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STUDYING THE PROCESS OF PRODUCING SODIUM SILICATE AND FLUORIDE FROM Na_2SiF_6 BY HYDROLYSIS WITH SODIUM HYDROXIDE

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Abstract. In this paper, to return acid-soluble silicon dioxide to the initial stage of the process of defluoridation of EPA in the form of a sodium silicate solution, the solid phase that has passed through the stages of filtration and washing is hydrolyzed with a NaOH solution. The hydrolysis products of Na_2SiF_6 are NaF and CaF_2. Results of studies on the influence of the norm on the degree of hydrolysis and the change in the L:S ratio, as well as on the chemical composition of the solid and liquid phases during the hydrolysis of Na_2SiF_6 with sodium hydroxide.

Keywords: silicon dioxide, sodium silicate, Na_2SiF_6, sodium hydroxide, defluoridation.

Introduction. On a global scale, the main part of phosphate raw materials - apatites and phosphorites - is processed into phosphorus fertilizers by decomposition using the sulfuric acid method to produce EPA and phosphogypsum waste according to the reaction.

$Ca_5(PO_4)_3F + 5H_2SO_4 + nH_2O = 3H_3PO_4 + 5CaSO_4 \cdot nH_2O + HF$

As a result of the synthesis of H3PO4, HF is released into the gas phase, which enters into a chemical reaction with silicon substances of the raw material to produce silicofluoride and hydrofluorosilicic acid [1,2].

During the synthesis of EPA, complex processes occur, as a result of which fluorine is distributed in three directions:

1. Fluorine remains and is found as hydrofluorosilicic acid, its salts and hydrolysis products
2. Emissions into the gas phase as SiF_4^- and HF
3. Converts to waste phosphogypsum. The presence of fluorine in three directions is related to the composition of phosphate raw materials, technological conditions and equipment [3,4].

The processes of fluorine transition into the gas phase have not yet been fully studied. Fluoride gases mainly enter the gas phase in the form of SiF_4^- and HF. The gas phase also contains mechanical impurities and aerosols, which contain non-volatile fluoride substances and volatile substances (POF_3, HPF_5, etc.). As a result, phosphorus passes into the composition of the resulting fluoride salts [5]. There are several known studies of the physical and chemical processes occurring during the processing of phosphates [6,7]. Today, in industry, fluorine is obtained mainly from the gas phase. Only 13% of the fluorine contained in phosphate raw materials is extracted. A considerable proportion of fluorine is contained in the fertilizer. It then enters the soil, groundwater and reservoirs and harms the environment. In this regard, the worst situation is with ammophos, which is characterized by the maximum amount of fluoride substances, and in water-soluble form (27.4-40.5% of its content in the raw material) [8,9]. It follows that one of the main tasks must be considered to reduce the amount of fluorine in fertilizers, which allows plants to prevent the transfer of fluoride into the soil and waterways and increase its extraction rate [10]. The degree of fluorine distribution differs significantly depending on the type of phosphorus raw material. For example, for Kola apatite there is 73% in acid, 15% in phosphogypsum, and 12% of the original fluorine in the gas phase. The following data were obtained for Kovdor apatite: in acid - 83%, in phosphogypsum - 10%, in the gas phase - 5% [11].

Experimental part

At the end of the hydrolysis process, the pulp was poured into thermostatically controlled cylinders to settle the pulp. Next, the condensed part was filtered, and the solid phase was washed with water. In this case, the following reaction occurs in the process:

$$Na_2SiF_6 + 6NaOH = 6NaF\downarrow + Na_2SiO_3 + 3H_2O$$

Most of Na_2SiF_6 undergoes hydrolysis even at the stoichiometric rate of NaOH. The presence of some excess NaOH (up to 120% of stoichiometry) makes it possible to increase the hydrolysis rate to 99.6%. Excess NaOH must also be fixed at a constant level, the ratio of Na_2O:F in solution, Na_2SiF_6, supplied to purify EPA from fluorine. Excessive amounts of NaOH increase the stability of Na_2SiO_3. According to kinetic experiments, the hydrolysis of Na_2SiF_6 with NaOH occurs very quickly. The dependence of the degree of hydrolysis of Na_2SiF_6 with NaOH was studied at a norm of the latter of 120% at different temperatures (Fig. 2.1). With increasing temperature, the rate of hydrolysis increases greatly. A low temperature of 40-50 °C is already sufficient to carry out hydrolysis.

