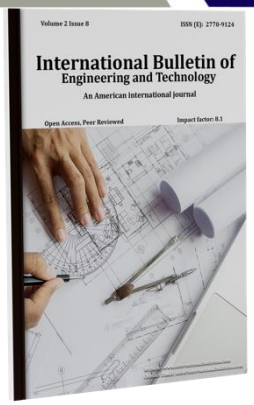


INFLUENCE OF TECHNOLOGICAL PARAMETERS ON THE DEGREE OF SEDIMENTATION OF SODIUM SILICO FLUORIDE BY SODIUM SULPHATES AND HYDROPHOSPHATES

Khodjamkulov S.Z [1]
Mirzakulov Kh.Ch [2]
Zoirov S. S. [3]
[1-3] Department of Chemical Technology, Termez Institute of Engineering and Technology, Termez 190100, Uzbekistan
[2] Faculty of Chemical Technology, Tashkent Institute of Chemical Technology, Tashkent, 100011, Uzbekistan
https://doi.org/10.5281/zenodo.10820308

Abstract. The results of studies on the production of sodium cremofluoride from extraction phosphoric acid based on phosphorites of the Central Kyzylkum Mountains using solutions of sodium sulfate and hydrogen phosphate are presented. Optimal technological parameters for the separation of sodium silicofluoride from acid have been established, at which the degree of fluorine precipitation from 40.29 to 41.44% is achieved. The conditions for settling sodium silicofluoride and its separation have been identified. The resulting product contains 91.28% Na_2SO_4 and 99.28% Na_2SiF_6 with Na_2HPO_4.

Keywords: Extraction phosphoric acid, fluorine, silicofluoride, sodium sulfate, sodium silicate.

Introduction

Literary data have shown that during the chemical interaction of phosphorites with sulfuric acid, a large proportion of fluorine is present in the acid in the form of fluoride and hydrofluorosilicic acid [1,2]. When MOPC CC is used as a phosphate raw material, after its sulfuric acid decomposition, three phases are formed, in which the total amount of fluorine in the phosphate raw material is as follows: liquid phase (EPC) - 40-45%, gas phase - 40-45%, solid phase (phosphogypsum)-10-20% [3-5]. In accordance with this, to purify EPA obtained from CC MOPC from fluorine, Na_2SO_4 and Na_2HPO_4 were used, which precipitated fluorine in the form of Na_2SiF_6. A complete chemical analysis of EPA gave the following results, wt. %: P_2O_5 - 21.05; CaO - 0.25; MgO - 0.94; Al_2O_3 - 1.13; Fe_2O_3 - 1.10; F - 1.23; SO_3 - 3.57; Na - 0.17; SiO_2 - 0.18[6-9]. Suspensions of Na_2SO_4 and Na_2HPO_4 in EPA are also necessary to prevent local interference [10].

Experimental part

Experiments on cleaning EPA from fluorine were carried out in laboratory conditions in a cylindrical quartz glass reactor with a stirrer inside. The rotation speed of the stirrer was measured with a tachometer. The estimated amounts of sodium sulfate and phosphate for the precipitation of sodium silicofluoride were calculated based on the ratio 2Na:6F. The rate of sodium sulfate and phosphate varied from 100 to 200% of the stoichiometry for the formation of sodium silicofluoride. The experiments were carried out at a temperature of 70°C, the experiment time was 45 minutes, with further deposition at a temperature of 30°C for two hours [11,12]. Table 1 and Figure 1, in accordance with experimental data, show the dependence of the degree of fluorine precipitation and the composition of defluorinated EPA on the rate of sodium sulfate and hydrogen phosphate. In the case of precipitation of Na_2SiF_6, sodium sulfate with an increase in its rate in the range from 100 to 200%, the degree of defluoridation increases from 32.43 to 40.29%, and when using Na_2HPO_4 this figure also

increases from 37.30 to 41.44%. Graphs of the dependence of the degree of defluoridation and the degree of dealkalinization of EPA on the norm of Na_2SO_4 and Na_2HPO_4 are given in Fig. 1.

