Optimization of Decomposition Process of Karatau Phosphorites

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Abstract

Phosphorous-acid process of Karatau phosphorites' decomposition has been studied. The impact of temperature, time and acid rate on decomposition process of phosphate raw material, the conditions ensuring maximum degree of phosphorite decomposition have been identified. Variance estimate of experiment results' reproducibility has been carried out by mathematical statistics method; the coefficients of regression equations have been set. The significance of regression equation coefficients has been checked up by Student's criterion, and the adequacy of regression equation to experiment has been checked up by Fisher's criterion. With the use of utopian point method the parameters of studied raw materials' decomposition have been optimized.

Introduction

One of main types of the fertilizers widely applied in agro-industrial complex are phosphorus containing mineral fertilizers obtained by acidextraction processing of natural phosphates – apatites and phosphorites [1-2]. As scientific publications testify [3-8] acid methods differ by number of potential possibilities.

In the work [9] the properties of Koksu and Dzhanatas phosphorites of Karatau deposit have been studied, possibility of applying circulating method to obtain double super phosphate with fodder properties have been identified. Here, high norm of a consumption of phosphoric acid, necessary for complete decomposition of natural phosphates, is provided at the expense of circulation of phosphoric mother solution saturated by dihydrogen phosphate. At the same time this, socalled, cyclic way of processing of off-grade phosphatic raw materials with receiving of highquality fertilizer and also fodder phosphate has not received practical application yet. For its successful industrial realization additional researches are necessary, allowing the obtainment of new scientific data in the context of optimization of processing of poor Karatau phosphorites making up the most part of balance of Kazakhstan phosphatic ores. In such a case, alongside with obtaining highquality products it would be possible to considerably expand phosphatic raw materials source of the country as well [10].

Process of phosphatic ores processing involves formation of the waste polluting the atmosphere, soils and water reservoirs. At the enterprises of the phosphoric industry large-tonnage firm wastes have been accumulated. Storage of the latter in natural conditions influences the chemical processes proceeding in the system of "firm wastes - soil water". In work [11] on the basis of long-term researches it is established that firm wastes phosphogypsum) (phosphoric slag and are constantly exposed to the impact of acid fallout with formation of soluble salts of manganese, strontium and other heavy metals with their subsequent transition to environment. Degree of

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transition of toxic components from wastes into a liquid phase depends on the size of granules, time of contact, a ratio of a firm and liquid phase.

Inorganic substances with the raised content of magnesium and gypsum carbonate in wastes of phosphoric industry can absorb completely phosphorus from water solutions and natural waters [12].

Implemented researches by authors of the present message will help to solve a number of the engineering and environmental problems connected with rather effective way of processing of phosphatic raw materials.

Aim of the research is decomposition process research of Karatau phosphorite of Kokdzhon deposit by a liquid phase recycling method, determination of optimum parameters of decomposition process of phosphatic raw materials.

Experimental

Material

The given work considers phosphoric acid decomposition process of Karatau phosphorite of Kokdzhon deposit. Phosphoric acid decomposition of phosphorites represents a complex physical and chemical process, the main qualitative characteristic of which is degree of decomposition of K_p raw materials, filtration of the insoluble rest.

The coefficient of K_p decomposition shows completeness of development of phosphatic raw materials and is determined by the content of the insoluble rest.

Researches were conducted with the use of sample of Karatau phosphorite of Kokdzhon deposit the structure of which is given in Table1.

 Table 1

 Chemical composition of Kokdzhon phosphorite sample

The content of basic components, %								
P_2O_5	CaO	MgO	Fe ₂ O ₃	A1 ₂ O ₃	F	CO ₂	н.о.	H ₂ O
26.13	45.28	1,84	0,68	0,97	1.93	8.78	8,43	5.96

