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ПРОБЛЕМЫ И ПЕРСПЕКТИВЫ ПРОИЗВОДСТВА И КВАЛИФИЦИРОВАНИЯ ФОСФОРНОЙ КИСЛОТЫ

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Квалифицирование фосфорной кислоты осуществляется в зависимости от использования фосфатов различных месторождений и необходимого качества конечных продуктов. Получение фосфорной кислоты нужного качества осуществляется с учетом трех аспектов: ресурсо-энергетического, экологического и комплексности переработки. Рациональное использование природных ресурсов и уменьшение загрязнения окружающей среды является определяющим фактором при выборе технологических режимов комплексной переработки сырья с сокращением объёмов отходов всех видов или перевода их в формы, легко поддающиеся вторичной переработке или специальному хранению. Отсутствие экономически обоснованных технологий переработки фосфогипса обусловливает его преимущественное складирование. Вторым компонентом, требующим утилизации, является фтор. В связи с этим, очистка фосфорной кислоты от фтора должна использовать технологии, реализующие улавливание выделившихся в газовую фазу фтористых соединений. Это актуально с точки зрения комплексности переработки сырья с извлечением редкоземельных элементов. Применение механохимической активации позволяет достигать наноразмерного уровня. В меньшей степени указанный аспект относится к стадии сернокислотного разложения, протекающего с участием трёх фаз: твёрдой, жидкой и газовой. В свою очередь, структура поверхности газожидкостного слоя играет роль энергетического барьера для испарения. Для установления основных энергетических закономерностей концентрирования и дефторирования в тарельчатом аппарате и оптимизации процесса была разработана теплофизическая модель, в которой область эффективных параметров определялась путём совместного решения ряда уравнений относительно искомых ингредиентов в диапазоне концентрации фосфорной кислоты 52-65%. Решение задачи комплексной очистки экстракционной фосфорной кислоты может осуществляться адсорбционными методами, которые позволяют удалить в той или иной степени практически все примеси.

Ключевые слова: фосфорная кислота, апатитовый концентрат, механохимическая активация, механохимический синтез, нанотехнология, редкоземельные элементы, адсорбент

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PROBLEMS AND PROSPECTS OF PRODUCTION AND QUALIFICATION OF PHOSPHORIC ACID

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The qualification of phosphoric acid is carried out depending on the use of phosphates of various deposits and the necessary quality of the final products. An acquisition of phosphoric acid of the required quality should be carried out taking into account three aspects: resource-energy, ecology and complex processing. Solving the problems of one aspect entails solving the problems of the other aspects. The rational use of natural resources and the reduction of environmental pollution is the determining factor in the choice of technological regimes for complex processing of raw materials with a reduction in the volume of waste of all kinds or transferring them into forms easily recyclable or specially stored. The absence of economically sound technologies for processing phosphogypsum determines its preferential warehousing. The second component that requires recycling is fluorine. In this regard, the purification of phosphoric acid from fluorine should use technologies that realize the trapping of fluorine compounds released into the gas phase. This is relevant from the point of view of the complexity of processing raw materials with the extraction of rare-earth elements. The use of mechanochemical activation makes it possible to achieve a nanoscale level. To a lesser extent, this aspect relates to the stage of sulfuric acid decomposition, proceeding with the participation of three phases: solid, liquid and gas. In turn, the surface structure of the gas-liquid layer plays the role of an energy barrier for evaporation. To establish the basic energy patterns of concentration and defluorination n the disc apparatus and to optimize the process, a thermophysical model was developed in which the range of effective parameters was determined by the joint solution of a number of equations for the desired ingredients in the phosphoric acid concentration range of 52-65%. The solution of the problem of complex purification of wet-process phosphoric acid can be carried out by adsorption methods that allow to remove to some extent almost all impurities.

Key words: phosphoric acid, apatite concentrate, mechanochemical activation, mechanochemical synthesis, nanotechnology, rare earth elements, adsorbent

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Obtaining phosphoric acid is an example of one of the large-tonnage world production of chemical technology. According to the analytical data the global phosphoric acid production in 2016 year in terms of P_2O_5 was 48 million tons. Among them 4.2 million tons were produced in Russia [1].

The raw material for phosphoric acid is phosphate concentrates of igneous and sedimentary origin, which opening is generally carried out by two methods: thermal and acid decomposition. The production of phosphoric acid by sulfuric acid decomposition of natural phosphates in the present and in near-term outlook is carried out with the following operations: dissolution of phosphate mineral in sulfur-phosphate solution, crystallization of calcium sulphate, separation by filtration of production solution and treatment of the resulting acid with the concentrating in various devices mainly up to 52-55% P_2O_5 [2, 3].

