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# **Separation of Phases Formed During the Process of Desfluorization of Extraction Phosphoric Acid with Sodium Phosphates**

**Khodjamkulov S.Z., Khujamberdiev Sh.M., Melikulova G.E.,  
Mirzakulov Kh.Ch., Shaymardanova M.A.**

Assistant Professor, Department Industrial Technology, Termez State University. Termez, Uzbekistan  
Assistant Professor, Department Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical  
Technology. Tashkent, Uzbekistan

Junior Researcher, Department Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical  
Technology. Tashkent, Uzbekistan

Professor, Department Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical Technology.  
Tashkent, Uzbekistan

PhD Student, Department Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical Technology.  
Tashkent, Uzbekistan

**ABSTRACT:** The article provides data on the development of a technology for defluorinating extraction phosphoric acid from phosphorites of the Central Kyzylkum using sodium phosphates, followed by phase separation and filtration of the sediment. The possibility of practically complete defluorination of the extraction phosphoric acid and obtaining a transparent acid is shown. Under these conditions, a fairly loose, well-filterable precipitate is formed.

**KEY WORDS:** Extraction Phosphoric Acid, Sodium Phosphate, Defluorination, Filtration, Sediment, Phase Separation, Precipitant, Sedimentation Rate.

## **I. INTRODUCTION**

In Uzbekistan, serious attention is paid to the problems of environmental protection from large-tonnage man-made, household waste, protection of soil, water resources from the ingress of various chemical and harmful substances into them [1-4].

## **II. LITERATURE REVIEW**

At the enterprises of the chemical industry, more than 700 thousand tons of phosphorites of the Central Kyzylkum (CK) are annually processed into extraction phosphoric acid (EPA) and phosphorus-containing fertilizers [5-7]. The content of fluorine in phosphorus-containing fertilizers produced in the republic, such as ammophos, PS-Agro, suprephos, enriched superphosphate, ranges from 2 to 4%. This is due to the fact that during sulfuric acid decomposition of CK phosphorites, 40.5% of fluorine passes into the gas phase, 5.4% is removed with phosphogypsum, and 54.1% remains in the EPA [8]. The low solubility of fluorine compounds in the composition of mineral fertilizers in a large sea prevents the removal of fluorine from the soil by thawed, rain and irrigation waters, as well as assimilation by plant organisms. However, the annual increase in the amount of applied mineral fertilizers, the use of chemical plant protection products, defoliants can change the solubility of fluorine compounds to the formation of assimilable forms by plants and animals. Many plants are capable of accumulating significant amounts of fluoride. So, tea contains from 57 to 1370 mg of fluorine per 1 kg, and in cotton plant up to 400 mg [4, 9, 10]. Moreover, fluoride accumulates in cotton seeds. The amount of fluoride absorbed by plants increases with the use of NPK fertilizers [3]. The intake of an excess amount of fluoride is negative not only on plants, but also on humans, animals, and fish. Fluorine compounds in water and air, even in small quantities, have a very harmful effect on living organisms [11-13].

On the other hand, fluorine compounds are a valuable chemical raw material and, despite the ever-increasing needs of the world economy for fluorine compounds, at present they are practically not extracted and remain in the composition

of mineral fertilizers. Therefore, studies aimed at processing CK phosphorites to obtain defluorinated EPA, which allows solving economic and environmental problems - reducing the content of fluoride in fertilizers and obtaining fluoride salts are very topical and relevant.

### III. RESEARCH METHODOLOGY

For the conditions of Uzbekistan, the most acceptable method for defluorination of EPA is the sedimentation of fluorine compounds from acid with sodium compounds in the form of sodium silicofluoride [14-17].

One of the bottlenecks in the defluorination process is the separation of the precipitate of silicofluorides, since they are deposited in the form of small crystals with a highly developed specific surface. The data available in the literature on the study of the processes of sedimentation of silicofluorides and or the stable part of EPA, depending on various parameters and the ways of intensifying the separation of solid and liquid phases, are not sufficient for the development of an effective technology for obtaining defluorinated EPA.

The required amount of alkali metals for defluorination was calculated based on the 6F : 2Na ratio. The rate of alkali metals was varied from 100 to 200% of the stoichiometry for the formation of sodium silicofluoride.

