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STUDY OF THE PROCESS KINETICS OF ACID-THERMAL DECOMPOSITION OF FLUOROPHOSPHATE SEDIMENT BY EXTRACTION PHOSPHORIC ACID FROM PHOSPHORITES OF CENTRAL KYZYL KUM

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Abstract: In this paper, the kinetic and thermal processes of obtaining phosphoric acid by defluorinating Central Kyzylkum phosphorites were studied. In this, the effects of different temperatures on the level of fluorine release on the decomposition of phosphoric acid were studied, and the best result was obtained at a temperature of 200 0C and 60 minutes.

Keywords: Central Kyzylkum phosphorites, phosphoric acid, thermal, kinetic, decomposition kinetics.

Аннотация: В данной работе изучены кинетические и термические процессы получения фосфорной кислоты путем дефторирования фосфоритов Центральных Кызылкумов. При этом изучалось влияние различных температур на уровень выделения фтора на разложение фосфорной кислоты, причем лучший результат был получен при температуре 200 0С и 60 мин.

Ключевые слова: фосфориты Центральных Кызылкумов, фосфорная кислота, термическая, кинетическая, кинетика разложения.

To determine the conditions for the decomposition of fluorophosphate sediment (FPS) formed during the defluorination of extraction phosphoric acid (EPA) from phosphorites of the Central Kyzylkum (CC) and to establish the patterns of the process, the necessary data on the kinetics of acid-thermal decomposition of the sediment[1; pp. 37-39].

PFO isolated from EPA under optimal conditions has the following composition wt.% Na_2O – 9.03, CaO – 15.75, SO_3 – 22.15, P_2O_5 – 1.35, MgO – 0.44, F – 18.7 R_2O_3 – 1.36. The decomposition of the sediment was carried out with defluorinated EPA with a concentration of (20.8% P_2O_5) at a rate of H_3PO_4 for interaction with Na_2O of 600% of the stoichiometry [2; pp. 14912-14916].

When studying the kinetics of processes occurring in heterogeneous systems, it is important to know whether they occur under given conditions in the kinetic and diffusion regions. To clarify this, it is necessary to study the influence on the speed of the process of two main factors - hydrodynamic (intensity of movement) and temperature. Therefore, the variable variables during the experiments were the temperature of sediment decomposition (140, 160, 180 and 200 ^oC)

and the rotation speed of the stirrer (n=20 and 35 cm $^{-1}$) [3; pp. 15192-15196]. As a parameter characterizing the decomposition of FPO EPA, the degree of fluorine release into the gas phase was chosen, the dependence of which on the process conditions is given in Table 1.

Table 1

Dependence of the degree of fluorine release from fluorophosphate sediment on the technological parameters of the phosphoric acid decomposition process

No.	Temperature about C	Degree of fluoride release, (%) after time, min.							
		5	10	15	20	thirty	40	50	60
Mixer rotation speed -20 s $^{-I}$									
1	140	3.85	17.19	24.97	29.21	38.83	43.29	48.29	50.78
2	160	20.17	37.37	45.99	51.63	58.31	64.20	68.48	72.56
3	160	46.81	60.12	66.96	71.05	78.25	83.05	87.00	89.05
4	200	63.95	75.11	82.29	86.29	82.74	92.20	94.01	94.71
Mixer rotation speed-35 s $^{-1}$									
5	140	3.15	9.92	15.61	18.07	31.11	43.01	49.03	55.45
6	160	14.06	28.88	39.42	47.73	61.85	67.07	72.96	76.90
7	180	48.87	62.43	69.65	74.90	82.24	85.61	88.69	91.11
8	200	69.08	81.09	85.88	89.29	91.14	93.09	94.46	96.35

During phosphoric acid decomposition, areas of self-acceleration of the reaction are observed in the initial sections of the kinetic curves, and this effect is more pronounced the higher the process temperature [4; pp. 18-21, 5; C. _ 324-332].. Processing of integral curves using various kinetic equations showed that the process of phosphoric acid decomposition of PFO is most adequately described by the following equation:

$lg\frac{1}{1-\gamma} = K\sqrt{\tau}$or

$$\left(lg\frac{1}{1-\gamma}\right)^2 = K^2 \cdot \tau$$

where: -degree of sediment defluoridation , τ –time, min.

At temperatures above 180 ^{o} C, the dependence $lg\frac{1}{1-\gamma}$on $\sqrt{t}$is linear, and at 160 and 140 ^{o} C a kink is observed in the curves, dividing them into 2 straight sections: I - the initial stage of the process, II - the final stage.

^{2} = K $_{1}$ in equation (2) , we get:

$$\left(lg\frac{1}{1-\gamma}\right)^2 = K_1 \cdot \tau$$

where: K $_{1}$ – reduced rate constant, min $^{-1}$; τ-time, min.

The rate constant values found graphically are presented in Table 2.

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Based on the data on the dependence of logK on 1/T, which is displayed as a linear dependence, the activation energy values for the initial and final stages of the process were calculated by the Arrhenius equation. $К_1 = К_0 e^{-\frac{Ea}{RT}}$They are 38.46-39.74 kcal /mol for the initial stage of decomposition and 20.77-21.88 kcal /mol for the final stage of the process.

Table 2
Decomposition rate constants of FPO EPA

Temperature, ^oC	rotation speed C^{-1}	K_1, min^{-1}	
		Initial stage	Final stage
140		$3.60 \cdot 10^{-5}$	$11.56 \cdot 10^{-4}$
160	20	$3.61 \cdot 10^{-4}$	$60.84 \cdot 10^{-4}$
180		-	$222.0 \cdot 10^{-4}$
140		$2.21 \cdot 10^{-5}$	$10.89 \cdot 10^{-4}$
160	35	$4.0 \cdot 10^{-4}$	$73.96 \cdot 10^{-4}$
180		-	$237.2 \cdot 10^{-4}$

By processing the experimental results, equations were obtained that make it possible to calculate the degree of defluoridation of the sediment during its phosphoric acid decomposition, depending on the process parameters , which have the form:

Initial stage of the process:

$$\left(\lg\frac{1}{1-\gamma}\right)^2 = 3{,}6643 \cdot 10^{16} \cdot e^{[(39700+300)/RT]} \cdot \tau$$

$$n = 20\, c^{-1}, \quad 140 \le t \le 180{,}2 \le \tau \le 5$$

where: t – process temperature, ^oC , τ – duration, min

$$\lg\left(\frac{1}{1-\gamma}\right)^2 = 6{,}4316 \cdot 10^{16} \cdot e^{[(38490+310)/RT]})$$

$$n = 35\, c^{-1}, \quad 140 \le t \le 180{,}10 \le \tau \le 26$$

Final stage of the process:

$$\left(\lg\frac{1}{1-\gamma}\right)^2 = 1{,}7321 \cdot 10^{8} \cdot e^{[(20870+350)/RT]} \cdot \tau$$

$$n = 20\, c^{-1}, \quad 140 \le t \le 180, \quad \tau = 5$$
$$t \ge 180, \quad 0 \le \tau \le \tau_{КОН}$$

$$\left(\lg\frac{1}{1-\gamma}\right)^2 = 6{,}55 \cdot 10^{8} \cdot e^{[(21870+380)/RT]} \cdot \tau$$

$$n = 35\, c^{-1}, \quad 140 \le t \le 180, \quad \tau > 25$$
$$t \ge 180, \quad 0 \le \tau \le \tau_{КОН}$$

Thus, the kinetics of the decomposition of FPO EPA was studied with the establishment of the kinetic parameters of the process. A kinetic equation has been found that adequately describes the decomposition process in the range under study.

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