Basically, the qualifying phosphoric acid is carried out with two-way:

1) Depending on the use of phosphates of different fields having significant differences on composition. On the territory of the Russian Federation beside the dominant use of apatite-nepheline ore of Khibinskaya group Beloziminskoe and Oshurkovskoe deposits are the most perspective and best, as well as several others. First of all among them the phosphate Karatau mine, partly Egoryevskoe and Vyatka-Kama can be pointed out [4].

2) Depending on the required quality of the final products and the further processing of phosphoric acid the purified phosphoric acid of improved qualification is obtained according to State Standard. For this purpose special cleaning methods are applied, which are often combined with a concentration process [5]. At the present time, in addition to the dominant use of phosphoric acid for fertilizer production (over 80%) feed phosphates are about 6% of acid and more than 8% are technical and food ones [6].

In the frame of each qualification the positive changes in the quality, physical-chemical and performance are motivated with the constant improvement of existing and the creation of fundamentally new technologies. By-turn, the development of modern technology involves taking into account the increasing scarcity of natural resources and the need for their rational use, and to reduce the negative impact on the environment. At the production of phosphoric acid the possibility of allocating and utilization at various steps of the rare earth elements is important, which in turn determines the complexity and re-cyclicity of the technology used [7].

Thus, obtaining the required quality of phosphoric acid should be carried out with considering three aspects: energy resources, environmental protection, and complexity of processing. At the same time, all three from mentioned above aspects are indissoluble connected, and technological solution of one problem necessarily entails to the solution of other.

Due to a large-scale production of phosphoric acid, phosphogypsum is the most valuable waste. For example: in 2016 in Russia about 18 million tons of phosphogypsum (in terms of dry calcium sulfate dehydrate) were formed. Depending on the quality of raw materials per 1 ton of P_2O_5 about 4.2-6.8 tons of phosphogypsum are formed in phosphoric acid [2]. The absence of economically proved technologies processing phosphogypsum into target products specifies its preferential warehousing, which has a negative impact on the environment. Implementation of the various environmental activities to eliminate this negative action requires additional costs.

The second component in quantity respect in the phosphate raw material requiring disposal is fluorine. For technologies that may be considered with respect to technical and economic expediency of isolating the intermediate product (hydrogen fluoride or fluorosilicic acid) the technologies providing the concentrating phosphoric acid to a content of more than 41% of P_2O_5 can be considered.

An emission of fluorine compounds to the gas phase at a production of phosphoric acid is drawn to special attention due to their carcinogenic character. They have a 2nd class of toxicity (MPC of fluorine in air – 0.5 mg/m^3). Therefore, cleaning the EPC from fluorine at the preparation of high-purity grades of acid should use technology, realizing trapping of fluorine compounds evolving to gas phase. This is relevant in terms of the complexity of the processing raw materials with the extraction of rare earth elements.

Khibinsky apatite concentrate contains about 1% of oxides of rare earth elements, which constitute the dominant part of the light rare earth group (lanthanum, cerium, praseodymium, neodymium).

In Russia, up to 85% of apatite concentrate is currently undergone with sulfuric acid opening to obtain phosphoric acid. Thereby, the bulk of the rare earth elements (0.5-0.7%) is deposited as a waste into calcium sulphate (hemihydrates or dehydrate). The rest of the rare earth elements remains in phosphoric acid solutions in a form of suspensions or poorly soluble salts. Upon receipt of fertilizers by ammonation of phosphoric acid this part of the rare earth elements is irrevocably lost at the fertilizers application [6, 8].

Considering the scale of production of phosphoric acid, isolation of rare earth elements from its solutions is the most accessible and attractive. But the rare earth elements isolation from phosphogypsum is a labor-consuming and cost-based process.

The analysis of the accumulated experimental data in a frame of researches on complex processing of apatite concentrate sets out the main requirements for the technological processes of the associated extraction of Sr, Ln, F.

Therefore, the basic principles of creation of technologies at production of phosphoric acid are: the resource-saving, energy saving, ecological safety and complexity of processing raw materials which are expressed in discharge coefficients and also in changes in the physic-chemical and operational characteristics of the received products. From this viewpoint the systems realizing nanotechnologies with use of mechanochemical activation and mechanochemical synthesis will have the special prospect [9].

The use of mechanochemical activation allows achieving a nanoscale level with a partial rupture of molecular bonds in the process as a whole. This is due to the exergetic approach, which can be approached and according to which we will deal with thermal exergy due to the difference in the composition of the acids in the system and at the outlet and, accordingly, temperatures and pressures.

