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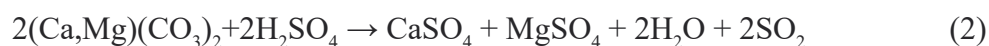E-mail: danel01kz@gmail.com

KINETICS AND MECHANISM OF DECOMPOSITION OF LOW-QUALITY PHOSPHORITES OF THE ZHANATAS DEPOSIT

Abstract. The production of extractive phosphoric acid (EPA) is one of the largest in the main chemical industry. The main part of the produced phosphoric acid is obtained by dihydrate from 24.5% of phosphorite P_2O_5. Depending on the quality of the processed raw materials, an acid containing 22-32% P_2O_5 can be obtained. The dihydrate method is one of the most developed in industrial practice. Its improvement is mainly associated with the introduction of new hardware solutions aimed at intensifying the process, optimizing and stabilizing the temperature regime (regime). The modern development of phosphoric acid production can undergo significant technological changes. thermal phosphoric acid as well as extraction phosphoric acid, and for this extraction the phosphoric acid goes through a two-stage purification process. Fertilizer DAP contains diammonium phosphate and monoammonium phosphate, as well as several additives containing primary phosphoric acid. Extraction phosphoric acid differs not only in P_2O_5 concentration, but also in the content of impurities. The main additives to the extraction phosphoric acid are sulfuric acid, calcium, magnesium, iron, fluorine, aluminum, silicon, sodium, potassium and dimensional substances. Almost all of them affect the composition and technology of diammonium phosphate. During the ammonization process, some impurities from the extracted phosphoric acid are converted to a water-insoluble form, which affects the rheological properties of the reservoir, solubility and nutrient absorption. The main component of the extraction phosphoric acid is sulfuric acid, which, when neutralized, turns into ammonium sulfate. Ammonium sulfate is a stable azygroscopic salt that can be used as a fertilizer on its own. The presence of ammonium sulfate stabilizes the granulation process; therefore, it is recommended to add sulfuric acid from thermal phosphoric acid to the diammonium phosphate composition.

Key words: fertilizer, ammonium sulfate, extraction phosphoric acid, diammonium phosphate, decomposition.

Introduction. Scientists of the Department of Chemical Technology of Inorganic Substances of the non-profit joint-stock company of M. Auezov South Kazakhstan University are studying effective methods of improving chemical and physical processes [1]. The article discusses one of the ways to further improve the technology for the production of phosphoric acid from off-balance phosphorites of the Zhanatas deposit.

A feature of the decomposition of phosphate raw materials containing carbonates [1] are chemical reactions:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2H_3PO_4 \qquad (1)$$

$$2(Ca,Mg)(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2H_2O + 2SO_2 \qquad (2)$$

At relatively low temperatures, the rate of decomposition of carbonates and phosphates is about the same. However, as temperatures rise to 80°C, the rate of carbonate decomposition increases rapidly [2,3]. This leads to the fact that at the initial stage of decomposition of the mineral gray acid often interacts with the carbonate-forming phosphorite with the strong release of carbon dioxide and the reaction mass.

In conventional known technologies, operating in a mixture of phosphorite and apatite [4], the extractor is dosed together with the phosphate raw material. In this case, sulfuric acid is fed together with the circulating

acid entering the extractor. Calcium sulfate, formed as a result of the rapid reaction of phosphorite with sulfuric acid, gets on the still insoluble apatite particles and prevents the sulfuric acid from spreading over the surface of the unreacted apatite particles [5]. In addition, the high rate of formation of calcium sulfate leads to the precipitation of small crystals. These factors explain the slower decomposition of apatite, an increase in the time of formation of small crystals, and a decrease in the productivity of the filtration stage [6].

Materials and methods. To study the kinetics and mechanism of phosphorite decomposition, Zhanatas used phosphorite of the next composition,%: P_2O_5-18.14, CaO-25.1, MgO-2.43, AI_2O_3-1.01, Fe_2O_3-0.58, F-3.0, CO_2-12.55, I.R (insoluble residue)-24.8.

