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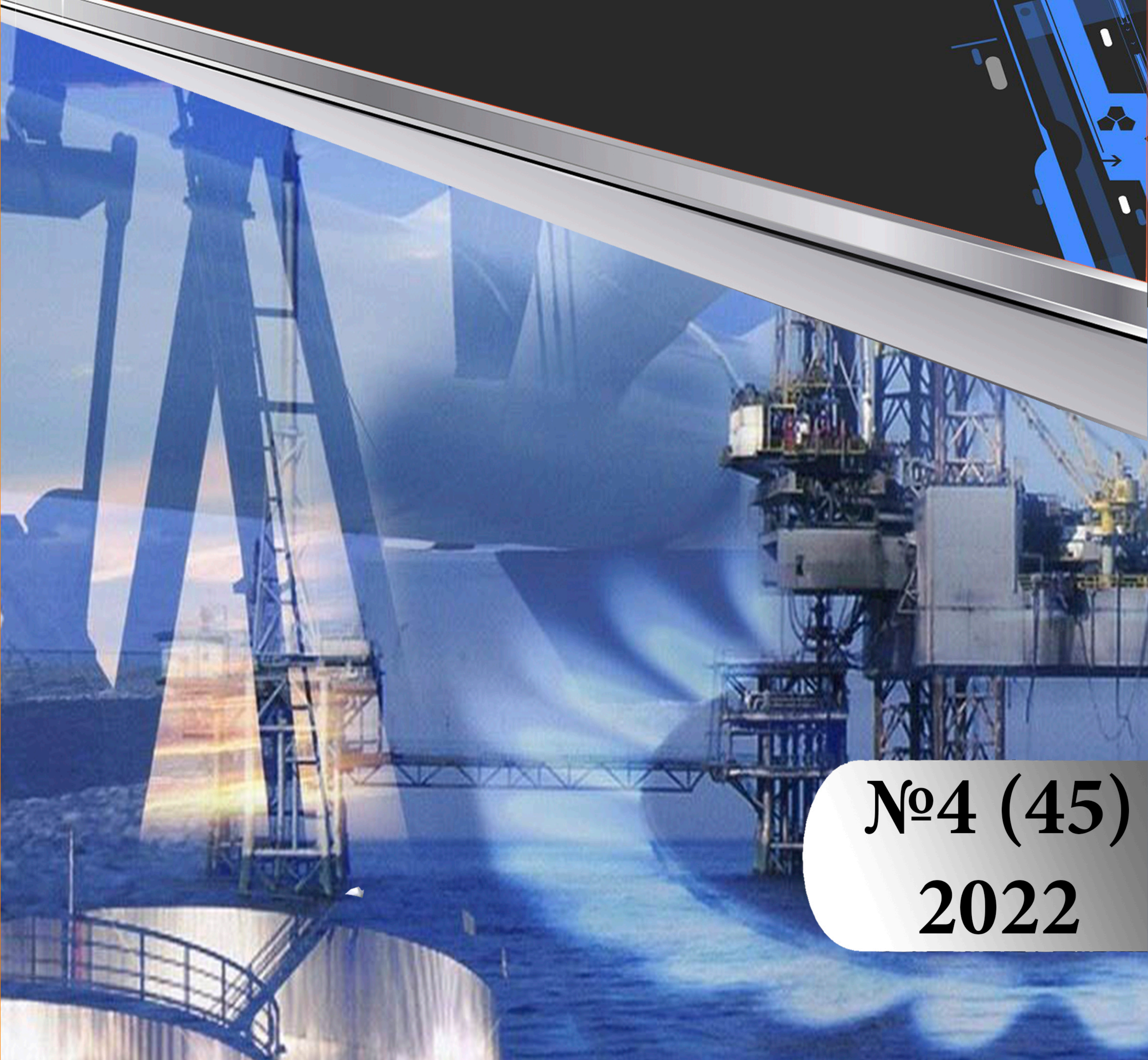

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WAX ANTI-SETTLING AGENTS BASED ON FATTY ACIDS AND ALCOHOLS FOR WAXY OIL

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ABSTRACT

The issues of obtaining and studying the depressant activity of an additive based on maleic anhydride and a mixture of unsaturated carboxylic acids with C_{18} carbon atoms, that is, linoleic ($C_{18}H_{32}$) and ($C_{18}H_{29}$), which were isolated from vacuum distillates of cotton soap stocks are considered in this article. The authors propose a new composition of the wax anti-settling agent - "Amingoss". According to the proposed method, fatty acids are esterified with methanol with air at 110-150 0C to a hydroxy acids' content of 20-60 wt.%, followed by condensation with ethanolamines in a molar ratio of acid: ethanolamine 1:1, in a toluene medium by azeotropic distillation of the reaction water. Fatty acids with an acid number 95 mg KOH/g are oxidized with air at 110-150°C of temperature for 18 hours to a hydroxy acids' content of 22.8 wt.%. According to the proposed method, fatty acids are esterified with methanol with air at 110-150 0C to a hydroxy acids' content of 20-60 wt.%, followed by condensation with ethanolamines in a molar ratio of acid: ethanolamine 1:1, in a toluene medium by azeotropic distillation of the reaction water. Fatty acids with an acid number 95 mg KOH/g are oxidized with air at 110-150°C of temperature for 18 hours to a hydroxy acids' content of 22.8 wt.%. The depressant activity of the composite wax anti-settling agent (further depressant additive) was studied specifically on the Kumkol, Ashchisai oils and the Kumkol-Akshabulak oil mixture (60:40).

Key words: paraffins, oil, additive, pipeline, viscosity, amingoss, fatty acid, methanol.

INTRODUCTION

Transportation of highly paraffinic oil through existing oil pipelines is economically more rational for companies involved in the transport of hydrocarbons. The produced oil in Kazakhstan is delivered to the destinations through the pipelines of the system of "KazTransOil" JSC, which is the national operator of the main oil pipeline of the Republic of Kazakhstan, which owns more than 5 thousand km of oil pipelines [1]. The work oil's pipeline transportation today is fraught with a number of difficulties, since it is known that most of the oils of Kazakhstan fields are highly viscous, paraffinic [2]. Paraffin compounds in various amounts are almost always present in the produced oil, in particular, there is enough paraffin in the oils of the South Torgai depression (Kumkol, Aryskum, Akshabulak, Nuraly and others), which contain up to 15% or more of paraffins [2]. It is believed that oil for transportation should contain no more than 6% paraffins [3]. Serious problems arise in the pipeline during oil transportation, due to the crystallization of paraffins and an increase in the viscosity of oil: the pressure in the pipeline increases, the consumption of electricity for pumping equipment and their wear, the throughput of the pipeline decreases. In cold climatic regions, oil transportation is even more complicated due to paraffin deposits directly on the inner walls of pipelines, that is, the cross section of the pipeline narrows and, as a result, productivity decreases. [4,5]. To reduce paraffin deposits on the pipelines' walls during oil pumping, various methods are used, among which heat treatment of oil through certain distances of the pipeline, the use of chemicals to reduce viscosity, and others are still used. Today, among the numerous methods of combating paraffin deposits during oil transportation, the most effective is the introduction of chemical reagents that prevent or inhibit the deposition of paraffins. Surfactants and pour point depressants are used as such reagents. In addition to preventing paraffin deposits, pour point depressants improve the rheological properties of oil, reduce the pour point, which is important for its further transportation it is their advantage. One way to improve the properties of high-viscosity and high-solidity oils is to introduce synthetic components into their composition, which can be used as low molecular weight olefins, long-chain alpha-olefins, and their co-oligomers. In this case, long-chain alkyl radicals, aromatic hydrocarbons with long alkyl radicals, and heterocyclic compounds act as carriers of depressant properties [6]. The depressants and paraffin inhibitors in use are quite effective currently, but their production is complex and many of them are still expensive. In the chemical reagents market for the oil industry, the range of inhibitors of asphalt, resin and wax deposits (ARPD) is limited, which are effective and relatively inexpensive [7]. In connection with the above, the development of technologies for obtaining new depressant compositions and inhibitors of paraffin deposits for highly solidifying and high-viscosity oils based on local raw materials is of great practical importance [8,10]. Currently, the development of new technologies for the production of depressant additives based on cheap available raw materials and characterized by good viscosity-temperature properties is an urgent task for the transportation of high-viscosity oils. [11]. The criteria for evaluating the effectiveness of depressant additives to oils in solving the above problems are the reduction in the pour point and their rheological characteristics [12-14].

The aim of this work is to obtain and study the depressant activity of an additive based on maleic anhydride and a mixture of unsaturated carboxylic acids with C_{18} carbon atoms, that is, linoleic ($C_{18}H_{32}$) and ($C_{18}H_{29}$), which were isolated from vacuum distillates of cotton stocks. Previously, these acids were obtained by us from the tars of the distillation of fatty acids by their alkaline saponification, neutralization with sulfuric acid, and subsequent isolation by gasoline extraction. The fatty acids obtained in this way contained a number of impurities, which affected the purity and relatively high cost of the final product [11].

MATERIALS AND METHODS

When obtaining a depressant action reagent, a mixture of linoleic and linolenic acids in a ratio of 1:1, maleic anhydride, and mono-ethanolamine were chosen as starting compounds. Further, when developing the composition, a stabilizer was used - technical gossypol. Linoleic monobasic carboxylic acid has two isolated double bonds in its structure, and linolenic acid has three isolated bonds, which makes it relatively easier to react with maleic anhydride. In the original soap stock, which is a product of cottonseed oil refining, its content is 25-25%. Linoleic and linolenic acids were taken from the soap stock vacuum distillation product. Linoleic and linolenic acids are in the form of geometric cis, tans isomers in cotton soap stock [12]. It should be noted that fatty acids, contained in a significant amount in the composition of soap stocks and distillation tars, having long chains of carbon atoms with a carboxyl group and a hydrocarbon radical, demonstrated a chemisorption ability, due to which they are in practical value for obtaining surfactants for various purposes [15].

RESULTS AND DISCUSSION

The use of additives based on ethylene-vinyl acetate copolymers to improve the low-temperature properties of oils and petroleum products is widely known. However, a significant disadvantage of such additives is their insufficiently good solubility in oils and oil products, as well as the selectivity of action to certain types of oils and oil products. Various methods are proposed for controlling the properties of finished ethylene-vinyl acetate copolymers to improve their solubility and increase the depressant properties of additives based on them [16].

We propose a new composition of a pour point depressant under the working title "Amingoss". According to the proposed method, fatty acids (FA) are esterified with methanol air at 110-150 ^{0}C to a content of hydroxy acids of 20-60 wt.%, followed by condensation with ethanolamines in a molar ratio of acid: ethanolamine 1:1, in a toluene medium by azeotropic distillation of the reaction water. Fatty acids with an acid number of 95 mg KOH/g are oxidized with air at a temperature of 110-150°C for 18 hours to a hydroxy acids' content of 22.8 wt.%. Oxidized fatty acids, toluene up to 50% for fatty ones are loaded into a batch reactor with a reflux condenser, heated to 80 ° C and monoethanolamine is introduced. In order to prevent foaming of the reaction mass, monoethanolamine is dosed within 2 hours, the heat of neutralization is removed by cooling the tank jacket with water. After the addition of monoethanolamine, the temperature is raised to the boiling point of the solvent (110°C). The reaction water is removed by an azeotropic mixture with a solvent. Condensation is carried out for 4-8 hours until the acid number of the reaction mixture is reduced to no more than 5 mg KOH/g; the degree of FA conversion is about 80%.

As noted above, "Amingoss" based on the composition, wt. %: esterified fatty acids - 40; ethanolamine - 40; toluene - 20, is also obtained according to the technological scheme shown in Fig. 1, but according to the following technological scheme. The solvent is loaded into the reactor 1 - toluene in an excess amount of 1,2 times relative to the final composition of the pour point depressant from the measuring tank 2 and the entire amount of esterified FA from the measuring tank 4, the mixture is heated to 80 ° C and the supply of ethanolamine from the measuring tank 6 is started. In order to prevent foaming of the reaction mass, ethanolamine is introduced in small portions over 2 hours, the heat of neutralization is removed by cooling the reactor jacket with water. After supplying the entire amount of ethanolamine, stirring is continued for 0.5 hour, then the temperature is raised to the boiling point of the solvent - 110 ° C. The reaction water is removed by an azeotropic mixture with part of the solvent. Condensation is carried out for 4 hours until the acid number of the reaction mixture is reduced to no more than 5 mg KOH/g; the content of toluene should not decrease below 20 wt%, the degree of conversion of esterified fatty acids is about 80%. The finished pour point depressant is drained through the lower fitting of the reactor and enters the filter 5, after filtering the finished commodity form of the pour point depressant enters the packaging.

