % of P_2O_5 is extracted in 15-20 minutes (table 2-4, Fig. 1-3).

Table 2

Influence of temperature and interaction time on the process of nitric acid decomposition of raw phosphate raw materials

№	Temperature, °C	Time, min	Degree of extraction, %		
			P_2O_5	CaO	F^*
1.	40	0,5	87,64	87,01	82,63
2.	40	1	91,51	91,09	84,40
3.	40	2	94,57	94,24	88,23
4.	40	3	95,83	96,00	91,00
5.	40	5	98,42	97,28	92,29
6.	40	15	98,71	97,59	94,10
7.	40	30	98,88	97,67	96,25
8.	50	0,5	88,47	88,44	84,68
9.	50	1	92,43	91,68	86,32
10.	50	2	95,57	95,39	89,70
11.	50	3	96,48	96,88	92,00
12.	50	5	98,87	97,85	93,51
13.	50	15	99,12	98,09	95,10
14.	50	30	99,23	98,20	97,39
15.	60	0,5	90,47	90,37	86,08
16.	60	1	94,14	93,32	88,00
17.	60	2	97,28	96,38	91,56
18.	60	3	98,04	97,20	93,33
19.	60	5	99,72	98,00	94,80
20.	60	15	99,89	98,23	96,48
21.	60	30	99,95	98,32	98,24

*

Total extraction of fluorine into the solution and gas phase.

III. RESULTS

The type of kinetic curves for NFS, MSK and MOFC is very similar and allows us to assume that the process of decomposition of phosphorites is two-stage (Fig. 1-3). Therefore, further calculations were made for the NSF and OIF. First, the speed of the process is determined by the speed of the chemical reaction of the acid with the phosphate substance (kinetic region),

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and then the limiting factor is the rate of diffusion of the acid to the mineral and the reaction products into the solution. Dependency of the LGK change in the table. time-dependent decomposition can be considered as consisting of three sections: kinetic – I, diffusion-III and intermediate, transition region-II. The straight-line nature of the LGK dependency is explained. from time to time in the diffusion domain shows that the process is described by a first-order equation.

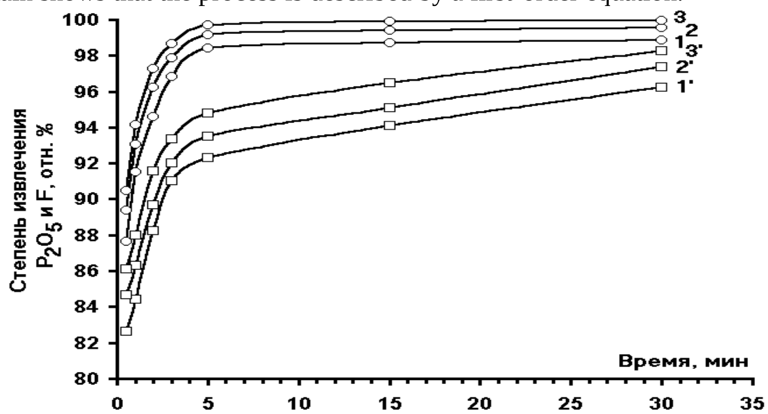

Fig. 1. kinetics of extraction of P2O5 (1, 2, 3) and F (1’, 2’, 3’) depending on the process temperature (1, 1’ - 40 °C, 2, 2’ - 50 °C, 3, 3’ - 60 °C) of NSF

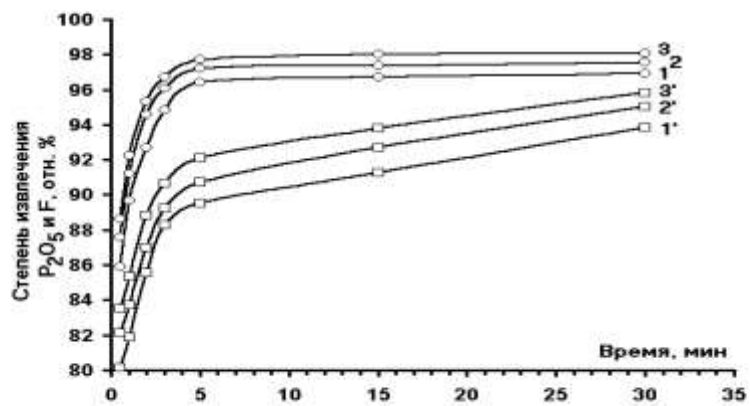

Fig. 2. kinetics of extraction of P2O5 (1, 2, 3) and F (1’, 2’, 3’) depending on the process temperature (1, 1’ - 40 °C, 2, 2’ - 50 °C, 3, 3’ - 60 °C) from MSK.

