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Determination of factors effecting the properties of water-air micro dispersion

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ABSTRACT

The article presents the results of laboratory studies on the effect of the liquid-gas ratio and the foaming agent type on the average water-air micro dispersion size obtained from the foaming agent solution. The size of microbubbles significantly effects the efficiency of flotation and depends on the type and concentration of foaming agent used for their production. A generator was used to obtain water-air micro dispersion. The works were performed to work out the water-air micro dispersion parameters of at different liquid-gas ratio and different performance of the generator. The following foaming agents were used as objects of research: sodium butyl aero flot (BTF), flotanol C-7, butyl triethylenetetramine (B-TETA) at a concentration of 0.5 g/dm^3. It has been established, that the optimal phase liquid-gas ratio was 1:1, the optimal capacity of the generator was 6-7.2 dm^3/h with an average particle size of air-water micro dispersion- 33-41 μm for BTF solution, 103-107 μm for C-7 solution, 90-93 μm for B-TETA solution. The type of foaming agent used in flotation effects the size and stability of microbubbles. It is established that the flotation agents can be arranged in the following line with respect to their ability to create micro dispersion: IIBK→Senfroth 580→B-TETA→OPSB→Flotanol C-7→T-92→BTF. The best results are shown by BTF that creates micro dispersion of 43-58 μm (t 20-40 °C) and stability of 80 sec with concentration of 0.5 g/dm^3.

Keywords: flotation, combined micro flotation, flotation reagent, water-air micro dispersion, microbubbles.

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Introduction

Low efficiency of flotation recovery of micron-sized particles from ores is one of the important reasons for large losses of valuable components at beneficiation plants [[1], [2]]. Beneficiation plants in all countries are engaged in solvation of this problem [[3], [4], [5], [6], [7], [8], [9], [10]]. One of the solutions to this problem is the use of combined microflotation with water-air micro-dispersion obtaining enabling to extract additional micro-dispersed valuable oreminerals, optimize the flotation process and obtain higher technological parameters [11], [12], [13]].

The problem is reduced to finding a microbubble production method [[14], [15], [16],

17]]. Spatial separation of the processes of microbubble formation and flotation is also important that willeliminate the pulp heating process in the flotation chamber and coalescence of bubbles, stabilizing formation process of micro dispersions homogeneous in size. All this in aggregate provides improved flotation performance of deeply milled ores to the micro-dispersed state, more complete recovery of finely dispersed valuable minerals

It is well known that classical flotation also uses different types of bubbles: macro-, medium- and micro-bubbles. Macro-bubbles that are transportable bubbles have a size of 300-500 μm, medium - 70-300 μmand micro - less than 70 μm. But, in conventional flotation, the amount of macro-bubbles (>90%) significantly exceeds the amount of medium and micro-bubbles. When stable micro dispersion sizes with the correct ratio of bubbles of different sizes is used, the flotation recoveryprocessformicroparticles is accelerated, the flotation time is reduced.

Scientists conduct researches to study sizes and stability of water-air microemulsion [[18], [19], [20]] obtained from the foaming agent solution. The effect of the water-air microemulsion (WAMD) nature on the flotability of sulfide minerals of non-ferrous metals and the properties of water-air microemulsion was studied in [21].

The purpose of this study is to study the effect of the liquid-gas ratio and the foaming agenttype on the average water-air micro dispersion size.

Thus, the problem to find more effective ways intended to obtain microbubbles for flotation of fine particles of minerals of non-ferrous and rare metals from minerals still remains relevant.

Experimental part

A generator was used to obtain water-air micro dispersion. The laboratory generator principle is that air and foaming solution is transferred through the inlet pipe of the dispersant head into the mixing chamberwith the help of metering pumps.

Additional mixing of the mixture is performed in the mixing chamber by means of the rotor part of the dispersator head. The mixture is thrown to the periphery and goes through the slot between the rotor and the stator due to the high circumferential speed. Its size is determined by the composition of raw materials and the required degree of dispersion. The rotating rotor crushes air bubbles with its teeth. The crushing degree of the final product depends on the viscosity of the medium, the foaming agenttype, the peripheral speed.

The properties of water-air micro dispersion are effectd by the ratio of air and foaming agent solution whose flow rate is regulated by dosing pumps with maximum capacity of 3.3 cm^3/s (12 dm^3/h).

The workswereperformedto work out the parameters of water-air micro dispersion at different liquid-gas (L:G)ratio, to study the effect of this ratio on the water-air micro dispersion size. Different L:G ratios were studied;theywere varied - L:G=1:0.75; L:G=1:1; L:G=1:1.25; L:G=1:1.5. The foaming agents used were sodium butyl aeroflot (BTF), flotanol C-7, butyltriethylenetetramine (B-TETA) at a concentration of 0.5 g/dm^3. Besides, tests were conducted at different dosing pump capacities.

The water-air mixture size obtained in the generator was analyzed using a Photocor Compact particle size analyzer. The operation principle of the analyzer was based on the method of static and dynamic light scattering (photon correlation spectroscopy). The size of the particles dispersed in the liquid was determined by measuring the correlation function of the fluctuations of the scattered light intensity and the integral scattering intensity. The analyzer laser power ranges from 2 to 35 mW.

Figures 1-3 show the dependencies of the average water-air micro dispersion size obtained from solutions of BTF, C-7, B-TETAfoamingagentson the liquid-gas ratio.

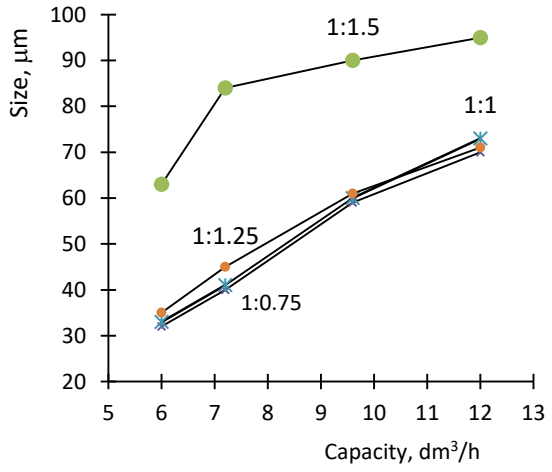

Figure 1 - Dependence of the average particle size of WWMD obtained from BTF solution on the L:G ratio at different pump capacities

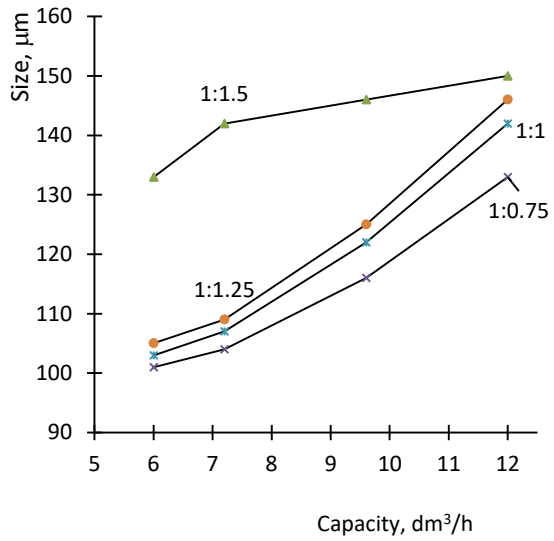

Figure 2 - Dependence of the average particle size of WWMD obtained from the C-7 solution on the L:G ratio at different pump capacities

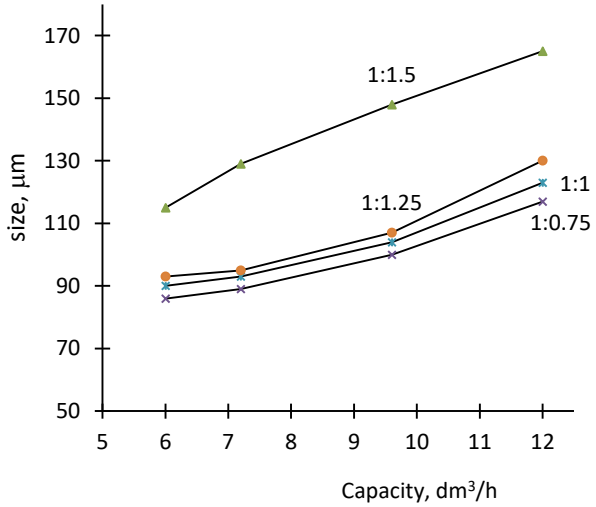

Figure 3 - Dependence of the average particle size of WWMD produced from B-TETA solution on the L:G ratio at different pump capacities

The result of the analyses shows that changes in the liquid-gas ratioeffects the final size of the water-air micro dispersion. The average water-air micro dispersion size increases for all solutions of foaming agents compared with other liquid-gas ratios at the liquid-gas ratio of 1:1.5. It indicates that thegas phase supply more than the liquid phase worsens the water-air micro dispersionproperties.

The final average water-air micro dispersion size is close to each other at liquid-gas ratios equal to 1:0.75, 1:1 and 1:1.25. It is required to properly adjust the generator (pumps) capacity and the liquid-gas ratio phases to obtain the optimum water-air micro dispersion size. Proper feeding of the gas phase, the optimal liquid-gas ratiohave a huge impact on the water-air micro dispersion formation. Increased supply of the gas phase results in an increase in the number of micro-bubbles with a smaller flow of the liquid phase (reagent solution). Not only the final size of the air-water micro dispersion but also the amount of created micro dispersionisimportantto obtain high performance in the flotation process, i.e. it is required to create a certain amount of air-water micro dispersion. The final amount of air-water micro dispersion created by quantity should provide recovery of all useful particles of slurry class not adsorbed by standard bubbles in the standard mode.

Discussion of the results

Analysis of the results shows that the liquid-gas ratio, equal to 1:1isthe optimum of all types of foaming agents. Figure 4 shows the dependence of the average water-air micro dispersion size obtained from 0.5 g/l solutions of BTF, C-7, B-TETA foaming agents at a liquid-gas ratio of 1:1.

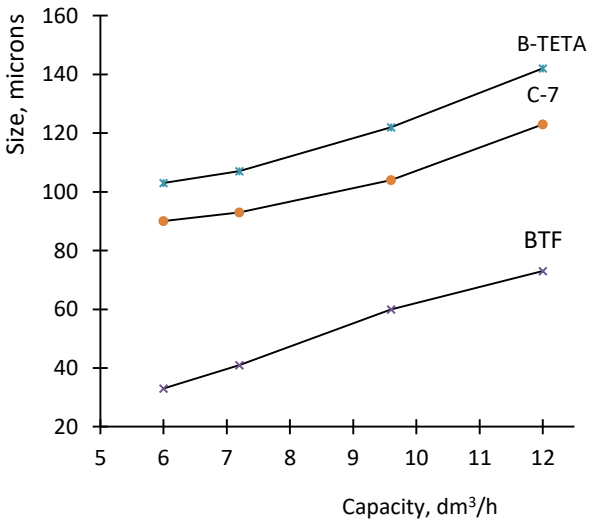

Figure 4 -Dependence of the average particle size of WWAMD obtained from BTF, C-7, B-TETAfoaming agent solutions at the ratio L:G = 1:1, on the generator capacity

The average size of the water-air micro dispersion obtained from 0.5 g/l BTP solution is 60-73 µm; from 0.5 g/l C-7 solution - 122-142 µm; from 0.5 g/l B-TETA solution - 104-123 µm at increased capacity of the liquid phase (9.6 l/h; 12 l/h). Analysis of the results shows that the water-air micro dispersion size for BTF solution increases by 100%; for C-7 solution by 20%; for B-TETA solution

by 15%at capacities of 9.6 l/h; 12 l/h. Thus, the generator capacity should vary between 6-7.2 l/hto create the optimum water-air micro dispersion size.

Thus, the parameters to be used to obtain water-air micro dispersion have been worked out, the effect of the phase ratio: liquid-gas on the micro dispersion properties has been studied. It has been established that the optimal liquid-gas ratio is 1:1, the optimal generator capacity - 6-7.2 l/h, and the average particle size of air-water micro dispersion is 33-41 µm for BTP solution, 103-107 µm - for C-7 solution, 90-93 µm - for B-TETA solution.

The researches to study micro dispersion properties depending on the flotation foamingagent used and their concentration were performed at the established optimum L:G ratio and generator capacity. The following foaming agents were studied: BTF, oxal T-92, propylene oxide butyl alcohol (OPSB),C-7, B-TETA, methyl isobutyl carbinol (MIBC), Senfroth 580 foaming agent. Here are some characteristics of these foaming agents.

BTF - sodium-butyl aeroflot ($(C_4H_9)_2S_2O_2PNa$, molar mass 264.3 g/mol) is an aqueous solution of sodium salt of dibutyl dithiophosphoric acid.

Oxal T-92 is a product of high boiling by-products of dimethyldioxane production. It contains more than 50 % of dioxane alcohols and esters and about 50 % of a mixture of 1, 2, 3 atom alcohols.

OPSB is a mixture of monobutyl esters of C_4H_9-O-$(C_3H_6O)_nH$ polypropylene glycols.

Flotanol C7 is an alkylpolyglycol based foaming agent. These foaming agents for sulfide ores were developed with optimal selectivity and are effective with ores containing nonferrous metals, platinum group minerals and precious metals.

B-TETA has four amino groups with four butyl radicals in its composition and is well soluble in water. It adsorbs on the surface of the bubbles, and changes their negative charges into positive ones, thus intensifying the flotation process.

MIBCwith the molecular formula $(CH_3)_2CHCH_2CHOCH_3$ is slightly soluble in water and can dissolve in most organic solvents.

Senfroth foaming agents consist of varying amounts of alcohol, polyethylene glycol and ethylene glycol. Senfroth 580 contains 37-50% alcohol, 38-51% glycol ether, ≥9% glycol with density of 0.903-0.96.

Such concept as water-air micro dispersionstability was introduced - it is time spent for destruction of emulsion. A flotation agent solution of 500 dm^3 is passed through the generator and water-air microemulsion is obtained for this purpose (Figure 5a). Then a stirrerand a stopwatch are turned on, and time spent for microemulsion destruction to a certain state is recorded (Figure 5b). The time taken tp break indicates the stability of the water-air micro dispersion.

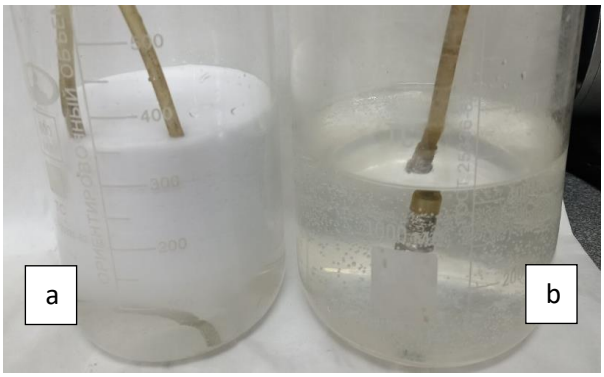

Figure 5 - View of water-air micro dispersion before (a) and after (b) destruction

Table 1 shows the dependence of water-air micro dispersion stability and size on the foaming agent type and concentration at the optimal speed of the generator of 6000 rpm.

The results of Table 1 show that:

- The optimal concentration for butyl aeroflot is 0.5 g/l, at which the particle size varies 43-58 µm (t 20-40 °C), the bubble stability is 80 sec;

- The optimal concentration for T-92 is 5 g/l, at which the particle size varies 41-43 µm (t 20-40°C), the bubble stability is 70-80 sec;

- The optimal concentration for OPSB is 5 g/l and more, at which the particle size varies 81-83 µm (t 20-40°C), the bubble stability is 60 sec;

- The optimal concentration for flotanol C-7 is 5 g/l, at which the particle size varies from 55 to 75 µm (t 20-40 °C), the bubble stability is 65-70 sec;

- The optimal concentration for B-TETA is 50 g/l, at which the particle size varies from 53-59 µm (t 20-40°C), the stability of the bubbles is 70-75 sec;

- Senfroth 580 foaming agent gives microbubbles with a stability of 60-65 seconds, the particle size from 73-85 µm (t 20-40°C)at a concentration of 5 g/l and more.

Table 1 - Dependence of -air micro dispersion stability and water size on the foaming agenttype and concentration at the optimal speed of the generator of 6000 rpm

Temperature, ^{0}C	Bubble size and bubble life at different concentrations (g/L)							
	0,05		0,5		5,0		50	
	Bubblestability, sec	Particlesize. µm	Bubblestability, sec	Particlesize. µm	Bubblestability, sec	Particle size,µm	Bubblestability, sec	Particlesize, µm
BTF								
20	55	90	80	42	70	65	70	65
30	45	100	80	43	65	73	70	69
40	40	110	80	41	65	76	70	67
50	35	120	70	65	65	75	70	66
60	35	123	70	68	65	72	65	73
70	30	142	60	81	60	83	65	75
80	25	150	50	85	50	93	55	86
T-92								
20	35	123	60	80	80	42	35	128
30	35	121	60	83	75	53	35	125
40	30	145	60	81	70	58	35	126
50	30	141	60	84	65	73	35	124
60	30	140	60	82	60	82	30	142
70	30	144	55	88	55	87	20	159
80	30	145	55	89	50	96	20	162
OPSB								
20	30	143	55	85	60	81	60	83
30	30	141	55	87	60	83	55	88
40	30	144	55	89	60	83	55	89
50	30	143	55	86	55	89	50	87
60	30	142	55	87	55	87	45	103
70	30	141	50	98	55	88	45	105
80	30	140	50	97	55	86	40	113
C-7								
20	30	143	40	112	70	55	75	55
30	30	142	40	116	70	57	75	54
40	25	153	40	114	65	75	70	58
50	25	156	40	113	65	74	70	59
60	25	151	30	145	60	82	65	72
70	25	154	30	147	55	88	65	71
80	25	152	30	143	55	87	65	71
B- TETA								
20	20	180	50	91	60	83	75	53
30	20	185	50	94	55	89	75	54
40	20	188	50	93	55	88	70	59
50	20	181	50	93	50	95	70	60
60	20	189	45	103	50	94	70	59
70	20	187	40	117	45	105	65	73
80	20	185	35	125	45	104	60	81
SENFROTH 580								
20					65	73	65	74
30					60	85	65	73
40					60	84	60	86
50					55	89	60	84
60					55	90	60	85
70					55	89	55	87
80					50	97	45	62

MIBC at a concentration of 50 g/l produces unstable microbubbles which quickly disintegrate within 10 seconds.

The flotation agents can be arranged in the following lineunder theor ability to create water-air micro dispersion: MIBC → SENFROTH 580→ B-TETA→OPSB→ Flotanol C-7→T-92→Butyl Aeroflot.

Attempts in the area of bubble formationare made to create more microbubbles. Reduction of the bubblesize increases the flotationefficiency. The asymmetric structure of foaming agent molecules and their low solubility in water contribute to their concentration on the interface L-G (or L-T), where they are oriented so that their hydrophilic group is directed to water, while the hydrophobic one (hydrocarbon radical) is directed to less polar phase (air, oil). Having a low surface tension, foaming agents reduce the surface tension of water and form a hydrate layer around the air bubble. It dramatically increases the stability of the air bubbles enabling to retain their original dispersibility [[22], [23], [24]]. The arrangement of the polar groups in the moleculeis essential for the surface activity of the substance. Foaming agent molecules adsorb more actively the more asymmetric the arrangement of hydrophilic and hydrophobic groups in the molecule is; the limiting location of the polar group is the end of the hydrocarbon radical. Bubbles should be elastic and elastic, i.e., deformable in addition to coalescence stability. Elasticity depends on the length of the hydrocarbon radicall middle homologues of the series of single-atom alcoholshaveespecially high elasticity.

Thus, the factors effecting the water-air micro dispersion properties are the temperature of the pulp, the speed of the generator, the concentration of foaming agent solution [19], as well as the L:G ratioregulated by the dosing pumps of the generator, as well as the foaming agenttype.

Conclusions

The effect of L:G phase ratio on the properties of water-air micro dispersion was studied. It was found that the optimum liquid-gas ratio is 1:1, the optimum capacity of the generator is 6-7.2 l/h, with the average size of the water-air micro dispersion is 33-41 μm for BTF solution, 103-107 μm - for C-7 solution, 90-93 μm - for B-TETA solution.

The type of foaming agent used in flotation effects the size and stability of microbubbles. It is established that the flotation agents can be arranged in the followinglinewith respect to ability to create micro dispersion: MIBC→Senfroth 580→B-TETA→OPSB→Flotanol C-7→T-92→BTF. The best results are shown by BTF that creates a micro dispersion of 43-58 μm size (t 20-40 °C) and stability of 80 sec.at concentration of 0.5 g/dm^3.

Conflict of interest

The correspondent author declares that there is no conflict of interest on behalf of all authors.

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Су-ауалы микродисперсияның қасиеттеріне әсер ететін факторларды анықтау

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ТҮЙІНДЕМЕ

Мақалада сұйық-газ фазасының қатынасы және көбіктендіргіш реагентінің түрі көбіктендіргіш ерітіндіден алынған су-ауа микродисперсиясының орташа мөлшеріне әсері бойынша зертханалық зерттеулердің нәтижелері берілген. Микрокөпіршіктердің мөлшері

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оларды өндіру үшін қолданылатын көбіктендіргіш реагентінің түрі мен концентрациясына байланысты флотация тиімділігіне айтарлықтай әсер етеді. Су-ауа микродисперсиясын алу үшін генератор қолданылды. Сұйық-газ фазаларының әртүрлі қатынасында және генератордың әртүрлі өнімділігінде су-ауалы микродисперсиясын алу параметрлерін анықау жұмыстары жүргізілді. Зерттеу объектілері ретінде концентрациясы 0,5 г/дм^3 құрайтын келесі көбіктендіргіш реагенттері пайдаланылды: натрий бутил аэрофлоты (БТФ), флотанол С-7, бутилтриэтилентетрамин (В-ТЕТА). Сұйық-газ фазаларының оңтайлы қатынасы 1:1, генератордың оңтайлы өнімділігі 6-7,2 дм^3/сағ құрайды, ал БТФ ерітіндісінен алынған су-ауа микродисперсиясының орташа мөлшері 33-41 мкм, С-7 ерітіндісінен - 103-107 мкм, В-ТЕТА ерітіндісінен - 90-93 мкм құрайды. Флотацияда қолданылатын көбіктендіргіш реагентінің түрі микрокөпіршіктердің мөлшері мен тұрақтылығына әсер етеді. Микродисперсия жасау қабілетіне қарай флотациялық реагенттерді келесі қатарға орналастыруға болады: MIBK → Senfroth 580 → В-ТЕТА → OPSB → флотанол S-7 → Т-92 → BTF. Ең жақсы нәтижелерді БТФ реагенті көрсетті, ол 0,5 г/дм^3 концентрациясында микробөлшектердің мөлшері 43–58 мкм (t 20–40 °C) және тұрақтылығы 80 сек құрайтын микродисперсия өндейді.