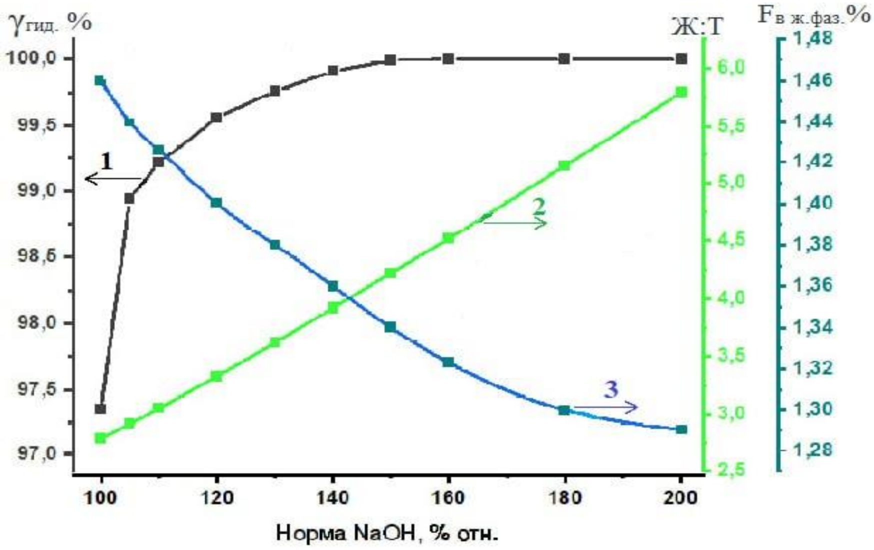

Figure -2.1. The influence of the NaOH rate on the phase composition and technological parameters of the Na_2SiF_6 hydrolysis process.

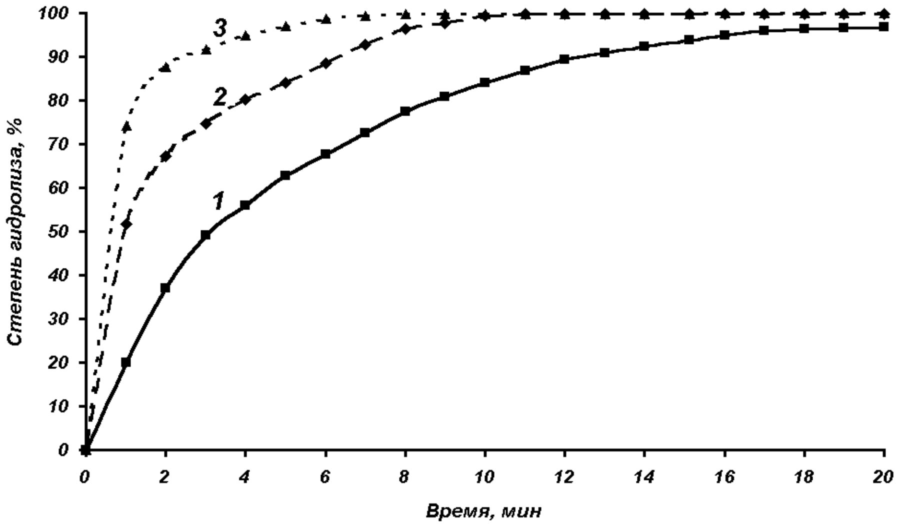

Figure 2.2. The influence of time on the degree of hydrolysis of Na2SiF6 in the temperature range of 20 – 60 °C.