In this regard, the influence of the rate of an alkaline precipitant, the required amount of alkali metals for defluorination, addition of phosphorite, the ratio of Na<sub>2</sub>O in a solution of sodium salts on the sedimentation rate of particles and the filtration rate of the precipitate formed during defluorization of EPA was studied. In the work used industrial EPC of Almalyk JSC "Ammophos-Maxam" composition (wt.%): P<sub>2</sub>O<sub>5</sub> - 22.4; F - 1.2; SO<sub>3</sub>w - 2.2; R<sub>2</sub>O<sub>3</sub> 2.3; R<sub>2</sub>O - 0.4 and suspensions 2.5. Experiments on the defluorination of EPA were carried out in a laboratory setup consisting of a glass reactor equipped with a stirrer.

In order to intensify the processes of decantation and filtration, we used a precipitant - CaSO<sub>4</sub>•2H<sub>2</sub>O, formed by the interaction of free sulfuric acid contained in EPA with phosphate raw materials. The amount of the latter was varied in the range of 0-120% of the stoichiometry for the formation of calcium sulfate dihydrate. At the same time, it was assumed that the resulting CaSO<sub>4</sub>•2H<sub>2</sub>O crystals have sufficient size and density, in comparison with the CaF<sub>2</sub>, Ca<sub>5</sub>F(PO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>SiF<sub>6</sub> and SiO<sub>2</sub> particles formed in the extraction suspension, and that large crystals during deposition should capture smaller particles in solid phase. It is known that the greatest effect of the precipitant follows at the moment of its formation [18]. Therefore, in the experiments, special conditions were created for the formation of CaSO<sub>4</sub>•2H<sub>2</sub>O. This was achieved by mixing phosphorite with the original EPA at a temperature of 70°C for 40 minutes. in a thermostated reactor. The resulting suspension was poured with stirring into measuring cylinders with a capacity of 100 cm<sup>3</sup>. The deposition time was recorded when a sufficiently clear phase boundary was reached. The sedimentation rate (W, m/h), the L:S ratio in the suspension (L:S), and the filterability (F) were determined by a known method [19]. The deposition rate was calculated using the formula:

$$W = \frac{l \cdot 60}{\tau}$$

where, *l*-path covered in time  $\tau$ , min. The L:S ratio in the suspension was calculated using the equation:

$$L : S = \left( \frac{j_p}{j_L} - 1 \right) : \left( 1 - \frac{j_L}{j_S} \right)$$

where,  $j_p$ ,  $j_L$ ,  $j_S$  - the specific gravity of the pulp, liquid and solid phases, respectively. Filterability was determined by the formula:

$$F = \frac{V_F * h_{sed}}{\Delta P * S * \tau}$$

where, F - filterability, m<sup>4</sup>/H-hour; V<sub>F</sub> - filtrate volume, m<sup>3</sup>; h<sub>sed</sub> - is the thickness of the filter cake layer, m;  $\Delta P$  - pressure difference, N/m<sup>2</sup>; S - filter area, m<sup>2</sup>;  $\tau$  - filtration duration, hour.

The average density of the solid phase, consisting of particles CaSO<sub>4</sub>•2H<sub>2</sub>O, CaF<sub>2</sub>, Ca<sub>5</sub>F(PO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>SiF<sub>6</sub>, SiO<sub>2</sub>, etc., is equal to 2450 kg/m<sup>3</sup>.

Filtration of suspensions was carried out on a Schott filter with a porosity of 100  $\mu$ m at a vacuum of 75-80 kPa. The precipitate was washed with hot water, acetone, dried at a temperature not exceeding 60°C and weighed. The filtration time was recorded by the appearance of a sediment mirror.

**IV. ANALYSIS AND RESULTS**

The initial EPA in the absence of phosphorite and a solution of alkali metal phosphates clears up rather quickly, but the upper acid layer, after the precipitation of the bulk of the sediment, remains cloudy and contains a significant amount of fine silty, suspended particles for a long, more than 10 hours, settling. The addition of an insignificant amount of CK phosphorite ( $N_{ph/r}$  50% of stoichiometry on  $SO_3$ ) at a mass ratio of EPA: phosphorite raw material - 100:(0.6-1.2) allows to drastically reduce the sulfate content in acid by almost 2 times (table 1).

The upper acid layer after settling, in contrast to the initial EPA, is noticeably lighter, which is due to the crystallization of calcium sulfate on suspended particles and their coprecipitation into the solid phase. The sludge mass increases by 1.7 times with an almost unchanged height of the clarified layer, which indicates a significant sludge compaction.