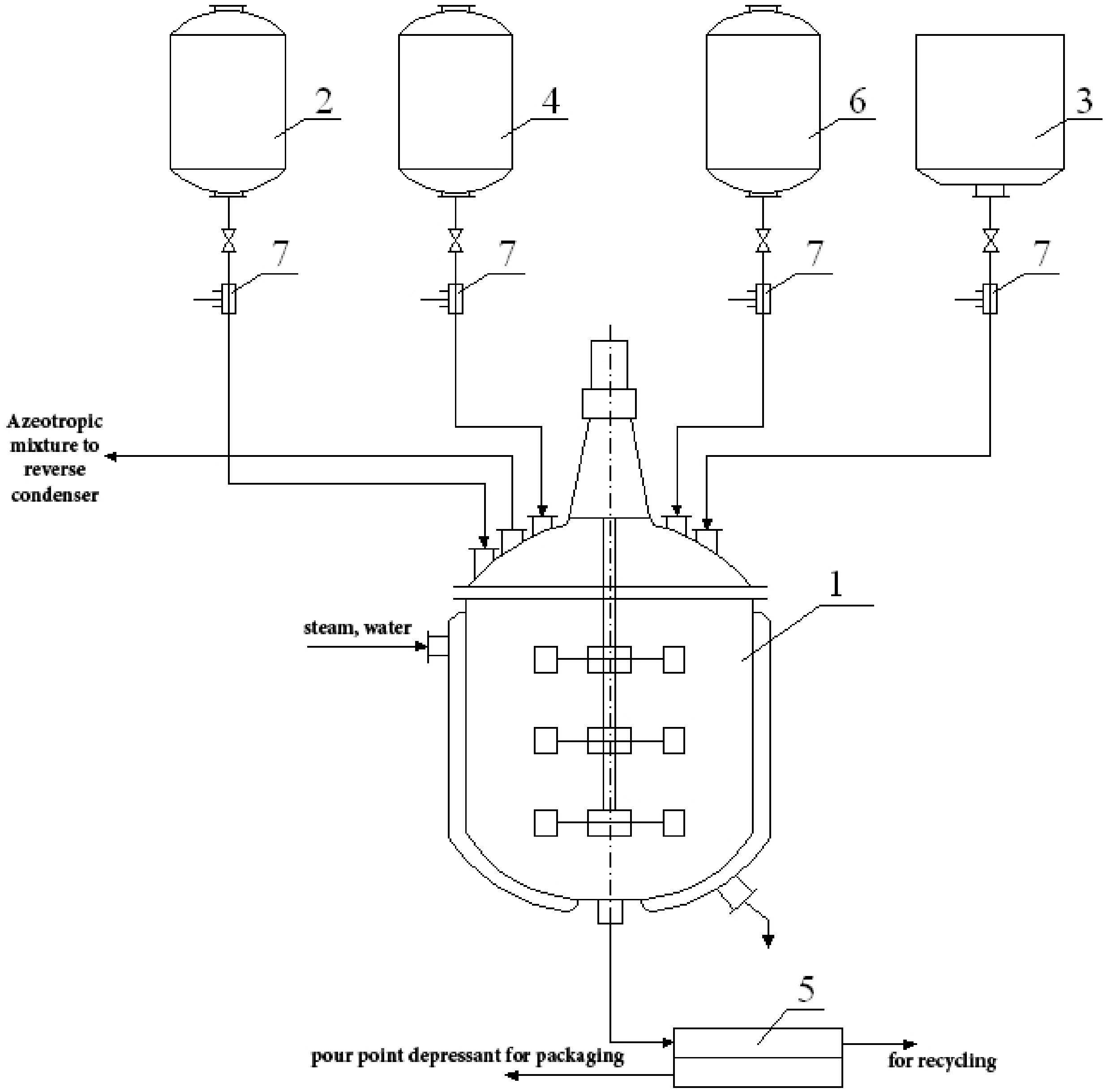

Fig. 1. Principal technological scheme for obtaining depressant additive "Amingoss": 1 - reactor-mixer; 2 - measuring cup of toluene; 3 - SEVA bunker; 4 - measuring of esterified FAs; 5 - filter; 6 - ethanolamine measuring, 7 - measuring - dosing devices.

The depressant activity of new composite pour point depressants was studied specifically on Kumkol, Ashchisai oils and Kumkol-Akshabulak oil mixtures (60:40). At the fields, heat treatment of oil to prepare for transportation and processing is carried out at a temperature of 60°C. It is believed that it is not economically feasible to carry out heat treatment above this temperature; in addition, low-boiling fractions of paraffins begin to separate from the oil, violating the hydrocarbon composition of the oil. Data on the study of the depressant activity of new formulations of pour point depressant are shown in the table.

Table 1 - Depressant activity of pour point depressant for oils from the Kumkol, Ashchisai fields and a mixture of Kumkol-Akshabulak oils.

Oil Sample	Content reagent, wt %	Depression ΔT, (°C)	Kinematic viscosity at 20°C, cSt	Efficiency of ARPD inhibition,%
Kumkol	0	0	8.7	-
	Heat treatment	5	7.2	60
	0.01	10	6.8	42
	0.03	19	6.3	54
	0.05	22	5.9	74
Ashchisai (kinematic viscosity at 50°C)	0	0	9.2	-
	Heat treatment	6	7.9	40
	0.01	8	7.6	68
	0.03	14	6.8	72
	0.05	19	6.5	77
Kumkol - Akshabulak (60:40)	0	0	20.3	-
	Heat treatment	5	19.5	62
	0.01	8	15.3	66
	0.03	12	13.2	72
	0.05	22	12.3	76

The results of the experiment indicate that during conventional heat treatment of Kumkol oil without pour point depressant additives at 60°C, the depression is about 5°C. It is known that thermal methods of influence are the most common, they are based on an increase in the internal energy of the oil system, leading to a weakening of intermolecular interactions between its individual components. Heat treatment of oil leads to the dissolution of high molecular weight paraffins and its homogenization, and during subsequent cooling at a certain rate, paraffin crystals are formed, on which asphalt-resinous substances are sorbed and prevent the deposition of new layers of paraffin on the crystals' surface. In this case, instead of needle-shaped paraffin crystals, plate-shaped crystals are formed. The presence of such a structure allows natural surfactants (surfactants) to influence the crystallization process in paraffinic hydrocarbon systems and participate in the formation of crystals of predominantly lamellar shape (petrolatum), which improves the aggregative stability of the dispersed system. In this regard, the ability of these modified paraffines to mutually combine and deposit on the pipeline wall is reduced. When pour point depressant is introduced into the dehydrated oil of the Kumkol field at concentrations of 0.01-0.05 wt%, a depression is observed equal to 21-

35°C and proportional to the concentration of the introduced pour point depressant, and its value is higher for the oils of the Kumkol field and is 33-35 ° C than for the oil mixture Kumkol-Akshabulak (22-29°C). For oils from the Ashchisai field, the depression was 19-30°C. At the same time, the kinematic viscosity for commercial oils from the Kumkol field decreases from 8.7 to 5.3-5.7 cSt, for commercial oils from the Ashchisai field - from 9.2 to 6.2-6.5 cSt, for the Kumkol-Akshabulak oil mixture with the introduction 0.05 wt% of pour point depressant, kinematic viscosity is reduced from 20.3 to 12.0-12.7 cSt.

The depressant was introduced in an amount of 0.05-0.1 wt.% per oil, the pour point of the studied samples of oil and petroleum paraffin was determined according to GOST 20287. Data on the study of the depressant activity of the new Amingoss additive in Kumkol oils and the Kumkol-Akshabulak mixture are shown in Fig. 2. The results of the experiment indicate that during conventional heat treatment of oil without the addition of pour point depressants at 60°C, the depression is 3–4°C. It was found that the introduction of the Amingoss additive into dry oil from 50 ppm and above increases the depressant activity, the intensity of which increases with increasing concentration.

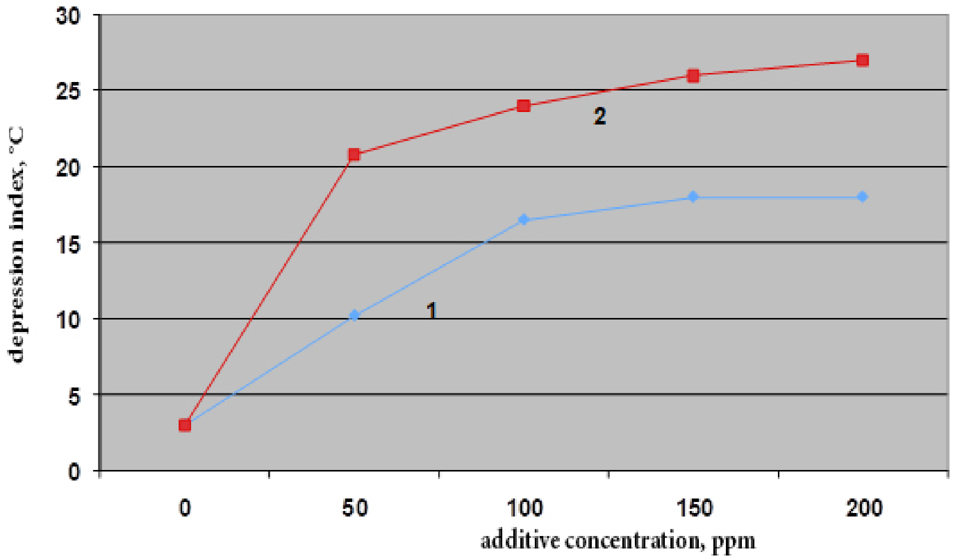

Fig. 2. Dependence of the depression index on the concentration of the additive "Amingoss" in oil: 1 - KK, 2 – KKA

According to the preliminary results of the research, the additive "Amingoss" shows a significant amount of depression at the same costs, compared with many well-known depressants. It follows from the results of rheological studies that the decrease in oil viscosity under the action of the studied depressants (new and known) occurs by a commensurable amount for all studied reagents – depressants.

Until now, there have been various theories explaining the loss of mobility of oil and oil products with decreasing temperature: micellar, solvation, crystallization [6,8]. In our case, when studying highly paraffinic oils, it is assumed that, according to the crystallization theory, the solidification of the tested oils is due to the formation of crystals. With a decrease in temperature, solid crystals of normal alkanes are released, which, sticking together, form a spatial network that binds the liquid phase. When added to paraffinic oil, the pour point depressant forms centers of crystallization of normal alkanes in the system and forms their accumulation in the form of druses, the crystals of which can be single or multicomponent.

Thus, the obtained pour point depressant Amingoss, the dosage of which is 0.05 wt%, and the depression index is 19-25 for samples of highly paraffinic oils. Kinematic viscosity with the introduction of pour point depressant of 0.05 wt. % for oil from the Kumkol field decreases from 8.7 to 5.3-5.7 cSt, for oil from the Ashchisai field - from 9.2 to 6.2-6.4 cSt, for oil mixture Kumkol-Akshabulak kinematic viscosity decreases from 20.3 to 12.0-12.7 cSt. The effectiveness of ARPD inhibition in the presence of pour point depressant in the oils of the Kumkol, Ashchisai fields and the Kumkol-Akshabulak commercial oil mixture, depending on the nature of the additive is 74-79%, 71-73% and 64-64%, respectively. The technical and economic indicators of the pour point depressant make it possible to recommend it for use not only on local, but also on main oil pipelines.

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STUDY ANTIMICROBIAL PROPERTIES OF FABRIC MATERIALS MODIFIED BY SILVER NANOPARTICLES

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ABSTRACT

This paper presents a technology for applying copper and silver films to cotton fabrics by combining photochemical and chemical methods for the reduction of compounds of these metals, in which the resulting metal-containing films have electrical conductivity inherent in metals. In this case, all the main processes presented in the work are carried out due to compounds sorbed by the tissue surface when they are wetted in appropriate solutions. This makes it convenient to use this technology in various medical institutions. There are a number of works showing the photochemical reduction of silver compounds when exposed to electromagnetic waves of sunlight, however, the resulting metal-containing films do not have electronic conductivity, because individual metal particles are surrounded by numerous wavelets, which in the material sense are emptiness. It is these wavelets that give the resulting films a black color. are reflected by light in the form of black shadows between individual metal particles.

Optimal conditions for the processing of fabric materials with silver nanoparticles have been developed. The antibacterial properties of fabric materials modified by silver nanoparticles have been investigated. It has been shown that fabric materials modified by silver nanoparticles have antibacterial activity to bacteria *St. Epidermidis*.

Keywords: fabric materials, modification, photochemical reduction, silver nanoparticles, antibacterial properties.

INTRODUCTION

Microbial contamination of medical devices and treatment rooms leads to several dangerous hospitals and device-related infections. Antimicrobial copper coatings are a new approach to fighting health-related infections (HAI). In recent years, the use of copper and silver to inhibit the spread of bacteria has been widely studied. Among the antimicrobial properties of copper and silver, it is worth noting its property, which effectively destroys the influenza A virus, including such a well-known methicillin-resistant strain of staphylococcal aura as "supermicrobious" MRSA, and the subtype H1N1, also known as "swine flu". The field of application of fabrics with copper and silver coating, as well as some of its compounds, is constantly expanding [1-3].

It is recommended to use such fabrics for the production of medical devices, various types of military clothing, sportswear, underwear and weapons, protecting them from various types of microorganisms.

Currently, the study of metal nanoparticles plays an important role in the development of nanotechnology. This is primarily due to the wide possibilities of their practical application, which take advantage of the unique properties of both nanoparticles and the materials modified by them. Silver nanoparticles are currently of considerable interest and can replace precious metals in nanoforms. This is because these particles have a unique set of valuable properties, which is a pronounced biological antimicrobial activity in relation to all biological objects, from viral particles to the human body. The annually increasing number of works devoted to the study of the antiviral and antibacterial activity of silver nanoparticles proves the increased interest of researchers in this issue from a basic and applied point of view.

Textile materials with antimicrobial properties are used for the manufacture of clothing, linen, dressings, sanitary ware, are effective as protection against infections. When developing new antimicrobial drugs, a number of criteria must be taken into account: the drug must be effective against a wide range of bacteria and fungi and at the same time not toxic to the body, not cause allergies or irritation. In addition, in the presence of some antimicrobial agents, microorganisms can become resistant and the formation of multidrug-resistant bacteria increases, which is one of the biggest difficulties. The use of copper nanoparticles to modify textiles is constantly expanding due to their high bactericidal properties. Currently, Research is underway on the use and modification of fabric materials with silver nanoparticles [4,5].