The study of the kinetics and mechanism of decomposition of phosphorite was carried out according to the following method [7,8]. In a three-necked flask located in a thermostat, load phosphate rock into a dilute solution (22% P_2O_5) heated to the required temperature. After 30 minutes, add the calculated amount of sulfuric acid. The temperature in the reactor is 75°C. The amount of sulfuric acid was calculated as the amount of total calcium bound to calcium sulfate. Acid levels were determined by stoichiometry in all experiments [9]. The total mixing time of the reagents was 5 hours.

Results. The results of the study are presented in Table 1.

Table 1. Influence of various parameters on the degree of decomposition of phosphate-silicon raw materials of the Zhanatas deposit.

Table 1. Stoichiometric value of sulfuric acid, temperature -75^{0}C.

№	Sulfuric acid concentration,%	Mixing time of phosphorite with circulating phosphoric acid, min.	The degree of decomposition of raw materials, %	
			by experience	in the middle
		L:S=2.5:1		
1	56	15	77.1	76.8
2	56	15	76.5	
3	75	15	71.2	70.5
4	75	15	69.8	
5	75	60	69.8	69.0
6	75	60	68.2	
7	92	15	74.2	70.5
8	92	15	66.8	
9	92	60	70.9	69.7
10	92	60	68.5	
		L:S=4:1		
11	92	60	75.2	75.2
12	92	60	75.2	

According to the analysis of Table 1, mixing phosphoric acid with phosphoric acid for 15-60 minutes does not indicate the actual effect on the degree of decomposition of phosphorite. Experiments 3.4 and 5.6 differ from each other only by mixing phosphoric acid, the degree of decomposition of phosphorite is 70.5 and 69.0%, respectively [10,11]. In experiments 7.8 and 9.10 it is 70.5 and 69.7% respectively. Increasing the ratio of L:S in the mass with 2.5:1 to 4:1 increases the rate of decomposition of all by 4-5% [12]. Therefore, the deposition of phosphate-silicon raw material at the site of Zhanatas was taken in an equal ratio of 2.5:1 in relation to L:S. Since its further increase is not economically important. After selecting the L:S relationship, the effects of time and temperature on the phosphorite decomposition were studied. The results of the study are presented in Figure 1.
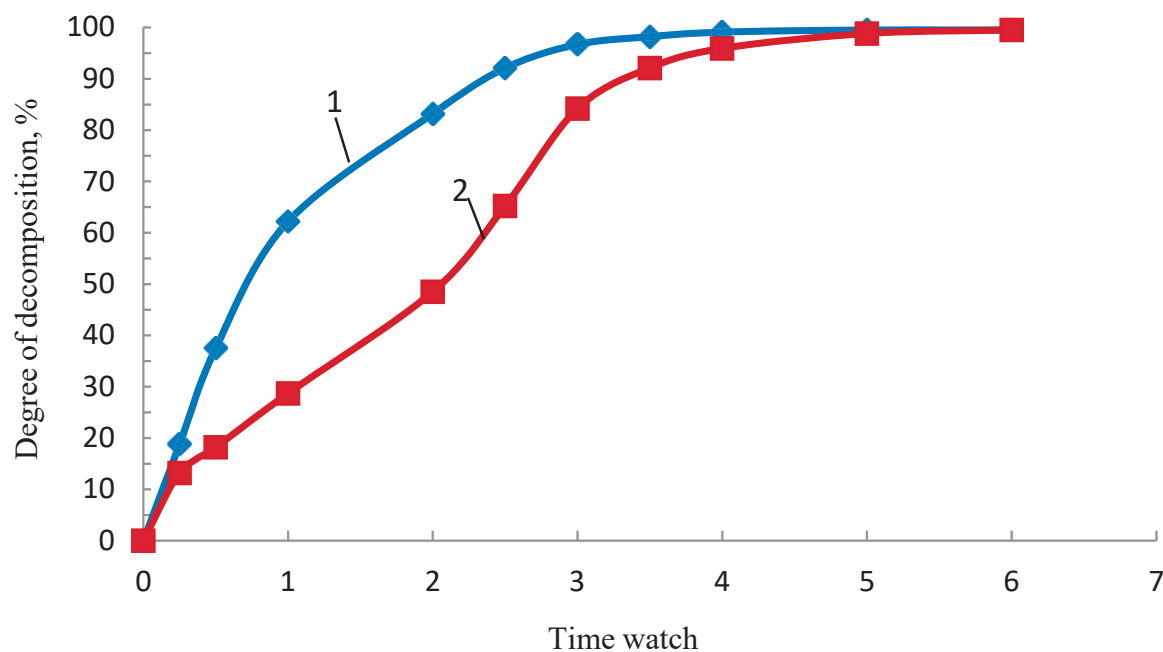
1 - temperature 95°C; 2 - temperature 75°C
Figure 1. The degree of decomposition of phosphorite is different.
Temperature dependence of process time.