Table 1. Influence of the phosphorite rate on the degree of sedimentation of suspensions during defluorination and desulfurization of EPA (process duration - 40 min; process temperature - 70°C; settling time - 120 min; settling temperature - 30°C

Experiment number	Phosphate raw material rate,%	Height of the clarified layer,%	Filtration rate, kg/m <sup>2</sup>	Sediment yield (per 100 g of EPA)	L:S ratio in suspension	L:S ratio in thickened suspension	Defluorination degree %	Degree of desulfurization niya,%
Without alkali metals								
1	-	87,4	170,49	1,78	55,18:1	6,95:1	13,85	0
2	25	83,1	182,50	2,40	40,98:1	6,92:1	14,72	30,01
3	50	82,7	254,44	3,01	32,63:1	5,65:1	16,34	47,84
4	75	66,7	250,80	3,65	26,91:1	8,69:1	22,33	66,70
5	100	65,0	245,41	4,70	20,80:1	7,28:1	23,50	91,20
6	120	60,7	230,24	5,28	18,50:1	7,26:1	24,00	95,00
In the presence of alkali metals in a solution $\Sigma R_2O:\Sigma P = 1:1$								
7	-	80,00	110,12	2,78	40,85:1	10,86:1	71,28	0
8	25	69,24	121,30	4,10	27,52:1	9,71:1	73,59	33,00
9	50	58,50	168,91	5,40	20,77:1	9,51:1	75,87	52,50
10	75	57,91	180,40	6,77	16,46:1	7,31:1	77,83	68,00
11	100	53,50	178,91	7,35	13,94:1	6,95:1	82,87	95,90
12	120	49,50	170,12	8,28	13,44:1	7,19:1	83,30	96,00

This is confirmed by the ratio L:S in the thickened part of the suspension, which is (5.5-10.86):1.

An increase in the amount of added phosphorite ( $N_{ph/r}$  - 75-100%) leads to almost complete defluorination of EPA and the production of a transparent acid. Under these conditions, a fairly loose, well-filterable precipitate is formed, represented mainly by calcium sulfate dihydrate with an insignificant amount of silica, which contains CK in phosphorite.

An increase in  $N_{ph/r}$  above stoichiometry practically does not contribute to further desulfurization, but leads to a sharp deterioration in the process of decantation and filtration of the sediment. This is due to the fact that in the process of interaction of excess phosphorite with phosphoric acid, the latter extracts Ca, Mg, Fe and Al cations into solution, increasing the viscosity of the acid, and the insoluble phosphorite precipitate with poor filtering properties dilutes well-filterable gypsum.

A similar picture is observed with the simultaneous addition of sodium phosphate solution to the initial EPA for defluorination and phosphorite (table 1).

In the absence of phosphorite, despite the fact that the phase separation occurs rather quickly, a poorly filterable, finely dispersed precipitate of silicofluorides in a mixture with suspended particles of the original EPA is formed. The clarified part remains cloudy for a day or more, although the content in it is no more than 0.2-0.3 mass. The filtration rate of such a sediment does not exceed 110.12 kg/m<sup>2</sup>·h.

Adding, together with a solution of alkali metal phosphates, phosphate rock in an amount of 75-100% of the stoichiometry for binding  $SO_3$ , it is possible to significantly increase the degree of defluorination (by 7-10 abs.%) and desulfurization to 70-90% (table 1). The filtration rate of the sediment increases by more than 1.5 times compared to the precipitate obtained without adding phosphorite. The liquid phase is transparent, does not contain suspended

particles, it is easily separated from the thickened part without agitation, despite the fact that L: S in suspension is (16.5-14.1):1. The thickened part is characterized by an almost optimal ratio of L:S, equal to (7.0-7.4):1, which makes it possible to carry out the subsequent processing of the precipitate into a solution of sodium phosphates and concentrated fluorine-containing gases without additional processing.

The indices of the process of defluorination and subsequent thickening of the suspension and filtration of the precipitate significantly depend on the composition of the precipitate, which is determined by the composition of the precipitation solution and the  $\sum Na_2O : \sum (F_{EPA} + F_{ph/r})$  ratio (table 2).  $\sum Na_2O = Na_3PO_4 + Na_2SiO_3$ , the content of acid-soluble silicon in EPA obtained from CK phosphorites is insufficient for the complete conversion of all fluorine into sodium silicofluoride, which causes a low degree of defluorination [1]. In this regard, experiments were carried out on the defluorination of EPA with sodium salts in the presence of sodium silicate in order to correct the ratio of  $SiO_2:F$  in EPA.