Methodology of the Research

In laboratory conditions a particular mass of phosphorite (12.5 g) was decomposed in the temperature-controlled glass reactor by thermal phosphoric acid with the content of 40% of P_2O_5 . Suspension agitating was being carried out by paddle mixer at the speed of the 300 rpm. Experimental conditions have provided formation of nonsaturated solutions according to Ca $(H_2PO_4)_2$ and absence of a secondary firm phase on grains of decomposed phosphate. Thus it is also possible to separate the insoluble rest without loss of production Ca(H₂PO₄)₂. With these purposes suspension was subjected to filtrations on a warmed funnel of Buhner at constant depression of 0.06 MPa. A precipitation on the filter was washed out by water and dried, defined the maintenance of P_2O_5 total and P_2O_5 of waters in it by standard methods according to National Standards (GOST) 21560-82 [2]. On the basis of analysis results the indicator of completeness of course of process or degree of P₂O₅ extraction into a solution in the form of decomposition factor according to the formula (1) has been calculated [9]:

$$K_p = 1 - \frac{m_{p(P_2 \, O_{5total} p - P_2 \, O_{5of \, water} p)}}{m_{ph} P_2 \, O_{5total} p h} \qquad (1)$$

Where m_p is weight of dry non soluble precipitation, g; m_{ph} weight of Ph taken for decomposition, g; of $P_2O_5 total^p$ and $P_2O_5^{p} of waters - the content of phospholic anhydride in dry precipitation, %; <math>P_2O_5^{ph} total - the content of P_2O_5 total in phosphorite, %.$

To define optimum conditions of phosphorite decomposition the experiment according to the orthogonal plan of the second order (size of a star shoulder is $\alpha = 1,414$, number of experiments in the plan center is $n_0 = 4$, total number of experiments is N = 18) have been conducted [13]. The dependences of the following criteria have been studied:

 y_1 - coefficient of Kokdzhon phosphorite decomposition, y_0 ,

- y₂ P₂O_{5total} in filtrated, washed out nonsoluble rest, %,
- y₃ time of filtration of out nonsoluble rest, min. From the following factors:
- z_1 of the temperature of (60-95°C),
- z_2 process duration (5-60 min),

 z_3 - norms of phosphorous acid from theoretically necessary ones (400-500%).

Results and Discussion

The Orthogonal Plan

The orthogonal plan and results of experiment are resulted in Table 2.

Table 2The orthogonal plan of the second order to $\kappa=3$ and experiment results
on Kokdzhon phosphorite decomposition.

#	\mathbf{x}_1	x ₂	X ₃	$y_1(K_p)$	y ₂ (total)	$y_3 \tau$ filtration
1	1	1	1	98.02	2.42	2.5
2	-1	1	1	90.01	9.45	7.37
3	1	-1	1	92.78	10.69	3.51
4	-1	-1	1	81.83	12.87	8.49
5	1	1	-1	99.42	1.32	2.14
6	-1	1	-1	89.5	9.16	8.35
7	1	-1	-1	87.22	11.65	3.24
8	-1	-1	-1	77.15	13.85	7.27
9	1.414	0	0	99.05	4.27	2,5
10	-1.414	0	0	82.88	11.64	7.06
11	0	1.414	0	93.03	8.32	6.24
12	0	-1.414	0	81.97	13.35	5.47
13	0	0	1.414	90.04	6.26	3.47
14	0	0	-1.414	89.58	7.86	4.06
15	0	0	0	91.14	7.9	5.67
16	0	0	0	91.4	6.9	5.25
17	0	0	0	91.01	8.9	5.38
18	0	0	0	92.03	8.8	5.7

Using calculation values 2, 3, 4

$$S_{\text{adequacy}}^2 = S_{\text{RSS}}^2 = \frac{\sum_{i=1}^n (y_i - \bar{y}_i)^2}{n - l}$$
 (2)

$$S_{\text{reproducibility}}^{2} = \frac{\sum_{\mu=1}^{m} (y_{i}^{0} - \bar{y}^{0})^{2}}{m-1}$$
(3)

$$_{\bar{y}}^{o} = \frac{\sum_{n=1}^{m} y_{i}^{o}}{m}$$
(4)

According to four experiments results for criteria y_1 , y_2 , y_3 dispersions of reproducibility in the plan center:

 $S_{y_1}^2 = 6,36; S_{y_2}^2 = 2,20; S_{y_3}^2 = 0,89$ have been defined.