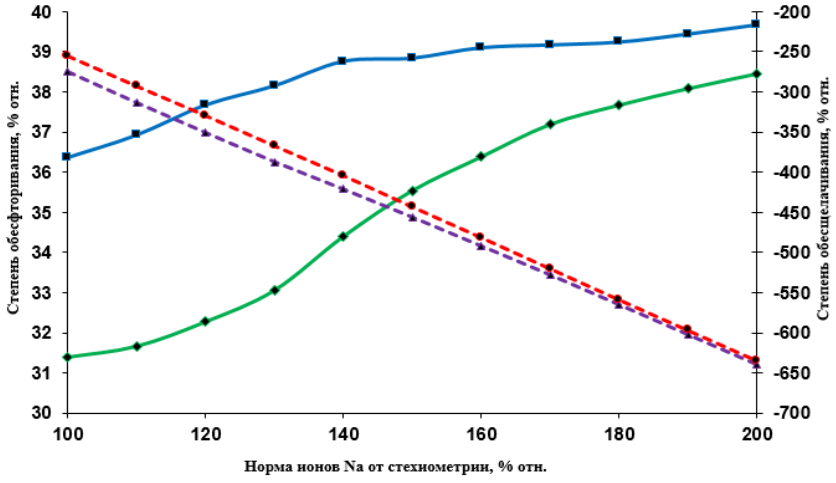
Table 1

Dependence of the composition of fluorinated EPA on the norm of sodium salts

Normal, %	Состав очищенной ЭФК, масс. %							
	Precipitating reagent			Level of defluoridation,	Precipitating reagent –			Level of defluoridatio
	P_2O_5	F	Na_2O		P_2O_5	F	Na_2O	
100	20,984	0,817	0,607	32,43	21,755	0,758	0,575	37,30
110	20,953	0,814	0,670	32,67	21,800	0,750	0,635	37,96
120	20,924	0,806	0,730	33,34	21,845	0,740	0,695	38,79
130	20,897	0,793	0,788	34,41	21,889	0,733	0,756	39,38
140	20,872	0,776	0,843	35,81	21,934	0,725	0,816	40,02
150	20,845	0,762	0,900	36,97	21,976	0,723	0,879	40,20
160	20,818	0,751	0,958	37,88	22,019	0,719	0,940	40,53
170	20,790	0,740	1,016	38,79	22,060	0,717	1,003	40,70
180	20,761	0,733	1,076	39,38	22,102	0,715	1,066	40,87
190	20,732	0,727	1,136	39,87	22,144	0,711	1,128	41,20
200	20,703	0,722	1,196	40,29	22,186	0,708	1,189	41,44

In the application for precipitation of Na_2HPO_4, compared to the use of Na_2SO_4, the degree of defluorination of EPA is slightly greater, because the precipitating agent contains phosphate ions. At the same time, the amount of P_2O_5 when using Na_2HPO_4 increases from 21.755 to 22.186%. When applied, Na_2SO_4 decreases from 20.984 to 20.703%.

When cleaning EPA from fluorine with sodium salts, sodium ions are added to the acid, which can be considered ballast. In the case of using Na_2SO_4 as a precipitant, increasing its rate from 100 to 200%. The amount of sodium in terms of sodium oxide in EPA increases from 0.609% to 1.198%. When using Na_2HPO_4 this parameter is 0.577 - 1.191%.



Rice. 1. Dependence of the degree of defluoridation and dealkalinization on the norm of Na_2SO_4 and Na_2HPO_4

Table 2 shows the dependence of the degree of defluoridation and dealkalinization of EPA on the time of interaction of Na_2SO_4 and Na_2HPO_4 with fluorine. According to experimental data [13] (Table 2), most of the fluorine (32.43 - 38.79%) forms poorly soluble compounds in the first 10 - 20 minutes. When sodium sulfate and phosphate are used as precipitants, the

proportion of fluorine remaining in the acid is in the range of 0.807-0.772% for 10 minutes and 0.777-0.739% for 30 minutes, and after 40 minutes the amount of fluorine decreases to 0.763-0.724% , respectively.