In modern conditions, research is rapidly developing to improve methods for modifying cellulose fibers to create a wide range of new, high-quality materials with biocidal properties. A unique way to solve this problem is to obtain materials containing silver nanoparticles. This is because these particles have a unique set of valuable properties. One of them is a pronounced biological antimicrobial activity, thanks to which silver nanoparticles can be used for environmental and medical purposes, for example, for disinfection of drinking water, in food packaging and textiles. Currently, many methods for obtaining silver nanoparticles are collected in the literature, for example, physical, chemical and biological their advantages and disadvantages are analyzed [6, 7]. The use of silver nanoparticles for the modification of textile materials is constantly expanding due to their high bactericidal properties and their low toxicity [8,9].

The modification of Textiles with environmentally safe compounds such as silver nanoparticles in order to provide effective biocidal properties for medical and sanitary products, dressing materials, fabrics, etc.

The purpose of this study is to obtain cellulose-containing materials with antimicrobial properties based on silver nanoparticles using a photochemical method. The synthesis of silver nanoparticles was carried out by reducing an aqueous solution of silver nitrate (AgNO3). All solutions were prepared in distilled water. In the process of obtaining silver nanoparticles, ascorbic acid ($C_6H_8O_6$) was used as an additional reducing agent.

MATERIALS AND METHODS

Experimental methods

Cotton fabric (article AA011228, cotton fabric is a natural and environmentally friendly material for planting silver film on the surface of fabric materials, which has bactericidal properties. Well absorbs moisture (adhesion), passes air, density 60 g/sq.m., composition consists of 98% cellulose, does not stretch during washing, elemental composition: C - weight. % 47.86; atomic% 55.01; O-weight. 52.14%; atomic % 44.99) material was used. Pre-washed fabric samples are processed with an aqueous solution of copper (II) chloride 50g/L, bringing them to a certain shape, size. We place samples (40 min, 1000-1200 W/m^2) in a place where sunlight falls unhindered. Maximum blackened specimens are washed and dried in distilled water. A monovalent chloride of copper is formed on the surface of the sample, which has semiconductor properties. After the formation of a semiconductor layer under the influence of photons of sunlight, photons provide additional energy, and excited electrons acquire the necessary oxidative ability to reduce monovalent copper. As a result, the following reactions occur:

$$2CuCl_2 + H_2O + R\text{-}OH = 2CuCl + 2HCl + R\text{-}OOH \qquad (1)$$

$$Cu\,Cl + e = Cu + Cl^- \qquad E = 0{,}137 \qquad (2)$$

After the formation of monovalent copper chloride, the samples are moistened by immersion in a solution of $AgNO_3$ 20 g/L for 5-10 minutes. Then the samples were dried under the influence of sunlight (40min, 500-600 W/m^2). Next, the samples were treated with a solution of A- $(OH)_2$ - 40 g/L. During the transformation of copper monochloride, the following reactions occur in silver:

$$AgNO_3 + HCl \rightarrow AgCl + HNO_3 \qquad (3)$$

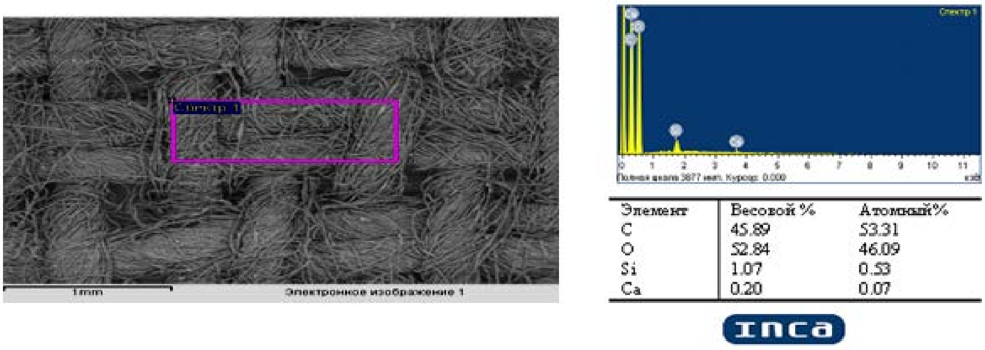
$$2AgNO_3 + C_6H_8O_6 + H_2O \rightarrow C_6H_8O_7 + 2Ag + 2HNO_3 \qquad (4)$$

1 as can be seen from the reaction, when the silver contained in an aqueous solution of silver nitrate is directly exposed to sunlight on the implementation of the process, the photons of sunlight are reduced under the additional influence of ascorbic acid to a metallic state, acting as a reducing agent. As a result, a thin silver film is formed on the surface of the fabric.

Determination of the effectiveness of antibacterial effects in cotton processing St. Epidermidis ATC 14990 test culture is carried out by means of artificial contamination. 20ml of Agar is poured into sterilized Petri dishes. Since the thickness of the agaric layer directly affects the results obtained, it is advisable to store it without exceeding the specified amount of food media. As a food medium, Endo and ISA environments were used. For breeding work on microorganisms, a mixture is prepared according to the St RK ISO 20743 standard [10]. The cultivation of prepared Agar is carried out. Petri dishes are kept at room temperature for 30 minutes and, after inoculation, a sample with antimicrobial properties is placed on the dried surface of the agar. The plates were kept at room temperature for 30 minutes and then placed on the thermostat at 28-37^{0}C for 1 to 5 days. The area of the udder of microbial growths is measured using a millimeter ruler.

RESULTS AND DISCUSSION

The starting fabric is dried by washing the samples in distilled water. An element and component analysis of the composition of fabric samples, brought into a certain shape, is carried out. The study of the composition of shells of various samples was carried out on a special raster electron microscope ISM-6490-LV (JEOL, Japan). Fig. 1 shows the electronic image and elemental composition of the source material.



Элемент	Весовой %	Атомный%
C	45.89	53.31
O	52.84	46.09
Si	1.07	0.53
Ca	0.20	0.07

Fig. 1. Electronic image and elemental composition of the original cotton sample.

Fig. 2 shows the result of an X-ray phase analysis of the primary tissue. As can be seen from the results of the analysis, the composition of the original fabric is cellulose.

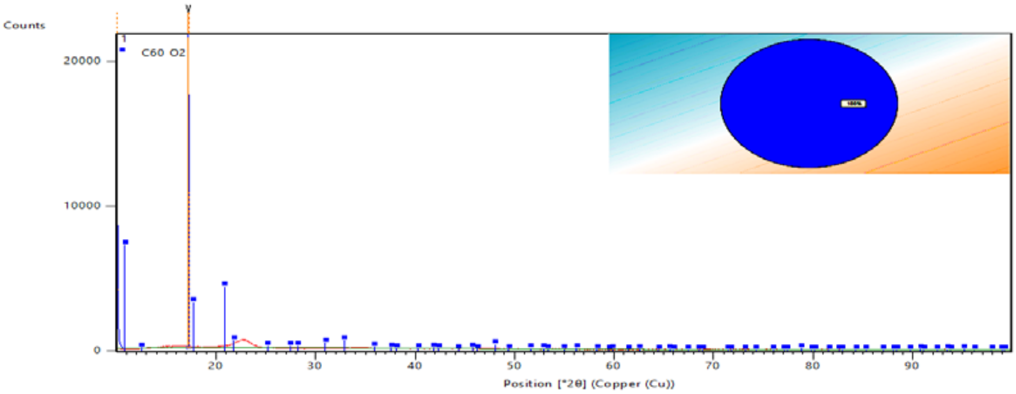
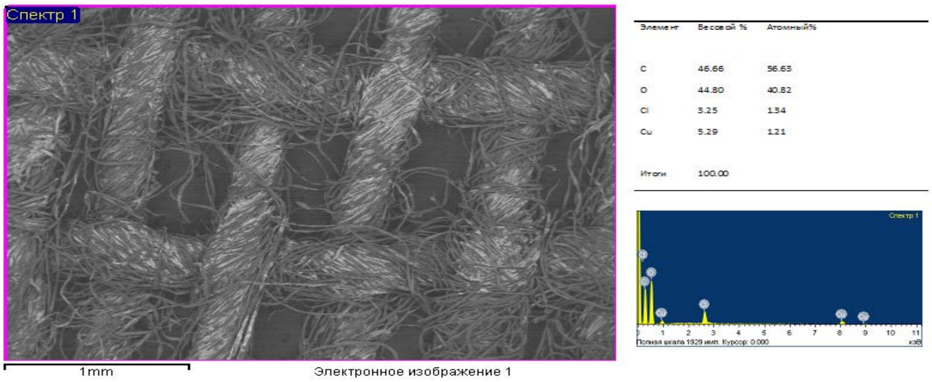


Fig. 2. Diffractogram of the original cotton pattern.

Under the action of photons of sunlight, the bivalent chloride of copper is reduced to monovalent chloride (1). A solution of ascorbic acid 40g/L is used as an additional reducing agent.

As a result of the reduction process carried out under the influence of sunlight, as shown in reaction 1, copper monochloride is formed, which has semiconductor properties. Under the influence of photons, copper monochloride is reduced to elemental copper (2). After maximum darkening, we wash and dry the samples with distilled water. Element and component analysis of the finished sample was carried out. The results of the analysis are presented in Fig. 3,4.



Элемент	Весовой %	Атомный%
C	46.66	56.63
O	44.80	40.82
Cl	3.25	1.34
Cu	5.29	1.21
Итоги	100.00	

Fig. 3. Electronic image and elemental composition of a cotton sample with a copper film on the surface.

Fig. 3 presents the elemental composition and electronic image of the film on the surface of the fabric sample treated with copper chloride. According to the results of the REM, the elemental composition corresponding to monovalent copper chloride was determined.

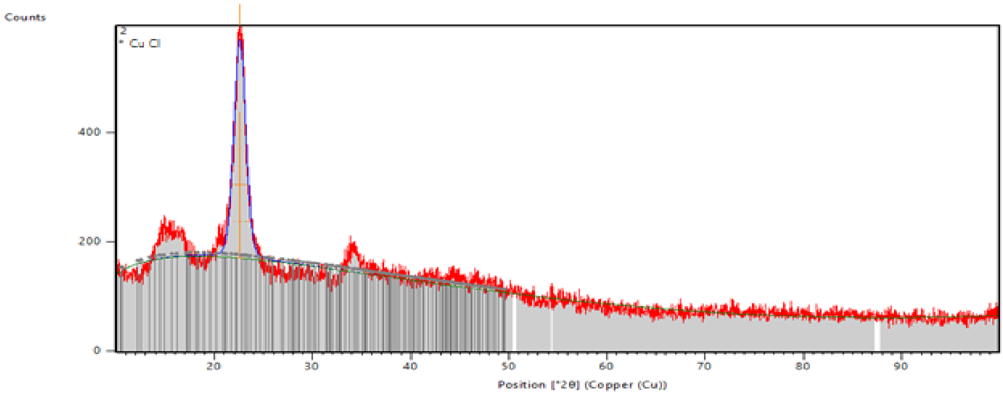


Fig. 4. Diffractogram of a cotton sample with a copper film on the surface

Fig. 4 shows the results of X-ray phase analysis of the surface layer of the fabric treated with a solution of copper (II) chloride. As can be seen from the diffractogram, it was found that the component composition of the sample surface is copper monochloride.

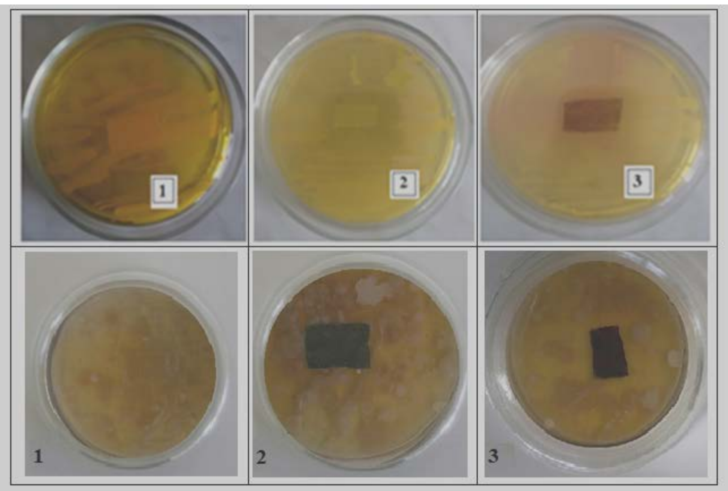


Fig. 5. Initial state of tissue samples with a film on the surface in an agricultural environment: 1) without film; 2) copper film sample; 3) silver film sample

Fig. 5 Shows The st of the original fabric, a fabric pattern with a copper and silver film on the surface. Activity against the bacterium Epidermidis has been cited. On the surface of a non-shell sample (Fig. 5.1), bacterial growth is observed, and on the surface of copper and silver shell samples (Fig. 5.2-5.3), bacterial growth is not observed. Therefore, the metal films obtained according to the results of the study are considered to have antibacterial destructiveness.

