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Research of the Process of Decomposition of Extractive Phosphoric Acid by Sodium Carbonate in the Presence of Sodium Silicate

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ABSTRACT: The article provides data on the defluorization of extraction phosphoric acid from phosphorites of the Central Kyzylkum with sodium carbonate in the presence of sodium silicate in order to correct the Si:F ratio. The optimal technological parameters for the purification of extraction phosphoric acid from phosphorites of the Central Kyzylkum from fluorine compounds have been established: the rate of sodium metasilicate, the total rate of metasilicate and sodium carbonate, the temperature and duration of the processes of acid defluorization and sedimentation of sodium silicofluoride sediment. In this case, the degree of defluorination reaches 80-85%. The obtained degree of defluorination is quite acceptable for the development of this technology in industrial conditions.

KEY WORDS: Extraction Phosphoric Acid, Carbonate, Sodium Metasilicate, Defluorination, Sodium Silicofluoride.

I.INTRODUCTION

Fluorine compounds are widely used in various industries. Significant amounts of fluorine compounds are used in metallurgy, the production of magnesium alloys, aluminum, beryllium, for the extraction of noble metals, in the building materials industry, the ceramic and glass industries.

II. LITERATURE REVIEW

The fluorine content in the earth's crust is 0.08%. The main raw materials for obtaining fluorine and its compounds are fluorspar and fluorite, as well as phosphate ores [1-3]. The reserves of fluorspar ores are limited and do not exceed 60 million tons. At the same time, the reserves of fluorine in phosphate ores, with their content of 2.7-3.0, are estimated at 900-1300 million tons, which is equivalent to 1700-2500 million tons of fluorspar. 90% of the world's fluorine reserves are found in phosphate raw materials, 80% of which is processed into phosphoric acid and phosphorus-containing fertilizers [4].

In the production of extraction phosphoric acid (EPA), 15-20% of fluorine goes into phosphogypsum, and 80-85% remains in the acid. Despite the great demand for fluorine compounds, it is practically not extracted and remains in the composition of mineral fertilizers, which leads to its accumulation in the soil [5].

The simplest and cheapest way to reduce the content of fluorine in fertilizers is its precipitation from EPA in the form of alkali metal silicofluorides [6-11]. Due to the specific features of the phosphorites of the Central Kyzylkum (CK), the known methods do not allow the acid to be sufficiently purified from fluorine due to the low content of acid-soluble forms of silicon. Therefore, studies were carried out on the defluorination of EPA with sodium salts - carbonate and metasilicate in order to correct the F: SiO_2 ratio in acid [12, 13].

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III. RESEARCH METHODOLOGY

For the experiments, we used EPA obtained on the basis of CK phosphorites with the following chemical composition (wt%): P_2O_5 - 20.89; CaO - 0.26; MgO - 0.87; Al_2O_3 - 1.37; Fe_2O_3 - 0.65; F - 1.21; SO_3 - 3.46; Na - 0.12; SiO_2 - 0.13. Experiments on the defluorination of EPA were carried out on a laboratory setup consisting of a glass quartz reactor placed in a thermostat. The reactor is equipped with a stirrer providing intensive mixing. The rotation speed of the electric motor was controlled by a rheostat and measured with a tachometer.

In the course of the experiments, the rate of sodium silicate for the formation of sodium silicofluoride, the total rate of sodium ions, the temperature of the process of defluorination and settling, and the time were varied. The chemical analysis of the initial, intermediate, and final products was carried out by known methods of chemical analysis [14].

IV. ANALYSIS AND RESULTS

Experiments on defluorination of EPA were carried out with a 20% sodium silicate solution, the process duration was 30 minutes, the temperature was 70°C, and the settling time was 120 minutes. The total rate of sodium salts was varied from 100 to 200%, and the rate of sodium silicate from 100 to 105% (table 1).

Table 1. Effect of the norm of Na_2SiO_3 and Na_2CO_3 on the composition of defluorinated EPA and the degree of defluorination (γF)