This temperature appears when NaOH is dissolved in a Na_2SiO_3 solution and the reaction between Na_2SiF_6 and NaOH. The optimal duration of hydrolysis: in the temperature range of 20-60°C is 4-30 minutes. Water washing of the solid phase with NaF leads to the formation of dilute solutions of Na_2SiO_3, which must be disposed of. In the developed technology, filter fluids are returned to the head of the process to maintain the L:S ratio and eliminate losses.

Therefore, the influence of various factors on processes was studied at a temperature of 40°C and humidity Na_2SiF_6 - 30%. (Table 1).

Table 1

Impact of circulating fluid on phase composition and process conditions

Concentration Na_2SiO_3, %	Degree of hydrolysis, %	Ratio. L:S	Chemical composition of the liquid phase, mass.%			Chemical composition of the solid phase, mass. %		
			Na_2O	SiO_2	F	Na_2O	SiO_2	F
Norma NaOH – 100 %								
5	97,360	2,41	10,992	11,90	1,25	72,98	0,67	45,56
10	97,160	2,41	13,45	14,29	1,24	72,92	0,73	45,58
15	96,910	2,41	15,96	16,68	1,23	72,85	0,77	45,61
20	96,260	2,42	18,54	19,02	1,21	72,65	0,92	45,68
Norma NaOH – 120 %								
5	99,570	2,84	14,45	10,57	1,25	73,64	0,15	45,31
10	99,530	2,83	16,56	13,01	1,23	73,63	0,16	45,31
15	99,470	2,83	19,48	15,44	1,22	73,61	0,17	45,32
20	99,610	2,83	22,01	17,87	1,21	73,56	0,19	45,32
Norma NaOH – 150 %								
5	99,990	3,48	18,29	9,02	1,24	73,82	0,01	45,26
10	99,950	3,47	20,82	11,46	1,22	73,80	0,01	45,26

15	99,900	3,47	23,36	13,90	1,21	73,79	0,02	45,27
20	99,870	3,47	25,90	16,35	1,2	73,78	0,03	45,27

The concentration of the circulating Na_2SiO_3 solution has virtually no effect on the degree of hydrolysis of Na_2SiF_6. The decrease in the degree of hydrolysis with increasing Na_2SiO_3 concentration can be explained by an increase in the viscosity of the liquid phase, which reduces the mobility of ions.
Hydrolysis of Na_2SiO_3 can be carried out with reverse solutions with a concentration of up to 30%. At concentrations above 30%, the viscosity of the resulting suspension increases.
The results of experimental data suggest that in the process of hydrolysis in a circulating solution of Na_2SiO_3, it is possible to synthesize NaF, which contains more than 98% of the main substance. You can use Na_2SiO_3 with a concentration of up to 40% by weight. Due to the implementation of the hydrolysis reaction with a circulating solution of Na_2SiO_3 with a concentration of 5-20%.
To separate sodium fluoride from the suspension formed during the hydrolysis of fluorophosphate precipitate with sodium hydroxide, the degree of clarification of the suspension was studied depending on the temperature and duration of the settling process [12].

Results and Discussion

The results of experiments on sodium fluoride slurry sedimentation showed that NaF crystals precipitate much faster (Fig. 3.1.). As can be seen from the figure, with increasing temperature and duration of the settling process, the degree of solution clarification increases and NaF precipitates into the solid phase quite quickly. In the range of heating degree 20-60°C, clarification interval up to 20 minutes, the clarification coefficient increases from 0.5 to 0.7, respectively. Further increases in the duration of the settling process lead to a slight increase in the degree of clarification of the suspension.