Түйін сөздер: флотация, комбинирленген микрофлотация, флотациялық реагент, су-ауа микродисперсиясы, микрокөпіршіктер.

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Определение факторов, влияющих на свойства водовоздушной микродисперсии

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АННОТАЦИЯ

В статье представлены результаты лабораторных исследований по изучению влияния соотношения фаз жидкое-газ и вида пенообразователя на среднюю крупность водо-воздушной микродисперсии, полученной из раствора пенообразователя. Размер микропузырьков существенно влияет на эффективность флотации, зависит от вида и концентрации вспенивателя, используемого для их производства. Для получения водо-воздушной микродисперсии использовали генератор. Проведены работы по отработке параметров получения водовоздушной микродисперсии при разном соотношении фаз жидкость-газ и разной производительности генератора. В качестве объектов исследований использованы вспениватели: бутиловый аэрофлот натрия (БТФ), флотанол С-7, бутилтриэтилентетрамин (Б-ТЭТА) при концентрации 0,5 г/дм^3. Установлено, что оптимальное соотношение фаз жидкость—газ составляет 1:1, оптимальная производительность генератора 6-7,2 дм^3/ч, при этом средняя крупность водовоздушной микродисперсии составляет 33-41 мкм для раствора БТФ, 103-107 мкм - для раствора С-7, 90-93 мкм - для раствора Б-ТЭТА. Вид вспенивателя, используемого при флотации, влияет на размер и устойчивость микропузырьков. Установлено, что по способности создавать микродисперсию флотореагенты можно расположить в следующий ряд: МИБК→ Senfroth 580→ Б-ТЭТА→ОПСБ→ флотанол С-7→Т-92→БТФ. Наилучшие результаты показывает БТФ, который при концентрации 0,5 г/дм^3 создает микроодисперсию крупностью 43-58 мкм (t 20-40 °C) и устойчивостью 80 сек.

Ключевые слова: флотация, комбинированная микрофлотация, флотореагент, водовоздушная микродисперсия, микропузырьки

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Development of the technology of integrated processing the Chelkar deposit potash ore

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ABSTRACT

With the huge explored reserves of potash salts in Kazakhstan, there is still no production of potash fertilizers, the demand for which is constantly growing. In this regard, research of processing of the largest Chelkar deposit ore into potash fertilizers and salts is an urgent problem. The article presents the research results of washed potash ore decomposition with nitric acid and nitric acid suspension filtration. The filtering properties and granulometric composition of the insoluble residue were studied, on what basis the decomposition mode with precipitate double washing was determined. To ensure good suspension filterability, washed, uncalcined ore should be used. Tests of a by-product, gypsum, as a gypsum binder were carried out, which confirmed its compliance with the normally hardening gypsum binder of the G-2 B grade. Advantage of the obtained gypsum is its environmental friendliness. Salts, which are chlorine-free water-soluble potassium-magnesium fertilizers have been obtained by crystallization from nitric acid solution. On the basis of results of experimental-and-laboratory tests, a basic flow scheme has been developed for obtaining potash and complex potassium-nitrogen-magnesium fertilizers from the Chelkar deposit ore.

Keywords: carnallite, Chelkar deposit, potash fertilizer, washing, decomposition, evaporation

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Introduction

Potassium is one of the most important nutrient elements for increasing crop yields. The potash fertilizer market has been steadily developing without significant declines for several decades. World consumption of potash fertilizers varies between 45-52 million tons of KCl or 28.4-32.9 million tons of K_2O. Although potassium chloride and potassium sulfate still hold the lion's share of the market, other potassium compounds also play an important role in crop production [[1], [2]]. Potassium sulfate is of the greatest importance as a chlorine-free fertilizer that combines well with micronutrients.

Most of developed potassium deposits are concentrated in Canada (Saskatchewan), in Russia (Verkhnekamskoye field), in Belarus (Starobinskoye field). Most common minerals in them are sylvine - 63%, sylvinite - 12-15%, carnallite - 17%, cainite - 19%, langbeinite - 23%, polyhalite - 16%. Rocks contain impurities of other salts such as gypsum, carbonates, clay particles. Of 120 potassium-containing minerals, only a small part is of industrial importance [[3], [4]].

Currently, Kazakhstan mineral fertilizer industry is at the stage of accelerated development and expanding the product range [5]. Despite the fact that there are huge reserves of potash ores in country's subsoil resources, there is no production of potash salts and fertilizers in the country. Poor knowledge of the ores' composition of known deposits and methods of their processing is the reason for this. The unique raw material base includes more than 6 billion tons of proven reserves of potassium chloride in the form of sylvinite, carnallite-sylvinite and polyhalite. Powerful deposits located in Aktobe, Atyrau and West Kazakhstan regions are considered as ones of the largest in the world. "Satimola", "Chelkar", "Inder" and "Zhilyansk" domes are the most studied ones [6]. Development of Zhilyansk and Chelkar potassium salts' deposits is the most ambitious of the projects proposed for implementation, for which "Kazakhstan Potash" received subsoil use rights in 2011. These deposits are reportedly owned by "Kazakhstan Potash" through a local subsidiary, "Batys Kaliy" [7]. Carnallite is a main component of the Chelkar deposit ore, and there are also 5-15% sylvite and 15-25% halite. The company carried out geological exploration and estimation of potash ore reserves. But until now, enterprises for potash salts' mining have not yet moved to the production stage. Considering the growing demand for potash in the country and in the world, mining and use of domestic potash ores are becoming increasingly important [6].

The authors [8] investigated the possibility of obtaining potassium sulfate from polyhalite ore of the Zhilyansk deposit by washing it with water from halite, calcining and dissolving in water, followed by gypsum separation. A review of scientific publications did not reveal information about the results of the study of Chelkar deposit potash ore by other researchers. The search for methods of Chelkar ore processing into potash fertilizers and salts is an urgent problem of potash fertilizer industry formation in Kazakhstan.

Preliminary study of the ore composition carried out by us earlier, showed that the natural salt has a complex non-uniform composition, it contains, in addition to the main potassium component, a large amount of halite, as well as glaserite and an insoluble residue in the form of calcium sulfate dihydrate [9]. The mineral halite is an impurity component in potash fertilizers, the removal of which from the ore composition will permit to enrich it in potassium [[10], [11], [12]]. Therefore a process of the ore washing from halite by the method of incomplete dissolution was studied and the optimal enrichment conditions were determined. In order to reach complete dissolution of potassium and magnesium salts, in particular, sulfates, the methods of dissolving a calcined ore with hot water and decomposition of washed raw materials with nitric acid were investigated. It has been established that the ore calcination although leads to the destruction of crystalline hydrates, but does not allow to complete transfer useful components into a soluble state for obtaining a water-soluble fertilizer. The operating parameters of nitric acid decomposition of the concentrated ore have been determined, namely temperature of 50°C, nitric acid concentration of 20%, the process time is 30 minutes, at which potassium and magnesium salts' complete dissolution takes place [9]. A formed suspension is separated by filtration into a nitric acid extract and an insoluble gypsum precipitate. To determine the conditions for obtaining well-filtering crystals of calcium sulfate dihydrate, an additional study of the process of washed ore nitric acid decomposition and formed suspension filtration was carried out.

Experimental part

Chelkar deposit potash ore is an object of the study. Nitric acid suspension obtained by decomposition of the ore washed from sodium salts was separated by filtration in a vacuum filtration plant under a vacuum of 0.06 MPa. The filter cake was washed with hot water; filtration productivity and precipitate washing performance were determined by dry washed precipitate. For the study, flame photometric and spectrophotometric methods of analysis were used. Microscopic spectral analysis of salts was carried out using a JSM-6490l V scanning electron microscope (Jeol, Japan). Semi-quantitative X-ray analysis of solid phase samples was carried out on a D8 Advance apparatus (Bruker). Processing of the obtained data of diffraction patterns and calculation of interplanar distances were carried out using the EVA software. The obtained solid waste was tested as a gypsum binder. To determine the setting time a Vic's OGTs-1 device was used, the compression strength was determined using a PGM-100MG4A press. Sedimentation analysis of the insoluble residue was performed using a FSK-6 photo sedimentometer. The total standard measurement uncertainty and standard deviation

for liquid and solid composition analyzes is calculated from 3 replicate measurements of the sample, taking into account sample weighing, calibration, and measurements on the flame photometer and spectrometer.

Results and discussion

The results of experimental laboratory tests of processing the Chelkar deposit potash ore show that the use of pre-calcined washed ore for nitric acid decomposition leads to formation of poorly filterable, practically non-separable suspension. At that the filtration productivity is 160 kg/m^2·h by dry precipitate (Table 1, experiment 1), which is obviously associated with gypsum dehydration and it transition to finely dispersed anhydrite during ore calcination. X-ray phase analysis of the dried, washed insoluble residue identifies calcium sulfate mainly in the form of anhydrate (76%) with gypsum content of 21% (Figure 1) [9].

Table1 - Indicators of the filtration process of nitric acid extract

Experiment	Composition of insoluble residue, %			Filtration productivity, kg/m^2·h	Average square particle diameter, μm	Specific surface area, cm^2/g
	SO_4^{2-}	CaO	MgO			
1	66.05	35.60	0	160	31	4855
2	55.59	29.25	0.36	3200	70	702

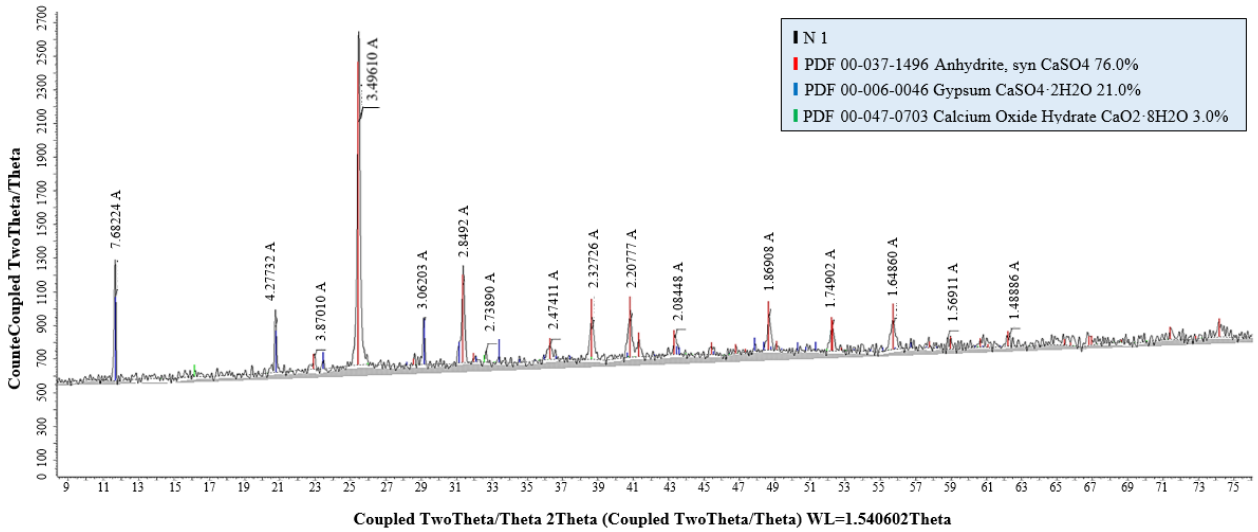

Figure 1 - X-ray diffraction pattern of the insoluble residue after nitric acid decomposition of calcined raw material

Fine-crystalline anhydrite clogs the filter pores and leads to significant deterioration in precipitate filtration properties [13]. To study possibility of eliminating this limiting stage and intensifying the filtration process, the decomposition of washed ore, which was not subjected to preliminary calcination, was investigated. At that as a result of nitric acid interaction, an insoluble gypsum precipitate remains in the solid phase, which is one of the components of natural potash ore; gypsum dehydration in this case does not occur. This leads to precipitation of coarse-crystalline precipitate and to increase extract filtration productivity by 20 times, up to 3200 kg/m^2·h by dry washed precipitate (Table 1, experiment 2). This suspension filterability increase is confirmed by sedimentation analysis of precipitates, which indicates an increase in particle size from 31 to 70 microns and a decrease in the specific surface of the precipitate by almost 7 times when using uncalcined ore instead of calcined one (Figures 2, 3; Table 1). As follows from Figure 2, about 50% of gypsum particles obtained in the first experiment have a root-mean-square diameter of 1-4 microns, while for the second experiment more than 30% of gypsum particles have a size from 60 to 100 microns. The difference in precipitate composition is also indicated by the results of spectral microscopic analysis (Figures 4, 5). Recalculation of composition of the main

component calcium sulfate on the content of calcium and sulfur shows the presence of only calcium sulfate dihydrate (≈100% $CaSO_4 \cdot 2H_2O$) in precipitate 2, and ≈90% of anhydrite ($CaSO_4$) in precipitate 1.

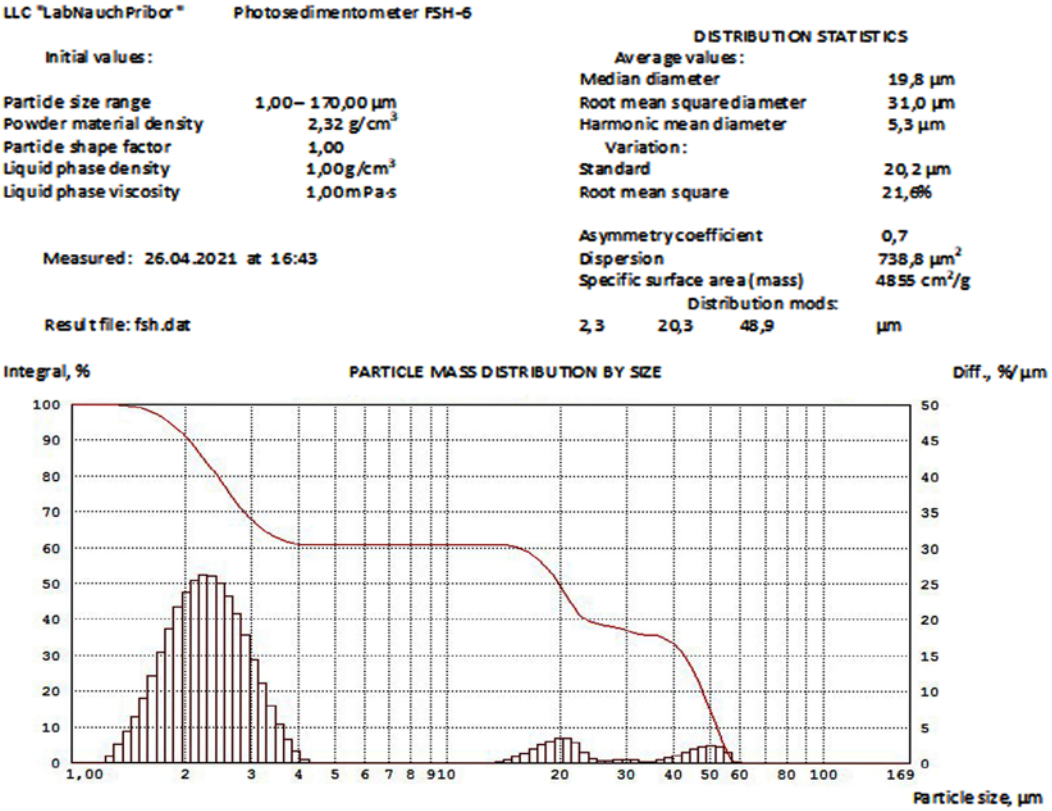

Figure 2 - Results of sedimentation analysis of calcium sulfate obtained by decomposition of calcined ore

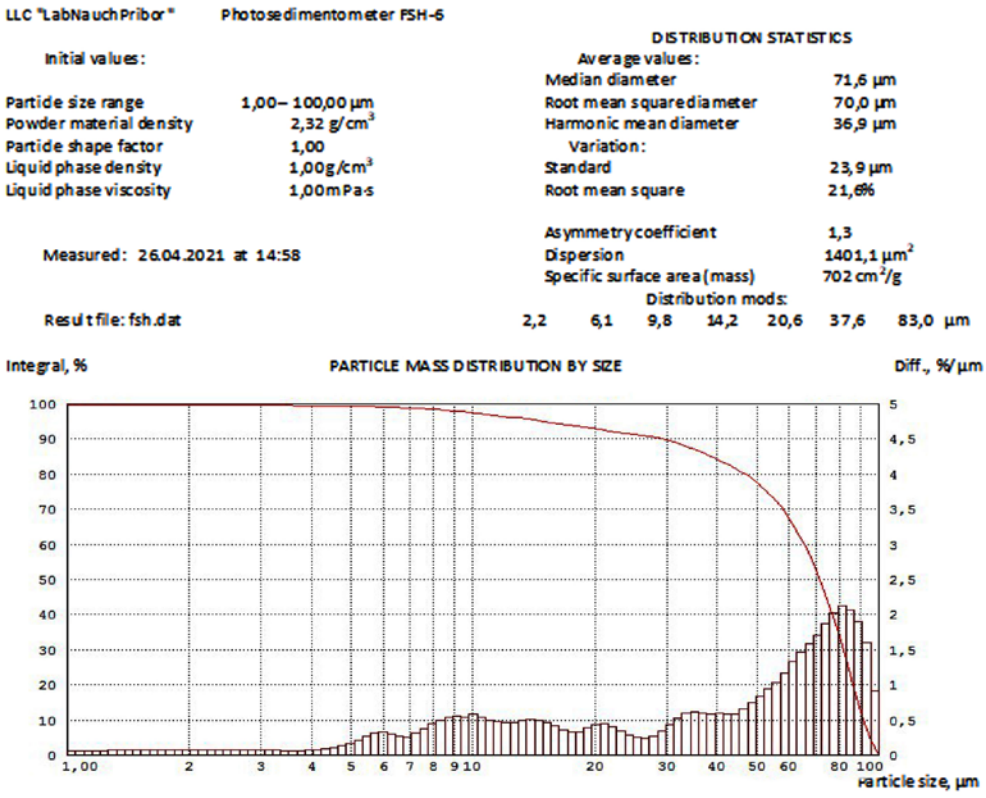

Figure 3 - Results of sedimentation analysis of calcium sulfate obtained by decomposition of uncalcined ore

Element	Weight,%
O	51.40
Al	0.18
Si	0.95
S	20.69
Ca	26.78
Total	100.00

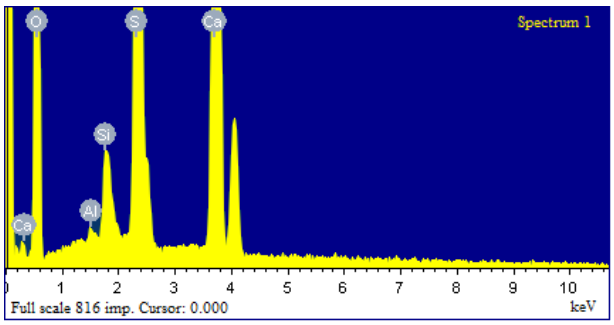

Figure 4 - Spectrogram of the insoluble residue obtained by decomposition of calcined ore (Sample 1)

Element	Weight, %
C	2.47
O	55.00
Mg	0.34
Si	0.74
S	18.04
Ca	23.41
Total	100.00

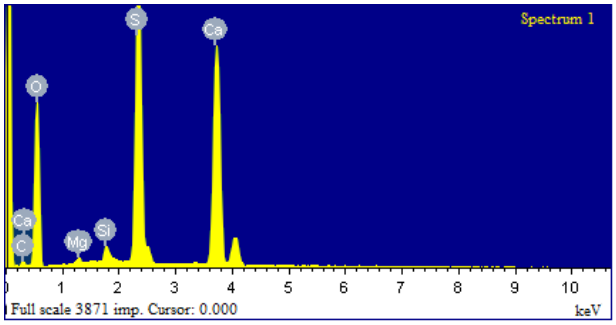

Figure 5 - Spectrogram of the insoluble residue obtained by decomposition of uncalcined ore (Sample 2)

The gypsum precipitate separated by filtration is a waste product, it does not practically contain impurities (Table 1) and therefore, after washing from mother liquor, it can be used in other chemical-technological processes. To wash out the insoluble residue, a counter-current two-stage washing scheme was used with water feed to the second stage and washing water to the first washing. The washing water obtained after the first stage of washing the insoluble residue was used for dilution to the required concentration of nitric acid fed for decomposition. The composition of filtrate and washing water is shown in Table 2.

Filtration productivity at the washing stages is at the level of this indicator for the main filtration. Crystallization of potassium-magnesium salts from nitric acid extract was carried out by partial solution evaporation at a constant temperature of 75°C and drying the separated crystals. At that the obtained crystalline product does not contain nitrogen, which remains in the mother liquor. The mother liquor was ammoniated to pH = 6 and dried to obtain nitrogen-potassium-magnesium chlorine-free water-soluble fertilizer in the form of sulfates and nitrates.

Table2 - Composition of the liquid phase after the decomposition of washed ore with 20% nitric acid

Liquid phase type	Content in liquid phase,%				Filtration productivity, kg/m^2·h
	K_2O	MgO	SO_4^{2-}	N	
Filtrate	4.53	2.54	10.91	2.03	3200
1 washing water	2.28	0.79	2.53	0.51	3320
2 washing water	1.21	0.36	1.71	0.20	3385

The dried gypsum by-product was tested to meet the standard requirements as low calcined gypsum binder. For this, the gypsum was calcined at a temperature of 160°C for 1 hour, then a gypsum dough of standard consistency was prepared and the setting time was determined on a Vic's device. For strength testing, samples of cubes were prepared, and 2 hours after the gypsum binder contact with water, the compression strength was determined using a press. Setting

beginning of 8 minutes and setting end of 10 minutes were determined, as well as the compressive strength of the samples was 2.189 MPa. These indicators determine the tested binder as normally hardening gypsum binder (index B) of the G-2 B grade.