Discussion. As you can see in Figure 1, the curves show that when the temperature rises from 75°C to 95°C, the decomposition time of phosphorite decreases by 2 times [13,14]. The increase in the rate of decomposition of phosphorite with increasing temperature is explained by an increase in the rate of chemical reactions [15]. In this case, the viscosity of the liquid decreases, and the diffusion rate of the components increases.
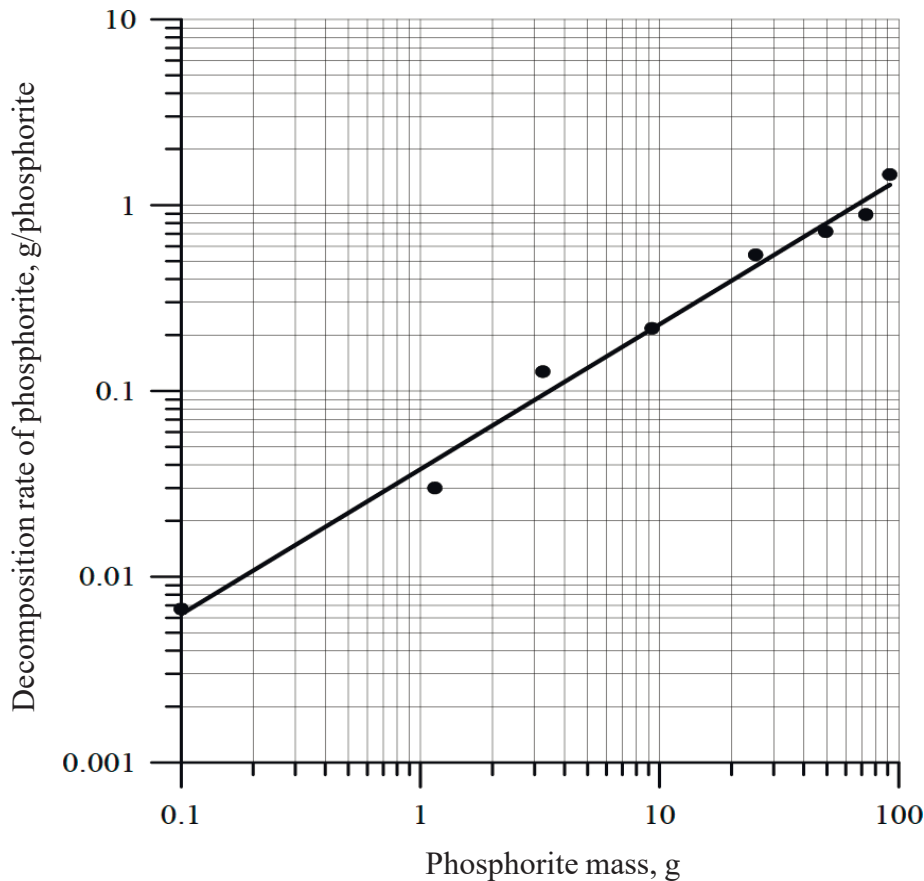

Figure 2 - The rate of decomposition of phosphorite in raw materials.
mass fraction dependence (in logarithmic coordinates).