Table 2

The influence of the duration of the process of interaction between sodium sulfate and phosphate salts on the composition of fluorinated EPA

Mixing duration	Composition of purified			Degree of defluoridatio	Deallerizati on degree,
	P_2O_5	F	Na_2O		
Precipitating reagent– Na_2SO_4					
10	20,832	0,806	0,923	33,34	-671
20	20,838	0,790	0,915	34,66	-664
30	20,842	0,776	0,907	35,83	-658
40	20,847	0,762	0,900	36,98	-652
60	20,849	0,756	0,897	37,48	-641
Precipitating reagent– Na_2HPO_4					
10	21,960	0,771	0,905	36,24	-656
20	21,966	0,754	0,895	37,64	-647
30	21,972	0,738	0,887	38,97	-640
40	21,978	0,723	0,879	40,20	-633
50	21,979	0,719	0,877	40,53	-632
60	21,980	0,717	0,876	40,70	-631

A more significant change in the degree of fluorine removal from EPA is caused by the temperature of the process (Table 3). The experimental data obtained show that with increasing temperature the degree of defluoridation of the original EPA increases. This factor is explained by an increase in the rate of chemical interaction of sodium salts with hydrofluorosilicic acid.

Results and Discussion

Analysis of X-ray diffraction patterns (Fig. 2) of the product formed during the purification of EPA Na_2SO_4 and Na_2HPO_4 showed a clear presence of interplanar distances (4.40; 4.20; 3.32; 3.05 Å; 2.89; 2.55; 2. 51; 2.77; 2.21; 2.13; 2.10; 2.02; 1.956; 1.846; 1.785; 1.755; 1.658; 1.621; 1.579 Å, etc.), which belong to sodium silicofluoride [14].

Analysis of X-ray diffraction patterns showed that the resulting sodium silicofluoride from the purification of EPA from fluorine using Na_2HPO_4 (Fig. 2, X-ray diffraction 1) does not contain impurities, as well as the product that precipitates when using sodium sulfate (Fig. 2, X-ray diffraction 1), contains an admixture of $CaSO_4 \cdot 2H_2O$, which is confirmed by the presence of its interplanar distances in the X-ray diffraction pattern. In addition to X-ray phase analysis, infrared spectroscopic analysis of the products formed during the purification of EPA from fluorine was also carried out.

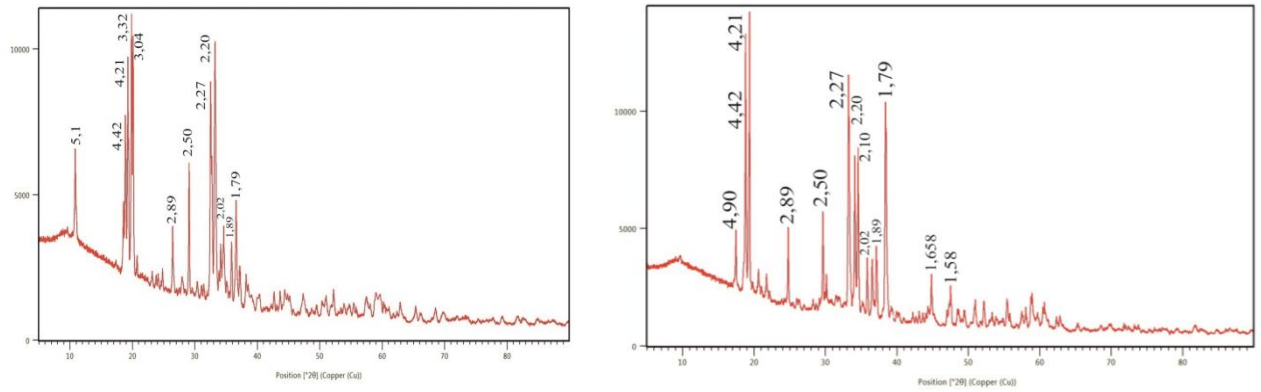


Figure-2. X-ray diffraction pattern of the product obtained by purifying EPA from fluorine using Na_2SO_4(1) and Na_2HPO_4(2).