Experimental laboratory tests of the technology of studied potash ore processing confirmed the experimental results and allowed to establish optimal parameters for all stages of processing and to determine consumption coefficients for initial raw materials and reagents. Based on the results obtained, a basic flow scheme was developed for obtaining potash and complex potassium-nitrogen-magnesium fertilizers from the Chelkar deposit ore (Figure 6).

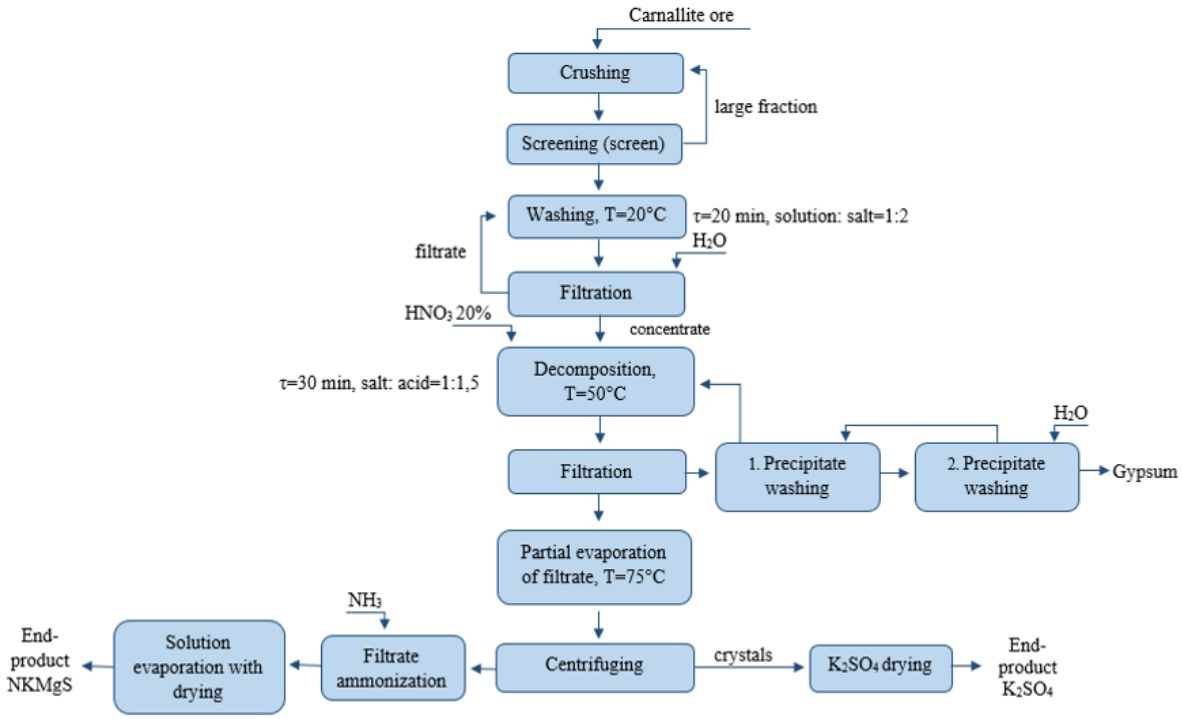

Figure 6 - Basic flow scheme forprocessing of Chelkar deposit potash ore

Crushed potash ore is washed from sodium salts in a screw dissolver with circulating mother liquor at a temperature of 20°C for 20 minutes with mass ratio of solution:salt = 1:2. The obtained suspension is separated in a settler, a clarified solution is returned to the dissolver for washing, and the thickened precipitate is fed to a vacuum filter and washed with water with the same L:S ratio. If necessary, a part of the solution can be evaporated to obtain a production salt, food sodium chloride. The washed ore is decomposed in an extractor with a stirrer with 20% nitric acid solution at a temperature of 50°C for 30 minutes with salt:acid ratio = 1:1.5. The suspension is separated by filtration on a vacuum filter. Washed with water and filtered cake, which is an insoluble gypsum residue, is sent for drying and further to the consumer. The washing water is returned to the reactor for nitric acid decomposition.The nitric acid extract is evaporated in an evaporator at a temperature of 75°C until crystallization from a solution of potassium and magnesium sulfate, which is then separated on a centrifuge. The mother liquor is ammoniated to pH = 6, evaporated and crystals are dried in a direct-flow drum dryer. The scheme is flexible and can be transformed to obtain only one type of nitrogen-potassium water-soluble fertilizer. The proposed technology is protected by an utility model patent "Method for processing potash ores to obtain potassium sulfate" [14].

Conclusions

As a result of completed research, the technology has been developed for obtaining potash and complex potassium-nitrogen-magnesium

fertilizers from the Chelkar deposit ore. The stage of filtration of nitric acid suspension obtained by washed potassium ore decomposition with nitric acid has been studied. Filtration properties and particle size distribution of the insoluble precipitate were investigated, on the basis of which the decomposition mode was determined. Tests of dried gypsum showed its compliance with a normally hardening gypsum binder (index B) of grade G-2 B, which can be used as a binder in the construction industry for manufacture of gypsum plaster, partition wall plates and panels, decorative and other details in buildings and constructions. An advantage of the obtained gypsum is its environmental friendliness due to impurity absence in its composition. The obtained crystalline products do not contain soluble chlorides, they are completely water-soluble potassium-magnesium and nitrogen-potassium-magnesium fertilizers. An advantage of the developed technology is absence of solid and liquid production wastes and possibility to integrated use all components of the Chelkar deposit natural potash salt.

Conflict of interests

On behalf of all authors, the correspondent author declares that there is no conflict of interests.

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Челқар кен орнындағы калий кенін кешенді өңдеу технологиясын әзірлеу

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ТҮЙІНДЕМЕ

Қазақстанда калий тұздарының барланған орасан зор қоры бар болғанымен, үнемі сұранысы өсіп келе жатқан калий тыңайтқыштарын өндіру әлі де жоқ. Осыған байланысты ең ірі Челқар кен орнының кенін калий тыңайтқыштары мен тұздарына өңдеуді зерттеу өзекті мәселе болып табылады. Мақалада жуылған калий кенінің азот қышқылымен ыдырату және азот қышқылы суспензиясын сүзуді зерттеу нәтижелері берілген. Ерімейтін қалдықтың фильтрлеуші қасиеттері мен гранулометриялық құрамы зерттелді, соның негізінде тұнбаны қосарлы жуумен ыдырату режимі анықталды. Суспензияның жақсы сүзгіштігін қамтамасыз ету үшін жуылған, күйдірілмеген кенді пайдалану керек. Қосалқы өнім – гипстің гипс байланыстырғыш ретінде сынағы жүргізілді, бұл оның Г-2 Б маркасының қалыпты қататын гипс байланыстырғышына сәйкестігін растады. Алынған гипстің артықшылығы – оның экологиялық тазалығы. Азот қышқылы ерітіндісінен кристалдану нәтижесінде суда еритін хлорсыз калий-магний сульфатты тыңайтқыштарын көрсететін тұздар алынды. Тәжірибелік-зертханалық сынақтардың нәтижелері негізінде Челқар кен орнының кенінен калий және күрделі калий-азот-магний тыңайтқыштарын алудың үздіксіз технологиялық сызбасы әзірленді.

Түйін сөздер: карналлит, Челқар кен орны, калий тыңайтқышы, жуу, ыдырау, буланy

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Разработка технологии комплексной переработки калийной руды месторождения Челкар

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АННОТАЦИЯ

При огромных разведанных запасах калийных солей в Казахстане до сих пор отсутствует производство калийных удобрений, спрос на которые непрерывно растет. В связи с этим исследование процесса переработки руды крупнейшего месторождения Челкар в калийные удобрения является актуальной проблемой. В статье приведены результаты исследования разложения отмытой калийной руды азотной кислотой и фильтрования азотнокислой суспензии. Изучены фильтрующие свойства и гранулометрический состав нерастворимого остатка, на основании чего определен режим разложения с двухкратной промывкой осадка. Для обеспечения хорошей фильтруемости суспензии следует использовать отмытую не прокалённую руду. Проведены испытания побочного продукта - гипса в качестве гипсового вяжущего, которые подтвердили соответствие его нормально твердеющему гипсовому вяжущему марки Г-2 Б. Преимуществом полученного гипса является его экологичность. Кристаллизацией из азотнокислого раствора получены соли, представляющие бесхлорные водорастворимые калийно-магниевые удобрения. На основании результатов опытно-лабораторных испытаний разработана принципиальная поточная схема получения калийных и сложных калийно-азотно-магниевых удобрений из руды месторождения Челкар.

Ключевые слова: карналлит, месторождение Челкар, калийное удобрение, отмывка, разложение, выпаривание

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Obtaining modified sorbents based on natural raw materials of Kazakhstan and research of their properties

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ABSTRACT

Kazakhstan takes a leading position in the production of uranium. During the hydrometallurgical processing of uranium-containing raw materials, a significant amount of liquid industrial waste is generated, such as waste solutions that require disposal. One of the most effective methods of cleaning liquid objects contaminated with radionuclides is sorption methods. Synthetic sorbents are not always justified due to their high cost and natural ones due to their low sorption capacity. The production of modified ion-exchange materials based on their combination is an urgent problem in the nuclear industry. The authors considered options for modifying natural aluminosilicate and coal-mineral raw materials of Kazakhstan. For research, zeolite from the previously unexplored Kusmurun deposit and shungite from the Koksu deposit were selected. It is proposed to modify natural sorbents with a tributylphostat and di-2-ethylhexylphosphoric acid mixture in kerosene, a mixture of phosphoric acid and polyacrylamide, technogenic raw materials. The probable mechanism of modification by each of the methods is considered. The sorption properties of the modified sorbents have been studied, and their mechanical strength has been determined.

Keywords: natural sorbents, modification, uranium sorption, mechanical strength.

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Introduction

Recently, more and more attention has been paid to the ecological safety of the republic, in connection with the increased threat of environmental pollution by radionuclides, particularly uranium. When processing uranium-containing raw materials, a significant amount of liquid technogenic wastes are formed. The main method of utilization is sorption, which requires the use of inexpensive sorbents of complex action.

Such sorbents can be obtained based on domestic natural raw materials. The significant disadvantages of natural sorbents include low sorption capacity, which can be increased by developing effective and inexpensive methods for their modification.

Various options for obtaining sorbents with improved sorption and kinetic properties are used. Many of them are based on the introduction of additional functional groups into the sorbent structure, which leads to the formation of new

adsorption centers, increasing the sorption capacity and selectivity of the sorbent. For this purpose, use is made of inorganic materials modified with amidoxime or iminodiacetate groups and, salts of heteropoly acids [[1], [2]]. Sorbents with amidoxime groups on various carriers have shown high efficiency in the extraction of radionuclides, as well as good kinetic properties [[3], [4], [5], [6]].

To isolate radionuclides from complex technological solutions, sorbents with diphyryl, aminophosphinate, carbamoylmethyl-phosphinate, and other phosphorus-containing functional groups have been developed, which can produce stable complexes with radionuclides [[7], [8], [9], [10]].

The most promising sorbents with functional groups fixed on polymer matrices that form complex compounds are materials obtained on the basis of natural minerals and radionuclide extractants. Such "solid-phase extractants" are characterized by good sorption properties [11].

The synthesis of organopolymers occupies a special place in the production of modified sorbents. This is how an organozeolite was synthesized on the basis of natural zeolite-containing tuffs and a water-soluble polymer of polyhexamethylguandine, epichlorohydrin as a cross-linking agent, which simultaneously exhibits cation-exchange, anion-exchange and bactericidal properties [12]. The sorbent is highly selective to oxygen-containing anions and uranium carbonate complexes.

All described methods were developed using foreign raw materials and expensive modifying reagents, many of them are difficult to implement.

Among the works of domestic scientists, the most interesting are examples of modification of zeolite and shungite, previously activated with sulfuric acid, copper (II) and nickel hydroxides, which are given in [13]. The authors discussed modified sorbents' features and general regularities of uranium sorption. It is shown that the use of pre-activated and modified shungite and zeolite for the sorption of uranium makes it possible to increase its extraction in comparison with the use of natural sorbents. However, the laborious process of modification is a limiting factor in the widespread use of sorbents obtained by this method.

Thus, a common disadvantage of the described methods is the complexity of implementation, high cost, and the use of scarce reagents. Therefore, in modern economic conditions, the development of effective and inexpensive sorption materials using cheap local raw materials remains relevant.

Research methodology

The modification of natural sorbents was carried out with organic extractants and, phosphoric acid in combination with polyacrylamide. Zeolite from the Kusmurun deposit and shungite from the Koksu deposit after preliminary flotation was used as natural sorbents [14].

When flotation of shungite, kerosene KO-25, TU 38.401-58-10-01 was used as a collector, as a foaming agent - T-80 - a mixture of derivatives of heterocyclic alcohols: mono- and dihydric alcohols of dioxane and pyran series, TU 20.14.60-029 - 05766801-2016. We also used liquid glass (sodium silicate), state standard GOST 13078-81 and quicklime (calcium oxide), state standard GOST 9179-77.

Modification experiments were carried out as follows: 10 g of a natural sorbent (zeolite or shungite) was poured with a solution of the sum of extractants (di-2ethylhexylphosphoric acid and tributyl phosphate) in kerosene. The resulting compositions were kept for 72 h, dried at room temperature, and then in an oven at 100 ° C.

Modification with phosphoric acid and polyacrylamide was carried out under the following conditions: a weighed portion of the natural sorbent in an amount of 10 g was treated with a dilute (1: 4) solution of phosphoric acid, after 12 hours the sorbent was washed to remove excess acid, dried and filled with a solution of polyacrylamide (concentration - 20 g / l), leaving for 12 hours. Then the polyacrylamide solution was poured off, the sorbents were washed with distilled water and dried.

Testing of the sorption capacity of the modified sorbents was carried out under static conditions. Sorption was carried out for 4 hours at room temperature (~ 25°C) at the ratio S:W = 1:5. Desorption was carried out with a solution of 1M sodium carbonate in a static mode at a ratio of S: L = 1: 10.

In the course of the research, the mechanical strength of the modified sorbents was also determined in comparison with the initial ion-exchange materials.

In order to determine the effect of activators on mechanical strength, 6 samples were made in the form of pressed briquettes from pre-modified sorbents. Pressed briquettes were made using a PSU-10 hydraulic press designed for static compression testing of standard samples of building materials. The method for modifying natural

sorbents for the manufacture of pressed briquettes, according to the numbering, is presented in Table 1.

Table 1 - Methods for modifying natural sorbents

Zeolite	1. Initial
	2. Initial Modified with a mixture of di-2-ethihexylphosphoric acid and tributyl phosphate in kerosene. (Di-2 EGPK + TBP + kerosene)
	3.Modified with phosphoric acid and polyacrylamide (H_3PO_4 + PAA)
Shungite	4. Initial
	5. Modified with a mixture of di-2-ethihexyl phosphoric acid and tributyl phosphate in kerosene. (Di-2 EGPK + TBP + kerosene)
	6. Modified with phosphoric acid and polyacrylamide. (H_3PO_4 + PAA)

2 series of experiments were carried out. In the first, the samples were pressed at a 200 kg / dm^3, water was used as a binder, and briquettes in the form of a cylinder (r = 8, h = 16) were obtained, which were carefully dried and compressed until the first crack. Compression speed 0.1 mm / sec.

In the second, the samples were pressed at 300 kg / dm^3, liquid glass was used as a binder, the studies were carried out similarly to the previous one.

Analysis methods

The quantitative content of uranium in solutions before and after sorption was determined on an Optima 8000DV inductively coupled placma atomic emission spectrometer (ICP).

IR spectra were obtained on an Avatar 370 FT-IR spectrometer in the spectral range of 4000-400 cm-1 from preparations in the form of a tablet prepared by pressing 2 mg of a sample and 200 mg of KBr. Experiment attachment: TrancmissionE.S.P.

To determine the strength of modified sorbents in comparison with the original used a universal floor testing machine AutographAG-X 100 kN, Shimadzu GmbH, Japan.

The discussion of the results

On the basis of natural raw materials from Kazakhstan, various options for modifying natural minerals have been developed. [15]. The most promising were the methods that included the treatment of natural minerals with organic extractants: di-2 ethylhexylphosphoric acid in combination with tributyl phosphate, phosphoric acid in combination with polyacrylamide. In the course of the research, we used a previously unexplored zeolite from the Kusmurun deposit and shungite from the Koksu deposit after preliminary flotation. We have proposed and tested three options for shungite beneficiation technology. The most promising was the method described in [14]. The product obtained in the flotation process can be classified as shungite concentrate.

IR spectroscopic studies of modified natural sorbents (Figs. 1, 2) showed that when zeolite is modified with a mixture of extractants, the sample contains plagioclase spectra of the albite type $Na[AlSi_3O_8]$ – 762, 747, 726, 647, 590, 528, 465 cm^{-1}. Possibly present: Heulandite $Ca[Al_2Si_7O_{18}] \cdot 6\ H_2O$ - 3428, 1032, 523, 465 cm^{-1}, lamentitis $Ca[AlSi_2O_6]_2 \cdot 4\ H_2O$ - 3572, 1032, 762, 523 cm^{-1}, phillipsitis K, $Ca[Al_3Si_5O_{16}] \cdot 6H_2O$ – 3428, 1639, 1032, 590 cm^{-1}, quartz α-SiO_2 – 696, 465 $см^{-1}$, calcite $CaCO_3$ – 1797, 1428, 878, 714 cm^{-1} [16], di-2 ethylhexyl phosphoric acid ($C_{16}H_{35}PO_4$) - 2960, 2931, 2874, 2861, 1461, 1384 cm^{-1} and tributyl phosphate ($C_{12}H_{27}PO_4$) - 2960, 2874, 1461, 1384 $см^{-1}$ [17], and when modifying shungite - quartz SiO_2 – 1165, 1080, 798, 778, 694, 513, 463 cm^{-1}, calcite $CaCO_3$ – 1796, 1420, 875, 712 cm^{-1} ν(OH) - 3438 cm^{-1}, δ(OH) – 1637 cm^{-1} [16], [18], [19]. Possibly present: muscovite $KAl_2[(OH,F)_2|AlSi_3O_{10}]$ – 1030 cm^{-1} [16], group $[SO_4]^{2-}$ – 624, 601 cm^{-1}, ди-2 ethylhexylphosphoric acid ($C_{16}H_{35}PO_4$) - 2960, 2930, 2873, 2860, 1030, 601 cm^{-1}, tributyl phosphate ($C_{12}H_{27}PO_4$) - 2960, 2873 cm^{-1} [18].

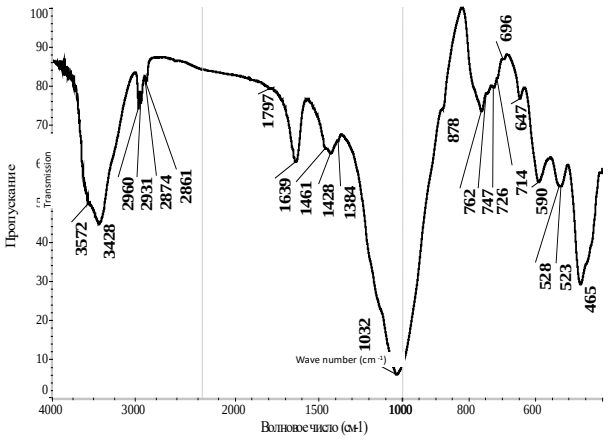

Figure 1 – IR spectrum of zeolite modified with a mixture of Di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene

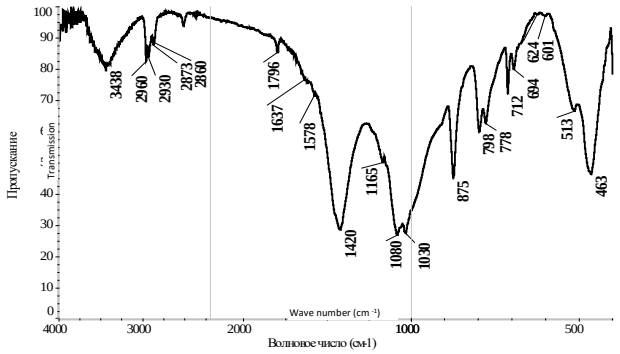

Figure 2 – IR spectrum of shungite after flotation modified with a mixture of di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene

Figure 3 shows the IR spectra of shungite modified with a mixture of phosphoric acid and polyacrylamide. The sample contains quartz SiO_2 – 798, 779, 694, 469 cm^{-1}, calcite $CaCO_3$ – 1794, 1425, 875, 713 cm^{-1}, dibasic calcium phosphate, dihydrate (brushit) $CaHPO_4 \cdot 2H_2O$ - 3539,3488, 3308, 3161, 1649, 1202, 1139, 1121, 1073, 1004, 987, 875, 798, 661, 577, 528 cm^{-1} [20]. Wavenumber band 1578 cm^{-1} falls into the area of manifestation of vibrations of polyacrylamide [21].

When zeolite is modified with a mixture of phosphoric acid and polyacrylamide, no new compounds are formed in the sample matrix. To the available minerals (Figure 1) is added, similarly to shungite, a band at the wavenumber 1578 cm^{-1}, falling into the area of polyacrylamide vibrations.

From the presented figures it follows that when modifying zeolite and shungite with a mixture of di-2 ethylhexyl phosphoric acid, tributyl phosphate and kerosene, we obtain sorbents with fixed functional groups on the surface of the polymer matrix. The sorption of uranium, in this case, will be accompanied by complexing compounds. This method allows the use of known extractants for synthesis in relatively cmall amounts.