According to the analysis shown in Figure 2, the dependence of the decomposition rate on the current value of the mass fraction of phosphorite flour shows that a wide range of changes in the concentration of phosphate raw materials does not change and is determined by the equation:

$$\frac{dddddddd}{dddddddd} = 0.038ddddd^{0.78}$$

m - mass fraction

Fig. 3 shows the temperature dependence of the efficiency of decomposition of phosphorite. The figure shows that for the decomposition of 98% of phosphorite it takes more than 6 hours at 75°C, respectively, at other temperatures 85°C - 4.5 hours, 95°C - 3.5 hours, 120°C - 3 hours.
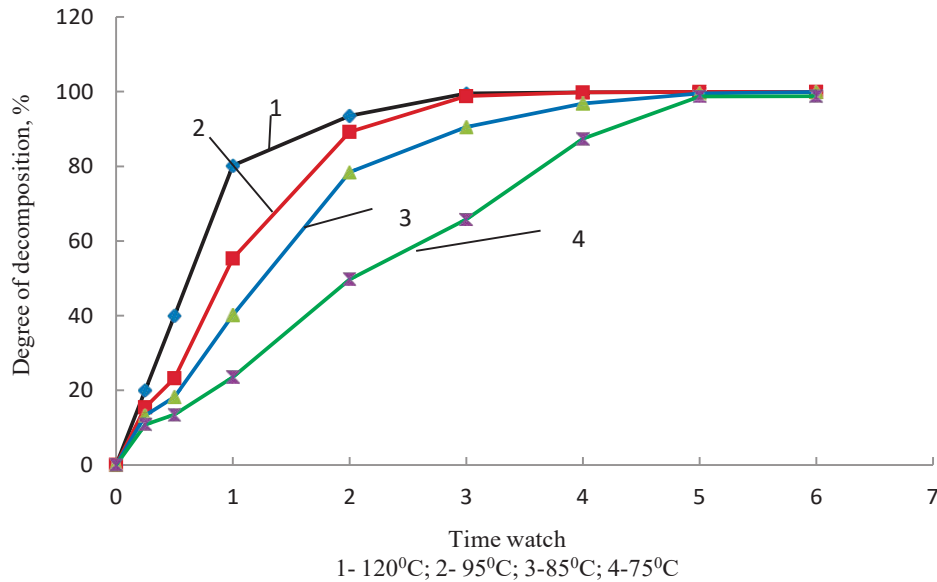

1- 120⁰C; 2- 95⁰C; 3-85⁰C; 4-75⁰C

Figure 3. Temperature dependence of the efficiency of phosphorite decomposition.

Fig 4 showsthe effect of P_2O_5 concentration and temperature on the crystalline composition of phosphogypsum formed during the decomposition of phosphate raw materials.
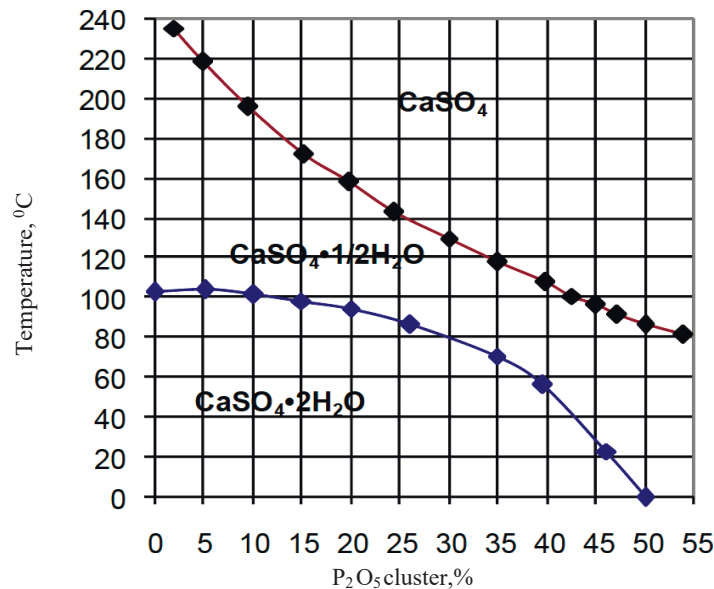

Figure 4. Influence of P_2O_5 concentration and temperature on the composition of phosphogypsum crystals.

As can be seen from Figure 4, the deposition of crystals of gypsum dihydrate can occur at temperatures below 95°C. In this case, the process takes 5 hours. At 70°C, the extraction process is completed only after 6 hours (curve-4 in Figure 3). As seen in Figure 4, the process is completed in 3 hours at 120°C. Thus, the process of obtaining EPA at a temperature of 120°C can be described as a polyhydrate process.