Table 1 - The results of the study of antibacterial properties

Number of samples	Film composition	Result
		S.epidermidis
1	The original sample	0
2	Copper	19mm (82%)
3	Silver	24mm (100%)

CONCLUSION

By combining photochemical and chemical processes occurring in the sorption layer on the surface of cotton under the influence of sunlight, copper and silver films are obtained that adhere well to the fabric, as well as have electrical conductivity, by absorbing the fabric in solutions of $CuCl_2$ 50g/L, $AgNO_3$ 20g/L and ascorbic acid (40g/L). As a result of these processes, a film with dispersed copper particles is formed on the fabric. This film can serve as a catalyst for chemical silvering. Tissue with a silver film on the surface of the sample was found to have activity against the bacterium *St. Epidermidis*. Optimal conditions for processing fabric materials with copper and silver nanoparticles have been developed. It was found that the treatment with the selected composition gives antimicrobial properties of the treated tissue, improves the physical and mechanical characteristics.

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INVESTIGATION OF THE CONDITIONS OF CRYSTALLIZATION OF CALCIUM SULFATE IN THE PROCESS OF CONVERSION OF CALCIUM CHLORIDE DISTILLER LIQUID

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ABSTRACT

Laboratory studies of the conversion of calcium chloride with natural sodium sulfate were carried out and the optimal parameters of the conversion process of calcium chloride and the consumption rate of sodium sulfate, as well as the conditions of crystallization of calcium sulfate, were determined. It was found that the formation of calcium sulfate crystal nuclei at 80^0C occurs as overgrown snowflakes and the length of the crystals is in the range of 140.0 - 218.7 microns, and the thickness of the crystals is from 14.81 microns to 32.52 microns. The results of the conducted complex of studies will make it possible to obtain a product of conversion sodium chloride and additionally construction gypsum; eliminate the formation of "white seas" of distiller liquid, thereby solving the most important task of ensuring environmental safety of soda ash production, significantly reduce payments for the placement of liquid production waste.

Keywords: distiller liquid, sodium sulfate, sodium chloride, gypsum.

INTRODUCTION

In the chemical industry, a special place is occupied by the production of soda ash.As you know, the most well-known and widely used method for producing soda ash in the world is the so-called ammonia method, which produces about 70% of the global production of soda. At the same time, this method has a significant drawback - for 1 ton of soda ash produced, 8-10 m^3 of non-recyclable chloride effluents containing 110-120 g/l $CaCI_2$, 55-58 g/ l NaCI, small impurities $CaCO_3$, $CaSO_4$, $Mg(OH)_2$, SiO_2,etc. are formed. At the same time, about 1.5 tons of calcium and sodium chlorides are removed from the process for 1 ton of soda with distiller liquid. With discharges, about 30% of raw materials are lost, as a result of which the degree of sodium use is no more than 70%. At the existing soda ash production facilities, sludge accumulators – "white seas" occupy huge territories with an area of several hundred hectares, which causes pollution of the natural environment and leads to damage to the health of people, animals, plants and soil conditions [1].

The processing of distiller liquid for the production of soda ash using sodium sulfate is accompanied by the formation of gypsum: two- and semi-aqueous calcium sulfate. Gypsum as a building material is used in the cement industry and as part of composite materials [2,3].

MATERIALS AND METHODS

In the studies, a model solution of distiller liquid was used, corresponding to the composition of the distiller liquid obtained under real technological conditions in accordance with the data of the Sterlitamak plant. Natural sodium sulfate, were acquired by Araltuz LLP.

The reaction was carried out in a 0.5 L glass flask with a reverse refrigerator, stirrer. After the conversion time has elapsed, the unit is switched off and the suspension is separated by filtration on a vacuum filter unit, after drying, the solid phase was analyzed for the content of basic and impurity components using chemical analysis and a JSM-6490LV scanning electron microscope with INCA Energy 350 energy dispersive microanalysis system and HKL Basic polycrystalline samples structural and textural analysis system. Precipitation was also subjected to physico-chemical analysis by the XFA method on the Dron-3 device [4].

RESULTS AND DISCUSSION

The crystallization process of calcium sulfate is characterized by mass transfer in the boundary layer and the rate of phase transformation at the crystal boundary. The interaction of a growing crystal with the environment and the mechanism of the transition of a substance from a solution on its face is considered by the diffusion theory of growth [5].

The process of gypsum crystallization consists of two stages of formation of $CaSO_4{\cdot}2H_2O$ crystal nuclei and crystal growth. The formation of embryos can occur at a certain temperature and at a certain saturation. The number of embryos arising per unit volume per unit time depends on the process conditions. Therefore, the spontaneous formation of the number of crystallization centers in a supersaturated solution depends on time.

The formation of calcium sulfate crystals is influenced not only by the temperature and duration of the process, but also by the consumption rate of sodium sulfate [6].

$$Na_2SO_4 + CaCl_2 + 2H_2O \Leftrightarrow 2NaCl + CaSO_4{\cdot}2H_2O$$

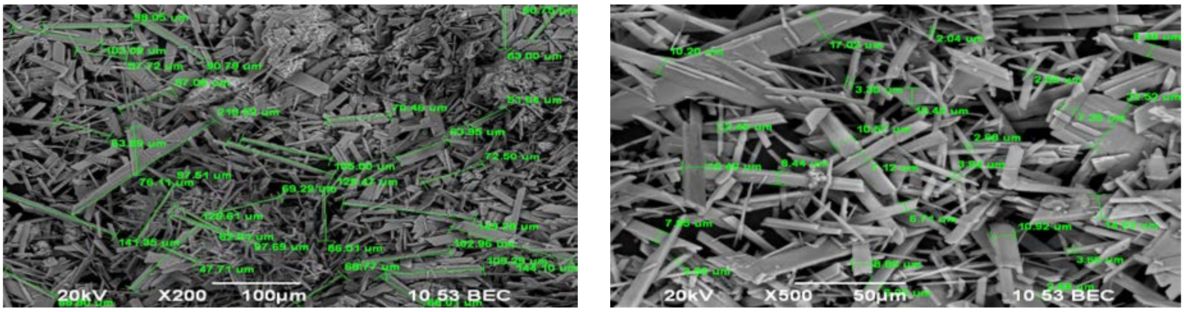
In order to determine the effect of temperature rise on the growth of $CaSO_4{\cdot}2H_2O$ crystals, studies were carried out at a temperature of 80^0C and a time of 15-60 min., the norm of sodium sulfate is 102%. The resulting washed gypsum precipitate was examined on a SEM and XFS device. Table 1 shows the results of the experiment of obtaining gypsum during the conversion of calcium chloride in a distiller liquid.

Table 1 - The size of $CaSO_4{\cdot}2H_2O$crystalsobtained at a temperature of 80°C

No.	Temperature, °C	Time, min.	Crystal size, microns	
			length	thickness
1	80	15	from 20.1 to 140.2	from 1.40 to 14.81
2	80	30	from 51.16 to 153.6	from 1.60 to 16.92
3	80	45	from 37.12 to 158.7	from 2.15 to 22.00
4	80	60	from 47.71 to 218.7	from 2.04 to 32.52

It can be seen from the data in Tables 1 that the length of gypsum crystals increases with increasing duration of the process and reaches from 140.0 microns to 218.7 microns, the thickness of calcium sulfate from 14.81 microns to 32.52 microns.

Fig. 1 shows micrographs of $CaSO_4 \cdot 2H_2O$ obtained at $80^{O}C$ and a time of 60 min.



A-crystallength

B-crystal thickness

Fig. 1. Micrograph of washed $CaSO_4 \cdot 2H_2O$

From the micrograph (Fig.1) of gypsum, it can be seen that $CaSO_4 \cdot 2H_2O$ crystals have large plate-shaped and partially needle-shaped crystals.

The results of the energy dispersion analysis of gypsum are shown in Fig. 2.

Element	Weight, %	Atomic, %	Connection, %
O	54.96	72.84	
Na	0.14	0.17	Na_2SO_4-0.46
S	18.22	12.05	
Cl	1.20	0.72	NaCI-0,97
Ca	23.46	12.41	$CaSO_4$-76.31

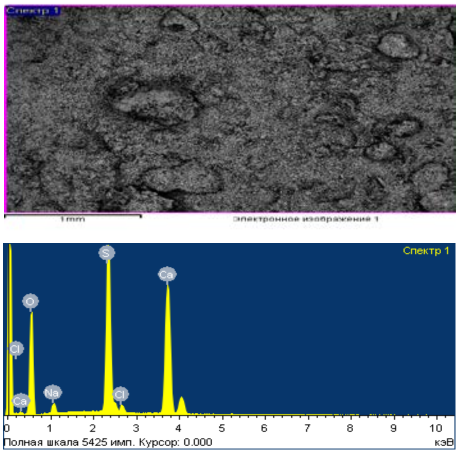


Fig. 2. Composition of $CaSO_4 \cdot 2H_2O$obtained at a temperature of $80^{O}C$, time 60 min.

Fig. 2 shows that the resulting gypsum contains $CaSO_4$-76.31%,Na_2SO_4-1.17%, NaCI-1.97%.

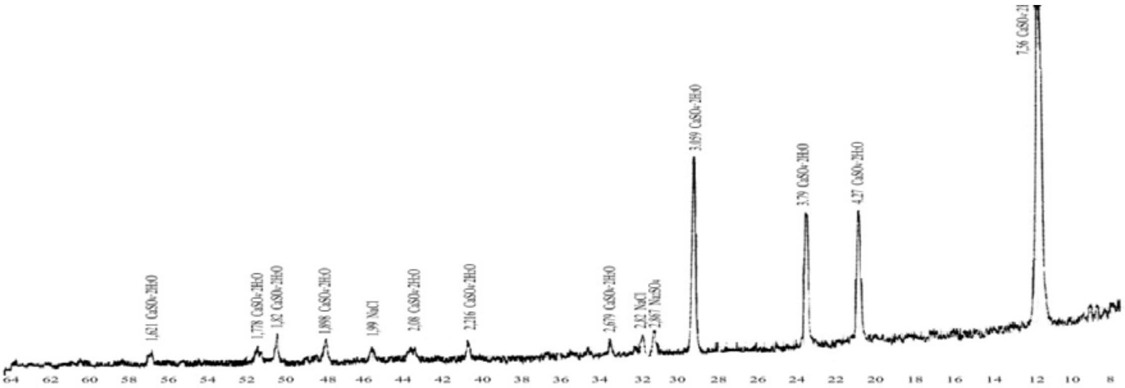


Fig. 3.X-ray of the sediment $CaSO_4 \cdot 2H_2O$

The radiograph of dried gypsum showed that the radiograph shows a compound whose intensity corresponds to 7,56, 4,27, 3,79, 3,059, 2,679, 2,216, 2,08, 1,898, 1,82, 1,778, 1,621A^{O}$CaSO_4 \cdot 2H_2O$,as well as a compound with an intensity of2,08A^{O}$CaCO_3$, 2,82, 1,99A^{O}NaCI.

CONCLUSION

Based on the conducted complex of studies, it was found that during the conversion of calcium chloride with sodium sulfate, the formation of nuclei of $CaSO_4 \cdot 2H_2O$ crystals occurs in the form of overgrown snowflakes and the length of the crystals increases to 218.7 microns, and the thickness of the crystals to 32.52 microns.

The conversion of calcium chloride with sodium sulfate makes it possible to obtain conversion sodium chloride and construction gypsum, as well as to exclude the formation of "white seas" of distiller liquid.

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STUDY OF MASS EXCHANGE PROCESS IN WET CLEANING PROCESSES OF WASTE GASES GENERATED IN SUPERPHOSPHATE PRODUCTION

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ABSTRACT

In the article, the method of calculation of the process of purification of waste gases generated in the production of superphosphate in a wet method in a rotor-filter experimental apparatus is given. Also, the results of the experiment on the absorption of hydrogen-fluoride gas contained in waste gas into the solution of technical soda in water are given, and the equation for calculating the mass transfer coefficient is recommended. Theoretical and experimental studies mainly selected the optimal values of variable factors. These studies have great practical application in the production of superphosphate mineral fertilizers for the purification of fluorine-containing gases generated in a rotary-filter experimental apparatus. This research work is also aimed at cleaning the gases produced and released into the atmosphere in the production of superphosphate and reducing environmental pollution. An effective method of exhaust gas cleaning was chosen and the optimal construction of the apparatus was developed. The developed semi-industrial experimental apparatus with a rotor-filter was used in the treatment of exhaust gases produced in the AS-72M workshop of Ferg'onaazot JSC.

Keywords: absorption, mass transfer, soda ash, filter material, partial pressure, component, hydrogen fluoride, emission gases, liquid flow, gas flow, hole diameter.

INTRODUCTION

Today, ecology and environmental protection are the most important tasks in every part of the Earth. It is known that the impact of emission gases, liquid and solid wastes on ecology and environmental damage is significant. Among these wastes, the impact of toxic waste gases generated in the production of mineral fertilizers is enormous. This research work is also aimed at cleaning the gases produced and released into the atmosphere in the production of superphosphate and reducing environmental pollution. An effective method of exhaust gas cleaning was chosen and the optimal construction of the apparatus was developed. The developed semi-industrial experimental apparatus with a rotor-filter was used in the treatment of exhaust gases produced in the AS-72M workshop of Ferg'onaazot JSC.

MATERIALS AND METHODS

Research on the treatment of waste gases generated in the production of superphosphate was carried out in two stages.

At the first stage, the composition and physicochemical properties of the waste gas mixture formed during the production of superphosphate mineral fertilizer were studied. Accordingly, in the production of superphosphate, 15000÷4500 mgr in 1m^3 gas mixture.

amount of hydrogen-fluoride and 1900÷2800mg of dust was determined. The physical and chemical properties of hydrogen fluoride were studied [1].

At the second stage of the research, in order to determine the optimal value of the device, the adsorbent consumption, the gas flow rate to be cleaned, and the diameter of the filter hole were selected as variable factors. A 30% solution of soda ash in water was used as an adsorbent [2].