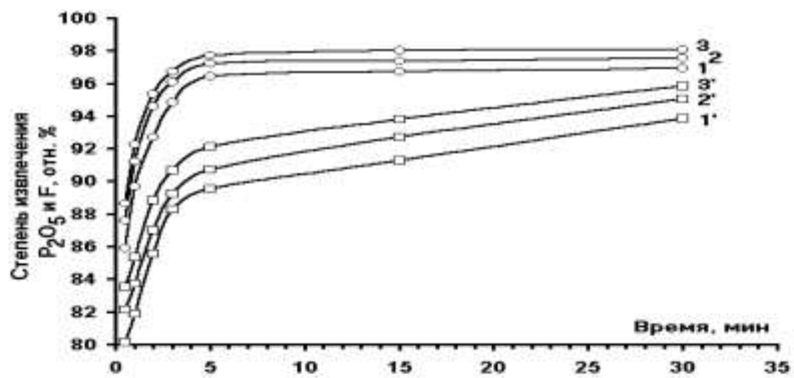

Fig. 3. kinetics of extraction of P_2O_5 (1, 2, 3) and F (1’, 2’, 3’) depending on the process temperature (1, 1’ - 40 °C, 2, 2’ - 50 °C, 3, 3’ - 60 °C) from the MOFC.

The average values of the speed constants (taking into account the transition region for 1 min) for the NSF have the following values: K40 – 1.008; K50 – 1.012; K60 – 1.013 min-1. The temperature coefficient of the reaction rate for this region does not exceed 1.00, which is typical for diffusion processes.

Table 3

Influence of temperature and interaction time on the process of nitric acid decomposition of washed dried concentrate

№	Temperature,°C	Time, min	Degree of extraction, %		
			P_2O_5	CaO	F*
1.	40	0,5	85,89	85,70	80,15
2.	40	1	89,68	89,72	81,87
3.	40	2	92,68	92,83	85,58
4.	40	3	94,86	94,56	88,27
5.	40	5	96,45	95,82	89,52
6.	40	15	96,74	96,13	91,28
7.	40	30	96,90	96,20	93,87
8.	50	0,5	86,69	87,11	82,14
9.	50	1	90,53	90,30	83,73
10.	50	2	93,65	93,96	87,01
11.	50	3	95,51	95,43	89,24
12.	50	5	96,90	96,38	90,70
13.	50	15	97,15	96,62	92,68
14.	50	30	97,29	96,73	95,02
15.	60	0,5	88,66	89,01	83,50
16.	60	1	92,26	91,92	85,36
17.	60	2	95,33	94,93	88,81
18.	60	3	96,71	95,74	90,65
19.	60	5	97,73	96,53	92,11
20.	60	15	98,00	96,76	93,79
21.	60	30	98,08	96,85	95,82

Total extraction of fluorine into the solution and gas phase.

The dependence of the reaction rate constant on temperature obeys the Arrhenius equation and is empirically expressed by the equation:

$$K=1{,}04\cdot e^{-11{,}49/T}$$

The average values of the speed constants for the MOFC are: K40-1.545; K50-1.642; K60 – 1.717 min-1. The temperature coefficient of the reaction rate for this region does not exceed 1.16, which is also typical for diffusion processes.

The dependence of the reaction rate constant on temperature is empirically expressed by the equation:

$$K= 9{,}0\cdot e^{-550{,}2/T}$$

The lgK values calculated from the equation for the MOFC for temperatures of 45 and 55oC fit well on the graph (Fig. 4).

