THE INFLUENCE OF SOME TECHNOLOGICAL PARAMETERS ON THE PROCESS OF PRECIPITATION THE HYDROCHLORIC ACID EXTRACTION OF PHOSPHATES

ABSTRACT.

The process of obtaining fertilizing precipitate based on the interaction of off-balance ore phosphorites of Central Kyzylkum and chemically enriched phosphorite concentrate with hydrochloric acid, followed by precipitation of hydrochloric acid extraction with suspension of calcium hydroxide. The optimal parameters of the precipitation were determined for the first time in our country. The resulting samples of precipitates under optimal conditions contain in their composition 23.63-24.19% $P_2O_{5(t.)}$, 21.09-21.38% $P_2O_{5accep.}$by 2% citric acidto those 26.97-28.41% $CaO_{(t.)}$, 23.52-25.59% of $CaO_{accep.}$by 2% citricacid. The degree of precipitinogen equal 94.01-98.05%. Physical and chemical studies (x-ray phase analysis) of the mineralized mass and products of its processing were also carried out.

Keyword: *mineralized mass, hydrochloric acid, precipitate, degree of precipitation.*

1. INTRODUCTION.

At the Kyzylkumphosphorite plant at the stage of phosphate raw material sorting, off-balance ore is formed during the enrichment process, the so-called mineralized mass with content of 12-14% P_2O_5, which is still stored. The volume of this raw material accumulated to date is more than 10 million tons. It is not suitable for the production of high-quality phosphorus-containing fertilizers by sulfuric acid extraction. One of the real ways of processing of the poor phosphate in phosphate fertilizers is hydrochloric acid decomposition.

In the scientific and technical literature there is information on the production of feed and fertilizer precipitate based on decomposition of Karatau and Kyzylkumphosphorites with a content of 24.57% and 20.04% P_2O_5, respectively [1-3].

In this work, the possibility of obtaining fertilizing precipitate by decomposing the off-balance ore of phosphorites Of Central Kyzylkum and chemically enriched phosphorite concentrate with hydrochloric acid followed by precipitation of hydrochloric acid extraction with suspension of calcium hydroxide was studied.

2. OBJECTS AND METHODS OF RESEARCH.

For carrying out laboratory experiments used off-balance ore (mineralized mass) containing

weight.%: 14.60 P_2O_5, CaO 43.99; 14.11 CO_2, 1.58 SO_3; 10.82 i.r.; CaO : P_2O_5 = 3.01, chemical enriched phosphate concentrate (ChEPC) composition weight.% : 22.74–P_2O_5; 39.00–CaO; 3.52–CO_2; 0.78–Ci; 2.52 – SO_3; 17.25-i.r.; CaO:P_2O_5=1.72, obtained during the enrichment of the mineralized mass with hydrochloric acid and hydrochloric acid, which is waste of the production of caustic soda of JSC "Navoiazot". The concentration of hydrochloric acid varied from 25 to 32%.The rate of hydrochloric acid was taken 100% of stoichiometry on CaO in the feedstock. Rules of $Ca(OH)_2$ for the deposition of P_2O_5 (in the form $CaHPO_4$) take 80, 90, 100 and 110%. The use of more concentrated hydrochloric acid is due to the fact that the decomposition of high-phosphate phosphorites observed abundant foaming, which prevents the maintenance of normal technological regime. This significantly reduces the performance of the equipment. The method of the experiments was identical as in [4].

3. RESULTS AND DISCUSSION.

The results of obtaining the precipitate from the mineralized mass are given in table 1. From data of table 1 shows that with the increase in the rate of the neutralizing agent at the same concentration of acid is observed to increase $P_2O_{5(t.)}$(t.-total) and$CaO_{(t.)}$in the obtained samples of the precipitate.

For example, at 25 % concentration of hydrochloric acid with the increase in the rate of $Ca(OH)_2$ from 80% to 110%, the content $P_2O_{5(t.)}$and$CaO_{(t.)}$.in the samples obtained, the precipitates increased from 23.49 to 24.19% and from 25.13 to 27.82%, respectively.