The following equations were used to clean the waste gases generated during the production of mineral fertilizers in the rotor-filter experimental apparatus [3-7].

The amount of the hydrogen-fluoride component in the initial gas mixture is determined as follows, m^3/h:

$$V_b = V_{b.ar} \cdot x_{bHF} \tag{1}$$

where $V_{b.ar}$ –is the amount of gas mixture supplied to the device, m3/hour; x_{bHF} – volume fraction of hydrogen-fluoride in the gas mixture, %.

The amount of hydrogen-fluoride in the gas leaving the device, m^3/h:

$$V_{ch} = V_{b.ar} \cdot x_{oxHF} \tag{2}$$

where x_{oxHF} –is the volume fraction of hydrogen fluoride in the purified gas flow (outlet), %.

The amount of hydrogen fluoride absorbed into the absorbent, m^3/h:

$$V_{yut} = V_b - V_{ch} \tag{3}$$

and

$$G_{yut} = \frac{V_{yut} \cdot T_0}{T} \cdot \rho_0 \tag{4}$$

where V_{yut} –is the amount of gas absorbed by the absorbent, m^3/h; T^0 - absolute temperature, K; T is working temperature, K.

The average driving force of the absorption process in the apparatus is determined as follows.

The partial pressure of the hydrogen-fluoride component at the entrance to the rotor-filter is determined from the following equation, kPa:

$$P_{b.HF} = P_{ap.} \cdot x_{b.HF} \tag{5}$$

The molar fraction of hydrogen fluoride in technical soda leaving the apparatus:

$$x_{m.HF} = \frac{\dfrac{G_{yut}}{M_{FH}}}{\dfrac{G_{yut}}{M_{FH}} + \dfrac{Q_{abs.}}{M_{havo}}} \tag{6}$$

The exhaust gases from three-stage stirred reactors have a mixer temperature of 65^0C, and at this temperature the Henry coefficient for hydrogen fluoride is 1,0 kPa. According to it, the partial pressure of hydrogen fluoride in the equilibrium state with the gas mixture is determined as follows, kPa:

$$P^*_{b.HF} = K \cdot x_{m.HF} \tag{7}$$

The force driving the absorption process in the lower part of the apparatus, kPa:

$$\Delta P = P_{b.HF} - P^*_{b.HF} \tag{8}$$

The partial pressure of the hydrogen-fluoride purified gas stream at the outlet of the mixer is determined, kPa:

$$\Delta P_{chiq} = P_{ap} \cdot x_{ox\,HF} \tag{9}$$

The average driving force of the mass transfer process in the experimental device is determined as follows, kPa:

$$\Delta P_{o'rt} = \frac{P^*_{b.HF} - \Delta P_{chiq}}{2,3\lg \dfrac{P^*_{b.HF}}{\Delta P_{chiq}}} \tag{10}$$

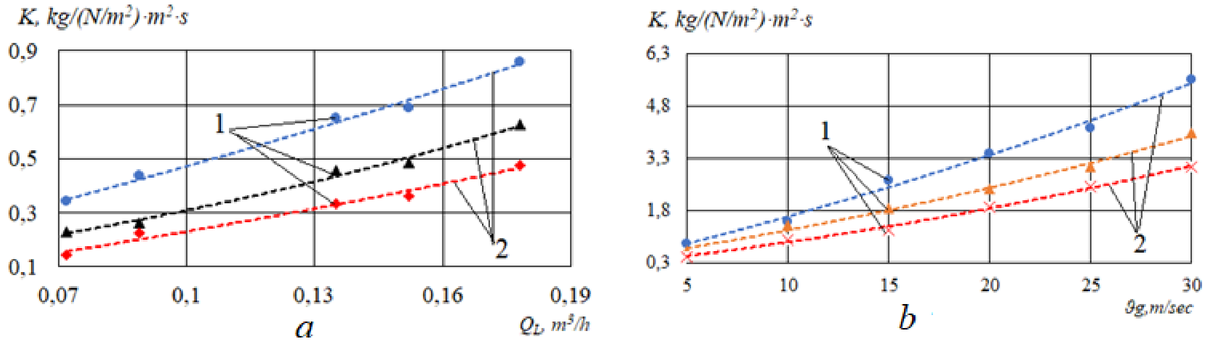
It was recommended to use the following equation to determine the mass transfer coefficient of absorption of hydrogen-fluoride into a solution of technical soda in water in a rotor-filter experimental apparatus, kg/(m^2·s·kPa):

$$K = \frac{G_{yut}}{\left(6,28 \cdot R_F \cdot L_B - 0,785 \cdot d_F{}^2 \cdot n_{tesh}\right) \cdot \Delta P_{o'rt}} \tag{11}$$

in this R_F – drum radius, mm; L_B – drum length, mm; d_F – diameter of the filter material hole covered with the drum, mm; n_{tesh}– number of holes.

RESULTS AND DISCUSSION

The following results were obtained in the absorption of hydrogen fluoride produced in the production of superphosphate into a solution of technical soda in water [3].



1-experimental values; 2-theoretical values;

Fig. 1. *a*–dependence of fluid consumption on the mass transfer coefficient; *b*-dependence of the gas velocity on the mass transfer coefficient

Fig. 1*a* shows the variation range of the mass transfer coefficient K when the consumption of absorbent liquid is Q_L=0.072÷0.178 m^3/h and the speed of the gas flow to be cleaned is 5 m/s. According to it, the secondary value of liquid consumption is Q_L=0.072m^3/hour and the diameter of the filter holes covered on the surface of the drum is d_F=2mm; d_F=3mm; When d_F=4mm, the value of the mass transfer coefficient is K=0.340 kg/(N/m^2)·m^2·s, and the maximum value of absorbent consumption is Q_L=0.178m^3/hour, when the value of the mass transfer coefficient is K=0.861kg/(N/m^2) ·m^2·s was found to increase.

In Fig. 1*b*, the range of the gas flow rate to be cleaned is ϑ_G=5÷30m/s and the absorbent liquid flow is Q_L=0.178 m^3/hour, and the diameter of the filter holes covered on the surface of the drum is d_F=2mm; dF=3mm; The variation range of the mass transfer coefficient when d_F=4mm is given. According to it, mass transfer coefficient reached the smallest value K=0,475 kg/(N/m^2)·m^2·s at binary value of gas velocity ϑ_G =5m/s. It was also observed that the value of the mass transfer coefficient increased by K=5,550 kg/(N/m^2)·m^2·s when the gas velocity increased to ϑ_G =30m/s.

Also, as a result of processing the data given in Figures 1 *a* and 1 *b*, the following empirical functions were obtained and the error between experimental and theoretical values was determined.

The following empirical functions are available for the speed of the purified gas flow ϑ_G =5m/s and the range of absorption fluid consumption QL=0.072÷0,178 m^3/hour.

filter diameter $d_Ф$=2mm, $y = 4.7104x^2 + 3.5504x + 0.0694$ $R^2 = 0.9923$ (12)

filter diameter $d_Ф$=3mm, $y = 9.391x^2 + 1.3992x + 0.07450$ $R^2 = 0.9914$ (13)

filter diameter $d_Ф$=4mm, $y = 3.8917x^2 + 1.9431x - 0.0035$ $R^2 = 0.9830$ (14)

The following empirical functions can be obtained in the range of the velocity of the purified gas flow ϑ_G =5÷30m/s and the absorption liquid consumption Q_L=0.178 m^3/hour.

filter diameter d_F=3mm, $y = 0.0014x^2 + 0.1344x + 0.125$ $R^2 = 0.9922$ (15)

filter diameter d_F=3mm, $y = 0.0013x^2 + 0.0836x + 0.2605$ $R^2 = 0.9929$ (16)

filter diameter d_F=4mm, $y = 0.0012x^2 + 0.0606x + 0.1525$ $R^2 = 0.9955$ (17)

From these empirical functions, it can be seen that the difference between experimental and theoretical values was 2%. As a result of processing the values obtained on the basis of theory and experiments, the following conclusions were drawn.

CONCLUSION

Purification of fluorine-containing gases produced during the production of superphosphate mineral fertilizers in a rotor-filter experimental apparatus with a 30% solution of technical soda in water resulted in the following results. An equation for calculating the mass transfer coefficient representing the absorption process in the rotor-filter apparatus that cleans gases in a wet method was recommended. The value of the gas flow rate to be cleaned is the largest and the largest value of the mass transfer coefficient was observed at the smallest value of the filter material hole diameter and the highest absorbent consumption, while the decrease of the gas velocity and the largest value of the filter material hole diameter was observed.

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INFLUENCE OF CARBON ON THE FORMATION OF CALCIUM CARBIDE FROM PHOSPHORITE KARATAU

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ABSTRACT

The article presents the results of the influence of the amount of carbon on the extraction of calcium into calcium carbide during the complex processing of phosphorites from the Karatau deposits. he study was carried out by thermodynamic modeling using the HSC-6.0 software package, based on minimizing the Gibbs energy, at a pressure of 1 bar in the temperature range of 500-2200 °C, the amount of carbon varied from 44 to 60%. It has been established that with an increase in the amount of carbon from 44 to 60%, the amount of CaC_2 formed increases; the maximum $\alpha Ca(CaC_2)$ is 58.35% at 2000 °C and 44% carbon, and at 60% carbon the maximum $\alpha Ca(CaC_2)$ increases to 84.72% at 1900 °C; high calcium content in carbide (86.76-87.09%) is observed at 60% carbon in the temperature range of 2000-2100 °C; the volume of the obtained calcium carbide of the highest grade is 322.76-323.86 dm^3/kg.

Keywords: phosphorite, thermodynamic modeling, carbon, calcium carbide, ferroalloy, phosphorus.

INTRODUCTION

There are several large deposits of phosphorites in Kazakhstan, with explored reserves of 483 million tons of P_2O_5 [1]. When phosphorus is obtained from phosphorites by the electrothermal method [2], 10–11 tons of dump slag is formed for each ton of phosphorus, into which all calcium and the main part of silicon pass [3]. The existing technology for obtaining phosphorus is characterized by a low degree of integrated use of raw materials (no more than 50%), and production waste - phosphorus slags occupy land and negatively affect the ecology of the region [4]. For the development of the phosphorus sub-sector and its economy, it is necessary to increase the degree of integrated use of raw materials. We propose a complex electrothermal processing of phosphorites with a high degree of complex use of raw materials with simultaneous production of gaseous phosphorus, calcium carbide and silicon-containing ferroalloy in an electric furnace [5]. This technology will make it possible to obtain up to 2.0-2.2 tons of high-quality calcium carbide and from 3.0 to 3.4 tons of ferrosilicon grades FS25 and FS45.

The article presents the results of the influence of the amount of carbon on the extraction of calcium into calcium carbide during the complex processing of phosphorites from the Karatau deposit.

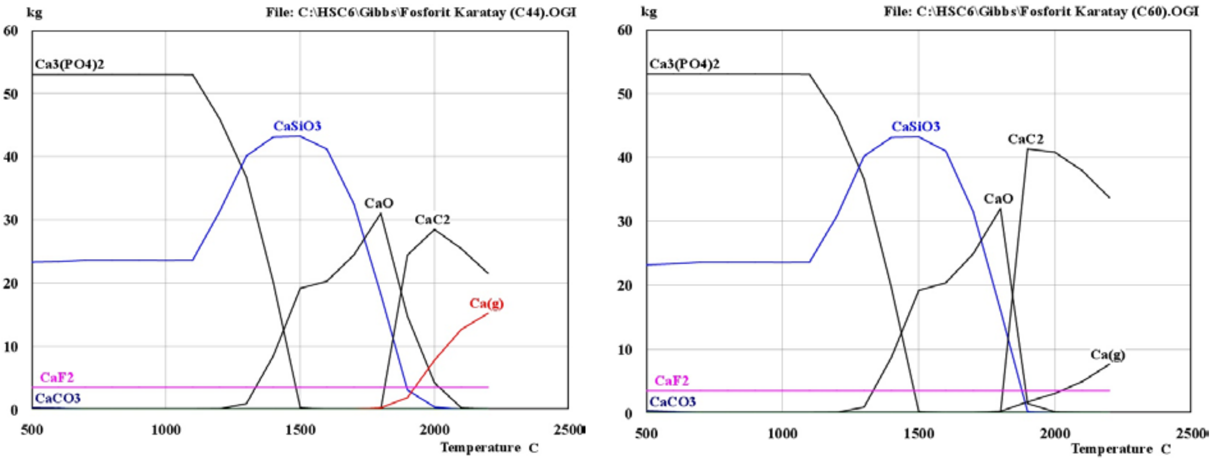
MATERIALS AND METHODS

The study was carried out by the method of thermodynamic modeling, using the HSC-6.0 software package [6], and the calculation of the equilibrium degree of distribution of elements between substances using the algorithm developed in M. Auezov SKU. [7]. Studies of the influence of carbon were carried out at a pressure of 1 bar in the temperature range 500-2200 ^{0}C. The amount of carbon in the Karatau-carbon-iron phosphorite system varied from 44 to 60%, the amount of iron was constant at 13.2%.