The average activation energy of the process is 4.56 kJ/mol. Activation energy that characterizes reactivity

Table 4

The effect of temperature and time of interaction on the process of decomposition of the nitric acid washed burnt toconcentrate

№	Temperature, °C	Time, min	Degree of extraction, %		
			P_2O_5	CaO	F*
1.	40	0,5	87,20	86,58	82,22
2.	40	1	91,05	90,64	84,76
3.	40	2	94,10	93,20	87,29
4.	40	3	95,40	94,57	88,52
5.	40	5	98,30	96,98	91,20
6.	40	15	98,67	97,35	94,10
7.	40	30	98,88	97,67	98,38
8.	50	0,5	88,92	88,00	84,63
9.	50	1	92,90	91,22	86,54

10.	50	2	96,38	95,28	89,20
11.	50	3	97,02	96,40	90,29
12.	50	5	99,37	97,49	92,43
13.	50	15	99,78	97,90	95,55
14.	50	30	99,89	98,20	98,52
15.	60	0,5	90,02	89,92	85,65
16.	60	1	93,67	92,86	88,32
17.	60	2	96,80	95,90	91,10
18.	60	3	97,56	96,72	92,05
19.	60	5	99,54	97,65	99,22
20.	60	15	99,85	97,95	96,00
21.	60	30	99,92	98,32	98,78

*Extraction of fluorine into the solution and into the gas phase in total.

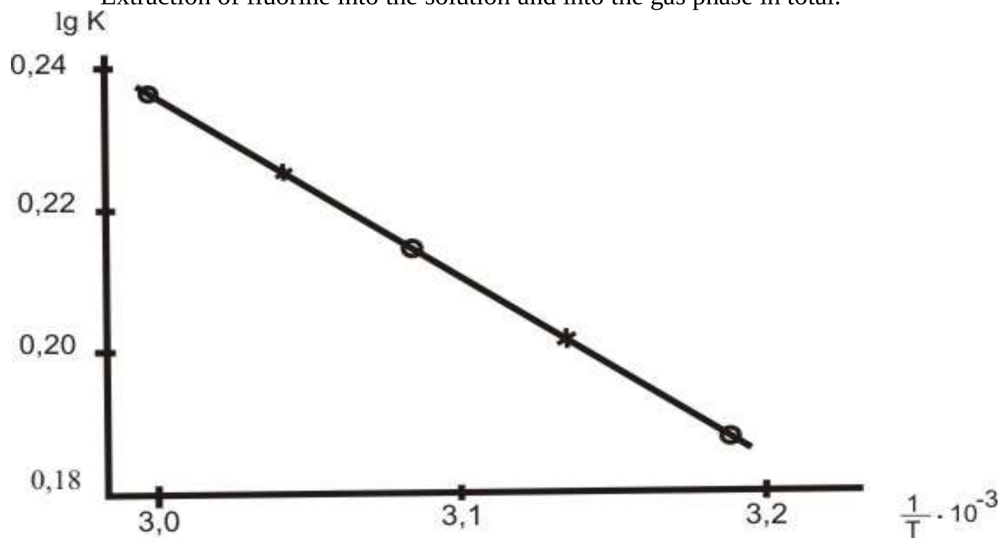

Fig. 4. Dependence of the reaction rate constant on temperature. o-experimental, x-calculated values of K.

IV. DISCUSSIONS

substances in the process of nitric acid extraction, for MOFC is significantly lower than for other phosphorites. Thus, for Karatau phosphorites it is 14.32 kJ/mol, for Apatite concentrate it is 41.87 kJ / mol [14].

In all cases, the degree of Cao extraction into the solution is slightly lower than P_2O_5 and does not exceed 98.3% as much as possible.Incomplete decomposition of calcium minerals is due to the presence of poorly soluble gypsum in phosphorite[15].

Thus, the conducted research has shown that the phosphorites of Central Kyzylkum belong to in all cases, the degree of Cao extraction into the solution is slightly lower than P_2O_5 and does not exceed 98.3% as much as possible .Incomplete decomposition of calcium minerals is due to the presence of poorly soluble gypsum in the phosphorite.

V. CONCLUSIONS

Highly reactive raw materials and that a high degree of decomposition of the phosphate substance with 55 % nitric acid, with a norm of 110% acid, is achieved at any studied temperature. The optimal temperature of the decomposition process is 45-50 oC. At these parameters, more than 99% of P_2O_5 is extracted into the solution in 10-15 minutes.

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