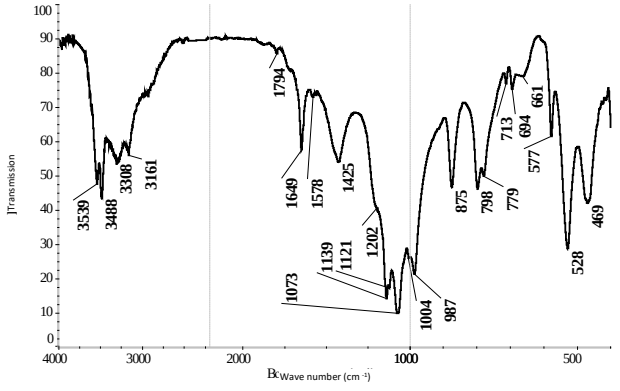

Figure 3 – IR spectrum of shungite after flotation modified with a mixture of phosphoric acid and polyacrylamide

When natural sorbents are modified with a mixture of phosphoric acid and polyacrylamide, for example, shungite, as a result of the interaction of the matrix with modifiers, new compounds are formed, in particular, calcium compounds interact with orthophosphoric acid to form dibasic calcium phosphate. In addition, it can be assumed that when natural sorbents are modified with this mixture, a gel-like film of polyacrylamide is formed on the surface of the matrix, which contributes to an increase in the sorption capacity of sorbents. [22].

Thus, it follows from the data obtained that the mechanicm of the formation of modified sorbents based on a matrix of zeolite and shungite by a mixture of extractants di-2 ethylhexylphosphoric acid, tributyl phosphate and kerosene and a mixture of phosphoric acid and polyacrylamide have different nature.

The uranium content in waste solutions, as a rule, is 5-15 mg/dm^3. In this regard, we have adjusted the productive solution in accordance with the given uranium concentration and studied the sorption process by modified natural materials. The initial uranium concentration was 11,9 mg/dm^3. The kinetic dependences of the sorption of uranium in a static mode from the imitate showed that with all the described modified sorbents it is possible to extract uranium by more than 90% already in the first 45-50 minutes.

In the course of the research, the possibility of repeated use of modified sorbents for the extraction of uranium from liquid radioactive waste was also studied, for which the concentration of di-2-ethylhexylphosphoric acid and tributyl phosphate, as well as phosphoric acid and polyacrylamide, was doubled when modifying zeolite and shungite. Sorption and desorption by modified sorbents were carried out in a static mode, alternating the processes of sorption and desorption. The research results are presented in Table 2.

Table 2 - Results of experiments on sorption and desorption of uranium

Stage	*Process*	*Zeolite*		*Shungite*	
		Uranium content, mg/dm³	*The degree of extraction %, degree of desorption%*	*Uranium content, mg/dm³*	*The degree of extraction %, degree of desorption%*
I	Sorption	0.79	93.36	0.046	99.6
	Desorption	9.50	85.51	10.62	89.6
II	Sorption	7.18	39.66	0.06	99.5
	Desorption	0.39	8.68	8.06	67.99
III	Sorption	7.41	37.73	0.96	91.93
	Desorption	0.30	6.35	3.8	32.09

It follows from the table that with an increase in the concentration of the modifier, shungite can be used repeatedly. For zeolite, this relationship is not observed.

One of the main factors in sorption is the mechanical strength of the sorbents. We have determined the mechanical strength of the modified sorbents in comparison with the initial ion-exchange materials [23].

The mechanical strength of a material is characterized by its ability to resist various external mechanical influences and is characterized by ultimate strength:

1) when compressed; 2) when stretched; 3) flexural strength and 4) abrasion resistance. We investigated the compressive strength of natural sorbents.

The results obtained are shown in Figure 4, which shows the effect of activators and a binder reagent on the mechanical strength of natural sorbents.

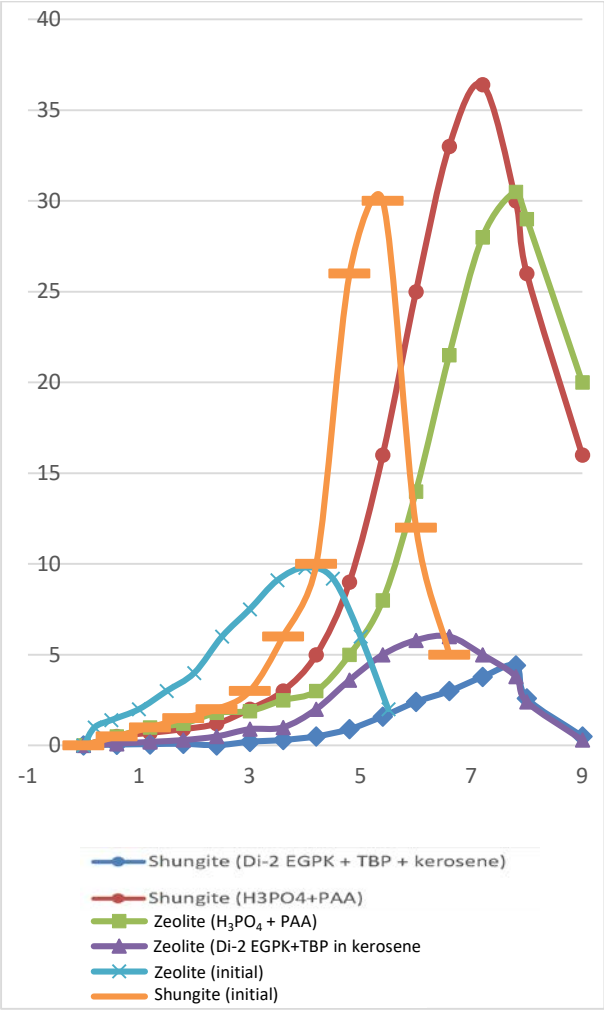

Figure 4 - Dependence of the degree of deformation of the sample on the stress for different methods of modification

Based on the studies carried out, it can be concluded that the ability of resistance to external mechanical influences (in our case, to compression) during the treatment of zeolite and shungite with phosphoric acid and polyacrylamide increases significantly, and in the case of using a mixture of extractants in kerosene with kerosene it decreases.

It also follows from the figure that the difference in the degree of deformation of the initial sample of zeolite and that modified with a mixture of orthophosphoric acid and polyacrylamide significantly exceeds the similar difference for shungite. At the same time, the decrease in the degree of deformation of a zeolite sample modified with a mixture of extractants in relation to the initial raw material is significantly less than in shungite.

Thus, the optimal options for modifying natural minerals have been determined using the example of zeolite and shungite, and the physicochemical properties of the obtained modified sorbents have been investigated.

It should be noted that the modified sorbents, especially the first two options, have proven themselves well in the testing process. These sorbents can be used for analytical purposes, as well as in low-tonnage production conditions. Their widespread use for the disposal of large volumes of liquid uranium-containing waste is unprofitable. Currently, work in this direction continues. In order to reduce the cost of modified sorbents, studies are being conducted on the possibility of using technogenic raw materials as modifiers, in particular, phosphorus slag, which is a waste of the phosphorus industry and is formed during the electrothermal production of yellow phosphorus. According to the performed physicochemical studies, the main phase of the phosphorus slag - calcium silicate - is represented by the amorphous phase of volostanite. The slag also includes multicomponent glass, cmall amounts of calcite, ankerite. Phosphorus is present as lazulite.

Analysis of scientific and technical literature in the field of calcium silicate synthesis showed that rational and environmentally friendly options include methods based on the interaction of the initial components in an aqueous medium at elevated temperatures and, in some cases, pressure, i.e. hydrothermal method. The hydrothermal method allows not only the synthesis of hydrosilicates, but also affects their structure and particle morphology. Hydrothermal conditions

simulate the formation of minerals in the earth's interior. Calcium carbonate and sodium chloride are commonly used as the aqueous phase.

During research, it was found that during the hydrothermal treatment of slag in a carbonate medium with an increase in temperature, the amorphous phase is transformed into a crystalline phase, and the morphology of particles also changes: the conglomerates existing in the initial sample gradually change their shape and turn into particles of an acicular structure (Fig. 5, 6). During the hydrothermal treatment of phosphorus slag with sodium chloride, its amorphous structure is retained.

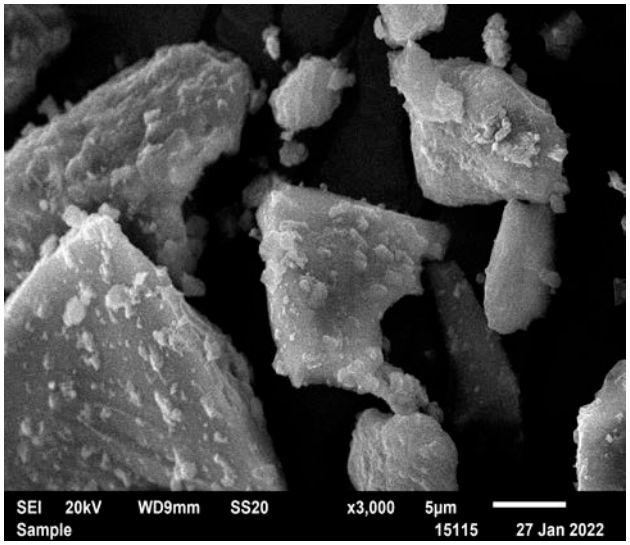

Figure 5 - The microstructure of the original phosphorus slag with an increase in x3000

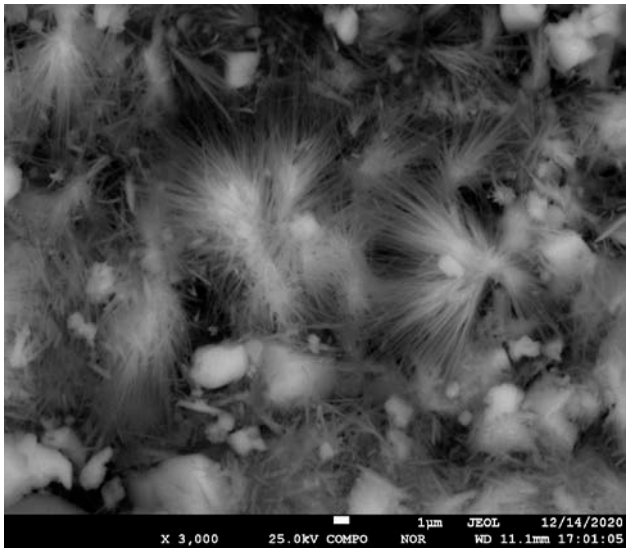

Figure 6 – Particles of activated (Na_2CO_3 - 150 g / dm^3, t - 230 ° C) phosphorus slag with an increase x3000

Several options for modifying natural minerals have been developed. An indicator of one or another modification method is the sorption process.

The best option for modifying natural minerals (zeolite or shungite) is mixing a natural sorbent with phosphoric slag activated in a chloride or carbonate medium and processing with a polyacrylamide solution.

The structure of the phosphorus slag activated with sodium chloride solution is partially retained even after it has been modified by natural minerals. This is especially clearly seen on the example of shungite (Fig. 7).

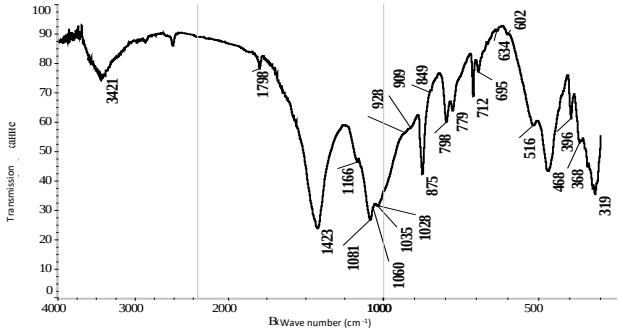

Figure 7 - Infrared spectrum of modified shungite

IR spectroscopic analysis of a sample of modified shungite showed the presence of: calcite - $CaCO_3$ – 1798, 1423, 875, 849, 712 cm^{-1}, quartz - SiO_2 – 1166, 1081, 798, 779, 695, 516, 468, 396, 368 cm^{-1} [[16], [24]]. The band at a wavenumber of 319 cm^{-1} falls within the range of bond manifestations Ca – O [25]. There are: wollastonite - $CaSiO_3$ - 1081, 1060п, 1035, 928п, 909п, 516, 468 $см^{-1}$ [16], muscovite - $KAl_2[(OH, F)_2| AlSi_3O_{10}]$ – 1028, 928 $см^{-1}$ [[16], [26]], multicomponent glass - 1035, 928 cm^{-1} [27]. Stretching vibrations of bonds Si–O–Si - 1035 cm^{-1}, shoulder at 928 cm^{-1} corresponds to stretching vibrations of terminal bonds Si–O–Si [28], bassanite - $Ca[SO_4] \cdot ½ H2O$ – 634, 602, 468 cm^{-1} [29].

When activated with sodium carbonate - in the process of modification, the structure is transformed.

Studies have established that the sorption capacity of modified sorbents increases when dressing natural minerals with phosphorus slag. If the slag modified with slag activated in a chloride medium sorbs both uranium and iron, then in a carbonate medium it is mainly iron. This property can be used to separate them.

Thus, the possibility of using technogenic raw materials - phosphorus slags - as modifiers of natural minerals has been shown.

Conclusions

In the course of research, methods have been developed and tested for modifying natural sorbents, which make it possible to actively extract uranium. The modifiers were a mixture of di-2-ethylphosphoric acid and tributyl phosphate in kerosene, phosphoric acid, polyacrylamide and technogenic raw materials. On the basis of IR spectroscopic studies, a prediction was made regarding the mechanism of interaction of modifiers with the matrix of a natural sorbent. It is shown that the mechanism of the formation of modified sorbents based on a matrix of zeolite and shungite with a mixture of extractants di-2 ethylhexylphosphoric acid and tributyl phosphate in kerosene and a mixture of phosphoric acid and polyacrylamide is of a different nature.

The properties of modified sorbents have been studied, and their sorption capacity and mechanical strength have been assessed. It is shown that the degree of uranium extraction by modified sorbents exceeds 90% already in the first 45 - 50 minutes.

It was found that when processing both zeolite and shungite with a mixture of phosphoric acid and an acid and polyacrylamide, the mechanical strength of the sample increases, and a mixture of extractants (di-2ethylhexylphosphoric acid and tributyl phosphate) in kerosene helps to reduce its value.

The possibility of using technogenic raw materials - phosphorus slags - as modifiers of natural minerals is shown.

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Қазақстанның табиғи шикізатының негізінде модификацияланған сорбенттерді өндіру және оның қасиеттерін зерттеу

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ТҮЙІНДЕМЕ

Қазақстан уран өндіруде жетекші орын алады. Құрамында ураны бар шикізатты гидрометаллургиялық өңдеу кезінде сұйық техногендік қалдықтардың едәуір мөлшері – қайта өңдеуге қажет ететін қалдықтар ерітінділері түзіледі. Радионуклидтермен ластанған сұйық заттарды тазалаудың тиімді әдістерінің бірі сорбциялық әдістерді қолдану болып табылады. Синтетикалық сорбенттерді пайдалану олардың жоғары құнына байланысты әрқашан ақтала бермейді, ал табиғи сорбциялық қабілеті төмен болғандықтан. Модификацияланған ион алмастырғыш материалдарды олардың комбинациясы негізінде өндіру атом өнеркәсібінің өзекті мәселесі болып табылады. Авторлар Қазақстанның табиғи алюмосиликатты және көмір-минералды шикізатын модификациялау нұсқаларын қарастырды. Зерттеуге бұрын зерттелмеген Қосмұрын кен орнының цеолиті мен Көксу кен орнының шунгиті таңдалды. Табиғи сорбенттерді трибутилфостат пен керосиндегі ди-2-этилгексилфосфор қышқылының қоспасымен, фосфор қышқылы мен полиакриламид қоспасымен, техногендік шикізатпен модификациялау ұсынылады, сонымен қатар органоминералды синтездеу нұсқасы ұсынылды. Әдістердің әрқайсысы бойынша өзгертудің ықтимал механизмі қарастырылады. Модификацияланған сорбенттердің сорбциялық қасиеттері зерттеліп, механикалық беріктігі анықталды.

Түйін сөздер: табиғи сорбенттер, модификация, уран сорбциясы, механикалық беріктігі.

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Получение модифицированных сорбентов на основе природного сырья Казахстана и исследование их свойств

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АННОТАЦИЯ

При гидрометаллургической переработке урансодержащего сырья образуется значительное количество жидких техногенных отходов – сбросных растворов, требующих утилизации. Одним из наиболее эффективных приемов очистки загрязненных радионуклидами жидких объектов является использование сорбционных методов. Применение синтетических сорбентов не всегда оправдано ввиду их высокой стоимости, а природных – ввиду низкой сорбционной емкости. Получение модифицированных ионообменных материалов на основе их сочетания является актуальной проблемой атомной промышленности. Авторами рассмотрены варианты модифицирования природного алюмосиликатного и угольно-минерального сырья Казахстана. Для исследований выбраны цеолит не изученного ранее месторождения Космурун и шунгит месторождения Коксу. Предложено модифицировать природные сорбенты смесью трибутилфостата и ди-2-этилгексилфосфорной кислоты в керосине, смесью фосфорной кислоты и полиакриламида, а также техногенным сырьем. Рассмотрен вероятный механизм модифицирования каждым из способов. Изучены сорбционные свойства модифицированных сорбентов и определена их механическая прочность.

Ключевые слова: природные сорбенты, модификация, сорбция урана, механическая прочность.

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Study of the possibility of using zeolite and diatomite in the treatment of oil-contaminated wastewater

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ABSTRACT

Numerous harmful substances of anthropogenic origin that are released into the environment, including petroleum products, are the result of the uncontrolled discharge of industrial wastewater into natural water bodies. Operation of oil refining and petrochemical industry enterprises, gaseous emissions and effluents of industrial enterprises, numerous oil and NP spills as a result of accidents and fires at oil storage facilities and oil refineries lead to pollution of water and soil with considerable amounts of crude oil and products of its processing and create a serious threat to the ecology of regions of Kazakhstan. A cardinal solution to the problem of protection of water bodies from pollution by wastewater polluted by oil and NP is to organize such water management of enterprises, under which the system of recycling water supply is developed as much as possible and the discharge of wastewater into water bodies is minimized.

Currently, the sorption method of water purification is the most environmentally safe and expedient. When selecting a sorbent for sorption much attention is paid to its sorption characteristics and the availability of raw materials. In addition, the choice of a sorbent depends on such factors as the quality requirement for purification, the condition of pollutants, the stages of purification and others. A wide range of natural sorption materials used in water treatment and water treatment is known. Natural materials based on modified diatomites and zeolites from Kazakhstan deposits are investigated in this work.

Keywords: oil, petroleum products; sorbents; chemical and thermal modifications; sorption purification, wastewater.

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Introduction

Numerous harmful substances of anthropogenic origin that get into the environment, including oil products, are the result of the uncontrolled discharge of industrial wastewater into natural water bodies.

The discharge of oil and its components into the environment (air, water and soil) causes changes in the physical, chemical and biological properties and characteristics of the natural habitat and disrupts natural biochemical processes.

The significant ecological load, rendered by the processes of oil refining on the condition of water bodies, is evidenced by the data of Table 1, which shows the typical rates of cooling water consumption and discharged wastewater.

Wastewater discharged into surface waters contains gasoline, kerosene, fuel and lubricating oils, benzene, toluene, xylol, fatty acids, phenols, glycerides, steroids, pesticides and organometallic compounds. The listed compounds make about 90 and more of the total amount of all organic impurities polluting the environment [[1], [2], [3]].

The purpose of this work is to study the possibility of the practical application of zeolite and diatomite for wastewater treatment.

Experimental part

The technology of wastewater treatment from oil pollution using sorbents of natural origin makes it possible to get the maximum effect at the post-treatment stage and provides an opportunity to reverse water supply. It consists of the application of the optimal combined method of wastewater treatment based on a combination of traditional reagent methods of treatment with sorption methods. Modified natural sorbents such as zeolites and diatomites are used as sorbents.

The purpose of this work was to select the optimal method of modifying diatomaceous powder and zeolite material and to reveal possibilities of applying the obtained sorbents in wastewater sorption treatment.

Significant excess of pollutants (pollutants) concentration in discharged water leads to a proportional increase in the concentration of these substances in water bodies. Only at some enterprises, there is a continuous analysis of the composition of wastewater and by integral indicators: the value of pH, by harmful impurities (EP) pollutants (pollutants). Whereas the content of organic compounds, oil, oil products, heavy metals and toxic ions is often left without control. Therefore, operational control over the content of petroleum hydrocarbons in wastewater and natural waters is a very important problem.

Standard methods have been developed to control the content of NP in the air, water and soil. They are based on chromatographic (gas and liquid chromatography) or spectral methods (infrared and fluorescence spectroscopy). Gas chromatography makes it possible not only to determine the total content of NP (like other methods), but also to identify and quantify individual hydrocarbons that are part of oil products. The latter circumstance makes it possible to really assess the danger of oil pollution, to detect its source (to determine the type and brand of NP) and to take measures to eliminate the consequences of pollution.

Chromatographic methods of analysis are currently one of the most frequently used methods for operational control over the content of petroleum hydrocarbons in water.

Knowing the hydrocarbon composition of the mixture of petroleum products, we can say to which particular petroleum products (gasoline, kerosene, diesel fuel, etc.) this pollution refers. And this is a direct way to the source of pollution, which is easy to identify on the basis of the results of research of water polluted with quite a particular type of fuel or mixture of various petroleum products (gasoline and fuel oil, kerosene and lubricating oils, diesel fuel, etc.) [[4], [5], [6], [7]]. Identification of the oil hydrocarbons corresponding to the peaks on the chromatogram was performed by the "fingerprints" method, comparing the desired chromatogram with the chromatographic spectra of oil products of different types.