Table 1

Basicchemical contents of precipitates

Norm$Ca(OH)_2$ %	Chemical contents of precipitates, %						
	$P_2O_{5(t.)}$	$P_2O_{5accep.}$ by 2% citric acid	$P_2O_{5w.s.}$	$CaO_{(t.)}$	$CaO_{accep}$by 2% citric acid	$CaO_{w.s.}$	Cl
Concentration of hydrochloric acid – 25%							
80	23.49	20.68	1.87	25.13	22.49	1.48	0.90
90	23.81	20.96	1.51	26.19	23.44	1.35	0.93
100	23.96	21.09	1.22	26.97	24.14	1.24	0.96
110	24.19	21.29	1.01	27.82	24.90	1.21	1.02
Concentration of hydrochloric acid – 30%							
80	23.40	20.83	1.92	25.16	22.59	1.50	0.90
90	23.66	21.06	1.54	26.20	23.52	1.37	0.94
100	23.79	21.15	1.25	27.51	24.70	1.27	0.97
110	24.01	21.38	1.04	28.05	25.18	1.26	1.05
Concentration of hydrochloric acid – 32%							
80	23.32	20.83	1.99	25.20	22.70	1.56	0.95
90	23.52	21.01	1.59	26.31	23.70	1.41	1.00
100	23.63	21.10	1.28	27.59	24.85	1.32	1.03
110	23.84	21.29	1.08	28.41	25.59	1.30	1.10

A similar pattern is observed at other concentrations of hydrochloric acid. The same rules of the precipitator, increasing the concentration of hydrochloric acid there is some increase in $CaO_{(t.)}$and$CaO_{w.s.}$(water solubility)in the resulting products, and the content $P_2O_{5(t.)}$ reduced. For example, when using 25 % hydrochloric acid at the rate of precipitator 100% content $CaO_{(t.)}$,$CaO_{w.s.}$and chlorine, respectively, are 26.97; 1.24 and 0.96%, and when using 32% acid, they are equal to 27.59; 1.32 and 1.03%. Under this content $P_2O_{5\ (t.)}$.in the resulting precipitates is equal to 23.96 and 23.63%, respectively, for the acid concentration of 25 and 32%. Means use more concentrated hydrochloric acid, leads to some deterioration of the quality of the precipitate.This fact is explained by the fact that the application of more concentrated hydrochloric acid is bad wash of $CaCl_2$

from wet phosphorite concentrate. From [4] it is known that when using lower concentration of acid, there is abundant foaming, which reduces the performance of the reactor. In addition, huge amount of weak calcium chloride solution is formed, which requires large investment for its processing. Therefore, it is advisable to use more concentrated acid.

Figure 1 shows the dependence of changes in the degree of precipitation of hydrochloric acid pulp from the norm of the precipitator and the concentration of hydrochloric acid.