RESULTS AND DISCUSSION

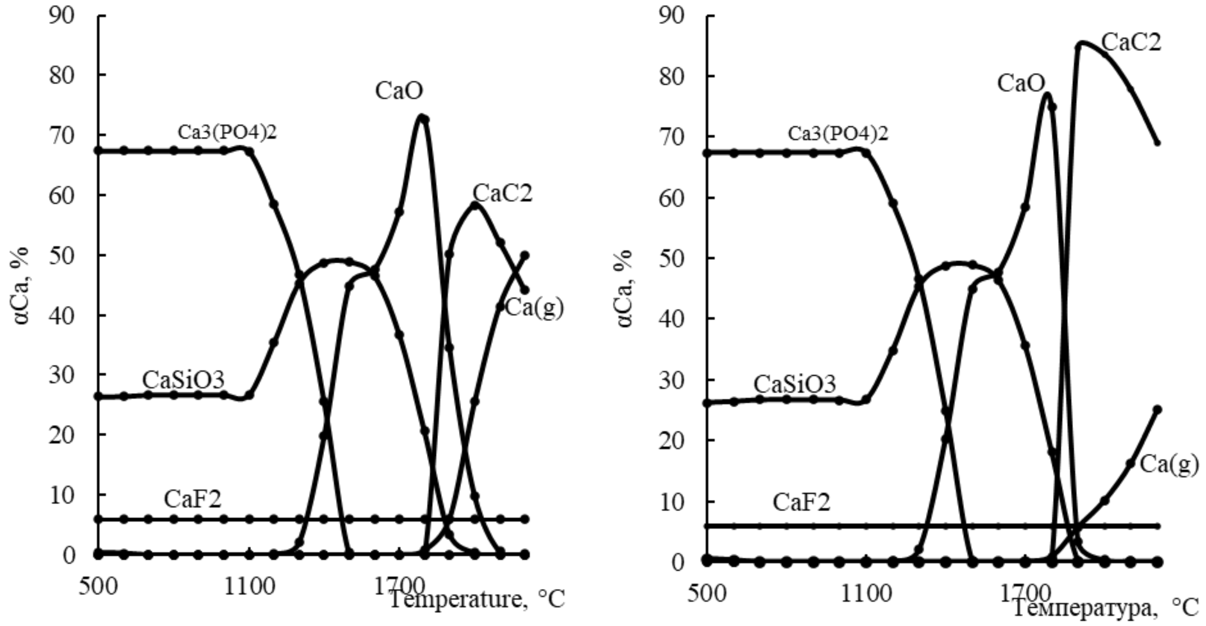
Fig. 1 shows the results of the quantitative distribution of calcium-containing substances in the Karatau-carbon-iron phosphorite system at different amounts of carbon, obtained using the HSC-6.0 software package (Equilibrium Composition option). Fig. 1 shows that calcium in the system is in the form of $CaSiO_3$, CaO, CaC_2, Cag, $Ca_3(PO_4)_2$, CaF_2, $CaCO_3$. With an increase in the amount of carbon from 44 to 60%, the amount of CaC_2 formed increases.

Fig. 2 shows the equilibrium degree of distribution of calcium in the system Karatau phosphorite - carbon - iron at the amount of carbon 44% and 60%.



I-44% carbon, II-60% carbon

Fig. 1. Effect of temperature on the quantitative distribution of calcium-containing substances in the phosphorite Karatau - carbon - iron system

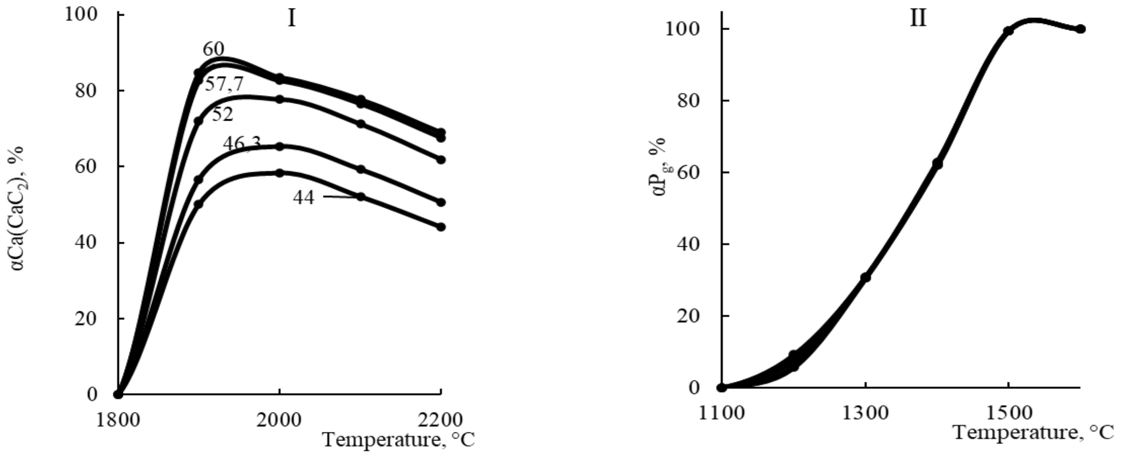


I-44% carbon, II-60% carbon

Fig. 2. Influence of temperature on the equilibrium distribution of calcium in the system in the phosphorite Karatau - carbon - iron system

Fig. 2 shows that in the temperature range of 500-1100 ^{0}C calcium in the system is in the form of $Ca_3(PO_4)_2$, $CaSiO_3$, CaF_2. With an increase in temperature, an increase in the degree of distribution of calcium in CaO, CaC_2 and Ca_g is observed. The decrease in the degree of distribution of Ca in CaC_2 with increasing temperature is due to the decomposition of the carbide.

Fig. 3 shows the results of calculating the equilibrium degree of distribution of calcium into calcium carbide ($\alpha Ca(CaC_2)$, %) and phosphorus into the gas phase depending on the temperature and amount of carbon.

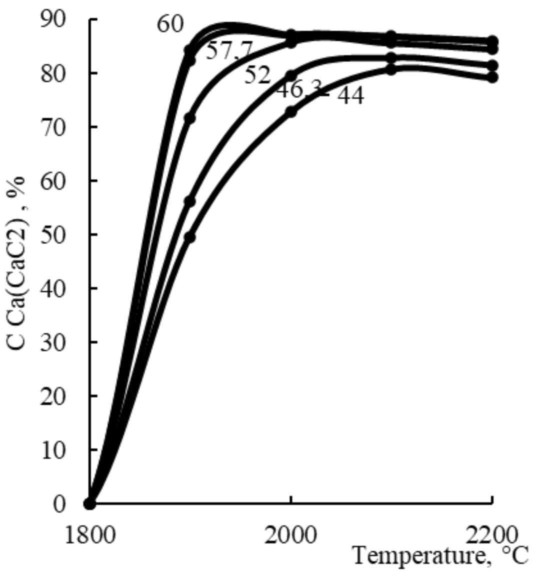


The numbers near the lines are the amount of carbon,%

Fig. 3. Influence of temperature and amount of carbon on the transition of calcium to carbide (I) and phosphorus to gas (II)

Fig. 3 shows that an increase in carbon from 44 to 60% leads to an increase in the degree of extraction of calcium into calcium carbide from 50.07 to 84.72% at a temperature of 1900 ^{0}C. The maximum degree of transition of calcium into carbide at 44% carbon is 58.35% at 2000 ^{0}C, and at 60% carbon the maximum αCa(CaC$_2$) is equal to 84.72% at 1900 ^{0}C. It follows that with a larger amount of carbon, the maximum degree of transition of calcium into carbide occurs at a lower temperature. An increase in the amount of carbon does not affect the degree of extraction of phosphorus into the gas. Phosphorus begins to pass into gas at a temperature of 1100 ^{0}C, and at a temperature of 1600 ^{0}C it is 99.99% for each amount of carbon.

Fig. 4 shows the effect of the amount of carbon and temperature on the concentration of calcium in calcium carbide, and in table 1 on the volume of technical carbide.



The numbers near the lines are the amount of carbon,%

Fig. 4. The effect of temperature and the amount of iron on the concentration of calcium in calcium carbide

Table 1 - The effect of temperature and the amount of iron on the volume of technical calcium carbide, dm^3 / kg

Amount of carbon, %	Temperature, °C			
	1900	2000	2100	2200
44	184.38	270.51	300.19	294.28
46.3	208.91	295.42	308.02	302.76
52	266.43	318.67	318.25	314.02
57.7	306.00	323.14	321.98	318.58
60	313.07	323.86	322.76	319.60

Fig. 4 shows that a high calcium content in carbide (86.76-87.09%) is achieved at 60% carbon in the temperature range of 2000-2100 ^{0}C. At the same time, the displacement of the obtained calcium carbide is 322.76-323.86 dm^3/kg. At 44% carbon, the maximum concentration of calcium in carbide (81.39%) is observed at a temperature of 2200 ^{0}C, and the displacement is 300.19 dm^3/kg.

CONCLUSION

Based on the results of studies of the influence of the amount of carbon on the extraction of calcium into calcium carbide during the complex processing of phosphorites from the Karatau deposit, it was found that:

-calcium in the system is in the form of $CaSiO_3$, CaO, CaC_2, Ca_g, $Ca_3(PO_4)_2$, CaF_2, $CaCO_3$;

-with an increase in the amount of carbon from 44 to 60%, the amount of CaC2 formed increases; the maximum $\alpha Ca(CaC_2)$ is 58.35% at 2000 ^{0}C and 44% carbon, and at 60% carbon the maximum $\alpha Ca(CaC_2)$ increases to 84.72% at 1900 ^{0}C;

-high calcium content in carbide (86.76-87.09%) is observed at 60% carbon in the temperature range of 2000-2100 ^{0}C; the volume of the obtained calcium carbide of the highest grade is 322.76-323.86 dm^3/kg.

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POSSIBILITY OF FORMATION OF IRON, CARBIDE AND PHOSPHORUS SILICIDES FROM THE SYSTEM $Ca_3(PO_4)_2$-$nSiO_2$-mFe-xC

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ABSTRACT

The article presents the results of studies of equilibrium production from $Ca_3(PO_4)_2$ and SiO_2 in the presence of iron and phosphorus carbon, calcium carbide and ferroalloy. The studies were carried out by calculating the change in Gibbs energy and entropy using the HSC-6.0 software package (Reaction Equations option), based on minimizing the Gibbs energy. Based on the results obtained on the interaction in the $Ca_3(PO_4)_2$-$nSiO_2$-mFe-xC system, it was found that the temperature of the start of the joint reduction of phosphorus, the formation of calcium carbide and iron silicides depends on the mole fraction of silicon in iron silicide and is 1555.8-1631,2 °C. With an increase in the mole fraction of silicon in the silicide from 0.375 (Fe_5Si_3) to 0.5 ($FeSi_2$), an increase in the temperature of the onset of interaction in the system is associated with an increase in silicon iron in the silicide, which has a higher affinity for oxygen than iron.

Keywords: Gibbs energy, enthalpy, phosphorus, calcium carbide, ferroalloy.

INTRODUCTION

When searching for the optimal conditions for obtaining yellow phosphorus during the electric smelting of phosphorites, a series of studies was carried out at the Lennigiprokhim Institute on the joint carbon-thermal reduction of phosphorus, calcium and silicon from the $Ca_3(PO_4)_2$-SiO_2 system [1], as well as the patterns of formation of high-silicon ferrophosphorus [2]. It was found that at 1500 ^{0}C (real temperature in the furnace) the rate of reduction of phosphorus is 30 times higher than the rate of reduction of silicon from SiO_2. Silicon reduction becomes more intense in the subelectrode region at temperatures above 1700 ^{0}C. Therefore, the Si content in industrial ferrophosphorus during a hot furnace run and an overestimated amount of coke can reach 15% [3].

With stable operation of phosphorus furnaces, the degree of reduction of Si and its transition to ferroalloy (ferrophosphorus) does not exceed 1%. Therefore, almost all silicon passes into waste slag, the yield of which per 1 ton of phosphorus is 9–12 tons [4–5]. Thus, the existing method of electrothermal production of phosphorus does not meet modern requirements for the complex processing of raw materials. In this regard, this article presents the results of studies of equilibrium production from $Ca_3(PO_4)_2$ and SiO_2 in the presence of iron and phosphorus carbon, calcium carbide and ferroalloy [6].

MATERIALS AND METHODS

The studies were carried out by calculating the change in the Gibbs energy (ΔG^o) and entropy (ΔH^o) from $Ca_3(PO_4)_2$-$nSiO_2$-mFe-xC systems to obtain CaC_2, P4(gas) and silicon silicides ($FeSi_2$, FeSi, Fe_5Si_3, Fe_3Si). The calculations were carried out using the HSC-6.0 software package (Reaction Equations option).