Figure 3 shows the energy dispersive spectrum and quantitative composition of the elements of sodium hexafluorosilicate on a scanning electron microscope.

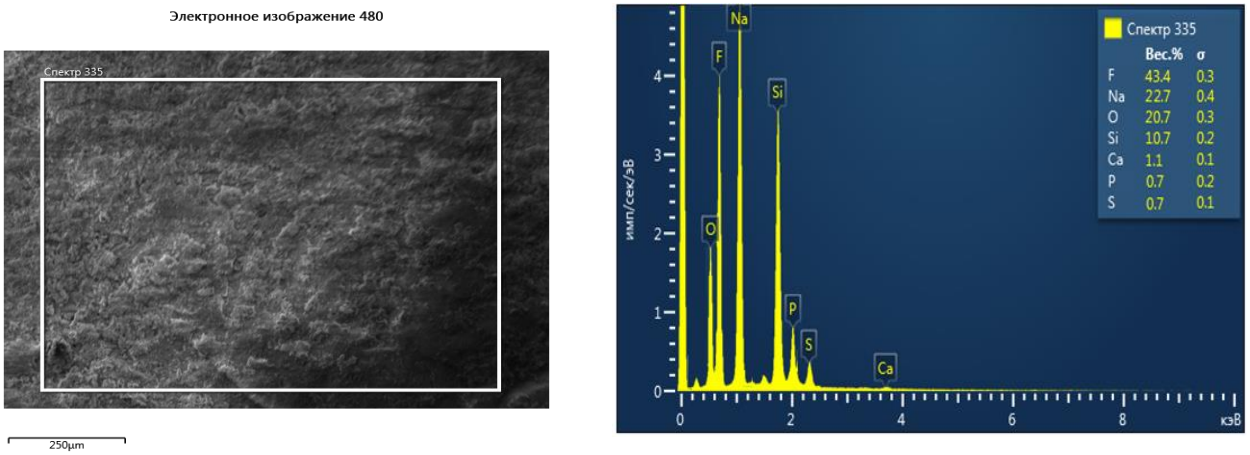


Figure 3. Energy dispersive spectrum and quantitative composition of sodium hexafluorosilicate elements

The results of scanning electron microscopy (SEM) analysis indicate the following composition: F-43.49%, Na-22.7%, O-20.7%, Si-10.7%, Ca-1.1%, P -0.7%, S-0.7, which corresponds to their content in sodium hexafluorosilicate.

Conclusion

The precipitate was obtained at a rate of 100% and the use of sodium hydrogen phosphate had a higher content (99.43%) of Na_2SiF_6 compared to the use of sodium sulfate (90.73%), this is explained by the fact that sulfate ions interact with calcium ions to form gypsum, which precipitates together with sodium silicofluoride, which reduces the content of the latter in the sediment. Thus, when defluoridating EPA with sodium sulfates and hydrogen phosphates, the degree of defluoridation does not exceed 40%. Increasing the rate of defluoridating reagents (more than 110-120%), temperature (more than 50°C) and process duration (more than 30 minutes) does not lead to a noticeable increase in the degree of defluoridation of EPA.

References:

1.Ходжамкулов С.З., Асамов Д.Д., Бардин С.В., Мирзакулов Х.Ч. Обесфторивание экстракционной фосфорной кислоты солями натрия // Журнал «Химия и химическая технология» – Ташкент, 2008. № 2. - С. 16-19.

2.Ходжамкулов С.З., Асамов Д.Д., Бардин С.В., Мирзакулов Х.Ч. Разработка технологии обесфторивания экстракционной фосфорной кислоты Центральных Кызылкумов с рециклом силиката натрия. Кимёвий технология. Назорат ва бошқарув, 41-45 бет.