The temperature dependence of the rate constant of the process has the form of the Arrhenius equation:

$$\ln K = 4.5 - \frac{EEEE}{RRRRRRRR}$$

Based on the data obtained, the activity energy of the process was calculated:
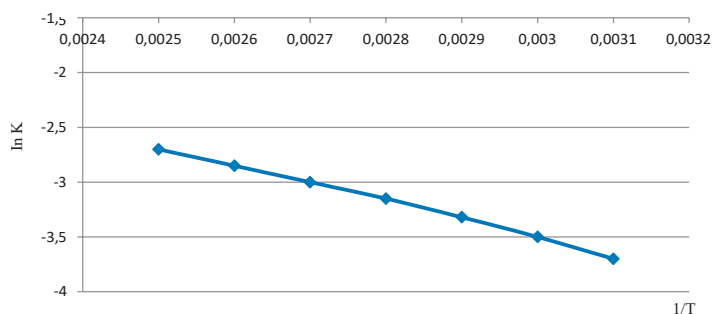$E_{active} = 5.33 kJ/mole$

Figure 5. Reverse temperature dependence of stability of process speed.

The values of the stability of the process in dihydrate mode at 75.80 and 95°C and the value of the stability of the speed at 120°C, when the process is in semi-hydrate mode, are located on the same straight line as the coordinates of Arrenus 5. the transition from dihydrate to semi-hydrate mode is preserved [7,15]. The resulting value of activation energy – 5.33 kJ/mole testifies to the fact that the diffusion process is a threshold stage of the extraction process. However, intensive mechanical mixing of the entire volume of the system used in the experiments does not affect the rate of decomposition of phosphate raw materials [16]. This indicates that the critical period represents a slow process of diffusion, which occurs directly in the raw material.

Conclusion. Based on the results of the study, the following most effective indicators for phosphate-siliceous raw materials from the Zhanatas deposit were selected:

- The process time for the extraction of the dihydrate is 4-6 hours.The temperature of the extraction process is 85-90⁰C.

To achieve effective and accurate research results, modern instruments and equipment were selected. The chemical composition of off-balance phosphorites of the Zhanatas deposit was determined, on the basis of which the mineralogical composition of the ore was calculated, taking into account the X-ray phase and IR spectroscopic analysis. Mineral content in phosphate-silicon raw materials(%): phosphorite, silicon, dolomite. For the extraction of phosphoric acid, an off-balance phosphate-silicon raw material from the Zhanatas deposit was selected.

The coefficient of decomposition of effective silicophosphate raw materials by the method of extracting phosphoric acid from off-balance phosphate-silicon raw materials of the Zhanatas deposit is 98⁰C; leaching coefficient of phosphogypsum 98.5-99.0; the time of the extraction process for the dihydrate is 240-390 min; The temperature of the extraction process is 85-90⁰C. indicators are defined.

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ЖАҢАТАС КЕН ОРЫННЫҢ БАЛАНЫСТАН ТЫС ФОСФОРИТТЕРІНІҢ ЫДЫРАУ КИНЕТИКАСЫ ЖӘНЕ МЕХАНИЗМІ

Аннотация. Экстракциялық фосфор қышқылын (ЭФҚ) өндіруі негізгі химия өнеркәсібіндегі ең ірі өндірістердің бірі. Өндірілген фосфор қышқылының негізгі үлесі дигидратты әдіспен 24,5% P₂O₅ фосфориттен өндіріледі. Өңделетін шикізатты сапасына байланысты құрамында 22-32% P₂O₅ болатын қышқыл алуға мүмкіндік береді. Дигидратты әдісі өндірістік тәжірибеде ең дамыған әдістердің бірі болып табылады. Оны жақсарту негізінен процесті қарқындатуға, температура тәртібін (режимін) оңтайландыруға және тұрақтандыруға бағытталған жаңа аппараттық шешімдер қабылдау жолында жүреді. Фосфор қышқылы өндірісінің заманауи дамуы маңызды технологиялық өзгерістерге ұшырауы мүмкін. термиялық фосфор қышқылынан, сонымен қатар экстракциялық фосфор қышқылы