Three groups of reactions were considered:

I group:

$$Ca_3(PO_4)_2+2SiO_2+18C+Fe=FeSi_2+3CaC_2+12CO_{(g)}+0.5P_{4(g)} \quad (1)$$

$$Ca_3(PO_4)_2+1.75SiO_2+17.5C+Fe=0.25FeSi+0.75FeSi_2+3CaC_2+11.5CO_{(g)}+0.5P_{4(g)} \quad (2)$$

$$Ca_3(PO_4)_2+1.5SiO_2+17C+Fe=0.5FeSi+0.5FeSi_2+3CaC_2+11CO_{(g)}+0.5P_{4(g)} \quad (3)$$

$$Ca_3(PO_4)_2+1.25SiO_2+16.5C+Fe=0.75FeSi+0.25FeSi_2+3CaC_2+10.5CO_{(g)}+0.5P_{4(g)} \quad (4)$$

$$Ca_3(PO_4)_2+SiO_2+16C+Fe=FeSi+3CaC_2+10CO_{(g)}+0.5P_{4(g)} \quad (5)$$

II group:

$$Ca_3(PO_4)_2+SiO_2+16C+Fe=FeSi+3CaC_2+10CO_{(g)}+0.5P_{4(g)} \quad (5)$$

$$Ca_3(PO_4)_2+1.5SiO_2+17C+2Fe=0.75FeSi+0.25Fe_5Si_3+3CaC_2+11CO_{(g)}+0.5P_{4(g)} \quad (6)$$

$$Ca_3(PO_4)_2+2SiO_2+18C+3Fe=0.5FeSi+0.5Fe_5Si_3+3CaC_2+12CO_{(g)}+0.5P_{4(g)} \quad (7)$$

$$Ca_3(PO_4)_2+2.5SiO_2+19C+4Fe=0.25FeSi+0.75Fe_5Si_3+3CaC_2+13CO_{(g)}+0.5P_{4(g)} \quad (8)$$

$$Ca_3(PO_4)_2+2.75SiO_2+19.5C+4.5Fe=0.125FeSi+0.875Fe_5Si_3+3CaC_2+13.5CO_{(g)}+0.5P_{4(g)} \quad (9)$$

$$Ca_3(PO_4)_2+3SiO_2+20C+5Fe=Fe_5Si_3+3CaC_2+14CO_{(g)}+0.5P_{4(g)} \quad (10)$$

III group:

$$Ca_3(PO_4)_2+3SiO_2+20C+5Fe=Fe_5Si_3+3CaC_2+14CO_{(g)}+0.5P_{4(g)} \quad (10)$$

$$Ca_3(PO_4)_2+2.5SiO_2+19C+4.5Fe=0.75Fe_5Si_3+0.25Fe3Si+3CaC_2+13CO_{(g)}+0.5P_{4(g)} \quad (11)$$

$$Ca_3(PO_4)_2+2.25SiO_2+18.5C+4.25Fe=0.625Fe_5Si_3+0.375Fe_3Si+3CaC_2+12.5CO_{(g)}+0.5P_{4(g)} \quad (12)$$

$$Ca_3(PO_4)_2+2SiO_2+18C+4Fe=0.5Fe_5Si_3+0.5Fe_3Si+3CaC_2+12CO_{(g)}+0.5P_{4(g)} \quad (13)$$

$$Ca_3(PO_4)_2+1.5SiO_2+17C+3.5Fe=0.25Fe_5Si_3+0.75Fe_3Si+3CaC_2+11CO_{(g)}+0.5P_{4(g)} \quad (14)$$

$$Ca_3(PO_4)_2+1.25SiO_2+16.5C+3.25Fe=0.125Fe_5Si_3+0.875Fe_3Si+3CaC_2+10.5CO_{(g)}+0.5P_{4(g)} \quad (15)$$

$$Ca_3(PO_4)_2+SiO_2+16C+3Fe=Fe_3Si+3CaC_2+10CO_{(g)}+0.5P_{4(g)} \quad (16)$$

RESULTS AND DISCUSSION

In table 1, as an example, the Critical final table of temperature of thermodynamic indicators (ΔH^o, ΔS^o, ΔG^o, reactions, lgKr) of reaction 1. It can be seen that with increasing temperature, the reaction equilibrium shifts from left to right ($\Delta G = 0$ of this reaction is observed at 1631, 2 ^0C).

Fig. 1 shows the effect of temperature on ΔG^o and ΔH^o of the texture of the 1st group, on the image of the 2nd group of the second, on the image of the 3rd - the larger group.

Table 1 - Effect of temperature on the thermodynamic parameters of reaction 1

Ca3(PO4)2+2SiO2+Fe+18C=FeSi2+3CaC2+12CO(g)+0.5P4(g)

T **C**	**deltaH** **kJ**	**deltaS** **J/K**	**deltaG** **kJ**	**K**	**Log(K)**
500	4402.18	2370.00	2569.81	2.33E-174	-173.63
600	4387.34	2352.02	2333.68	2.40E-140	-139.62
700	4372.42	2335.86	2099.27	2.04E-113	-112.69
800	4355.01	2318.84	1866.54	1.38E-91	-90.86
900	4332.76	2298.89	1635.82	1.44E-73	-72.84
1000	4312.98	2282.68	1406.78	1.90E-58	-57.72
1100	4292.89	2267.50	1179.27	1.37E-45	-44.86
1200	4253.70	2239.95	953.92	1.49E-34	-33.83
1300	4234.20	2227.14	730.57	5.50E-25	-24.26
1400	4214.05	2214.75	508.44	1.34E-16	-15.87
1500	4194.78	2203.57	287.53	3.38E-09	-8.47
1600	4161.69	2185.36	68.18	1.26E-02	-1.90
1700	4142.54	2175.40	-149.86	9.28E+03	3.97
1800	4102.85	2155.65	-366.14	1.68E+09	9.23
1900	3914.39	2065.37	-573.96	6.27E+13	13.80
2000	3893.63	2056.03	-780.03	8.43E+17	17.93
2100	3873.25	2047.25	-985.19	4.86E+21	21.69

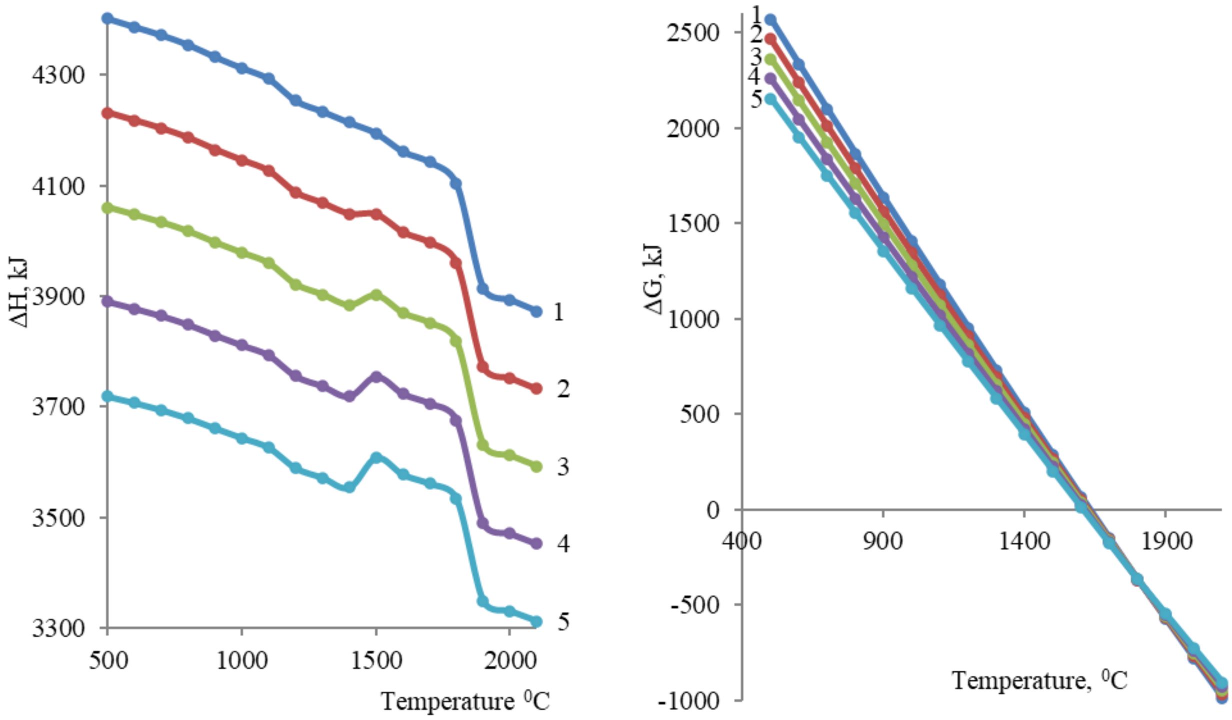

Fig. 1. Influence of temperature on ΔG° and ΔH° reactions of group 1

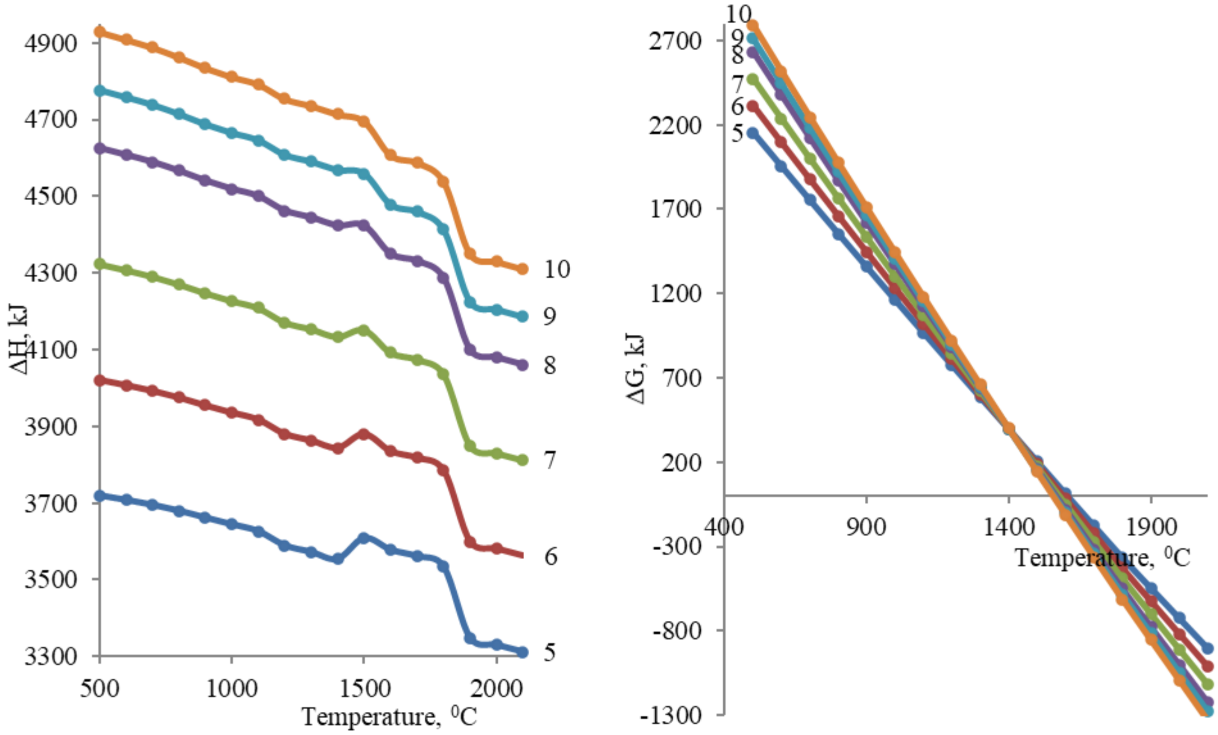

Fig. 2. Influence of temperature on ΔG° and ΔH° reactions of group 2

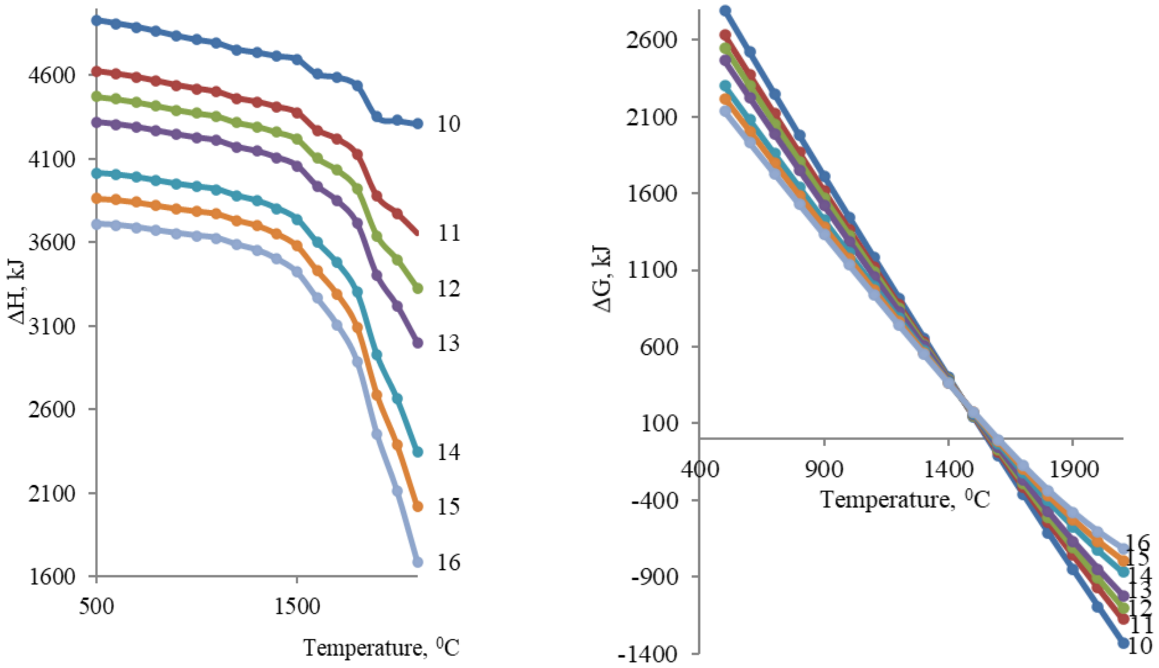

Fig. 3. Influence of temperature on ΔG° and ΔH° of group 3 reactions

It can be seen from the above material that all 16 reactions are endothermic (ΔH for all reactions is a positive value). The observed breaks in the dependences ΔH=f(T) are associated with phase or modification transitions of the reaction participants. If there is a decrease in ΔH^{o}, then these transitions refer to the starting substances, and if an increase, then it indicates the transitions of the reaction products.