3.Ходжамкулов С.З., Мирзакулов Х.Ч., Меликулова Г.Э., Усманов И.И. Исследование процесса обесфторивания экстракционной фосфорной кислоты из фосфоритов Центральных Кызылкумов // Журнал «Химия и химическая технология» - Ташкент, 2020. № 2. –С. 37-39.

4.Ходжамкулов С.З., Хамзаев Н.Ж. Техник фосфат кислотасини фтордан тозалаш. Академик А.Ғ.Ғаниевнинг 90 йиллигига бағишланган “Аналитик кимё фанининг долзарб муаммолари” VI республика илмий-амалий анжумани. - Термиз. 2020, 111-112 б.

5. Ходжамкулов С.З., Хайитов Ш.М., Мирзакулов Х.Ч., Меликулова Г.Э. Исследование процесса обесфторивания экстракционной фосфорной кислоты Центральных Кызылкумов солями калия // Журнал «Фан ва технологиялар тараққиёти». - Бухоро, 2019. № 4. - С. 41-45.

6. Ходжамкулов С.З., Мирсаидов М.Х., Мирзакулов Х.Ч. Исследование процесса получения кемнефторида натрия из экстракционной фосфорной кислоты // Умидли кимёгарлар 2015. XXII научно-техническая конференция молодых ученых, аспирантов и студентов. –Ташкент, 2015. С.74-75.

7. Ходжамкулов С.З., Зоирова Х.С., Шерматова Х.М. Экстракцион фосфат кислотасини натрий тузлари билан фторсизлантириш жараёни тадқиқоти // «Аналитик кимё фанининг долзарб муаммолари» IV республика илмий-амалий анжумани. –Термиз, 2014. 137 б.

8. Ходжамкулов С.З., Зоирова Х.С., Мирзакулов Х.Ч. Обесфторивание экстракционной фосфорной кислоты солями натрия // Биогеоэкологические проблемы. “Узбекистана республиканской научной и научно-технической конференции”. – Термез. 2016. С.301.

9. Ходжамкулов С.З., Мирзакулов Х.Ч. Определение оптимальных технологических параметров процесса обесфторивания экстракционной фосфорной кислоты // V-республиканская научно-практическая конференция «Актуальные проблемы аналитической химии», посвященная 85-летию академика А.Г.Ганиева. –Термез 2017. С.174-176. (247).

10.Ходжамкулов С.З., Набиев Д., Зоирова Х.С., Мирзакулов Х.Ч. Исследование процесса обесфторивания экстракционной фосфорной кислоты Центральных Кызылкумов солями натрия. Ўзбекистоннинг биогеоэкологик муаммолари республика илмий ва илмий-техник анжумани материаллари 15 март 2016 йил. Термиз, 302-303 б.

11.Muratov B A, Turaev Kh Kh, Umbarov I A, Kasimov Sh A, Nomozov A K. Studying of Complexes of Zn(II) and Co(II) with Acyclovir (2-amino-9-((2-hydroxyethoxy)methyl)-1,9-dihydro-6H-purine-6-OH), Int J Eng Trends Technol. 2024; 72(1); 202-208. https://doi.org/10.14445/22315381/IJETT-V72I1P120.

12.Shaymardanova M A, Mirzakulov Kh Ch, Melikulova G, Khodjamkulov S Z, Nomozov A K, Shaymardanova Kh.S. Study of process of obtaining monopotassium phosphate based on monosodium phosphate and potassium chloride. Chemical Problems. 2023; 3 (21): 279-293. https://doi.org/10.32737/2221-8688-2023-3-279-293.

13.Nomozov A K, Beknazarov Kh S, Khodjamkulov S Z, Misirov Z Kh. Salsola Oppositifolia acid extract as a green corrosion inhibitor for carbon steel. Indian J Chem Technol. 2023; 30(6): 872-877. doi: 10.56042/ijct.v30i6.6553.