To a lesser extent, this aspect refers to the step of sulfuric acid decomposition of apatite concentrate, which takes place with the participation of three phases: solid, liquid and gas. At the same time, the solution of the energy problem of mechanochemical technology is closely related to the question of the possibility and optimization of the participation of the liquid or gas phase at intermediate steps of synthesis.

It was shown in [11] that due to transformation of mechanical energy of destruction and a rupture of bond at the molecular level (10^{-9} m) there is an increase in excess free energy of Gibbs. This value is applied for the description of non-equilibrium states in thermodynamics and expresses affinity of the activated substance in the course of transition of it in a stable state. As a result, physical and chemical properties of a product and first of all its solubility are improved considerably.

Another effect of mechanochemical activation of phosphorites is their defluorination (by 30-40%), mainly due to heating of the system under treated by 85-90 °C [9, 10].

To determine the role of the gas and liquid phases with mechanochemical activation, it was proposed to use the relative degree of saturation of the multicomponent gas mixture [12].

$$\varphi=\sum_{i=0}^{n} z_i / K_i\left(T \cdot P\right), \qquad (1)$$

where: z_i is the composition of the initial gas mixture supplying the reactor; n is the number of components; $K_i(T, P)$ is the phase equilibrium constant; $i = CO_2, H_2O, O_2, N_2$.

The high energy efficiency of mechanochemical synthesis in a gas-liquid media is associated not so much with the grinding of solids in a liquid, as with the separation of a highly disperse solid phase from a liquid medium. Essentially, mechanochemical synthesis in a gas-liquid media is a combination of processes of dispersing the grinded component and condensation of the chemical reaction product formed in the liquid layer on the activated surface of highly dispersed particles [12].

Nanotechnologies at the mechanochemistry of liquid in a volume of the equilibrium fluid ("liquid-gas") were developed for the dehydration and de-fluorination processes of phosphoric acid using an intensive plate-type heat and mass transfer apparatus [11, 13]. In this case, the only kind of deformation is all-round compression, and the local mechanochemical state is characterized by the set of pressure P.

The affiliation of such systems to nano- is illustrated for the processes of dehydration and defluorization by the example of the evaporation of a spherical droplet into the gas phase, depending on its size by the Laplace equation:

$$P = 2\sigma/r, \qquad (2)$$

where σ – is the surface tension, r – is the droplet radius.

The pressure inside the droplet is increased at the decrease in a droplet radius.

For plate device operating in a foam mode with an intermediate gas-liquid layer the surface tension can be expressed in terms of the height of the layer, h, by the equation:

$$\delta=\int_0^h\left(P_h-P_t\right)dh, \qquad (3)$$

where P_h and P_t are the normal and tangential pressure components.

The r values calculated on the known formulas [8] are 50-80 nm.

In turn, the surface structure of the gas-liquid layer plays the role of an energy barrier for evaporation. Therefore, for a given mechanochemical nanoprocess, the higher interfacial surface of the layer and, correspondingly, the greater the pressure drop, the lower the temperature, the process can be carried out [15, 16]. In addition, it is known that the free energy of the interfacial surface (surface tension) is a function of its charge [14].

Change in a reactionary ability and physical and chemical characteristics at the mechanochemical activation of substance facilitates the transfer of charged particles which is carried out by diffusion on a surface in a type of growth of the last that leads to decrease in energy of activation of process of thermal dehydration. The plate-shaped device developed in JSC Voskresensky NIUIF was tested in experimental-industrial and industrial conditions and is universal one since it can be used as the concentrator, a deftorator and an absorber.

To establish the basic energy regularities of concentration and defluorination in the plate apparatus and to optimize the process, a thermophysical model was developed in which the range of the most efficient parameters (temperature, expenditure) were determined by combine solution a number of equations with respect to the desired ingredients in the phosphoric acid concentration range of 52-65%. This regime corresponds to the production of superphosphoric acid, in which not only dehydration and intensive defluorination occurs, but also phase transitions of orthophosphates to pyrophosphates, pyrophosphates to polyphosphates, etc. take place [15-18].

Changes in the physico-chemical properties of purified and untreated superphosphoric acid obtained in an industrial plate device in comparison with thermal phosphoric acid, close to the binary system ($2H_3PO_4 \cdot H_2O$), as well as with industrial superphosphoric acid (70% P_2O_5) obtained with a bubbling evaporator are presented in Table 1 [15, 16].

For the samples obtained in the plate device under mechanochemical activation conditions, not only the composition, the freezing point, the boiling point, the surface tension, the viscosity, etc. are corrected, but also the temperature of its formation decreases, which in turn predetermines a significant reduction of the total energy consumption for obtaining this product.