Table 1 - Norms of cooling water consumption and waste water disposal for refineries

Factory Profile	*Water consumption, m^3/t*			*Quantity of wastewater discharged into a water body, m^3/t*		
	turnover	fresh	Losses water	Polluted	Conditionally clean	all
Fuel profile with a shallow refining scheme oil refining	16.80	1.31	0.79	1.12	-	1.12
The same, with a deep processing scheme	39.60	1.90	0.76	1.14	-	1.14
Fuel and oil profile with a shallow oil refining scheme	41.20	2.71	1.10	1.22	0.39	1.61
The same, with a deep processing scheme	68.50	4.98	2.00	2.52	0.44	2.96

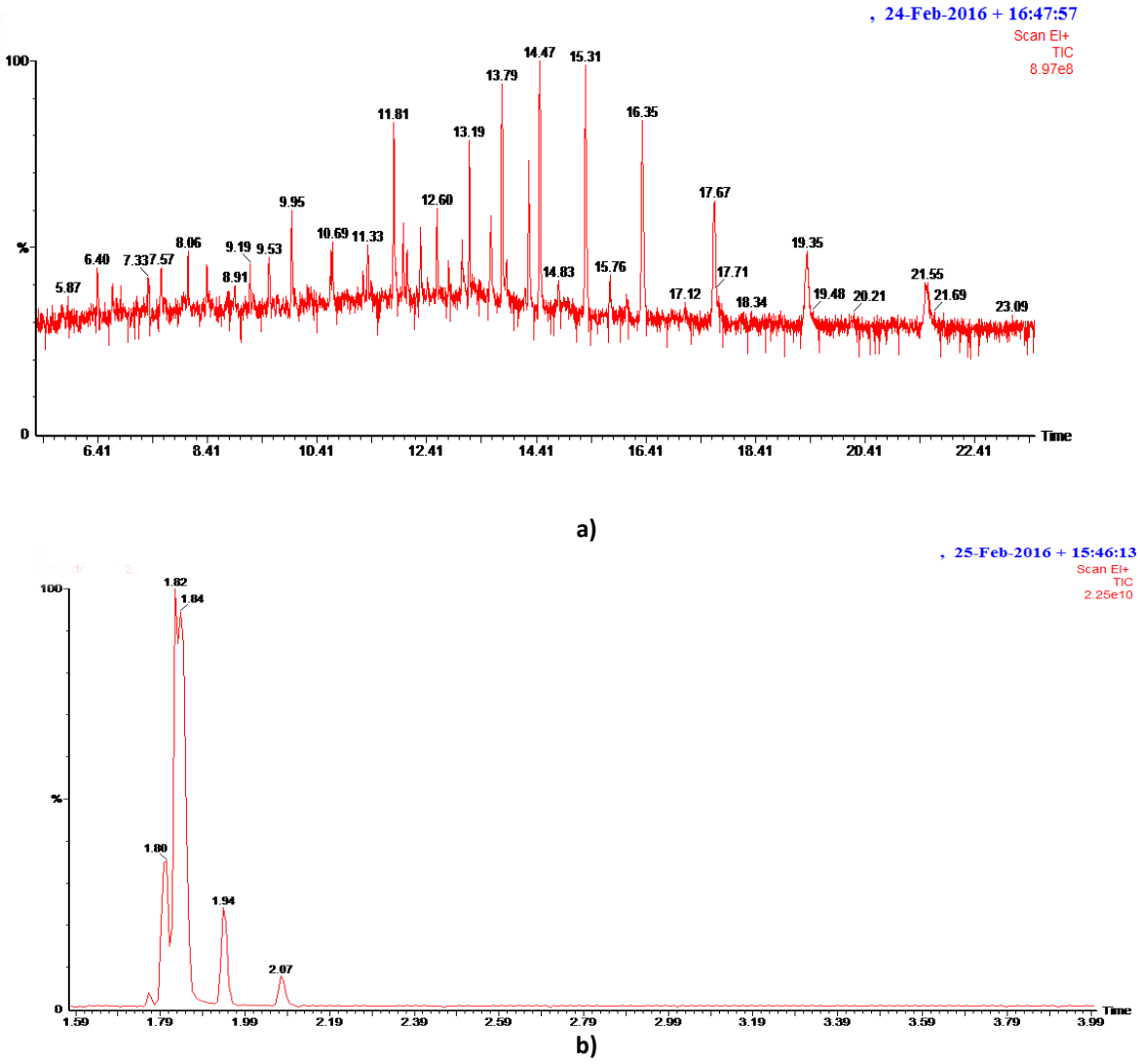

Figure 1 - Chromatograms of model solutions a) before and b) after purification with sorbents based on natural raw materials

Octane, 2,3,7-trimethyl (R=6,40); Dodecane, 2,6,10-trimethyl (R=7.337); Tetradecane (R=7,57); Heptadecane, 2,6,10,14-tetramethyl (R=8,06); Dodecane, 2,6,10-trimethyl (R=8.91); Hexadecane(R= 9.19); Pentadecane, 2,6,10-trimethyl (R=9.53); Pentadecane, 2,6,10,14-tetramethyl (R=9.95); Hexadecane, 2,6,10,14-tetramethyl (R=10.69); Hexadecane (R=11.33); Dibutyl phthalate (R=11.81); Eicosane (R=12.60); Docosane (R=13.19); Heptacosane (R=13.79); Tetracosane (R=14.47); Heptasiloxane, hexaamethyl (R=14,83); Heptacosane (R= 15,31).

By methods of GC and CHMS in the case of relatively light fractions of oil and refinery (about to C-12) can almost completely characterize the individual composition of mixtures. In heavy distillates, separate chromatographic peaks correspond mainly to n-alkanes and some isoalkanes. Other petroleum hydrocarbons are determined in the form of a blurred peak formed by the sum of undivided organic compounds. It has been established that gasoline fractions cover the range of n-paraffins C_5-C_{12}, light kerosene – C_8-C_{16}, diesel fuel – C_8-C_{25} (winter) and C_9-C_{27} (summer); the composition of various grades of mineral oils and greases correspond to n-paraffins C_{16}-C_{40}, C_{20}-C_{37} and C_{26}-C_{33}, and fuel oils – C_{14}-C_{38} etc.

The maximum losses of NP during their definition in water are connected with a stage of concentrating the extracts by evaporation.

The disadvantages of this technique are the considerable changes in the hydrocarbon composition of volatile NPs, which affects the reliability of identification of individual petroleum hydrocarbons. For intensively polluted waters it is reasonable to use the method excluding a concentrating stage (Table 2).

Table 2 – Losses of petroleum products in the process of separation of petroleum products from water samples with and without concentrating extracts

Petroleum product	Losses, %	
Gasoline	With Concentration	Without Concentration
Kerosene	76.3	33.5
Diesel fuel	61.21	30.7
Fuel oil	47.5	25.4
	4.5	27.3

Based on the work carried out, a method of wastewater treatment was developed. The proposed combined method of wastewater post-treatment has several advantages over existing ones:

- The possibility of regeneration of the sorbent, which allows used adsorbents to reuse in the treatment process or recycling;
- low cost of obtaining and using the sorbent as natural mineral raw materials are used;
- environmental safety of the purification process.

In order to achieve a deep degree of purification of oil-contaminated wastewater it was necessary to solve the following research tasks:

- study of wastewater treatment processes by combined methods at the pretreatment stage;
- study of physical and chemical properties of sorbent samples based on natural zeolite and diatomite materials;
-determination of sorption characteristics of sorbent samples in relation to oil and water.

Oil of Amangeldy gas and oil refinery "North West Konys" was used in the research as a model system. The main characteristics of oil are given in table 3.

Table 3 - Physical and chemical parameters of North-West Konys oil

Physico-chemical parameters	**Numerical values**
Features	***Indicators***
Density at 20^0C, kg/m^3	845
Curing temperature, ^{0}C	-3
Saturated vapor pressure, kPa (mm Hg)	45
Mass sulfur content, %	0.37
Mass water content, %	3.04
Mass content of mechanical impurities, %	0.07

Chemical modification by solutions of salts of metals of various natural materials allows receiving the sorbents having high sorption capacity on organic and inorganic substances. Modified sorbents with a surface nature and porous structure different from the original mineral, combine the useful properties of the original material and modified sorbents [[7], [8]].

Improved systems of wastewater treatment from petroleum products and suspended substances by filtration have been developed. Filters with granular loading, where modified zeolites and diatomite are used as sorbing materials, are the most effective for reducing pollution of the natural environment.

The mentioned natural materials are quite active in the natural state, but it is found to be advisable to activate them additionally by chemical or thermal method to increase and regulate the porous structure, change the chemical nature of the surface [[9], [10], [11], [12]].

To study the adsorption characteristics of the samples under study, a laboratory unit of flow-through type was used. The investigated filter powder was loaded into an adsorption column with a diameter of 10 mm. The height of a layer of the powder was 12 mm; investigated material was a powder with a density about of 0.5 g/cm^3 . Filtration was carried out at a pressure of 0.5-1 atm, the filtration speed was measured by changing the liquid level above the sorbent. Before filtration of a model wastewater system, distilled water was passed through the sorbent. The solution passed through the column was analyzed for the content of petroleum products. In accordance with the results of the analysis, the degree of purification = (Sis - Skonen)100 %/Sis, where Sis - the initial concentration of NPs in the studied water, mgl $^{-1}$; Skon - the final concentration of NPs in purified water, mgl $^{-1}$), total sorption dynamic capacity.

While studying different methods of thermochemical modification of diatomite and zeolite powders it has been experimentally determined that the treatment of initial powder with aluminum sulfate solution results in a material with maximum sorption capacity in relation to oil

Table 4 - Sorption properties of powders when treated with $Al_2(SO_4)_3$ solution of various concentrations

Mass fraction of aluminum sulfate in solution, %	Dynamic hydrocarbon capacity of the powder, mg/g	Hydrocarbon recovery from water, %
0.1	185	92
0.3	175	93
0.5	250	91
0.7	250	91
1.0	145	93
2.0	130	90

and oil products. The initial powder sorbents were modified by the aluminum sulfate solution in the following way: a solution of industrial aluminum sulfate was added to the powder suspension, then stirred for 15 minutes and the pH was adjusted to the necessary value by the ammonia solution. An excess of water from the suspension was separated on a centrifuge (600 rpm), then powders were heat-treated at 150 – 600 ^{0}C for 2 - 2.5 h.

While studying the degree of purification of CB and the sorption dynamic capacity for oil products at different concentrations of aluminum sulfate solution we came to the conclusion that its optimum quantity in the treated solution should be 0.03-0.08 g of aluminum per 1 g of powder. Such content of aluminum salt provides an optimum filtration rate of 0.15 mm/min (table 4).

The maximum degree of purification from oil products has been achieved in the temperature range of 300 - 450^{0}C when optimizing the powder's processing temperature.

Optimal conditions of chemical modification of the initial diatomite and zeolite powders are achieved by treatment of the source material with 0.1% aluminum sulfate solution, precipitation of aluminum hydroxide at pH=7-8 and thermal treatment at 200^{0}C for 2 hours.

The modified adsorbents provide the degree of wastewater treatment from oil products equal to 99,4%, which allows reducing the concentration of oil products in wastewater from 50 to 0.5 - 1 mg/l. The resulting powder has an adsorption capacity of 250 mg/g powder on petroleum products.

Since the oil refining industry is quite water-intensive, water use and sewage systems are constantly being improved in this industry to reduce water consumption and water disposal as much as possible. Water serves as an indispensable resource in organizing the production cycles of a refinery. It is used as:

- cooling agent for the end product;
- cooler of technological units and equipment;
- solvent for the preparation of reagent solutions;
- a source of steam;
- a source of condensate.

Wastewaters of refineries differ from each other in composition and degree of contamination. The indicators of effluents also depend on the quality of refined oil and the range of products produced. Normally, the effluents of a refinery contain or may contain the following substances: oil and oil products, gasoline and fuel oil, kerosene and lubricating oils, paraffin, sulfates, fatty acids, surfactants, phenol, carbamide, cyclic organic hydrocarbons, ammonium ions, etc.

A set of methods for continuous ecological monitoring of natural waters, as well as express methods, allow for timely determination of control parameters in the processes of industrial wastewater treatment. Compared with the existing ones, it gives a more accurate and realistic assessment of the danger of oil pollution and, accordingly, the adoption of measures to eliminate the consequences of pollution. Table 5 shows normative values of general properties of waste water and permissible concentrations of pollutants in wastewater.

When controlling water quality (sanitary-chemical and environmental analyses), only those methods of determination that are included in the State Register of methods of chemical analysis of the Republic of Kazakhstan are mandatory.

As a result of the research, innovative technological schemes of wastewater treatment using modified natural minerals (zeolite, diatomite) were proposed. (Figures 2 and 3).

Table 5 - Normative indicators of general properties of wastewater and permissible concentrations of pollutants in wastewater

Normative indicators	**Maximum permissible value of the indicator in the wastewater sample**
pH	6.0 - 9.0
Oil Products	10 mg/l
Temperature	40°C
Mineralization (dense residue)	3000 mg/l
Fats (dissolved and emulsified)	50 mg/l
Sulfides	1.5 mg/l
Nitrogen	50 mg/l
Posphore	12 mg/l
Suspended matter	300 mg/l

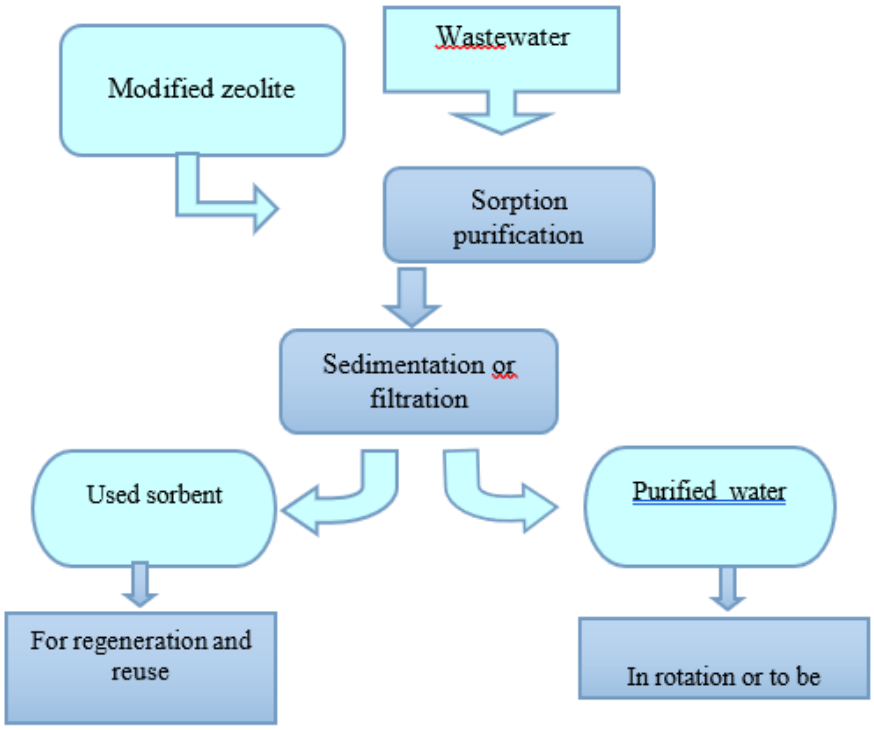

Figure 2– Schematic diagram of one-stage water treatment

One-stage treatment (figure 2) can be used when the degree of purification of the wastewater achieved in this case is sufficient and a deeper treatment is not required. In the case where the required degree of purification cannot be achieved in one stage, a two-stage treatment is recommended (figure 3).

In this case, the sorption process in the unit with countercurrent introduction of the sorbent is carried out under static conditions in two stages. By intensive mixing of treated wastewater in the main tank, with a given mass of sorbent (modified diatomites and zeolites) for a certain time, and the subsequent separation of sorbent from water in the settling tank for 24 hours the first stage of purification is carried out. Then in the second stage of cleaning fresh sorbent is added to the tank with partially cleaned water, reaching the lowest concentration of contaminants followed by sedimentation of the sorbent. The unused sorbent is fed to the first stage of purification, with its subsequent regeneration or use for other purposes [[5], [6], [7]].

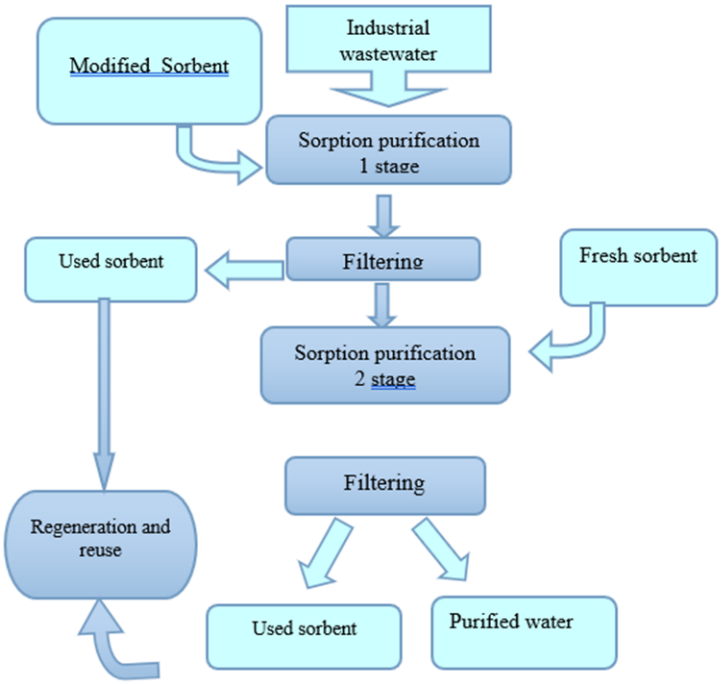

Figure 3 - Technological scheme of two-stage wastewater treatment

Conclusions

Approaches and methods of testing the proposed technologies of oil-contaminated wastewater treatment in the conditions of a real oil refinery (Taraz branch of Amangeldy GPP), with a view to further improvement, as they were mainly worked out on simulation models in laboratory conditions. We proposed new modified sorbents based on available and environmentally safe domestic natural raw materials: zeolites and diatomites [[8], [9]].

Diatomite, not treated thermally, which has high adsorption rates and low permeability values, can be used as an adsorbent for fine wastewater treatment in steady-state, in water treatment processes. The use of diatomite as an adsorbent for the fine treatment of wastewater, in contrast to the activated sludge usually used for this purpose. The advantage of using diatomite for fine purification of wastewater from contaminants is the ability to restore the adsorption properties of diatomite after calcination at 200-500 0C. Diatomite used for fine purification of wastewater from heavy metal cations can be regenerated or utilized.

Hardened diatomite, which has a relatively high permeability at a fairly low value of adsorption, can be used as a filtering material for coarse water purification. It is possible to use diatomite as a filtering material for water purification in the form of granules of fractions 0.5-1.0, 0.8-2.0, 1.0-4.0, 2.5-5.0 mm.

It is established that after diatomite is calcined at temperatures from 200 to 900 0C the number of reactive centers on its surface increases. It is recommended to use diatomite, which has high indices of adsorption and low values of permeability, not treated thermally as an adsorbent for fine purification of sewage in settling tanks, not as a replacement for activated sludge. It is recommended to use calcined diatomite, which has a relatively high permeability at a sufficiently low value of adsorption as a filtering material for rough treatment of water used in swimming pools, aquariums, dolphinariums. To increase the permeability, calcined diatomite can be used in the form of granules.

The developed complex of ecological express-analyses for research of sewage water, their approbation makes it possible to make a real-time assessment of sewage water. Approbation of the used methods of analysis of oil-contaminated wastewater in the conditions of the Central plant laboratory of Taraz branch of Amangeldy gas processing plant was carried out. [[13], [14], [15], [16], [17]].

The possibilities of combining different methods of treatment were investigated and the original scheme of wastewater treatment with sequential application of sorption, which allows purification of up to 92% on average, was proposed. This technology will reduce discharges of pollutants: oil products not more than 0.5 mg/l; phenol not more than 0.09 mg/l; suspended solids not more than 20 mg/l; chlorides (by Cl^-) not more than 600 mg/l; sulfates (by SO_4^{2-}) not more than 450 mg/l; surfactants not more than 0.4 mg/l. The proposed technology will reduce discharges of pollutants: oil products not more than 0.2 mg/l; phenol not more than 0.09; suspended solids not more than 20 mg/l; chlorides (by Cl^-) not more than 600 mg/l; sulfates (by SO_4^{2-}) not more than 450 mg/l; surfactants not more than 0.4 mg/l.

The developed high-efficiency, energy-saving technology of wastewater treatment has been successfully implemented.

The developed highly efficient energy-saving technology of wastewater treatment by the above-mentioned sorbents allows obtaining maximum effect at the post-treatment stage which ensures the recycling water supply. Raw materials for obtaining sorbents are modified diatomite and zeolite materials of Kazakhstan deposits.

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Мұнаймен ластанған ағынды суларды тазартуда цеолит пен диатомитті пайдалану мүмкіндіктерін зерттеу

Мырзалиева С.К., Багашарова Ж.Т., Акильбекова Ш.К.

Қазақстан Республикасының минералдық шикізатты кешенді қайта өңдеу жөніндегі ұлттық орталығы; әл-Фараби атындағы Қазақ Ұлттық Университеті, Алматы, Қазақстан

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ТҮЙІНДЕМЕ

Қоршаған ортаға түсетін көптеген зиянды заттар, соның ішінде мұнай өнімдері өнеркәсіптік ағынды суларды табиғи су объектілеріне бақылаусыз ағызудың нәтижесі болып табылады. Мұнай өңдеу және мұнай-химия өнеркәсібі кәсіпорындарының жұмысы, өнеркәсіп кәсіпорындарының газ тәрізді шығарындылары мен ақаба сулары, мұнай қоймалары мен мұнай айдау зауыттарындағы авариялар мен өрттер нәтижесінде мұнайдың және т.б. көптеген төгілуі су мен топырақтың шикі мұнай мен оны қайта өңдеу өнімдерінің елеулі мөлшерімен ластануына әкеп соғады. Қазақстан өңірлерінің экологиясына елеулі қатер төндіреді. Су қоймаларын мұнаймен ластанған ағынды сулармен ластанудан қорғау мәселесін түбегейлі шешу кәсіпорындардың осындай су шаруашылығын ұйымдастыру болып табылады. Онда айналмалы сумен жабдықтау жүйесі барынша дамып, су қоймаларына ақаба суларды ағызуды азайтады.Қазіргі уақытта суды тазартудың сорбциялық әдісі экологиялық жағынан ең қауіпсіз және көздеген мақсатқа сай болып табылады. Сорбцияны таңдағанда оның сорбциялық сипаттамаларына, шикізат базасының болуына көп көңіл бөлінеді. Сонымен қатар, сол немесе басқа сорбентті таңдау келесі факторларға байланысты: тазарту сапасына қойылатын талаптар, ластаушы заттардың күйі, тазарту сатылары және т.б. Суды тазартуда және суды тазартуға даярлауда қолданылатын табиғи сорбциялық материалдардың кең ауқымы бар. Бұл жұмыста Қазақстан кен орындарындағы модификацияланған диатомиттер мен цеолиттер негізіндегі табиғи материалдар зерттелді.