алуға болатынын және ол үшін экстракциялық фосфор қышқылы екі сатылы тазалау процесінен өткізіледі. Тыңайтқыш ДАФ құрамына диаммонийфосфат және моноаммонийфосфат, сонымен қатар бастапқы фосфор қышқылының құрамындағы бірнеше қоспалар кіреді. Экстракциялық фосфор қышқылы тек қана P_2O_5 шоғырымен ғана ерекшеленіп қоймайды, сонымен қатар құрамындағы қоспалармен де ерекшеленеді. Экстракциялық фосфор қышқылы құрамындағы негізгі қоспалар күкірт қышқылы, кальций, магний, темір, фтор, алюминий, кремний, натрий, калий және өлшемді заттар болып табылады. Олардың барлығы дерлік диаммонийфосфат құрамы мен технологиясына әсер етеді. Аммонизациялар үрдісі кезінде экстракциялық фосфор қышқылы құрамынан қоспалардың бір бөлігі суда ерімейтін формаға өтіп, қоймалжыңның реологиялық қасиетіне, қоректік заттардың ерігіштігі мен сіңірімділігіне әсер етеді. Экстракциялық фосфор қышқылы құрамындағы негізгі қоспа күкірт қышқылы, ол бейтераптау кезінде аммоний сульфатына өтеді. Аммоний сульфаты тұрақты азгигроскопиялы тұз, ол өздігінен тыңайтқыш ретінде пайдалануға болады. Аммоний сульфатының қатысуы түйіршіктеу үрдісін тұрақтандырады, сондықтан термиялық фосфор қышқылынан алынатын диаммонийфосфаттың құрамына күкірт қышқылын қосу ұсынылады.

Түйінді сөздер: тыңайтқыш, аммоний сульфаты, экстракциялық фосфор қышқылы, диаммонийфосфат, ыдырату.

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КИНЕТИКА И МЕХАНИЗМ РАЗЛОЖЕНИЯ НИЗКОКАЧЕСТВЕННЫХ ФОСФОРИТОВ МЕСТОРОЖДЕНИЯ ЖАНАТАС

Аннотация. Производство экстрактивной фосфорной кислоты (ЭФК) - одно из крупнейших в основной химической промышленности. Основную часть производимой фосфорной кислоты получают дигидратом из 24,5% фосфорита P_2O_5. В зависимости от качества обрабатываемого сырья можно получить кислоту, содержащую 22-32% P_2O_5. Дигидратный метод - один из наиболее развитых в производственной практике. Его улучшение в основном связано с внедрением новых аппаратурных решений, направленных на интенсификацию процесса, оптимизацию и стабилизацию температурного режима (режима). Современное развитие производства фосфорной кислоты может претерпеть

значительные технологические изменения: термическая фосфорная кислота, а также экстракционная фосфорная кислота, и для этой экстракции фосфорная кислота проходит двухступенчатый процесс очистки. Удобрение ДАФ содержит диаммонийфосфат и моноаммонийфосфат, а также несколько добавок, содержащих первичную фосфорную кислоту. Экстракционная фосфорная кислота отличается не только концентрацией P_2O_5, но и содержанием примесей. Основными добавками в экстракционную фосфорную кислоту являются серная кислота, кальций, магний, железо, фтор, алюминий, кремний, натрий, калий и размерные вещества. Практически все они влияют на состав и технологию диаммонийфосфата. В процессе аммонизации некоторые примеси из экстрагированной фосфорной кислоты превращаются в нерастворимую в воде форму, что влияет на реологические свойства резервуара, растворимость и поглощение питательных веществ. Основным компонентом экстракционной фосфорной кислоты является серная кислота, которая при нейтрализации превращается в сульфат аммония. Сульфат аммония-это стабильная азигроскопическая соль, которую можно использовать как удобрение самостоятельно. Наличие сульфата аммония стабилизирует процесс гранулирования, поэтому в состав диаммонийфосфата рекомендуется добавлять серную кислоту из термической фосфорной кислоты.

Ключевые слова: удобрение, сульфат аммония, экстракционная фосфорная кислота, диаммонийфосфат, разложение.

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