Table 1

Comparison of physico-chemical characteristics of superphosphoric acids

***Таблица 1.* Сравнение физико-химических характеристик суперфосфорных кислот**

Parameter	Unpurified superphosphoric acids. 65% P_2O_5 2.8% SO_4	Purified superphosphoric acids. 65% P_2O_5 0.25% SO_4	Thermal evaporated phosphoric acid. 65% P_2O_5 0.01% SO_4	Industrial superphosphoric acids. 70% P_2O_5 3.1% SO_4
1.T of freezing, °C	-35	-19	28.8	-41
2. Boiling point, °C	165	169	172	238
3. Content of polyforms, %	5.9	1.3	0.1	34
4. Density at 20 °C, g/cm^3	1.856	1.765	1.748	1.982
5. Viscosity at 20 °C, mPa	220	140	110	1800
6. Surface tension at 25 °C, N/m	0.081	0.078	0.076	0.085
7. Vapor pressure at 80 °C, kPa	5.33	3.12	2.65	6.11

Table 2 shows the activation energy and the temperature of phase transitions at the production of superphosphoric acids with mechanochemical activation in a plate device in comparison with the electric heating in a glass without mixing. The methodology for determining the parameters is indicated in the publications [14, 15].

Table 2

The activation energy and the temperature of phase transitions at the production of superphosphoric acids under various conditions

***Таблица 2.* Энергия активации и температура фазовых переходов при получении СФК в различных условиях**

Conditions for process	Steps of phase transitions					
	$H_3PO_4 \rightarrow H_4P_2O_7$		$H_4P_2O_7 \rightarrow H_5P_3O_{10}$		$H_5P_3O_{10} \rightarrow H_{n+2}P_nO_{3n+1}$	
	$\Delta E_{акт}$ kJ/mol	T, °C	$\Delta E_{акт}$ kJ/mol	T, °C	$\Delta E_{акт}$ kJ/mol	T, °C
Electric heating in a glass without stirring	72	110	32	180	17	280
Mechanochemical activation in the plate-shaped device	64	85	27	130	14	210

At pilot and industrial tests, the change in pressure of the system as a whole and on steps was used as measuring parameter the increase of which allows to reduce the concentrating temperature and which has a direct correlation with the coefficients of heat and mass transfer. These coefficients serve as a criterion for the efficiency and intensity of processes in a two-phase system. Table 3 compares the calculated parameters for different methods of concentrating and defluorination [16, 18].

All total energy and environmental benefits of the scheme for obtaining the superphosphoric acids that implements the mechanochemical activation in the "liquid-gas" system using an industrial plate device operating in "Balakovskie Mineralnye Udobreniya" are presented in Table 4 in comparison with other industrial schemes.

Obtaining superphosphoric acids is economically advantageous and expedient for production of liquid complex fertilizers in a form of ammonium polyphosphates because of the large amount of heat evolving at ammoniation. In addition, a high concentration of P_2O_5 in superphosphoric acids allows to reduce transportation costs in case of using this acid as a commercial product supplied to other regions.

Table 3

Comparison of methods of purification and defluorization of wet-process phosphoric acid by heat and mass transfer

***Таблица 3.* Сравнение способов очистки и дефторирования ЭФК по тепломассопередаче**

Concentrating method or apparatus	The fluorine content in wet-process phosphoric acid, %		Degree of defluorination, af,%	Inter-phase surface, S_0, m^2/m^2	The process temperature t, °C	Coefficient of a heat transfer, Kt, W(m^2 °C)	Coefficient of a mass transfer, Km kg/m^2
	Initial	Final					
Surface Steam Vacuum	0.6 – 0.7	0.35	56.9	-	150	250	73
Contact gas in the air-lift device	0.6 – 0.7	0.25	69.2	До 9	180	4070	89
Contact gas foam in the plate-shaped device	0.6 – 0.7	0.12	85.2	До 280	135	12700	110
Contact with the steam foam in plate-shaped device	0.6 – 0.7	0.05	93.8	До 500	145	18300	207

Table 4

Comparison of technical and economic indicators of industrial plants for the production of superphosphoric acids operating in the Russian Federation

***Таблица 4.* Сравнение технико-экономических показателей промышленных установок по получению СФК, действующих в РФ**

The name of indicators	Ammophos	Belorechensk "Mineral fertilizers"	Balakovo Mineral Fertilizers
Method of production	Cherepovets Vacuum surface, the form of «Спи-Батиньоль»	Contact, in the airlift device	Contact, in the plate-shaped device
Installed capacity (one thread), thousand tons/year P_2O_5	50	75	75
Content in superphosphoric acids	68 – 70 0.35 – 0.38	64 – 66 0.24 – 0.27	64 – 66 0.12 – 0.15
P_2O_5, %	195 – 202	170 – 180	130-140
F, %	512	4070	13130
Concentrating temperature °C	232.9	112.7	56.7
Heat transfer coefficient W/(m^2· °C)	- 0.286	6.85 1.0	1.2 0.25

At obtaining highly purified phosphoric acid, the technical and economic picture is somewhat different. Analysis of data on consumption of purified phosphoric acid, starting from 2000, indicates an annual increase by 3.3%, and the global volume reached 4000 thousand tons of P_2O_5 in 2015 [22].