Түйін сөздер: мұнай, мұнай өнімдері; сорбенттер; химиялық және термиялық түрлендіру; сорбциялық тазарту, сарқынды сулар.

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Исследование возможностей использования цеолита и диатомита в очистке нефтезагрязнённых сточных вод

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АННОТАЦИЯ

Многочисленные вредные вещества антропогенного происхождения, которые попадают в окружающую среду в том числе нефтепродукты являются результатом бесконтрольного сброса промышленных сточных вод в природные водоемы. Предприятия нефтеперерабатывающей и нефтехимической промышленности, газообразные выбросы и сточные воды промышленных предприятий, многочисленные разливы нефти и нефтепродуктов в результате аварий на нефтехранилищах и нефтеперегоннных заводах приводят к загрязнению воды значительными количествами сырой нефти и продуктов ее переработки и создают серьезную угрозу экологии регионов Казахстана. Кардинальным решением проблемы охраны водоемов от загрязнения сточными водами, загрязненными нефтью и нефтепродуктами, является организация такого водного хозяйства предприятий, при котором максимально развивается система оборотного водоснабжения и сводится к минимуму сброс сточных вод в водоемы. В настоящее время сорбционный метод очистки воды является наиболее экологически безопасным и целесообразным. При выборе материала для сорбции большое внимание уделяется его сорбционным характеристикам, и доступности сырьевой базы. Кроме того , выбор того или иного сорбента зависит от таких факторов как: требования к качеству очистки, состоянию загрязняющих веществ, этапов очистки и других. Известен широкий спектр природных сорбционных материалов, используемых в водоочистке и водоподготовке. В работе исследованы природные материалы на основе модифицированных диатомитов и цеолитов Казахстанских месторождении.

Ключевые слова: нефть, нефтепродукты; сорбенты; химическое и термические модифицирование; сорбционная очистка, сточные воды.

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Monitoring of displacements and deformations of the earth's surface at the Annensky field

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ABSTRACT

In connection with the ongoing depletion of mineral reserves located in relatively favorable conditions, at shallow depths, it is increasingly necessary to involve deposits located in complex mining and geological conditions; occurring at great depths, in complex, poorly studied and potentially dangerous conditions. The deposits developed by the underground method are no exception. Safe and efficient development of mineral deposits by underground method, occurring at great depths, is complicated by the fact that with an increase in the depth of mining, the nature of the course of deformation processes in the rock mass and the degree of their impact on the environment change. Studies of deformation processes, their control and forecast in many cases determine the efficiency and safety of the development of deposits of solid minerals. A practical forecast can be made as a result of continuous tracking in space and time of deformation processes. Currently, to determine the displacements and deformations of the earth's surface of the field, complex monitoring is used, which includes the following methods:

- methods of preliminary diagnostics of the rock massif;
- repeated high-precision leveling;
- satellite geodetic methods, primarily interferometry methods;
- other methods of instrumental observations in regional and local areas.

It should be noted that ground-based methods used for geomechanical monitoring of earth surface deformations, such as repeated geodetic leveling, as well as the use of satellite geodesy methods, do not fully reflect the temporal detail and spatial scale of the changes in the earth surface deformations. Today, the methods and technologies of space radar interferometry are of particular practical value, which make it possible to obtain areal estimates of vertical and planned displacements of the earth's surface with an accuracy of a few millimeters, regardless of illumination and cloudiness conditions. Space radar interferometry (CRI) is an effective tool for direct mapping of the earth's surface movements and deformations of structures over large areas of the study areas.

Keywords: monitoring, displacements of the earth's surface, deformation processes, high-precision leveling, radar interferometry.

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Introduction

The study of modern displacements and deformations requires high-precision geodetic measurements in the monitoring mode on the earth's surface of ore deposits [[1], [2], [3], [4]].

The sufficiently large experience of geodetic monitoring of deformation processes at deposits that is currently available shows [[5], [6], [7]] that subsidence of the earth's surface is widespread during long-term development of ore deposits and for the vast majority of the rate of technogenic subsidence is 1–2 cm/year, and the accumulated values do not exceed the first tens of centimeters. The consequences of such deformation processes can be the activation of landslide processes, the appearance of dangerous zones, displacement troughs [[8], [9]], etc.

At the Annensky field under study, as a result of the introduction of mining operations over many decades, vast areas of rock movement, subsidence

and collapse of the earth's surface have formed, which continue to this day.

In 2004 and 2006, large collapses occurred in the Annensky mountain region as a result of the destruction of inter-chamber pillars (ICP) and failures of interlayers between worked out overlapping sloping deposits. The combined displacement trough covered an area of about 2 km along the strike of the Ann-2-I-II deposit and 0.6 km along the dip. Large rupture cracks formed on the earth's surface along the boundaries of the shear trough. Dips formed in the western part of the Annensky quarry. In the western part of the trough on the surface, in the zone of smooth shifts, the communications network continues to be used: a road, three collectors, a power line-35kV, a power line-6kV, a communication line.

In this regard, further mining of mineral reserves in such difficult conditions in the subsidence trough area was prohibited. However, significant mineral reserves lie under the zones of possible collapses, which can lead to unjustified losses of balance ore reserves.

The conclusions of studies previously conducted by various organizations turned out to be largely contradictory regarding the conduct of mining operations in the area of the formation of a huge trough, and therefore did not lead to unambiguous decisions on the development of mineral reserves.

Therefore, the purpose of this article is to determine the weakened zones on the earth's surface of the Annensky mine using high-precision leveling and space radar interferometry, which increases the efficiency and safety of field development.

Experimental part

Studies of deformation processes, their control and forecast in many cases determine the efficiency and safety of the development of deposits of solid minerals. A practical forecast can be made as a result of continuous tracking in space and time of deformation processes.

The system of complex monitoring of deformations of the earth's surface should contain the following basic methods [[10], [11]]:

Visual monitoring of rock movements

Methods of local observations of rock movements are used in studies of the stability of individual local sections of a rock mass due to the formation of continuous cracks of considerable length.

At the same time, the elements of occurrence of each crack at several points, the planned and height reference of measurement points, the nature of the surface of the cracks and the material filling them are subject to study.

For local observations, simplified mine surveying observations are used with the establishment of the boundaries of distribution and the type of deformations of rocks, the determination of the speed and magnitude of deformations, the identification of the critical value of displacements preceding the onset of the active stage and the pre-calculation of the development of deformations in time.

Repeated high-precision leveling

Repeated high-precision leveling is performed with the necessary and sufficient accuracy, which can be obtained using modern instruments and observation methods, which make it possible to most fully eliminate systematic leveling errors.

To perform leveling at the Anennsky mine, a modern Leica DNA03 digital level is used, designed for the most complex work requiring increased measurement accuracy, with a set of three-meter invar rails with a BAR code, which ensure leveling with an RMS error of measuring elevations of ±0.3 mm per 1 km double stroke.

Downhole reflectometry

TDR (Time Domine Reflectometry) downhole reflectometry methods are based on the use of a coaxial cable as a rock deformation detector. To do this, the cable is lowered into the drilled well and attached to the rock surrounding it with an expanding cement slurry. An electromagnetic signal is passed through the cable. In the process of shifting the rock mass, local deformations of the cable occur, which affect the passage of the electromagnetic signal in the places of its deformation. These places are fixed by the TDR reflector and displayed on the screen of an oscilloscope or computer.

Space radar interferometry

Space radar interferometry is the most important part of an integrated system for monitoring the state and building a continuous situational map of the earth's surface deformations.

To determine the values of the absolute values of the displacement of the earth's surface that occurred in the time period under study, for the correct application of SAR - interferometry methods,

it is necessary to use a tandem pair of radar satellite images with a minimum value of the perpendicular baseline (distance between spacecraft) and having a minimum coherence value.

The discussion of the results

According to the data provided by the Annensky mine of Kazakhmys LLP, there are 4 profile lines on the earth's surface of the mine (Figure 1):

- profile line 65-65 bis;
- profile line 66;
- profile line 151;
- profile line 67.

According to the points of the network to determine the vertical movements of the earth's surface at the field, leveling of the II class of increased accuracy is designed. This technique provides for a combination of relatively fast observation with the achievement of a sufficiently high level of accuracy, which will reliably detect local anomalies in the vertical movements of the earth's surface with amplitudes of 3-5 mm and more. The practical accuracy of observations by the leveling method of the II class of increased accuracy is ±1 mm/km.

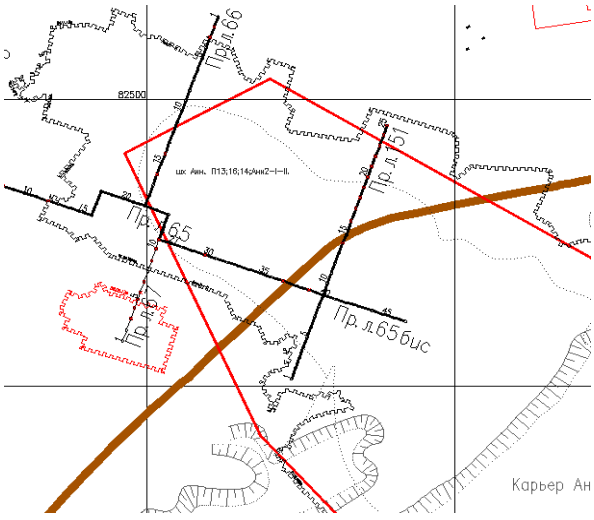

Figure 1 — Layout of profile lines at the Annensky field

Instrumental observations on the earth's surface of the Annensky mine have been carried out since 1976. Starting from 2009, in connection with the linking of elevations in all profile lines, the differences in measured observations were recalculated. Taking into account all linking marks, this research work provides an analysis of instrumental observations from 2011 to the present.

Profile line 65-65bis

On the profile line 65-65 bis, observations are made from 1 to 47 working benchmarks. In April 2009, in connection with the linking of the marks, they were recalculated from PP No. 146 for a difference of -0.0104 m. Also, the following observation benchmarks were excluded due to the destruction: 8, 12, 13, 25, 26, 37 and 39. In September 2010, due to linking, the marks were recalculated from the Sai triangulation to a difference of + 0.0099 m.

Taking into account all the recalculated marks, starting from 2011, a comparison was made of the excesses obtained as a result of the adjustment between the benchmarks of the profile line with the data of all cycles (Figure 2).

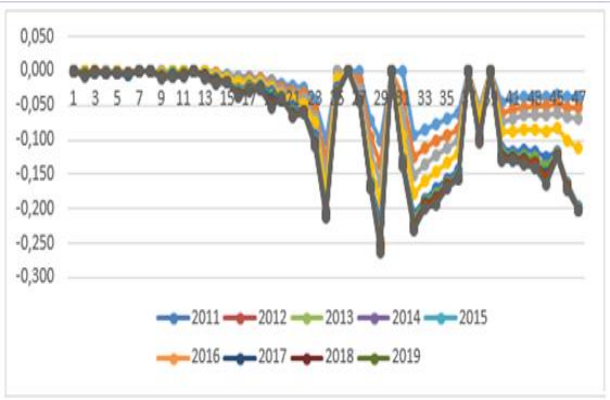

Figure 2 — Graph of subsidence according to the observational benchmarks of the profile line 65-65bis

Analysis of subsidence along the profile line 65-65bis, obtained from the results of multiple leveling, shows that intense subsidence is observed at working benchmarks 22, 23, 24, 28, 29 and 31. As can be seen from Figure 2, intense subsidence is noticeable in 2011 and 2015. It should be noted that with the conduct of mining operations and the development of the MCC in 2016, all the working benchmarks of the profile line 65-65bis were destroyed. In this regard, from 2016 to the present, instrumental observations are not possible in this area and require non-contact monitoring.

Profile line 66

On the profile line 66 observations are made from 1 to 19 working benchmarks. In April 2009, in connection with the linking of the marks, they were recalculated from PP No. 146 for a difference of -0.0104 m. Also, the following observation benchmarks were excluded due to the destruction: 2, 3, 13, 14 and 16. In September 2010, due to

linking, the marks were recalculated from the Sai triangulation to a difference of + 0.0099 m.

Taking into account all the recalculated marks, starting from 2010, a comparison was made of the excesses obtained as a result of the adjustment between the benchmarks of the profile line with the data of all cycles (Figure 3).

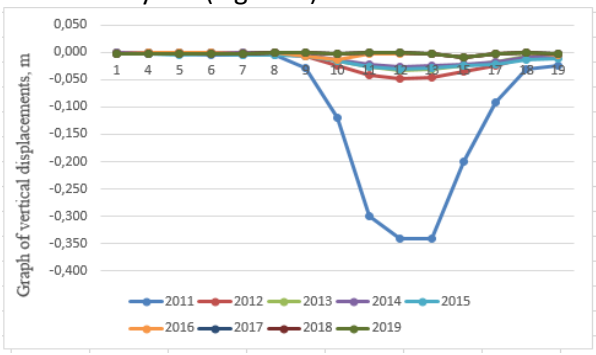

Figure 3 - Settling schedule along profile line 66 (according to observation benchmarks)

Analysis of subsidence along profile line 66, obtained from the results of multiple leveling, shows that intense subsidence is observed in the area of profile lines 10, 11, 12, 15 (Figure 3). Also, intensive subsidence is observed in 2011 and 2016 (Figure 3). For a more detailed analysis, it is necessary to carry out monitoring by the method of space radar interferometry.

Profile line 67

On the profile line 67 observations are made from 1 to 11 working benchmarks. In April 2009, due to the linking of elevations, they were recalculated from PP No. 146 (+25.501) for a difference of -0.0104 m. Also, the following observation benchmarks were excluded due to the destruction: 3, 4, 7, 9, 10 and 11. In September 2010, due to linking, the marks were recalculated from the Sai triangulation to a difference of + 0.0099 m.

Taking into account all the recalculated marks, starting from 2010, a comparison was made of the excesses obtained as a result of the adjustment between the benchmarks of the profile line with the data of all cycles (Figure 4).

Analysis of subsidence along the profile line 67, obtained from the results of multiple leveling, shows that intensive subsidence of the earth's surface is observed in 2010 (Figure 4). It should be noted that with the conduct of mining operations and the development of the ICP, 80% of the existing working benchmarks were destroyed. In this regard, for a more detailed analysis, it is necessary to monitor the method of space radar interferometry.

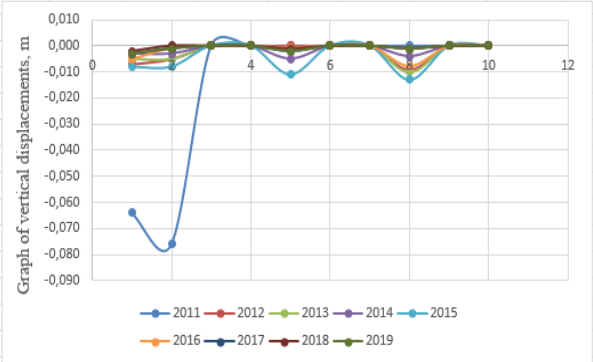

Figure 4 – Settling schedule along the profile line 67

Profile line 151

On the profile line 151 observations are made from 1 to 25 working benchmarks. In April 2009, due to the linking of elevations, they were recalculated from PP No. 146 (+25.501) for a difference of -0.0104 m. Also, the following observation benchmarks were excluded due to the destruction: 16, 17, 18, 19, 20, 21, 22, 23, 24 and 25. In September 2010, due to linking, the marks were recalculated from the Sai triangulation to a difference of + 0.0099 m.

Taking into account all the recalculated marks, starting from 2010, the comparison of the excesses obtained as a result of the adjustment between the benchmarks of the profile line with the data of all cycles was made (Figure 5).

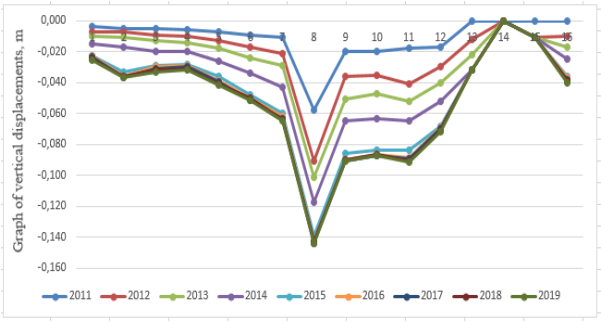

Figure 5 – Settling schedule along profile line 151 (according to observation benchmarks)

Analysis of subsidence along the profile line 151, obtained from the results of multiple leveling, shows that (Figure 5):

- The revealed features of modern vertical movements of the earth's surface in the area of the profile line, due to the mining of the MCC in the upper horizons and the mining of ores of the lower horizons, consist in constantly observed subsidence from the benchmark Rp No. 1 to the benchmark Rp No. 15. The most significant subsidence is observed in the area from the benchmark Rp No. 7 to Rp No.

12. The benchmark settlement rate is ≈ 50 mm per year.

For further study, the development of deformation processes, space radar surveys from the Sentinel satellite were used for the study area [12].

A pair of Sentinl-1B photographs with the following parameters are used for calculations:

- Measurement mode: Interferometric wide bandwidth (IW) measurement mode,
- Product: Level 1 Single View Complex (SLC),
- Incident angle: 29 - 46,
- Spatial resolution: 5 x 20 m,
- Sweep Width: 250 km,
- Subswath number: 2,
- Polarization: VV,
- Path: 22,
- Orbit: descending

For calculations, the following software products were considered: GMT5SAR and SNAP 6.0. Both of these programs differ in many ways, but they also have common features: they are open source software and allow you to process Sentinel-1 images.

After analyzing the advantages and disadvantages of software products, SNAP 6.0 software was chosen to perform the calculations. The input data processing algorithm in SNAP 6.0 software is as follows: registration, interferogram generation, interferogram filtering, unfolding phase and phase conversion to offsets, georeferencing.

The processing steps start with the selection and collection of the required data, usually in SLC (Single Look Complex) format, and end with a DEM or deformation map.

As a result of the work carried out, a map of displacements of the earth's surface of the territory of the Annensky mine was built, on which displacements of soils and soils in the subsidence trough up to 10 mm were recorded (Figure 6).

As a result of the work carried out, a map of displacements of the earth's surface of the territory of the Annensky mine was built.

Displacements of the earth's surface were determined and recorded according to observational data for the period using satellite images of 2018, 2019 and 2020 on the territory of the Annensky mine. The displacements took place in height both upwards during the formation of rock dumps, and downwards, as a result of the subsidence of the earth's surface. Comparative analysis showed that the obtained results are consistent with the data of ground-based measurements, as well as with the data of radar interferometry carried out by Sovzond LLC.

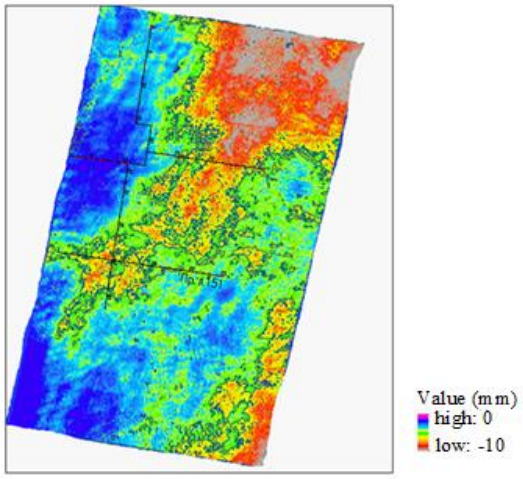

Figure 6 - Map of displacements of the earth's surface at the Annensky mine for the period 05.08.2020 – 06.25.2020.

To verify the results of SAR - interferometry, a planning map of ground mine surveying and geodetic observations was built in the study area of the Annensky mine. A comparative analysis of the displacements of the Earth's surface obtained by these methods was carried out, which showed their consistency. A continuous situational map of the problem areas of the Annenskoye field was compiled.

Also, the results of a comparative analysis of data on subsidence obtained by methods of differential interferometry and ground leveling are presented. Processed Sentinel data and profile lines 65 bis, 66, 67, 151 for the period 2018 to 2020 were selected as differential interferometry data. A detailed comparative analysis is shown in Figures 7-8.

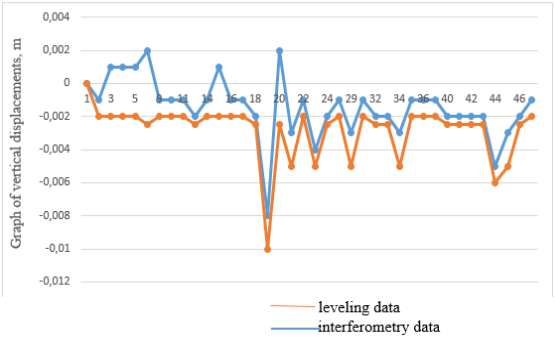

Figure 7 - Comparative analysis chart for profile line 65bis

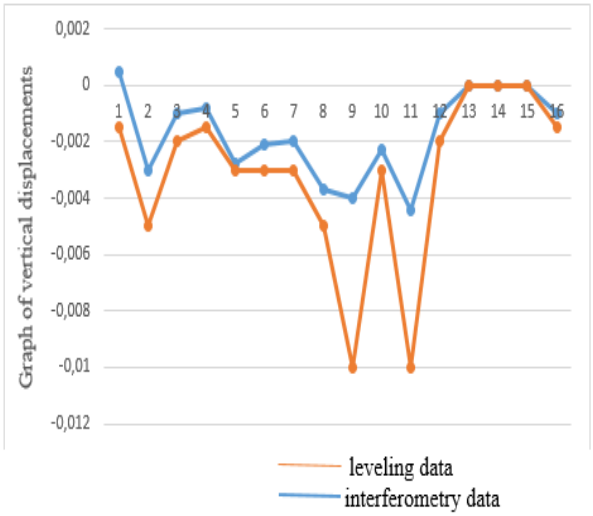

Figure 8 - Benchmarking chart for profile line 151

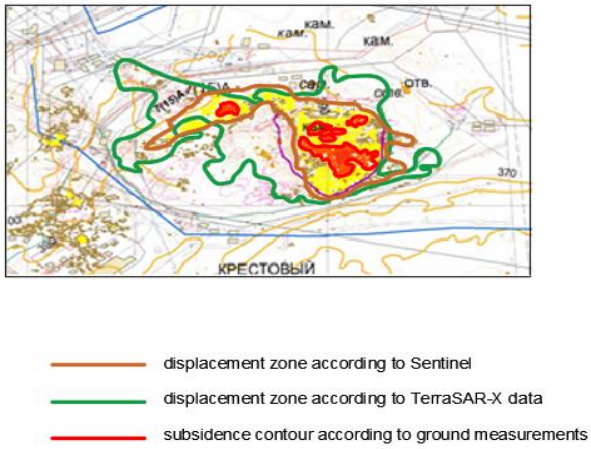

Figure 9 – Construction of a digital map of possible risk areas of subsidence of the earth's surface of the Annensky mine according to TerraSAR-X, Sentinel, ground measurements

Comparative analysis of the results of radar interferometry and showed the following.