Na ion rate, %	Chemical composition of EPA, wt. %			γ_F,%
	P_2O_5	F	Na_2O	
SiO_2 norm for the formation of Na_2SiF_6 - 100%				
100	20,19	0,42	0,26	63,43
110	20,20	0,34	0,28	70,70
120	20,21	0,26	0,30	77,97
130	20,20	0,23	0,35	79,99
140	20,19	0,21	0,40	82,01
150	20,18	0,20	0,45	82,72
160	20,17	0,19	0,51	83,43
200	20,10	0,19	0,76	83,93
SiO_2 rate for the formation of Na_2SiF_6 - 102%				
100	20,17	0,40	0,25	65,33
110	20,18	0,34	0,28	70,92
120	20,18	0,27	0,30	76,52
130	20,18	0,25	0,35	78,76
140	20,17	0,22	0,40	81,00
150	20,16	0,21	0,46	81,56
160	20,14	0,21	0,52	82,12
200	20,08	0,21	0,76	82,12
SiO_2 rate for the formation of Na_2SiF_6 - 105%				
100	20,13	0,44	0,27	61,71
110	20,14	0,37	0,21	67,74
120	20,14	0,30	0,32	73,77
130	20,14	0,27	0,36	76,38
140	20,13	0,24	0,41	79,00
150	20,12	0,24	0,47	79,23
160	20,10	0,24	0,53	79,46
200	20,04	0,23	0,77	79,65

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With an increase in the total norm of sodium ions for the formation of sodium silicofluoride, taking into account the acid-soluble form of silicon present in the acid, the content of P_2O_5 in the solution slightly decreases, and the sodium content increases. Thus, the content of P_2O_5 decreases from 20.89% to 20.10% with a total rate of 200%. At the same time, the Na_2O content in the solution is 0.26-0.51%. The introduction of sodium salts reduces the fluorine content in the acid from 1.21% to 0.19% at a rate of sodium metasilicate of 100% and a total rate of sodium salts of 200%. In this case, the degree of defluorination reaches 83.93%.

An increase in the norm of sodium metasilicate to 102 and 105% has practically no effect on the content of P_2O_5 and Na_2O in the acid. However, the fluorine content in the acid is slightly higher and with a total sodium salt rate of 150% it is 0.21% and 0.24%, respectively. The degree of defluorination is 81.56% and 79.23%, respectively. This degree of defluorination is also achieved with a total rate of sodium ions of 130-150% and a rate of sodium metasilicate of 100%.

An increase in the norm of sodium metasilicate above the stoichiometric value leads to the formation of a finely dispersed sediment, which settles for more than 2 hours and is poorly separated.

Experiments to determine the dependence of the degree of defluorination and the composition of EPA on the duration of interaction of an alkaline solution of sodium silicate with EPA were carried out at a sodium silicate rate of 100%, a total rate of sodium ions - 130%, a process temperature of 70°C, settling time - 120 min., and a settling temperature - 30°C. The results are shown in table 2.

Table 2. Influence of the process duration on the composition of defluorinated EPA and the degree of defluorination (γF)

Time, min	Chemical composition of EPA, wt%			γ_F, %
	P_2O_5	F	Na_2O	
10	20,19	0,26	0,33	77,31
20	20,12	0,24	0,32	78,91
30	20,20	0,23	0,32	80,04
40	20,20	0,23	0,31	80,51
50	20,20	0,22	0,31	80,62
60	20,20	0,22	0,31	80,74

With an increase in the duration of the defluorination process, the contents of P_2O_5 and Na_2O practically do not change. So, P_2O_5 in the first 30 minutes slightly increases from 20.19% after 10 minutes to 20.20 after 30 minutes, Na_2O decreases from 0.33% to 0.32%. The fluorine content under these conditions decreases from 0.26% to 0.23%, which corresponds to the degree of defluorination of 77.31% and 80.04%. A further increase in the duration of the defluorination process contributes to a slight increase in the degree of defluorination to 80.74% after 60 minutes.

Table 3 shows the data on the effect of the temperature of defluorination of EPA and settling on the chemical composition of the acid and the degree of defluorination with a process duration of 30 minutes.

Table 3. Influence of the process temperature and settling temperature on the EPA composition and the degree of defluorination

Temperature, ° C	Chemical composition of EPA, wt. %			γ_F, %
	P_2O_5	F	Na_2O	
Defluorination process				
40	20,18	0,28	0,34	75,75
50	20,19	0,26	0,33	77,76
60	20,20	0,24	0,32	79,41
70	20,20	0,23	0,32	80,04
80	20,21	0,22	0,31	80,90
The settling process				
20	20,21	0,21	0,31	81,50
30	20,20	0,22	0,31	80,80
40	20,19	0,27	0,33	77,10
50	20,18	0,33	0,37	71,10
60	20,13	0,45	0,43	61,30

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An increase in temperature from 40 to 80°C affects the degree of defluorination when the process temperature rises to 60°C. So, at a process temperature of 40°C, the degree of defluorination is 75.75%, at 60°C 79.41% and at 80°C 80.90%. The content of P_2O_5 is 20.19-20.21%, Na_2O 0.31-0.34% and fluorine 0.22-0.26%.
Temperature has a more significant effect on the settling process of defluorinated EPA. An increase in temperature contributes to a decrease in the degree of defluorination from 81.50% at a settling temperature of 20°C to 61.30% at 60°C. The content of Na_2O and F in the purified acid increases from 0.31% to 0.43% and from 0.21% to 0.45%, respectively. In this case, the content of P_2O_5 decreases from 20.21% to 20.13%.
An increase in the duration of the defluorinated EPA settling process at a total sodium salt rate of 130% and a settling temperature of 30°C leads to an increase in the defluorination degree from 72.21% at 30 minutes of settling to 83.34% at a process duration of 120 minutes (table 4).