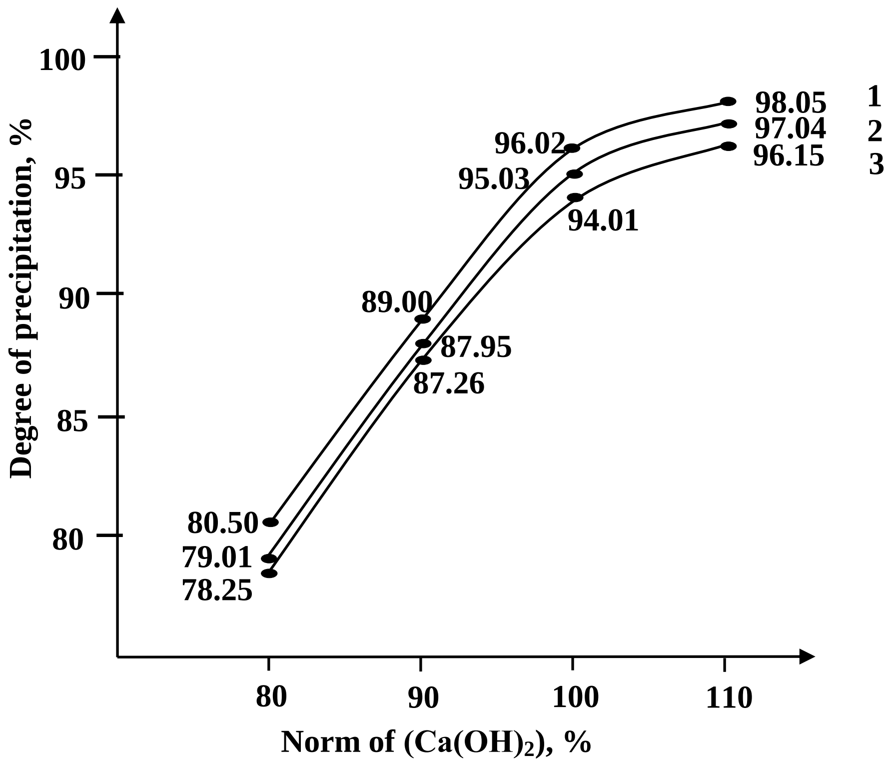


Fig. 1.Dependence of changes in the degree of precipitation of hydrochloric acid pulp from the norm of the precipitator. Concentration of HCl: 1 – 25%; 2 – 30% and 3-32%.

From fig.1 it can be seen that with the increase of the precipitator norm $Ca(OH)_2$ the degree of precipitation increases, but with an increase in the concentration of hydrochloric acid, the degree of precipitation decreases, but slightly. All the above concentrations of hydrochloric acid are optimal. The optimal rate of the precipitator $Ca(OH)_2$ is 100-110%. The degree of precipitinogen within 94.01-98.05%.

Further, to obtain fertilizer precipitate, the ChEPC was used, obtained on the basis of the mineralized mass of the above composition. The method of the experiments was identical as in the case of obtaining fertilizer precipitate from mineralized mass.

The data obtained are summarized in table 2. It is shown that with the increase of the norm of the precipitator $Ca(OH)_2$ the content of P_2O_5 in the obtained samples of precipitates increases. For example,at concentration of 25% HCI with an increase in the norm of the precipitator from 80 to 110% $P_2O_{5(t.)}$in the samples of the precipitate ranges from 24.12 to 26.98%. The degree of precipitation increases from 85.69 to 97.41%. Despite this, the relative content of digestible forms of P_2O_5 decreases. A similar pattern is observed at other acid concentrations. The optimal norms of the precipitator are 100-110%.Fertilizing precipitate obtained under optimal conditions, contains in its composition $P_2O_{5(t.)}$.from 26.04 to 26.98%.