1. The registered displacements of the earth's surface in the territory of the Annensky mine by the methods of radar and differential interferometry of Sovzond LLC, KazNITU-Grant, Sentinel are spatially confined to the sediment trough of the Annensky mine.

2. The zone of displacement (subsidence) of the earth's surface according to the data of the TerraSAR-X radar spacecraft, which has a higher spatial resolution (up to 1 meter), has more detailed detail and more accurately displays the contours of the intensive displacement trough obtained by ground surveying measurements.

3. The maximum absolute value of subsidence of the earth's surface within the subsidence trough of the Annensky mine, obtained according to Sentinel data from 05/08/2020 to 06/25/2020, was 10 mm.

Based on the results of the above analysis and comparative graphs, a digital map of possible risk areas of displacement and subsidence of the earth's surface of the Annensky field was built (Figure 9).

In conclusion, we note that the accuracy of differential interferometry methods for solving the problem of monitoring the movements of the earth's surface depends on the parameters of satellite imagery.

Conclusions

As a result of the application of integrated monitoring of the Annensky mine, displacements of the earth's surface were determined and recorded according to observational data for the period using satellite images of 2018, 2019 and 2020. The maximum absolute value of subsidence of the earth's surface within the subsidence trough of the Annensky mine from October 2018 to August 2020 was 0.8 cm. The displacements took place in height both upwards during the formation of rock dumps, and downwards, as a result of the subsidence of the earth's surface.

Thus, the results of the conducted research allow developing additional minerals and increasing the efficiency of the mining enterprise.

Conflict of interests. On behalf of all authors, we declare that there is no conflict of interest.

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Анненский кенішіндегі жер бетінің жылжуын және деформациясын бақылау

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ТҮЙІНДЕМЕ

Салыстырмалы түрде қолайлы жағдайларда, таяз тереңдікте орналасқан пайдалы қазбалар қорларының сарқылуының жалғасуына байланысты күрделі тау-кен-геологиялық жағдайларда орналасқан, үлкен тереңдікте, күрделі, нашар зерттелген және ықтимал қауіпті жағдайларда орналасқан кен орындарын тарту қажет. Жер асты әдісімен игерілген кен орындары да ерекшелік емес. Үлкен тереңдікте жатқан пайдалы қазбалар кен орындарын жерасты әдісімен қауіпсіз және тиімді игеру тау-кен жұмыстарының тереңдігінің ұлғаюымен, тау-кен массивындағы деформация процестерінің жүру сипатымен және олардың әсер ету дәрежесімен қиындайды. Деформациялық процестерді зерттеу, оларды бақылау және болжау көп жағдайда қатты пайдалы қазбалар кен орындарын игерудің тиімділігі мен қауіпсіздігін анықтайды. Практикалық болжам деформация процестерін кеңістікте және уақытта үздіксіз қадағалау нәтижесінде жасалуы мүмкін. Қазіргі уақытта кен орнының жер бетінің жылжуын және деформациясын анықтау үшін келесі әдістерді қамтитын кешенді бақылау қолданылады:

- тау жыныстары массивін алдын ала бақылау әдістері;
- қайталанатын жоғары дәлдіктегі нивелирлеу;
- спутниктік геодезиялық әдістер, ең алдымен интерферометрия әдістері;
- аймақтық және жергілікті жерлерде аспаптық бақылаудың басқа әдістері.

Қайта геодезиялық нивелирлеу, сондай-ақ спутниктік геодезия әдістерін қолдану сияқты жер беті деформацияларының геомеханикалық мониторингі үшін қолданылатын жер үсті әдістері жер беті деформацияларында болған өзгерістердің уақытша егжей-тегжейі мен кеңістіктік масштабын толық көрсетпейтінін атап өткен жөн. Бүгінгі таңда ғарыштық радиолокациялық интерферометрияның әдістері мен технологиялары ерекше практикалық құндылыққа ие болып отыр, олар жарық пен бұлттылық жағдайларына қарамастан, бірінші миллиметрге дейінгі дәлдікпен жер бетінің тік және жоспарлы жылжуының алаңдық бағаларын алуға мүмкіндік береді. Ғарыштық радиолокациялық интерферометрия (ҒРИ) - зерттелетін аумақтардың үлкен аудандарындағы жер бетінің қозғалысы мен құрылымдардың деформациясын тікелей картаға түсірудің тиімді құралы.

Түйін сөздер: кешенді бақылау, жер бетінің жылжуы, деформациялық процестер, жоғары дәлдіктегі нивелирлеу, радиолокациялық интерферометрия.

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Мониторинг смещений и деформаций земной поверхности Анненского рудника

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АННОТАЦИЯ

В связи с происходящим истощением запасов полезных ископаемых, расположенных в относительно благоприятных условиях, на небольших глубинах залегания, все чаще приходится вовлекать в добычу месторождения, расположенные в сложных горно-геологических условиях, залегающие на больших глубинах, в сложных, слабоизученных и потенциально опасных условиях. Не исключением являются и месторождения, разрабатываемые подземным способом. Безопасное и эффективное освоение месторождений полезных ископаемых подземным способом, залегающих на больших глубинах, осложняется тем, что с увеличением глубины ведения горных работ существенно изменяется характер протекания деформационных процессов в массиве пород и степень их влияния на окружающую среду. Исследования деформационных процессов, их контроль и прогноз определяют во многих случаях эффективность и безопасность разработки месторождений твердых полезных ископаемых. Практический прогноз может быть осуществлен в результате непрерывного слежения в пространстве и во времени за

деформационными процессами. В настоящее время для определения смещений и деформаций земной поверхности месторождения используют комплексный мониторинг, включающей в себя следующие методы:
- визуальный мониторинг подвижек горных пород;
- повторное высокоточное нивелирование;
- спутниковые геодезические методы, в первую очередь, методы интерферометрии;
- другие методы инструментальных наблюдений на региональных и локальных участках.
Следует отметить, что наземные методы, применяемые для геомеханического мониторинга деформаций земной поверхности, такие как повторное геодезическое нивелирование, а также применение методов спутниковой геодезии не полностью отражают временную детальность и пространственный масштаб произошедших изменений в деформациях земной поверхности. На сегодняшний день, особую практическую ценность приобретают методы и технологии космической радиолокационной интерферометрии, которые позволяют получать площадные оценки вертикальных и плановых смещений земной поверхности с точностью до первых миллиметров независимо от условий освещённости и облачности. Космическая радиолокационная интерферометрия (КРИ) представляет собой эффективное средство прямого картирования подвижек земной поверхности и деформаций сооружений на больших площадях исследуемых территорий.
Ключевые слова. комплексный мониторинг, смещения земной поверхности, деформационные процессы, высокоточное нивелирование, радарная интерферометрия.

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Increased recovery of free fine gold in the leaching process

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ABSTRACT

The current state of world mineral resources is characterized by a decrease in the quality of minerals. An increase in production and processing volumes is possible only through the development of new deposits and the involvement of off-balance ores, dumps and tailings, slags and other industrial wastes in the integrated mining process. More increasing the need for involving raw materials of complex composition, refractory, low-grade, with small reserves, technogenic mineral waste. It becomes more and more relevant as the discovery and exploitation of new deposits, allowing to increase the gold reserve of the Republic of Kazakhstan. The article presents the results of sorption leaching of ore in order to extract gold associated with sulfides, the processes of opening gold. A representative sample was taken and the phase composition of an additional explored ore body was studied at one of the deposits in Kazakhstan. The ore sample was prepared for research: three-time mixing by the ring-cone method, in general, three-stage quarting and mixing were performed. It should be noted that the methods for processing gold-bearing ore raw materials depend on many parameters, including the material composition and technological properties. Samples from the last quarting materials were selected for chemical, sieve and phase analyzes. It was found that the test sample contained 6.04 g / t Au and 7.9 g / t Ag, as well as fineness of gold within 0.01-0.25 mm phase analysis. Mineral gold formations can be easily soluble in cyanide solutions (native gold, electrum), partially soluble (maldonite, or practical are insoluble (tellurides). Gold in ores is present in the form of gold-colored sizes and shapes. Both physical (gravity, flotation) and chemical (cyanide, etc.) methods are used to extract it. Rational analysis also found that gold in the ore under study, crushed to a particle size of 90%, class 0.071 mm, gold is free and in intergrowths is 81.46%, gold associated with sulfides is 14.40%, in rock-forming minerals 1.66%. Based on the data obtained, it can be stated that when cyanidating ore, one should expect rather high rates of gold dissolution (80% or more). Gold extraction from ore with a content of 85% fraction -0.071mm-90.2%, with a content of 85% fraction- 0.071mm-98% with oxidative leaching. Full extraction of gold from ore is possible with sorption cyanide leaching with their preliminary oxidation. The paper considers economically feasible existing and promising technologies for gold extraction at the leading factories of Kazakhstan and abroad.

Keywords: gold ore, sorption leaching, chloroactive compound, sorbent, oxidizing agent.

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Introduction

The current state of world mineral resources is characterized by a decrease in the quality of minerals. An increase in production and processing volumes is possible only through the development of new deposits and the involvement of additionally explored raw materials in the complex, as well as the development of off-balance ores, heaps and tailings, slags and other industrial wastes. The most contemporary important problem of gold hydrometallurgy is the search for rational methods for its extraction from refractory ores and industrial wastes. It becomes more and more relevant as the discovery and exploitation of new deposits, allowing to increase the gold reserve of the Republic of Kazakhstan.

Kazakhstan has significant potential for gold-bearing mineral resources. One of these objects is the ore of one of the deposits of East Kazakhstan. The field was discovered in the 70s of the last century. Exploration of the deeper horizons of the deposit showed the presence of a richer sulfide type of ore.

At present, most gold processing plants process ores in which sulfide minerals are present. Gold in such ores is partially associated with sulfides, and partially is in a free state. In most cases, ores of this type are classified as refractory, and circumstances that exclude the use of enrichment methods are possible.

Technological mineralogy methods allow to identify useful and harmful minerals and their associations in ores, determine the features of their real composition and structure, the nature of relationships between themselves and with rock-forming phases, control, explain and predict the behavior of ores in technological processes. Cyanide leaching is the main method for extracting gold from ores both in traditional technology and in geotechnological mining. Sodium cyanide or potassium cyanide salts with a concentration of 0.02-0.3% are used as a reagent.

The dissolution of gold in cyanide solutions occurs in the presence of oxygen by the reaction:

$$2Au+4NaCN+SO_2+H_2O = 2Na[Au(CN)_2] + 2NaOH \quad (1)$$

From the reaction it is clear that gold passes into the solution in the form of a gold-cyanide salt of sodium, which dissociates in solution into ions:

$$Na[Au(CN)_2] = Na^+ + [Au(CN)_2]^- \quad (2)$$

The possibility of the occurrence of an electrochemical dissolution of gold is determined by the electromotive force equal to the potential difference of the anodic and cathodic processes. In addition, in the presence of a complexing agent, in particular, a CN ion, the activity of Au ions in solution decreases during the formation of a very strong $[Au(CN)_2]^-$ complex.

The instability constant of this complex is characterized by a very small value:

$$K = \frac{[Au]\times[CN]^2}{[Au(CN)_2]^-} = 5 \times 10^{-38} \quad (3)$$

Therefore, in the presence of CN ions, the activity of Au ions decreases sharply, which means that the potential of gold decreases and its oxidation becomes thermodynamically possible [[1], [2], [3], [4]]. The potential for dissolving gold with the formation of a cyanide complex is -0.611 V, while the potential of gold itself is equal to + 1.8 V.

At the same time, studies noted that an increase in the oxygen concentration in the solution increases the passivation of the gold surface and, as a result, there is a strong anodic inhibition of the dissolution process. An excess of alkali in a solution (pH-12) of hydrogen peroxide leads to the same effect, which contribute to the formation of thick oxide films on the metal surface. However, it should be noted that the addition of chloroactive compounds increases the rate of dissolution of the noble metal. This is in favor of the adsorption mechanism of passivation of gold by oxygen. A.N. Frumkin noted that when oxygen is adsorbed, along with a change in the double layer, the chemical nature of the metal surface changes, which should affect the rate of the dissolution process [[5], [6], [7]]. The addition of a chloroactive compound to the solution leads to the adsorption displacement of oxygen from the gold surface, its partial depassivation, and an increase in the dissolution rate. All of the above applies directly to free metallic gold. At the same time, the main problem for the gold mining industry is persistent sulfide ores and concentrates, in which gold is closely associated with pyrite and arsenopyrite. These minerals are chemically stable and are not amenable to direct leaching with solutions of acids and alkalis. For such raw materials, various methods of opening, grinding, bioleaching, roasting, oxidation of autoclaves, etc., were proposed before the cyanide process. The study of the decomposition of arsenopyrite and pyrite. showed that their chemical resistance is largely dependent on the nature of the solvent used. The most favorable conditions for the

oxidation of these minerals are created in alkaline solutions in the presence of an oxidizing agent.

The aim of the work was to conduct research and development of a sorption technology for the extraction of gold from further explored ores [[8], [9], [10], [11], [12], [13]].

Methods of analysis

X-ray phase analysis was carried out on a D8 Advance diffractometer (BRUKER), α-Cu radiation. Diffraction pattern shooting conditions: U = 35 kV; I = 20 mA; scale: 2000 imp; time constant 2s; shooting theta-2ta; detector 2 deg / min

Currently, most GEFs process ores in which sulfide minerals are present. Gold in such ores is partially associated with sulfides, and partially is in a free state. In most cases, ores of this type belong to the category of resistant. The raw material for gold extraction is gravity-flotation concentrate from ore enrichment. The methods of technological mineralogy make it possible to identify useful and harmful minerals and their associations in ores, to determine the features of their real composition and structure, the nature of relationships between themselves and with rock-forming phases, to control, explain and predict the behavior of ores in technological processes [[14], [15], [16], [17], [18]].

The raw material base of the gold mining industry of Kazakhstan is mainly represented by small (with reserves up to 25 tons) and medium (from 25 to 100 tons) deposits. However, the leading position is occupied by the deposits of Eastern, Northern and Central Kazakhstan. The search for the most effective integrated technology for extracting gold from mineral raw materials is an urgent task of the gold mining industry of Kazakhstan.

One of the key processes in the technology of processing of resistant fine-grained ores is the process of their opening, which provides access of the leaching reagent to the surface of micro- and nanoparticles of gold. The conducted studies of hydrometallurgical methods for extracting gold from low-sulfide ores allowed us to make a choice and justify the prospects for the use of pre-oxidation [[19], [20], 21]].

Experimental part

The object of research was the ore of the processing plant of the deposits of East Kazakhstan. In preparation for research, the sample was crushed in stages to a particle size of -2.5 + 0 mm, was quarting, mixed, and reduced in accordance with the standard sampling methodology (samples) for technological studies and the study of material composition. Ore crushing was carried out on laboratory jaw and roll crushers and grinding on ball, rod and bead mills and vibro-crusher. The ore sample is a finely ground material with a particle size of 100 % class – 0.071 mm. The chemical composition of the studied tailings sample is represented by the following main components, %: 4.27 Fe; 9.02 Fe_2O_3; 8.1 FeO; 0.010 As; 0.072 Zn; 0.016 Cu; 6.04 g / t Au; 7.9 g / t Ag.

Ore cyanidation products — solution and cake — were subjected to atomic adsorption and assay assays, respectively.

Electron microscopic studies of the basic sulfide mineral arsenopyrite extracted from the initial tailings sample were carried out using a JEOL JXA-8230 scanning electron microscope (Japan) equipped with an energy dispersive analyzer. As can be seen in fig. 1, pyrite in addition to the basic structural elements - iron and sulfur also contains gold and trace elements of copper and zinc.

From the results of a rational (phase) analysis of the gold in the ore, finely ground to a fineness of 90 % of the class –0.071 mm (table 1), it follows that the content of free gold in the intergrowths (cyanide gold) is 81.46 %. The presence of finely disseminated gold in sulfides is one of the main reasons for the technological persistence of mineral raw materials. 14.4 0% of gold is associated with sulfides, 2.48 % is associated with acid-soluble compounds. In the rock-forming minerals, the gold content (0.10 g / t, or 1.66 %).

Table 1 - The results of a phase (rational) analysis for gold of a crushed sample of the original ore with a particle size of 90 % of the class -0.071 mm

Forms of gold in ore	Gold allocation	
	g/t	%
Free form	4.92	81.46
Associated with acid-soluble minerals (carbonates, hydroxides, chlorites, etc.)	0.15	2.48
Associated with Sulfides	0.87	14.40
Finely interspersed in rock-forming minerals	0.10	1.66
Total in sample (balance sheet)	6.04	100.0

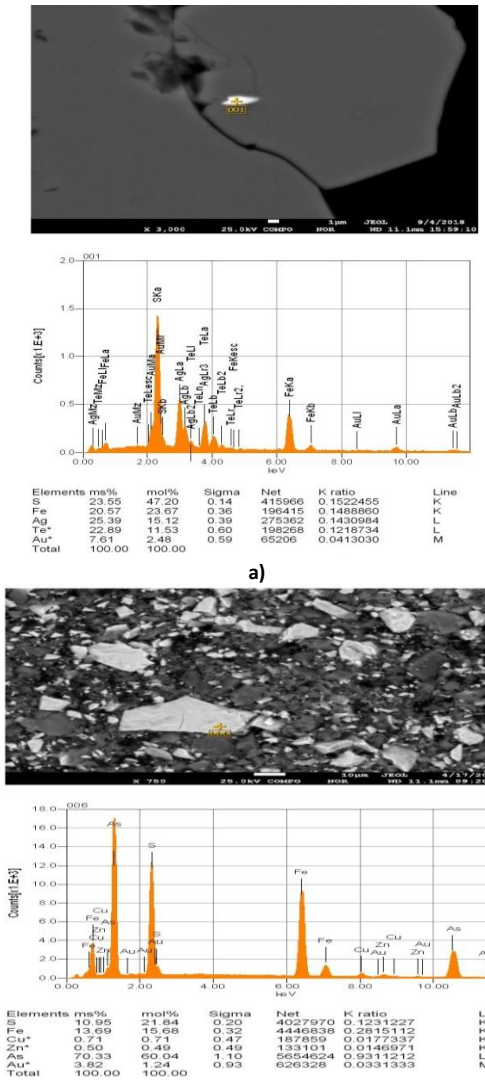

Figure 1 - energy dispersive analysis of the microstructures of gold (a) in pyrite and (b) in a fragment of arsenopyrite

The data of X-ray phase analysis of the sample showed that the bulk of the sample is represented by silicon oxide (54.7%). The proportion of pyrite in the sample (3.4%). Clinochlor is a mineral belonging to phyllosilicate ammonium and aluminum with hydroxyl, the proportion of which is 11.2% (figure 2).

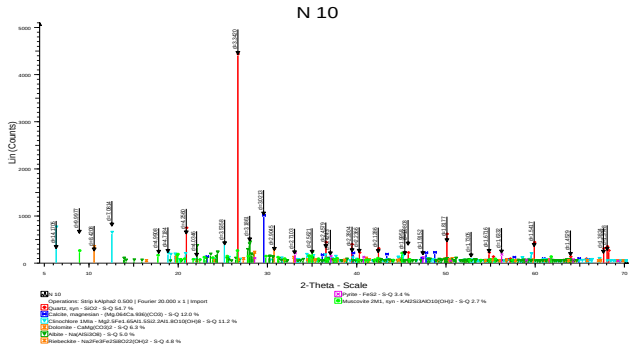

Figure 2 - Diffractogram of an ore sample

To find the forms of gold, a rational analysis of the ore sample was performed with the initial size class -0.05 mm and +0.05 mm. Under an optical microscope Axio Scope.A1, a polished section (∅ = 25 mm, m $_{weights}$ = 12-17 grams) formed from this material was studied. As a result, found 33 golden particles, of which:

• 26 particles in free form - 78.8%, Au dimension from 0.5 to 6.9 mkm, i.e. ultrafine, finely dispersed gold (Figure 3, 4);

• 7 particles in intergrowths with waste rock - 21.2%, with parameters - Au from 0.4 to 8.4 mkm (Figure 3). The particle size is in the range: Au (0.4-8.4 mkm), i.e. ultrafine (0.1-1.0 mkm) and finely dispersed gold (1.0-10.0 mkm) (according to Petrovskaya's classification "Native gold").