Table 4. Influence of the duration of settling on the degree of defluorination and the composition of EPA

Time, min.	Purified EPA composition, wt%			γ_F, %
	P_2O_5	F	Na_2O	
30	20,17	0,32	0,37	72,21
60	20,20	0,23	0,32	80,03
90	20,21	0,20	0,30	82,56
120	20,21	0,19	0,30	83,34
150	20,22	0,19	0,30	83,69

Based on the results obtained on the precipitation of sodium silicofluoride from EPA solutions, we studied the effect of the total rate and the ratio of sodium carbonate and metasilicate on the process of isolating sodium silicofluoride from EPA, previously desulfurized with washed fired CK fosconcentrate.
The total rate of sodium salts was changed from 150 to 300%, and their ratio was varied from 60:90 to 200:100 at a temperature of the defluorination process of 70°C and the duration of defluorination of 30 minutes. The results are shown in table 5.

Table 5. Effect of the total rate of precipitating reagents on the chemical composition of sodium silicofluorides

№	The rate of the precipitating agent,%			Chemical composition of the sediment, wt%								
	Na_2CO_3	Na_2SiO_3	Total norm	P_2O_5	CaO	MgO	SO_3	Na_2O	Fe_2O_3	Al_2O_3	F	H_2O
From andesulfurized EPA												
1	60	90	150	0,092	1,28	0,49	1,40	30,43	0,27	0,35	43,18	8,19
2	90	85	175	0,083	1,25	0,46	1,44	30,48	0,29	0,39	43,36	8,25
3	120	75	195	0,079	1,22	0,35	1,45	30,52	0,29	0,38	42,94	8,55
4	150	60	210	0,081	1,18	0,38	1,50	30,60	0,28	0,40	44,27	8,42
5	200	100	300	0,082	1,15	0,40	1,52	30,65	0,27	0,42	45,18	9,04
From desulfurized EPA												
1	60	90	150	0,391	0,38	0,49	0,22	30,40	0,46	0,32	50,46	8,18
2	90	85	175	0,372	0,35	0,46	0,25	30,48	0,45	0,33	50,73	8,21
3	120	75	195	0,423	0,32	0,35	0,32	30,62	0,43	0,33	50,97	8,45
4	150	60	210	0,432	0,28	0,38	0,35	30,71	0,42	0,35	51,15	8,98
5	200	100	300	0,521	0,25	0,40	0,42	30,88	0,40	0,36	51,46	9,35

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The compositions of sodium silicofluoride obtained from the initial EPA and pre-desulfurized EPA differ markedly. If the content of P_2O_5 in sodium silicofluoride obtained from non-desulfurized EPA is about 0.08%, then from desulfurized EPA the content of P_2O_5 is 0.39 - 0.52%, i.e. increases by 4.9-6.5 times depending on the total rate of precipitating reagents. The content of sulfates changes by analogy with the change in their content in EPA and amount to 1.28-1.37% and 0.30-0.45%, respectively, for sodium silicofluorides obtained from andesulfurized and desulfurized EPA.

The content of Na_2O in silicofluoride from EPA crude from sulfates is 30.43-30.65%, and in desulfurized 30.40-30.88%. Accordingly, the fluorine content varies from 43.18-45.18 to 50.46-51.46%, which indicates a higher fluorine content in the product from the desulfurized EPA.

When carrying out the process of defluorination in optimal conditions, a precipitate of sodium silicofluoride is formed, containing 70.83-74.11% of the main substance, when obtained from andesulfurized EPA, and 82.77-84.47% from desulfurized acid.

VI. CONCLUSION

Thus, the studies carried out on the enrichment of extraction phosphoric acid from CK phosphorites showed the possibility of obtaining phosphoric acid partially defluorinated by 80-85%. To do this, it is necessary to carry out the process of defluorination of EPA with a mixture of metasilicate and sodium carbonate at a total rate of 130-150% and a rate of sodium metasilicate of 100% of the stoichiometry for binding fluorine into sodium hexafluorosilicate, a temperature of 60-70°C and the duration of the defluorization process at least 30 minutes.

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