Table 2

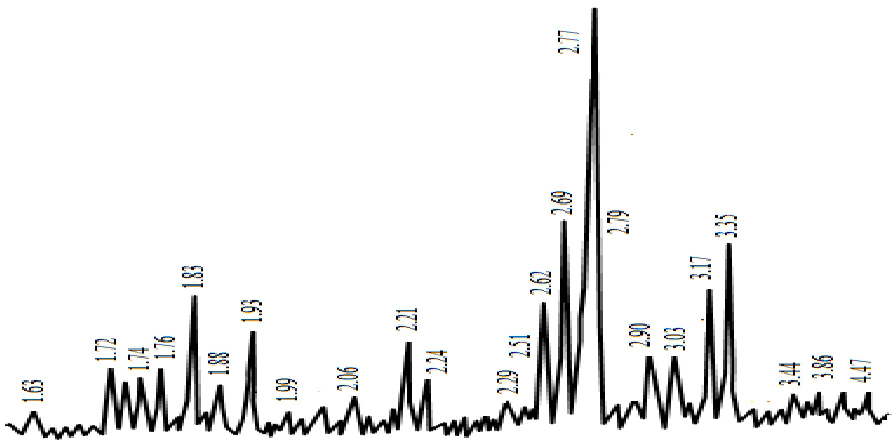
Basic chemical contents of precipitates

№ Experiences	The norm of $Ca(OH)_2$ for precipitation, %	Chemical contents of precipitates, %							Degree of precipitation, %
		$P_2O_{5\ (t.)}$	$P_2O_{5accep.}$ by 2% citricacid	$P_2O_{5w.s.}$	$CaO_{(t.)}$	CaO_{accep} by 2% citricacid	$CaO_{w.s.}$	Cl	
Concentration of hydrochloric acid – 25%									
1	80	24.12	20.92	1.79	24.36	21.92	1.51	0.87	85.69
2	90	25.23	21.31	1.50	26.27	23.12	1.30	0.91	90.41
3	100	26.22	21.64	1.23	28.01	24.18	1.23	0.96	95.28
4	110	26.98	22.52	1.02	29.20	24.63	1.20	1.03	97.41
Concentration of hydrochloric acid – 30%									
5	80	24.08	20.73	1.81	24.59	22.20	1.57	0.92	86.27
6	90	25.17	22.04	1.57	26.81	23.76	1.38	0.98	91.32
7	100	26.14	22.44	1.26	28.10	24.39	1.30	1.02	95.19
8	110	26.59	22.72	1.06	29.41	25.02	1.27	1.08	97.29
Concentration of hydrochloric acid – 32%									
9	80	24.01	20.76	1.84	24.73	22.50	1.60	0.96	86.59
10	90	25.07	22.15	1.59	26.75	24.01	1.40	1.00	91.22
11	100	26.04	22.48	1.28	28.05	24.53	1.32	1.03	95.09
12	110	26.47	22.73	1.09	29.27	25.20	1.30	1.10	97.12

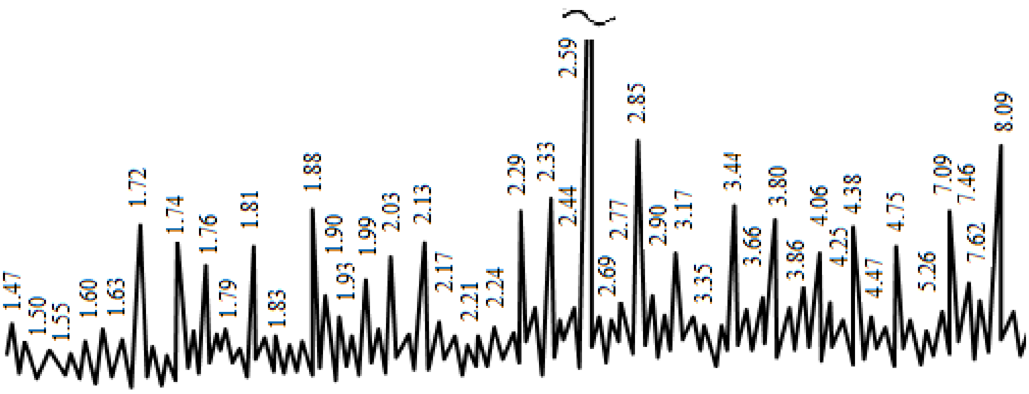
Content of $P_2O_{5accep.}$by 2% citric acid, ranging from 21.64 to 22.73%. The degree of precipitation at all acid concentrations is in the range from 95.09 to 97.41%. The precipitate with such indicators can be successfully used as single fertilizer in agriculture.

Further, X-ray phase analysis of phosphate raw materials, ChEPC and fertilizing precipitate was carried out, the results of which are shown in Fig. 2. The interpretation of the diffraction bands made by comparing the values of interplanar distances of phosphorites and known minerals, allows us to assume that the diffraction bands with the values of 3.44; 3.17; 3.03; 2.79; 2.69; 2.62; 2.24; 1.93; 1.88; 1.83; 1.76; 1.74 and 1.72 Å belong to fluorocarbon-Apatite strips with interosseous distances 3.86; 2.90; 2.51; 2.29; 2.06; 1.99 and 1.63 Å characterize the presence of calcite in phosphates