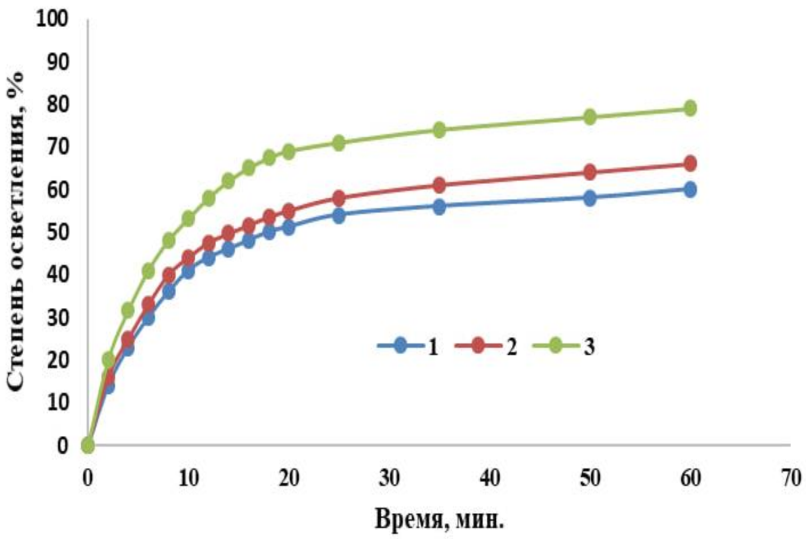

Figure. 3.1. Coefficient of NaF precipitation into the solid phase depending on time at temperature, °C: 20(1), 40(2), 60(3)

In order to intensify the settling process and maximize the thickening of the suspension, PAA were used; the results of the experimental data are shown in Fig. 3.2.

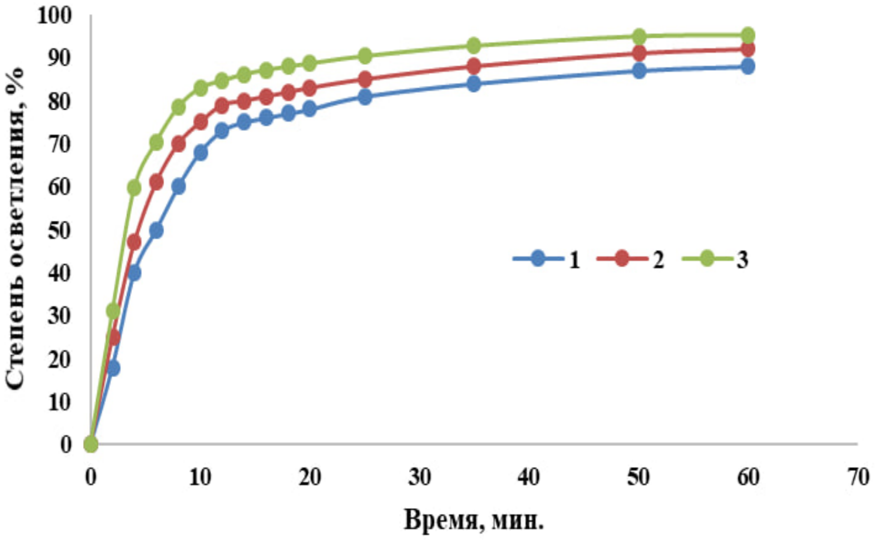

Figure 3.2. The effect of the clarification interval of a NaF suspension in a Na_2SiO_3 solution at temperature and the presence of PAA: 1 – 20 °C, 2 – 40 °C, 3 – 60 °C.

When using optimal quantities of PAA (PAA - 10 g/t), the degree of clarification of the suspension increases with increasing temperature and with a settling process duration of 20 minutes it ranges from 80 to 90%, respectively, that is, the degree of settling of the suspension increases by an average of 1.5 times.