Using calculating expressions 5 and 6

$$b_j = \frac{\sum_{i=1}^N x_{ji} y_i}{\sum_{i=1}^N x_{ji}^2} \quad j = 0, 1, 2, \dots, k;$$
(5)

$$b_{nj} = \frac{\sum_{i=1}^{N} (x_j x_n)_i y_i}{\sum_{i=1}^{N} (x_j x_n)_i^2} \quad n, j = 1, 2, \dots, k, \mu \neq j; \quad (6)$$

Regression equations coefficients have been revealed (Table 3)

	Table 3	
Regression	equations	coefficients

coefficients	y1	y ₂	y ₃
b0	89.892	8.645	5.204
b1	5.152	-2.473	-2.212
b2	4.468	-2.819	-0.088
b3	0.833	-0.234	0.003
b12	-0.386	-1.311	-0.259
b13	-0.129	0.104	0.049
b23	-1.391	0.416	-0.264
b11	0.068	-0.070	-0.061
b22	-1.661	1.367	0.476
b33	-0.508	-0.517	-0.567

The value of regression equation coefficients has been estimated by Student criterion by the formula (7). Adequacy of the equation of regression to experiment [13-14] has been checked up by Fisher's criterion according to the equations (8)

$$t_j \frac{|b_j|}{s_{bj}};\tag{7}$$

$$S_{RSS} = \sum_{i=1}^{n} \sum_{n=1}^{mi} (y_{in} - y_i)^2; \quad f_{RSS} = \sum_{i=1}^{n} m_i - l; \quad (8)$$

where S_{RSS} – residual sum of squares;

After excluding insignificant coefficients of regression equation, the adequate ones to the experiments have acquired the form of:

$$\begin{aligned} & \mathbf{y}_1 = 91,\!29 + 4,\!47 \cdot \mathbf{x}_1 + 4,\!47 \cdot \mathbf{x}_2 + \\ & 0,\!83 \cdot \mathbf{x}_3 - 1,\!39 \cdot \mathbf{x}_2 \cdot \mathbf{x}_3 - 1,\!66 \cdot \mathbf{x}_2^2 \end{aligned} \tag{9}$$

$$\mathbf{y}_3 = 5,31 - 2,21 \cdot \mathbf{x}_1 + 0,26 \cdot \mathbf{x}_1.\mathbf{x}_2 - 0$$

$$0,26 \cdot x_2 \cdot x_3 + 0,48 \cdot x_2^2 - 0,57 \cdot x_3^2 \tag{11}$$

where $x_1 = \frac{z_1 - 77,5}{12,38}$, $x_2 = \frac{z_2 - 32,5}{19,45}$, $x_3 = \frac{z_3 - 4,5}{0,35}$

Optimal Conditions of Phosphorite Process Decomposition

As a result of calculations with use of the regression equations (9, 10, 11) the maximum value of $y_1 = 99.71$, the minimum values of $y_2 = 0.75$ and $y_3 = 0.76$ under following conditions have been received:

For y_1 - decomposition coefficient of Kokdzhon phosphorite, %,

$x_1 = 1.414$	$z_1 = 95^{\circ}C$
$x_2 = 0.63$	$z_2 = 45 \min$
$x_3 = 1.414$	$z_3 = 500\%$
	in the filtered

For y_2 - P_2O_5 total in the filtered, washed out, insoluble rest, %,

$x_1 = 1.414$	$z_1 = 95^{\circ}C$
$x_2 = 1.414$	$z_2 = 60 \min$
$x_3 = 1.414$	$z_3 = 500\%$

For y_3 - time of filtration of the insoluble rest, min.,

$x_1 = 1.414$	$z_1 = 95^{\circ}C$
$x_2 = 0.77$	$z_2 = 48 \min$
$x_3 = 1.414$	$z_3 = 500\%$

Below the figures 1-9 shows dependences of temperature influence, duration of decomposition process and norm of phosphoric acid on degree of decomposition of Kokdzhon phosphorite, on the content of P_2O_5 total in the filtered insoluble rest and on duration of filtration of the insoluble rest are given.