It can be seen from the dependences ΔG^{o} =f(T) that during ΔG^{o} reactions it decreases with increasing temperature. The reaction start temperature (according to ΔG^{o} = 0) depends on the mole fraction of silicon in the silicide (β). For FeSi2 β=0.666, FeSi=0.5, Fe5Si3=0.375 and for Fe3Si= 0.25. Table 2 shows the influence of the mole fraction of Si in silicides (β) on the temperature of the start of reactions (Tн, ^{0}C).

Table 2 - Temperature of 1-16 reaction start

1 group							
№ reactions	1	2	3	4	5		
β*	0.66	0.621	0.583	0.54	0.50		
Tн, ^{0}C	1631.2	1625.7	1619.8	1613.4	1606.7		
2 group							
№ reactions	5	6	7	8	9	10	
β	0.50	0.428	0.40	0.384	0.382	0.375	
Tн, ^{0}C	1606.7	1591.1	1577.7	1566.1	1560.8	1555.8	
3 group							
№ reactions	10	11	12	13	14	15	16
β	0.375	0.357	0.346	0.333	0.3	0.277	0.25
Tн, ^{0}C	1555.8	1563.8	1568.3	1573.2	1584.4	1590.9	1598.1

*) mole fraction of silicon in iron silicide

Fig. 4 shows the graphic dependence of Tн=f(β) for reactions 1-10. It can be seen that with an increase in β, the temperature of the onset of reactions increases. This dependence is described by the equation:

$$T_H = -44973\,\beta^4 + 99812\,\beta^3 - 82578\,\beta^2 + 30336\,\beta - 2581.7 \qquad (17)$$

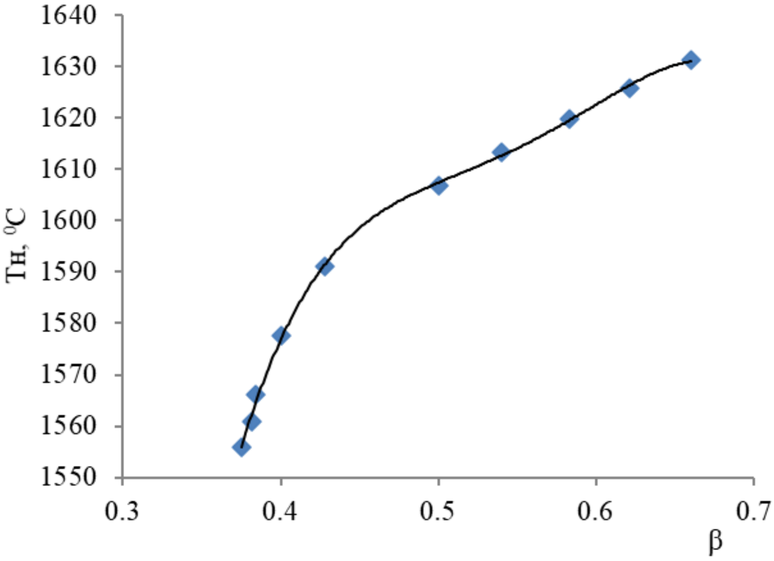

Fig. 4. Dependency Tн=f(β)

The established dependence is due to the fact that with an increase in β in the silicide, the proportion of Si increases, which, in comparison with iron, has a greater affinity for oxygen than iron.

CONCLUSION

Based on the results obtained on the interaction in the $Ca_3(PO_4)_2$-$nSiO_2$-mFe-xC system, the following conclusions can be drawn:

- the temperature of the beginning of the joint reduction of phosphorus, the production of calcium carbide and iron silicides depends on the mole fraction of silicon in the iron silicide and is 1555.8-1631.2 ^{0}C.
- with an increase in the mole fraction of silicon in the silicide from 0.375 (Fe_5Si_3) to 0.5 ($FeSi_2$), an increase in the temperature of the beginning of interaction in the system is associated with an increase in silicon iron in the silicide, which has a higher affinity for oxygen than iron.

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USE OF USED CATALYSTS AND INDUSTRIAL PRODUCTS OF ENTERPRISES IN THE PRODUCTION OF MICROFERTILIZERS

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ABSTRACT

Methods for solving an important environmental problem - the qualified use of spent catalysts and manganese-containing wastes from the production of nicotinic acid - are considered. The products obtained by the proposed technology can be used in the production of mineral fertilizers with microelements. Today, there are various ways of processing technogenic formations. Technological and environmental shortcomings of the pyrometallurgical scheme for extracting metals from waste and intermediate products determine the need to find more advanced ways for their complex processing. Foreign enterprises are actively searching for alternative technologies. Hydrometallurgical methods: acid, salt and alkaline leaching require the use of acid-resistant equipment for their implementation. The processing of nicotinic acid production wastes with the use of reducing agents makes it possible to achieve high selectivity in the extraction of metals into solution, as well as the possibility of their regeneration and does not require special structural materials.

Keywords: sulfuric acid, nicotinic acid, concentration, temperature, middlings, potassium iodide, trilon B, sodium toisulfate, xylenol orange indicator, starch.

INTRODUCTION

The intensification of the raw material sector of the economy of our country is now increasingly being carried out through the involvement in the processing of poor off-balance, difficult-to-enrich ores and dump tailings. Recently, it has become more and more economical to use recycled raw materials in order to extract useful materials for their further use. In particular, non-ferrous metallurgy and chemical industry wastes are secondary sources of valuable metals. There are technologies and methods for processing such waste, but due to a number of problems they are not widely used. To organize production facilities for the processing and disposal of secondary raw materials, municipal and state support is required, as well as the creation and modernization of recycling technologies in order to increase the economic benefits of the entire process.

There are many works in the literature on the use of chemical production wastes as sources of raw materials in the production of mineral fertilizers enriched with microelements [1–6].

When using waste as macro- or microfertilizers, in each specific case, it is necessary to study the chemical and phase composition of the waste, processing methods, the behavior of components, toxicological characteristics, agrochemical efficiency, and the development of a specific fertilizer technology. To increase the production of fertilizers with manganese, it is necessary to expand the search for waste, as well as research on the conditions for extracting the trace element from them.

The production of complex fertilizers containing various microelements in their composition is constrained mainly by the lack of cheap and affordable sources of raw materials for microelements.

In this regard, in the production of manganese-containing microfertilizers, manganese-containing wastes from the production of nicotinic acid, caprolactam permanganate purification, and phosphate slag deserve attention.

MATERIALS AND METHODS

Sulfuric acid (chemically pure H2SO4), potassium iodide (chemically pure KI), trilon B (chemically pure), sodium toisulfate (chemically pure Na2S2O3), xylenol orange indicator (chemically pure) .a), starch.

We have proposed methods for extracting microelements from the waste composition of the production of nicotinic acid - pyrolusite, %: 60 - 65 MnO4, 2-3 K2O, 0.2-0.5 salts of nicotinic acid.

To extract microelements from waste, an installation was assembled, which is a three-necked glass flask equipped with an electromechanical stirrer, a reflux condenser, a thermometer, and holes for feeding the reaction mixture and sampling.

RESULTS AND DISCUSSION

To clarify the possibility of using waste as an additive to enriched superphosphate, the extraction of manganese with acid solutions under conditions close to the fertilizer production technology was studied. The influence of various factors (concentration, T:L ratio, process duration and temperature) on the degree of extraction of manganese from waste by sulfuric acid (5-93%) was studied.

At 40 and 60% sulfuric acid concentration, the degree of extraction of manganese from the waste from the production of nicotinic acid with a duration of 10 minutes increases to 3.1% and 8.5% at 25°C and up to 7.3% and 30.1% at 85°C , respectively.

Table 1 - Extraction of manganese into sulfuric acid from nicotinic acid waste depending on the concentration

№	Factors	Extraction Mn,%	Conditions for the experiment
Effect of Sulfuric Acid Concentration			
1.	5	1.5	T:W=1:10 Temperature 25ºC
2.	10	1.6	
3.	15	2.2	
4.	20	2.8	
5.	30	2.9	
6.	40	3.1	
7.	60	8.5	
8.	93	3.5	

Table 1 continuation

9.	5	4.9	T:W =1:10 Temperature 85°C
10.	10	5.5	
11.	15	6.3	
12.	20	6.5	
13.	30	7.1	
14.	40	7.3	
15.	60	30.1	
16.	93	10.8	

A further increase in the concentration of sulfuric acid from 60 to 93% leads to a decrease in the degree of extraction of manganese to 3.5% at 25°C and to 10.2% at 85°C. (Table 1, Fig.1.).

As can be seen from the data obtained, the degree of extraction of manganese is very low and cannot meet the requirements for complex fertilizers in terms of their manganese content. To increase the degree of manganese extraction from nicotinic acid waste into sulfuric acid solutions, sodium sulfite and hydrazine were used as reducing agents.

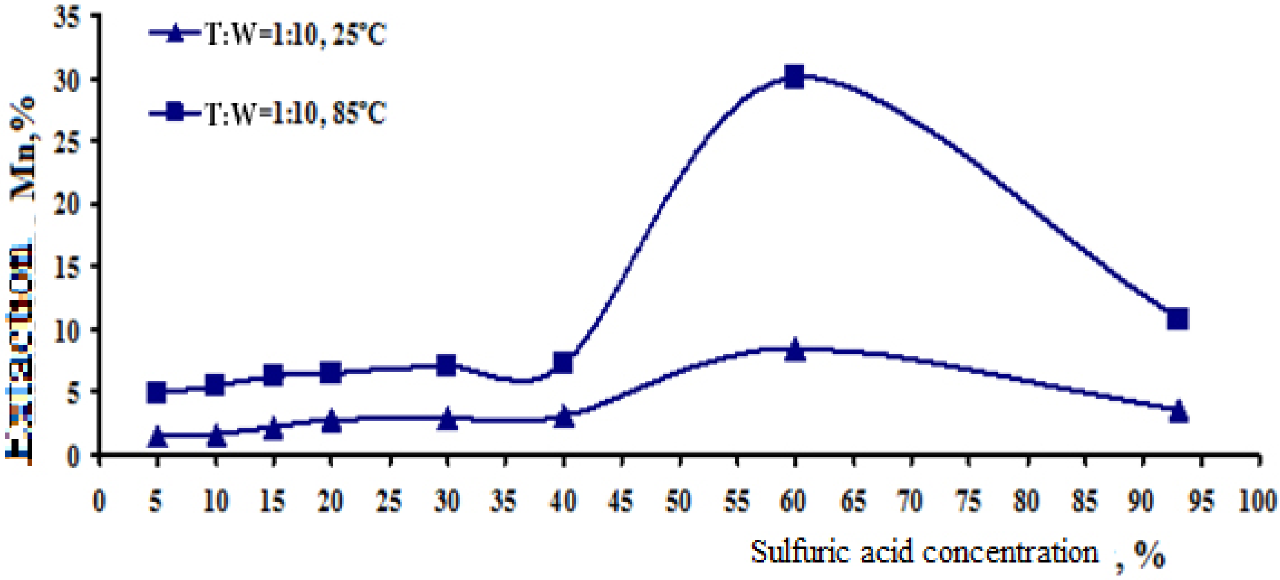

Fig. 1. Extraction of manganese into sulfuric acid from the waste of nicotinic acid at T:W = 1:10 depending on the concentration

Based on the redox potentials, it could be assumed that sodium sulfite (Eo = +0.17B) and hydrazine (Eo = 1.00B) will reduce manganese dioxide (Eo = +1.23B with the formation of a soluble compound of divalent manganese:

$$MnO_2+Na_2SO_3+H_2SO_4=MnSO_4+Na_2SO_4+H_2O$$

$$2MnO_2+N_2H_4+2H_2SO_4=2MnSO_4+2H_2+2H_2O$$

Introduced into sulfuric acid sodium sulfite in the amount of 1.8-5.0%. The influence of the concentration of hydrazine in the reaction mixture (0.5-5%) on the degree of extraction of manganese from the waste from the production of nicotinic acid in 15%, 40% and 50% sulfuric acid solutions was studied.

With an increase in the acid concentration, the degree of transition of manganese into the solution decreases. So, in the presence of 3.3% hydrazine, the extraction of the trace element in 15%, 40% and 50% solutions of sulfuric acid is 91.2; 49.0 and 27.6% respectively. Under optimal conditions (T:W=1:10, temperature 85°C, reducing agent concentration 4-4.5%), up to 99% manganese passes from the waste from the production of nicotinic acid into 15% sulfuric acid.

CONCLUSION

For the purpose of physical and chemical substantiation and development technologies of manganese-containing enriched superphosphate using cheap and affordable sources - manganese-containing waste from the production of nicotinic acid - pyrolusite, which contains 60-65% MnO_2, 2-3% K_2O, 0.2-0.5% salt of nicotinic acid in its composition - the extraction of manganese in sulfuric acid solutions. It has been established that the concentration of acid, the ratio of solid and liquid phases, and the temperature of the process have a significant effect on the extraction of trace elements. Sodium sulfite and hydrazine were used as reducing agents to increase the degree of manganese extraction from nicotinic acid waste into solutions of sulfuric and extraction phosphoric acids. It has been proven that at T:L=1:10 and a temperature of 85°C in the presence of reducing agents (sodium sulfite and hydrazine), almost complete extraction of manganese into sulfuric acid solutions is achieved, which makes it possible to recommend the waste from the production of nicotinic acid as a source of manganese raw materials for the production of manganese-containing mineral products. fertilizers.

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