In the initial unpaired phosphoric acid [19], all impurity components are in the form of strong complex salts containing sulphates, fluorides, iron, aluminum and rare earth elements, humates of iron, which create the structure of the solution.

The purification process with extraction of the necessary components will proceed than easier than more disordered (destructured) this system will be. The measure of disorder, removal from equilibrium according to the second law of thermodynamics, is the value of entropy. The use of mechanochemical activation for obtaining purified phosphoric acid for the destruction of structure mentioned above can be only the step in the general technological scheme by blowing fluorine in the plate deflator [19].

The solution of the problem of complex purification of phosphoric acid can be carried out successfully by adsorption methods that allow removing to some extent practically all of the above components.

Therefore, it can be concluded that the introduction into phosphoric acid solutions of sulfuric and nitric acids as well as ammonium hydroxide or their salts in a small amounts which are equivalent to content in system of salting out admixtures of Fe^{3+}, SO_4^{2-}, SiF_6^{2-} activates the process.

On basis of given points the technology of obtaining purified phosphoric acid of technical, food, medical quality with the simultaneous extraction and utilization of fluorine, silicon, calcium, iron, aluminum and rare earth elements compounds was developed. The technology is based on combining the processes of concentrating phosphoric acid, blowing fluoride compounds with hot flue gases (or steam) and sorption of all impurity ingredients on activated carbons in a single circular contour. The main apparatus of such a circuit are the column-type plate de-fluorinator operating in the foam mode and the adsorption column [16-18].

The initial carbon material is active carbon of BAU-A of GOST 6217-74 grade which is used as a sorbent for purification of wet-process phosphoric acid or as a raw material for chemical modification.

At this complex treatment, most fluoride compounds are transferred to the gas phase and utilized in a form of hydrofluoric acid, and the ions of calcium, aluminum, iron and rare earth elements are adsorbed on the coals, concentrated at the circulation of the production solution, and then desorbed under the regeneration of the adsorbents. The intensifying effect of sulfuric and nitric acids can also be used at the modification of standard coals and at the regulation of the content of their selective active sites by mechanochemical synthesis [8]. Regarding the extraction of rare earth elements from phosphogypsum, the specialists on a repulpation of the latter recommend all the same sulfuric and nitric acids with the subsequent sorption extraction of ingredients from the pulp.

The use of adsorbents allows to increase not only the depth of purification from compounds of iron, aluminum, silicon, sulfur, rare earth elements, but also to increase the rate of purification of fluoride compounds. Details of the purification of phosphoric acid from fluorine and other elements, as well as the extraction of rare earth elements by charcoal-type BAU modified with various additives, are given in the publication [16].

Concerning the rare earth elements sorption process, it should be noted that, in most researchers judgment, process mechanism is close to ion exchange and, in part, to molecular sorption. The acid itself (phosphoric acid) adsorbs on the coals physically and it can later be easily separated from the extracted components upon desorption [19].

A new approach is proposed for extracting rare earth elements from phosphoric acid, which represents the sorption separation of concentrated electrolytes on ion exchangers using the "acid retention" effect.

Table 5

The content of fluorine in phosphoric acid purified in different ways

***Таблица 5.* Содержание фтора в очищенной разными способами ЭФК**

Experimental conditions	Content of fluorine in purified phosphoric acid solution, mas. %	
	BAU	Carbon black P514
Initial phosphoric acid	2.2	2.2
Blowing fluoride compounds	0.95	0.95
Adsorption purification	1.47	0.27
Blowing in the presence of an adsorbent	0.35	0.04

A comparison of the various combinations of the use of adsorbents with blow-off in a plate-type concentrator-deflator for the preparation of purified phosphoric acid is given in Table 5 [23].

Realization of the described scheme for obtaining purified phosphoric acid with simultaneous extraction of rare earth elements in a large scale will allow classifying this scheme as an energy technology one combining the maximum use of raw materials and energy taking into account the energy principles mentioned above.

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