As the Figure 1 shows, with the raise of temperature in the range from 60 to 95°C the coefficient of decomposition of phosphatic raw materials linearly increases. With increase in duration of decomposition process the coefficient of decomposition increases reaching a possible maximum at 50 minutes (Fig. 2). Hereby nearly 70% of phosphatic raw materials decompose in 5 minutes.



Fig. 1. Influence of temperature on the degree of Kokdzhon phosphirite decomposition.



Fig. 2. Influence of time on the degree of Kokdzhon phosphirite decomposition.

Influence of phosphoric acid norm on decomposition process of phosphorite is shown in Fig. 3. As it is illustrated, in studied interval of

changes' norms of phosphoric acid the high factor of decomposition is observed and process proceeds stably.



Fig. 3. Influence of norm of phosphoric acid on the degree of Kokdzhon phosphorite decomposition.

In Figure 4 the influence of temperature on the content of P_2O_{5total} in the insoluble rest is shown. It follows that at temperatures of $60\div95^{\circ}C$ it is possible to spread out phosphatic raw materials rather fully. In such a case the content of P_2O_5 total can decrease in the insoluble rest and this is the evidence of completeness of the course of decomposition process.



Fig. 4. Influence of temperature on content of P_2O_{5total} in insoluble rest

The influence of duration of decomposition on the content of P_2O_{5total} in the insoluble rest is shown in Fig. 5. As it is illustrated, the increase of duration complete decomposition contributes of to decomposition of phosphatic raw materials. The in the content of P_2O_{5total} insoluble rest correspondingly decreases.



Fig. 5. Influence of time on the content of P_2O_{5total} in insoluble rest.

In Figure 6 the dependence of the content of P_2O_5 total in the insoluble rest on the norm of phosphoric acid is shown. As the Figure 6 shows, the content of P_2O_5 total in the insoluble rest at the norm of acid 400% reaches 0.75% and practically doesn't change at the norm of acid of 500%.



Fig. 6. Influence of norm of phosphoric acid on the content of P_2O_{5total} in insoluble rest.

One of important operations after decomposition of phosphatic raw materials is separation (filtration) of the insoluble rest for the purpose of receiving rather pure production monocalcium phosphate with fertilizing and fodder properties. To provide rather high production of filtratitons of the insoluble rest the filterability of the insoluble rest has been studied and optimized in laboratory conditions by us.

The Figure 7 illustrates the dependence of filtrations time of the insoluble rest on the process of temperature. At temperatures above 60°C it is possible to filter the insoluble rest quickly enough. Thus time of filtrations decreases up to 0.75

minutes. At temperature of 60°C the degree of decomposition of phosphatic raw materials is rather high, however at this temperature crystallization of mono calcium phosphate together with the insoluble rest begins and separation of the insoluble rest from production mono calcium phosphate becomes complicated.



Fig. 7. Influence of temperature on filtration time of the insoluble rest

The influence of duration of decomposition process on filterability of the insoluble rest is shown in Fig. 8. As it is seen, with increase of decomposition duration to 35 minutes the filterability of the insoluble rest is essentially accelerated. In this term, it is possible to separate the insoluble rest without the losses of mono calcium phosphate. At further increase of duration of decomposition process (more than 40 minutes) is saturated by the mono calcium phosphate because of complete decomposition of phosphorite mother solutions. As a result the filterability of the insoluble rest worsens; moreover, in this case, it is not possible to separate it from mother liquor without mono calcium phosphate losses.



Fig. 8. Influence of decomposition time on the time of filtration of the insoluble rest

Influence of norm of phosphoric acid on filterability of the insoluble rest is shown in Fig. 9. Filterability of the insoluble rest increases with increase of norm of acid and time of filtration is accelerated at the norm of 500 %.



Fig. 9. Influence of norm of phosphorous acid on time of filtration of the insoluble rest

Thus, almost complete development of phosphorite is provided with using 4-5-fold excess of phosphoric acid and duration of decomposition process of 50 minutes, since influence of temperature on the degree of decomposition of phosphorites positively s at temperature 60°C the system quickly cools down when filtering, the crystallization of mono calcium phosphate together with the insoluble rest, i.e. slugging of the product occurs.

Regression equation received as a result of processing experimental data adequately describes the studied process of decomposition of phosphate raw material and the obtained curves using this equation show visually the law of process proceeding being revealed.