Table 2. Influence of norm, concentration of alkali metal ( $Na_2O$ ) on the process of sedimentation of suspensions during defluorination of EPA (process temperature - 70°C; process duration - 40 min; settling temperature - 30°C; settling time - 120 min;  $N_{ph/r} = 75\%$ ).

Experience number	Mass ratio $Na_2O:F$	Height of the clarified layer, %	Sedimentation rate, m/h	L:S ratio in the initial suspension	L:S ratio in a thickened suspension	Sediment yield, %	Filtration rate, $kg/m^2 \cdot h$
1	0,4:1	47,2	1,07	18,82:1	8,13:1	5,85	98,8
2	0,6:1	51,7	1,27	18,43:1	8,53:1	6,06	120,8
3	0,8:1	54,3	1,38	18,09:1	8,83:1	6,35	165,3
4	1:1	54,3	1,39	17,96:1	8,86:1	6,58	176,7

As can be seen from the presented data, all other things being equal, an increase in  $\sum Na_2O : \sum F$  from 0.4:1 to 1:1 leads to an insignificant increase in the filtration rate of the sediment with a simultaneous compaction of the sediment (table 2). The height of the clarified layer with a decrease in L:S and an increase in the yield of the solid phase increases by 5-11%. Moreover, these indicators are significantly improved when using sodium phosphate solutions for fluorine precipitation. The filtration rate of the precipitate when defluorinated with a solution with a mass ratio of  $Na_2O : \sum F$  equal to 1:1 is  $176.7 kg/m^2 \cdot h$ .

Taking into account that in real technological conditions the sedimentation temperature is directly dependent on the ambient temperature and fluctuates in the range of 20-60°C, the effect of temperature on the sedimentation and filtration rate of the sediment formed during desulfurization and defluorination of the EPA CK was studied (table 3).

Table 3. Influence of sedimentation temperature on the process of suspension sedimentation during defluorination of EPA (duration - 40 min, phosphorite rate - 75%, sedimentation time - 120 min.)

Experience number	Deposition temperature, °C	Height of the clarified layer, %	Sedimentation rate, m/h	Sediment yield, %	L:S ratio in suspension	L:S ratio in a thickened suspension	Filtration rate, $kg/m^2 \cdot h$
1	20	59,2	1,29	7,0	16,01:1	7,16:1	178,2
2	40	60,4	1,58	6,5	17,31:1	7,57:1	209,45
3	50	60,9	1,67	6,2	18,29:1	7,88:1	307,57
4	60	61,0	1,68	6,2	18,31:1	7,90:1	309,41

With an increase in temperature from 20 to 60°C, the rate of sedimentation of the solid phase and the rate of filtration of the sediment slightly increase from the used solution of alkali metal phosphates. For example, at 20°C  $W_{sed}$  is 1.29 m/h, and at 60°C it reaches 1.68 m/h, and the filtration rate of the sediment increases from 178.2 to 309.41  $kg/m^2 \cdot h$ . At a temperature of 50°C, the bulk of the particles, up to 97-98%, settles in the first 30-40 minutes, and at 20°C within 2-2.5 hours.

A significant difference in the rate of sedimentation of particles and filtration of the sediment with an increase in the settling temperature is due to a sharp decrease in the density and, especially, in the viscosity of the liquid phase of the suspension with increasing temperature.

Under optimal process conditions, the maximum sedimentation rate of solid phase particles is 2 m/h with a degree of defluorination and desulfurization of 73-89 and 70-95%, respectively.



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## VI. CONCLUSION

Thus, the addition, together with the solution of alkali metal phosphates, of the CK phosphate raw material in an amount of 75-100% of the stoichiometry for  $\text{SO}_3$  binding makes it possible to significantly increase the degree of defluorination by 7-10% and desulfurization to 70-90%. The filtration rate of the sedimentate increases by more than 1.5 times in comparison with the precipitate obtained without the addition of phosphorite. With an increase in temperature from 20 to 60°C, the sedimentation rate of the solid phase and the filtration rate of the sediment slightly increase.

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