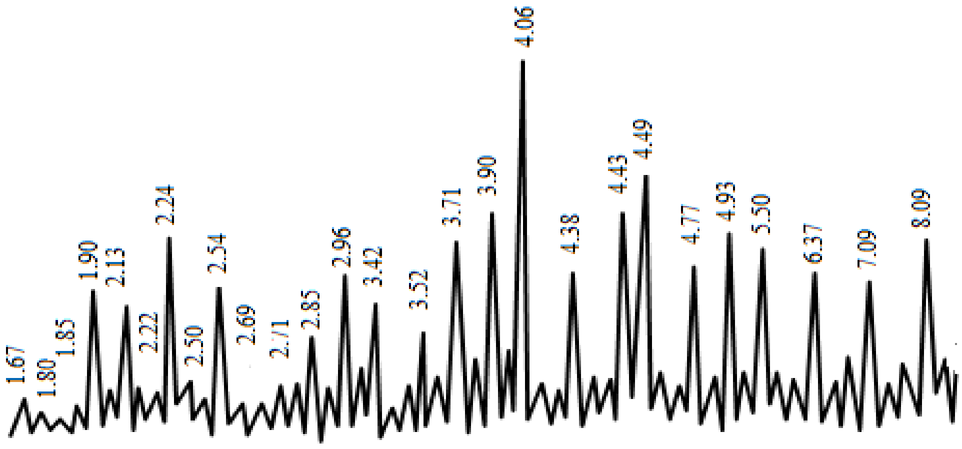
(Fig.2a) [5].The diffraction band 4.47; 3.35; 2.77 and 2.21 Å belongs to α-quartz. Quantitative relations between fluorocarbon, calciteand quartz correlate with the intensity of diffraction peaks related to these minerals. Radiograph ChEPC from raw material (Fig.2b) is characterized in that the x-ray diffraction bands appear with the values of 8.09; 4.06 and 2.13 Å for dicalcium phosphate, as in the enrichment of the saline mass there is a partial decomposition of percarbonates with the formation of dicalcium phosphate and interlayer distance with the main values of 4.47; 3.17; 2.85; 2.33; 2.24 and 1.90 Å for calcium chloride, since large amount of calcium chloride remains in the enriched phosphorite when washing acidic pulps with calcium chloride and water.



(a)



(b)



(c)

Fig. 2.Radiograph of phosphorus raw material (a), ChEPC (b) and precipitate (c).

The peak intensities belonging to fluorocarbonate-apatite increase, and the peak intensities for calcite decrease, because with the enrichment of phosphorites, the amount of calcite decreases due to the decomposition of its hydrochloric acid. X-ray of the fertilizing precipitate (fig. 2c) differs from x-ray MM and ChEPC that this x-ray is virtually no peaks belonging to fluorocarbonate and calcite, on the contrary, the intensity of the peaks belonging to the precipitate increases sharply. Also there are peaks related to monocalcium phosphate 4.93; 3.90; 3.71; 3.42; 2.96; 2.69 and 1.80 Å, aluminum phosphate 6.37; 4.77; 4.49; 4.38; 3.52; 2.71; 2.50; 2.24; 1.80; 1.90 and 1.67 Å and iron phosphate (III) 5.50; 4.43; 4.38; 2.85; and 2.54 Å.

The main disadvantage of hydrochloric acid production of the precipitate is the formation of solution of calcium chloride, which is utilized in various ways. For example, in Sweden [6] Boliden Chemi produces precipitate using hydrochloric acid technology, in which solution of calcium chloride is evaporated and sent to cement production. In Israel [7], calcium chloride solution is converted to magnesium chloride by magnesium oxide and hydrochloric acid is regenerated. And in our case, the resulting calcium chloride can be used as an inhibitor of corrosion of reinforcement in road construction and in the manufacture of tiles for sidewalks.

Thus, on the basis of the results of laboratory studies, the principal possibility of obtaining precipitate by the interaction of off-balance ore of phosphoritesofCentral Kyzylkums and ChEPC with hydrochloric acid is shown, followed by precipitation of calcium hydroxide by precipitation of calcium hydroxide bypassing the stage of separation of insoluble precipitate from hydrochloric acid solution.

4. CONCLUSION.

The process of decomposition of off–balance ore-waste thermal enrichment of phosphoritesofCentral Kyzylkum and ChEPC with hydrochloric acid was studied. For precipitinogen hydrochloric acid slurries used slurry of calcium hydroxide. The optimal parameters of the precipitation were determined. The resulting samples of precipitates under optimal conditions contain in their composition 23.63-24.19% $P_2O_{5(t.)}$, 21.09-21.38% $P_2O_{5accep..}$by 2% citric acid.26.97-28.41%

$CaO_{(t.)}$ and 23.52-25.59% $CaO_{accep.}$ by 2% citric acid in the case of using mineralized mass. Under optimal conditions of ChEPC obtained samples of the precipitates of the following composition: 26.04-26.98% $P_2O_{5(t.)}$, 21.64-22.72% $P_2O_{5accep.}$by 2% citric acid, 28.01-29.41% $CaO_{(t.)}$and 24.18-25.20% $CaO_{accep.}$by 2% citric acid. The degree of precipitation under optimal conditions is 94.01-98.05% and 95.19-97.41%, respectively, for mineralized mass and ChEPC.

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