Optimization by Utopian Point Method

The regression equation (8) allows calculating the values of the chosen criteria at any combination of the studied factors in the investigated range, analyzing influence intensity of separate factors on indicators of process and to define optimum conditions of phosphorite decomposition by a liquid phase method in conditions of mother solution recycling. Thus it is necessary to spread out fuller phosphorite as completely as possible; also it is needed to ensure high speed of filtration of the insoluble rest after the stage of decomposition of raw materials. To define the conditions ensuring high values of criteria of y_1 and low value of y_2 , y_3 , the method of utopian point has been used.

While using as the generalized criterion distance to utopian point [13-14]

$$d = \sqrt{\frac{(f_1^{*n} - f_1^{H}(x_i))^2 + (f_2^{*n} - f_2^{n}(x_i))^2}{+(f_3^{*n} - f_3^{n}(x_i))^2}}$$
(9)

where

$$f_j^n(x_i) = \frac{f_j x_i}{f_j^*}, j = 1, 2, \dots, q, x_i \in X, i = 1, 2, \dots, k,$$

Having used values of normal criteria distance to utopian point d will be received Table 4

Table 4Distance to utopian point d

#	y ₁	y ₂	y ₃	d
1	0.99	1.83	1.17	0.85
2	0.91	7.16	3.44	6.63
3	0.93	8.10	1.64	7.13
4	0.82	9.75	3.97	9.24
5	1.00	1.00	1.00	0.00
6	0.90	6.94	3.90	6.61
7	0.88	8.07	1.51	7.09
8	0.78	10.49	3.40	9.79
9	1.00	3.23	1.17	2.24
10	0.83	6.55	3.30	6.01
11	0.94	6.30	2.92	5.64
12	0.82	10.11	2.56	9.25
13	0.91	4.74	1.62	3.79
14	0.90	5.95	1.90	5.04
15	0.92	5.98	2.65	5.25
16	0.92	5.23	2.45	4.47
17	0.92	6.74	2.51	5.94
18	0.93	6.67	2.66	5.91

According to equation 1, 2 and 3 according to four experiments in the centre plan (experiments 15-18, Table 2) the dispersion of reproducibility (2, 3) for generalized criterion d has been calculated:

$$S_d^2 = 47, 74 \ 10^{-2}$$

On values of the generalized function d coefficients of the regression equation (4, 5) have

been counted, the significance of coefficients has been checked up by Student's criterion according to equation (6), adequacy of the regression equation to experiment has been checked up by Fisher's criterion (7).

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After an exception of insignificant coefficients the regression equation adequate to experiment looks like:

$$d = 5,26 - 1,88 \cdot x_1 - 2,02 \cdot x_2 - 0,95 \cdot x_1 \cdot x_2 + 1,23 \cdot x_2^2$$
(10)

In compliance with equation (10) optimum conditions of decomposition process of Karatau phosphorites corresponding to the maximum value of generalized criterion in the field of research have been defined.

As a result of calculations with use of the equation of regression (10) the maximum value of the generalized criterion d = 2.96, under following conditions has been received:

$$X_1 = 1,414$$
 $z_1 = 95^{\circ}C$ $X_2 = 1,414$ $z_2 = 60 \text{ min}$ $X_3 = 1,414$ $z_3 = 500\%$

Conclusions

As a result of carried out researches consistent patterns of decomposition of Karatau phosphorite of Kokdzhon deposit are determined. The optimum phosphoric acid mode of carrying out an extraction that allows receiving the maximum output of P_2O_5 has been identified.

Optimum conditions of phosphorite decomposition with application of the orthogonal plan of the 2nd order have been determined, mode technological parameters of the studied process have been found at observance of which it is possible to reach 99.71 % of degree of decomposition of phosphatic raw materials by phosphoric acid, the contents of P_2O_5 (total) in the insoluble rest of 0.75 %.

Using the method of utopian point the conditions providing high value of criterion of decomposition coefficient $K_p - y_1$, low value contents of P_2O_5 (total) in the insoluble rest $- y_2$, time of a filtration of insoluble rest $- y_3$ have been established.

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