When the settling process lasts 15 minutes, the degree of clarification of the suspension reaches its maximum value, i.e. 90% and above. A further increase in the duration of the settling process does not lead to a noticeable increase. Therefore, the optimal technological parameters and settling process are the following: temperature - 50-60°C; the duration of the settling process is 10-15 minutes and the amount of PAA is 10-12 g/t. Thus, as a result of the chemical interaction of sodium silicofluoride with sodium hydroxide, a solid phase of sodium fluoride precipitates, which is easily clarified and thickened[13].

In continuation of these studies, the influence of the amount of sodium silicate, the L:S ratio, and the degree of heating of the pulp on the rapidity of phase separation without and in the presence of PAA was considered. Without and in the presence of PAA, the research results are shown in Table. 3.2.

The data in Table 2 show that with an increase in the concentration of Na_2SiO_3 in increments of 10%, it is satisfactorily stable and its values are 24-26%. At a temperature of 20°C, L: S=1:1 and a Na_2SiO_3 solution concentration of 10%, the filtration rates were satisfactory. With an increase in temperature to 40°C, these indicators increase from 243.1 to 364.7 kg/m2 per hour. accordingly. Very high speeds are achieved at F: T = 4:1, when the considered indicators from 437.5 and 652.8 increase to 238.6 and 358.0 increase to 432.0 and 619.3 kg/m2 hour for dry sediment and sodium silicate 432.9 and 649.3 kg/m2 hour, respectively.

Table 3.2

Dependence of NaF filtration rate on Na2SiO3 concentration, L:S ratio and suspension temperature. ∆P – 400 mm Hg. Art.

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Ratio. L:S	Temperature, °C	Concentration of Na_2SiO_3 solution, wt.%						Concentration of Na_2SiO_3 solution, wt.%
		10		20		30		
		Filtration rate, kg/m^2 h						
		By dry sediment	For sodium silicate	By dry sediment	For sodium silicate	By dry sediment	For sodium silicate	
1:1	20	124,4	185,2	88,4	175	74,9	157,3	
	30	142,7	199,2	111,4	221	85,9	180,5	
	40	243,7	364,1	179,4	357	115,8	244,3	
2:1	20	152,7	207,3	111,8	221,8	91,8	193,2	
	30	187,1	251,7	149,9	278,9	112,5	210,3	
	40	296,2	442,9	214,5	394,9	145,9	283,9	

3:1	20	190,4	255,7	145,9	290	114,5	241,4
	30	231,5	316,2	185,4	350,5	139,1	269,8
	40	363,8	544,3	252,9	469,6	182,2	355,6
4:1	20	239,1	357,4	172,1	342,5	143,8	303,6
	30	289,2	432,3	220,8	439,7	173,7	367,4
	40	433,5	648,7	300,6	599,4	221,9	469,6

Phase separation in Na_2SiO_3 solution is complex. With an increase in the concentration of the Na_2SiO_3 solution from 10 to 20%, in some cases it decreases, and in some cases it increases. With these values, the maximum decrease in the filtration rate of the Na_2SiO_3 solution is 10.84%, and the increase is 13.54%. With a further increase in the Na_2SiO_3 concentration, the filtration rate through the liquid phase decreases.

With an increase in Na_2SiO_3 concentration, the complex nature of the change in filtration rate can be explained by the following considerations: with an increase in sodium silicate concentration from 10 to 20%, the values of these increases are greater than those obtained when changing the filtration time; with a further increase in the concentration of Na_2SiO_3 to 30%, the achieved filtration rate of Na_2SiO_3 does not compensate for the decrease in the filtration rate, because The time it takes for Na_2SiO_3 to pass through the filter increases sharply.

Conclusion Thus, according to experimental data, the optimal filtration conditions were determined in the presence and absence of PAA, as well as the established concentration and amount of added PAA, which allows rapid filtration of NaF and Na_2SiO_3 suspensions by 1.7 - 1.8 times. The optimal conditions for the process are as follows: liquid and solid phase ratio - 3-4:1, Na_2SiO_3 concentration - 20%, temperature - 30-40 °C.

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