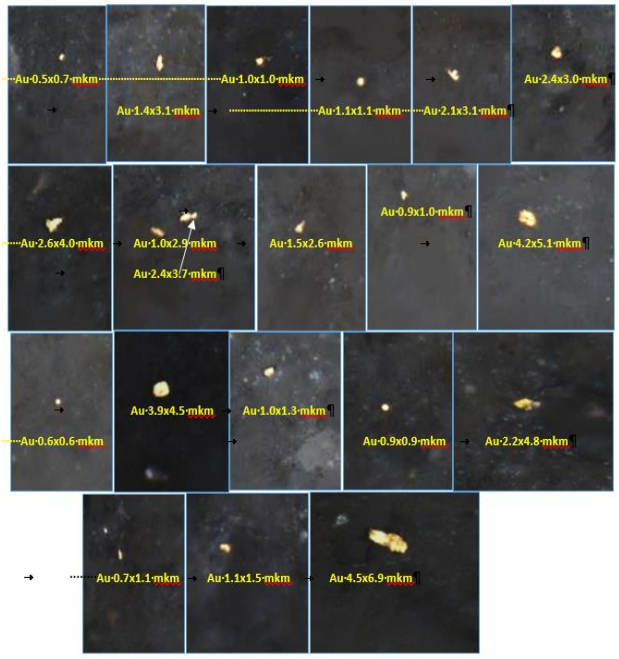

Figure 3 - Free gold in binder polystyrene

Below, in Figure 4, gold particles in the free state are noted, covered with oxidation films, possibly of goethite-limonite composition, which, in turn, gives them a reddish tint.

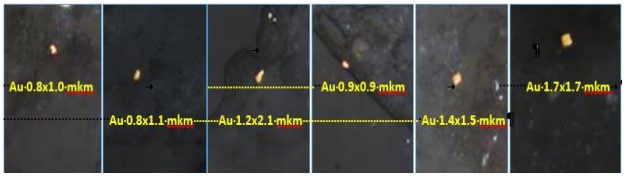

Figure 4 - Free gold particles covered with oxidation films

Table 2 - the results of the leaching of gold from the source ore

Nomination	Parameters		
	85% - 0,071mm	85% - 0,071 mm	85% - 0,071mm
Sample weight, g	300	300	300
The mass of the solution, g	900	900	900
CaO, kg/t 70% activity	1.5	1,5	1.5
The density of the pulp during cyanidation,% solid	30	30	30
The concentration of NaCN,%	0.1	0.1	0.1
pH	11.3	11.4	11.2
Type of sorbent / oxidizing agent, g	-	Gold Carb 207C	$Ca(ClO)_2$ +*Cl^{n+} 2.5
Au content in initial sample by assay, g/t	6.04	6.04	6.04
Au content in the tailings solid residue (cake), g / t	0.59	0.5	0.12
The degree of dissolution of Au,%	90.2	91.6	98.0

Under conditions of ore treatment with preliminary oxidation by a chloroactive complex of compounds (≈ 30% Ca $(ClO)_2$ + 70% * Cl^{n+}), subsequent washing of the cake with water and cyanide leaching (pH = 11.2 solid: liquid = 1: 3, and 1 g / dm3 NaCN, the duration of 24 hours of gold recovery is 98.0%. With direct cyanidation, the recovery rate was only 90.2%. Sorption recovery reached 91.6%.

Discussion of the results

The results presented in table 2 indicate that during direct, sorption and pre-oxidation leaching, the gold content in the leaching tailings decreases to 0.59-0.12 g/t and the degree of gold dissolution increases to 90.2-98.0%. During sorption cyanidation, the consumption of sodium cyanide and alkali (calcium oxide) increased slightly (Table 2). This is due to the fact that GoldCarb 207C activated carbon has the ability to sorb cyanide compounds and hydroxide ions. The increase in the consumption of sodium cyanide during the transition from direct cyanidation to sorption is associated with the sorption of CN-activated carbon ions.

Based on the results of the conducted research, the following modes for hydrometallurgical processing of ore from the Sekisovsky deposit are recommended:

- grinding fineness 55% -0.071 mm;
- the concentration of sodium cyanide in the liquid phase of the pulp is 0.1%, pH 10.5-11.0;
- the ratio of solid to liquid in the pulp S:L = 1:3 (the solid content in the pulp is 33.3%);
- cyanidation time is 24 hours;
- cyanidation of gold from ore is carried out in the presence of a sorbent (sorption leaching).

Carrying out the process in this mode allows 91.6% of gold to be dissolved from the ore with its almost complete extraction by the sorbent and to obtain tails of sorption cyanidation with a minimum gold content of 0.5 g/t.

When comparing test 1 and test 3 on a crushed product, it follows: after preliminary oxidative treatment of the material, the extraction is higher by 7.8% (98.0% compared to the test without oxidative treatment - 90.2%).

It follows from the above: in order to increase the extraction of gold from the ore of the Sekisovsky deposit by cyanidation, preliminary oxidative treatment has a positive effect.

Conclusion

It was revealed that the sulfide ore under study according to assay data contains 6.0 g / t gold, 7.9 g /t silver and belongs to the sulphide gold-quartz type. The ore is characterized by a multicomponent mineral composition with a predominance of iron-containing pyrite and is practically not affected by oxidation processes. The study of mineralogical and x-ray phase analysis and samples showed that the bulk of the ore is represented by pyrite with rare fragments of gold-bearing arsenopyrite. The only valuable component in the sample of industrial interest is gold, and silver recovery can be considered as an associated metal. Rational analysis found that in the ore under study gold is free and in intergrowths is 85.51%, gold associated with sulfides is 11.81%, in membranes 1.46%, in gangue 1.22%. However, the formation of various types of membranes covering the surface of free gold can to some extent slow down the cyanidation process. Thus, the use of preliminary oxidation by chloroactive compounds promotes a more complete recovery of noble metals by eliminating impurities of various types of membranes forming on the surface of free gold. In addition, the oxidizing properties of

chlorine can reveal sulfide gold-bearing minerals, such as pyrite and arsenopyrite, which also contributes to a more complete extraction. Thus, the use of a complex of chloroactive compounds made it possible to extract an additional 7.8% of gold from the sample under study compared with direct cyanidation, which ultimately amounted to 98% of gold transferred to a productive solution.

Conflict of interests. On behalf of all authors, the correspondent author declares that there is no conflict of interest.

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Шаймалау процесінде бос алтын алуды арттыру

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ТҮЙІНДЕМЕ

Әлемдік минералдық-шикізат ресурстарының қазіргі жай-күйі пайдалы қазбалар сапасының төмендеуімен сипатталады. Өндіру мен қайта өңдеу көлемін ұлғайту жаңа кен орындарын игеру және баланстан тыс кендерді, үйінділер мен қалдықтарды, шлактар мен өнеркәсіптің басқа да қалдықтарын кешенді игеруге тарту есебінен ғана мүмкін болады. Құрамы күрделі, төзімді, төмен сұрыпты, аз қоры бар, техногендік шикізатты өңдеуге тарту қажеттілігі барған сайын артып келеді. Ол Қазақстан Республикасының алтын қорын ұлғайтуға мүмкіндік беретін жаңа кен орындарының ашылуына және пайдаланылуына қарай барынша өзекті бола түсуде. Мақалада сульфидтермен астасқан алтынды алу мақсатында кенді сорбциялық сілтісіздендіру нәтижелері, Алтынды ашу процестері келтірілген. Өкілдік сынаманы іріктеу жүзеге асырылды және Қазақстанның кен орындарының бірінің жете зерттелген кен денесінің фазалық құрамы зерделенді. Кен сынамасын зерттеуге дайындау орындалды: "сақина-конус" әдісімен үш рет араластыру, жалпы үш сатылы квартылау және араластыру орындалды. Құрамында алтын бар кен шикізатын өңдеу әдістері материалдық құрамы мен технологиялық қасиеттерін қамтитын көптеген параметрлерге байланысты екенін атап өткен жөн. Химиялық, елек және фазалық талдауларға соңғы тоқсандағы материалдардан сынамалар алынды. Зерттелетін сынамада 6,04 г/т Au және 7,9 г/т Ag, сондай-ақ фазалық талдау арқылы 0,01-0,25 мм шегінде золотиннің ірілігі бар екені анықталды. Алтынның минералды түзілімдері цианид ерітінділерінде оңай ериді (табиғи алтын, электрум), ішінара ериді (мальдонит немесе іс жүзінде ерімейді (теллуридтер). Рудадағы алтын алтын мөлшері мен формасы түрінде болады. Оны алу үшін физикалық (гравитация, флотация) және химиялық (цианизация және т.б.) әдістер қолданылады. Рационалды талдау сонымен қатар зерттелетін кендегі алтынның 0,071 мм класының 90% - ына дейін ұсақталғаны, алтын бос және көшеттерде 81,46%, сульфидтермен байланысқан алтын 14,40%, тау жыныстарын құрайтын минералдарда 1,66% екендігі анықталды. Алынған деректер негізінде кенді циандау кезінде Алтынды еріту бойынша жеткілікті жоғары көрсеткіштерді (80% және одан жоғары) күту керек деп айтуға болады. Құрамында 85% фракция -0,071 мм-90,2% болса, 85% фракция-0,071 мм-98% болса, алдын ала тотығу кезінде кеннен алтын алу. Алтынды кеннен толық алу оларды алдын ала тотықтыра отырып, сорбциялық цианидті шаймалау кезінде мүмкін болады. Жұмыста Қазақстанның алдыңғы қатарлы фабрикаларында және шетелдерде алтын алудың экономикалық тұрғыдан орынды қолданыстағы және перспективалы технологиялары қарастырылды.

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Повышение извлечения свободного золота в процессе выщелачивания

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АННОТАЦИЯ

Современное состояние мировых минерально-сырьевых ресурсов характеризуется снижением качества полезных ископаемых. Увеличение объемов добычи и переработки возможно лишь за счет освоения новых месторождений и вовлечения в комплексную отработку забалансовых руд, отвалов и хвостов, шлаков и других отходов промышленности. Все более возрастает необходимость вовлечения в переработку сырья сложного по составу, упорного, низкосортного, с небольшими запасами, техногенного. Она становится все более актуальной по мере открытия и эксплуатации новых месторождений, позволяющих увеличить золотой запас Республики Казахстан. В статье приведены результаты сорбционного выщелачивания руды с целью извлечения золота, ассоциированного с сульфидами, процессы вскрытия золота. Осуществлен отбор представительной пробы и изучен фазовый состав доразведанного рудного тела одно из месторождений Казахстана. Выполнена подготовка пробы руды к исследованиям: трехкратное перемешивание методом «кольцо-конус», в целом выполнено трехступенчатое квартование и перемешивание. Следует отметить, что методы переработки золотосодержащего рудного сырья зависят от многих параметров, включающих в себя вещественный состав и технологические свойства. На химический, ситовой и фазовый анализы отобраны пробы из материалов последнего квартования. Установлено, что в исследуемой пробе содержится 6,04 г/т Au и 7,9 г/т Ag, а также крупность золотин в пределах 0,01-0,25мм фазовым анализом. Минеральные образования золота могут быть легко растворимы в цианидных растворах (самородное золото, электрум), частично растворимы (мальдонит, или практически нерастворимы (теллуриды). Золото в рудах присутствует в виде золотинразных размеров и форм. Для его извлечения применяют как физические (гравитация, флотация), так и химические (цианирование и т.п.) методы. Рациональным анализом установлено также, что золото в исследуемой руде, измельченной до крупности 90 % класса 0,071 мм, золото свободное и в сростках составляет 81,46 %, золото ассоциированого с сульфидами 14,40 %, в породообразующих минералах 1,66 %. На основании полученных данных можно констатировать, что при цианировании руды следует ожидать достаточно высоких показателей по растворению золота (80 % и более). Извлечение золота из руды при содержании 85% фракции -0,071мм-90,2%, при содержании 85% фракции-0,071мм-98% при предварительном окислении. Полное извлечение золота из руды возможно при сорбционном цианидном выщелачивании с предварительным их окислением. В работе рассмотрены экономически целесообразные действующие и перспективные технологии извлечения золота на передовых фабриках Казахстана и за рубежом.

Ключевые слова: золотосодержащая руда, сорбционное выщелачивание, хлоративное соединение, сорбент, окислитель.

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creative commons

The study the possibility of development of environment safety technology of creating polymer composites in the conditions of small innovative enterprises

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ABSTRACT

The creation of competitive products with a high degree of science intensity is impossible without the use of innovations. However, in their creation process does not always comply with the environmental safety requirements, which leads to negative consequences for the natural environment and human health. This article presents the results of research work group of authors to create wear-resistant polymer composites and their rational use in the processes of parts manufacturing machines running under the impact of the abrasive particles in the absence or limited admission Lube. A method of applying a metal coatings on fibers and powders, in which a metal coating layer with a thickness from 50 nm is applied to the surface by thermal decomposition organometallic compounds vapour using CVD-method, and device for molding polymer composites pressure. Developed innovative polymer composites based on polyamide-6.6 reinforced with metallic fibers and powders used for the manufacture of parts of construction, emergency rescue and other types of equipment. As a result of conducting a comprehensive study reported an increase resources manufactured parts relative serial assembly units. The ecological nature of the creating polymer composites in the conditions of small innovative enterprises was ensured by conducting the process in a closed cycle with the possibility of re-use of the reagents. This eliminated the flow of pollutants into the environment and allowed the implementation of the principles of resource and energy conservation.

***Keywords*:** CVD-method, organometallic compounds, polymer composites, resource saving, environment safety, innovations.

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Introduction

The functioning of innovative enterprises is one of the conditions for the progressive development of the economy of a modern state. The possibility of obtaining an innovative commercial product in medium and small-scale production provides undeniable advantages in the development of the sales market and the search for optimal product characteristics for the consumer. At the same time, in the conditions of small innovative enterprises, there are objective prerequisites for the implementation of technological processes, taking into account the requirements of technosphere safety, energy and resource saving through the development and implementation of low-waste technologies, as well as the involvement of regional natural resources in production processes [[1], [2], [3], [4]].

When creating a new composite at an enterprise operating on the basis of a scientific center (university, scientific institute, etc.), the possibility of approbation of the current results of scientific research (technologies and equipment) at the stages of development and experimental design is of particular importance. At the same time, the most difficult and interesting task is the choice of the optimal composition and technological regimes

that ensure the production of materials with desired physical, mechanical and operational properties. It is necessary to take into account the whole range of operating factors of machine parts and equipment for which it is intended, testing various options for the composition and ratio of the material components. Such tasks are of an explicit research nature and require deep study at the theoretical and empirical levels of research using the methods of thermodynamics, electron microscopy, energy dispersive X-ray spectroscopy, as well as bench and operational tests of samples of materials and parts of machines and equipment.

The purpose of this study is to analyze the possibilities and prospects for developing an environmentally friendly method for producing composites based on thermoplastics, the use of which in small-scale production will ensure the creation of an innovative product.

Experimental Part

Composites based on thermoplastics are widely used in various industries, including mechanical engineering and repair production in the manufacture and restoration of machine parts operating under the influence of wear factors and a corrosive environment. The required properties (wear resistance, hardness, heat resistance, shrinkage, etc.) are obtained by combining the characteristics of the matrix and filler [1].

To achieve optimal compatibility of the filler elements with the matrix, they were metallized by the CVD method of organometallic compounds in the technological modes presented in the works [[1], [5]].

The study of the quality of metal coatings was carried out using a two-beam system (small dual beam, FIB / SEM) in a scanning electron microscope Quanta 3D FEG.

Obtaining images and parts from polymer composites based on polyamide - 6.6 was carried out using a device for injection molding of thermoplastics and composites based on them under pressure [6].

Bench and operational tests of images and parts made of polymer composites were carried out on the basis of state and interstate standards:

- state standard 18616-88 “Plastics. Method for determining shrinkage”,
- state standard 11629-2017 “Plastics. Friction Coefficient Determination Method”,
- state Standard 21341-2014 “Plastics and ebonite. Method for determining heat resistance according to Martens".

Research discussion

As part of the research activities of the authors, the development of methods for obtaining wearresistant polymer composites for the manufacture and restoration of mating parts of road construction, emergency rescue, tillage and mining machines using the Chemical Vapor Deposition method (CVD), that is, "chemical vapor deposition”) of organometallic compounds (OMC). Using this method, it is possible to improve the characteristics of the filler elements of the composite through their metallization, achieving optimal adhesive compatibility with the matrix [[5], [6]].

The essence of the CVD method is to convert the initial OMC into a vapor state by evaporation or sublimation and deposition of the metal on the surface of the substrate heated to the decomposition temperature of the OMC.

Figure 1 shows the general scheme of the process.

$$\frac{[OMC]}{[OMC]} \xrightarrow[\text{liquid}]{\text{Evaporation}} \xrightarrow[\text{powder}]{\text{Sublimation}} [OMC] \xrightarrow[\text{gas}]{\text{Decomposition}} [Metal] + \begin{bmatrix} \text{Related} \\ \text{products} \end{bmatrix}$$

Figure 1 - General scheme for implementing the OMC CVD method

When implementing the OMC CVD method, an active atomic background is formed, which is accompanied by a spontaneous thermodynamically favorable arrangement of the substance on the metallized surface and contributes to obtaining a uniform metal coating with a thickness of 50 nm to 200 mm on substrates, incl. complex configuration (powder particles, fibers, etc.) [[5], [7]].

As initial metallization reagents, carbonyl, cyclopentadienyl and bisarene OMCs can be used, which have the volatility required for the CVD method, the absence of aggressiveness with respect to the substrate and the equipment used, as well as a relatively low decomposition temperature (up to 600°C), which is important for implementing the principle of energy saving of technological process [[8], [9], [10]].

When carbonyl organometallic compounds of nickel, iron, molybdenum, and other metals are

Table 1 – Nomenclature and Characteristics of Initial OMCs, Substrates, and CVD Metal Coatings

Substrate		Original OMC			Coating	
View	*Size, microns*	*View*	*Temperature, ℃*		*Basis*	*Thickness, microns*
			Evaporation / sublimation	*Expansions*		
Glass fibers	5 – 10 (diameter)	$Ni(CO)_4$	30	60 - 200	Ni	0.01 - 0.05
Carbon fibers		$Ni(C_5H_5)_2$	100	400 - 450	Ni	0.50 - 1.00
Particles of quartz sand	140 - 280	$Fe(CO)_5$	100	60 - 250	Fe	0.50 - 1.00
Metal powders PG-US25	125 - 200	$Mo(CO)_6$	40	130 - 400	Mo	0.08 - 0.10

used as initial reagents, the main reaction of the process is the thermal dissociation of OMC:

$$M_x(CO)_y \xrightarrow{t} xM + yCO,$$

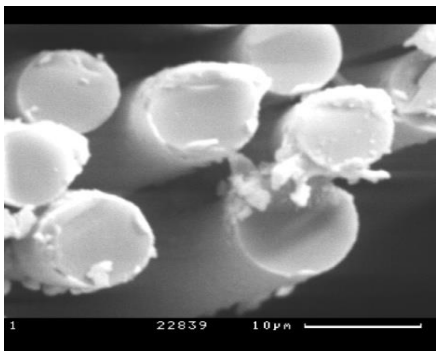
where M is a transition metal of groups V ... VIII of the Periodic system of chemical elements of D.I. Mendeleev;

t – decomposition temperature OMC, ℃.

The implementation of the process is based on changing its temperature regime at the stages of transferring the initial OMC to a vapor state and the interaction of the OMC with a substrate heated to the temperature of its decomposition. The ongoing chemical reactions are reversible, which makes it possible to ensure the cyclicity of metallization and to use the initial reagents that have not come into contact with the substrate in the repeated stages of the process. This ensures low waste and resource saving for technological processes of metallization using the CVD method.

Table 1 lists the filler (substrate) elements of composites obtained using the OMC CVD method [1].

Figure 2 shows the appearance of metallized powders and fibers obtained by the CVD OMC method.



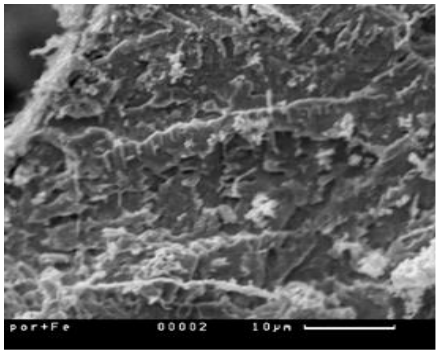


Figure 2 – Cross-section of glass fibers and quartz sand powder particles metallized by the CVD OMC method

To obtain composites based on thermoplastics using modified fillers by injection molding, to study and optimize their properties in order to achieve the characteristics required under specific operating conditions, a device has been developed, the scheme of which is shown in Figure 3.

With this device, which is compact and simple in design, it is possible to obtain a wide range of samples of materials and parts. The principle of its operation is based on filling the melt accumulator with 9 thermoplastic granules (formaldehyde-dioxolane copolymer, polyamide-6, polyamide-6.6, acrylobutadiene styrene plastic, low-pressure and high-pressure polyethylene, polypropylene, etc.) and a filler of the appropriate type (metallized powders, granules, fibers 5 - 7 mm long) in the required amount (from 1 to 50% (wt.) and their uniform heating to the melting temperature of the thermoplastic (180 - 250˚C)).

The formed melt, using a cylindrical pusher, fills the cavity of the mold 11, in which it is kept under pressure at the pressing temperature for a given time. Then the pressure is released, the mold 10 is cooled, the finished material sample (part) is removed [6].

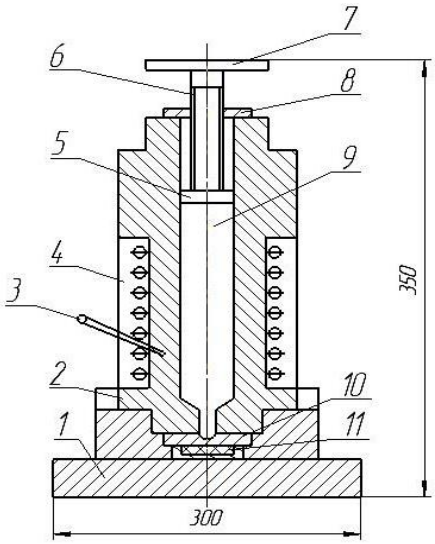


Figure 3 - Scheme of the device for molding composites under pressure: 1 - base; 2 - body; 3 – thermocouple; 4 - heater; 5 - cylindrical pusher with plasticator; 6 - stock; 7 - flywheel; 8 - threaded cover; 9 - melt accumulator; 10 - mold; 11 - mold cavity

Figure 4 shows a composite based on polyamide-6.6 (PA 66) with a filler in the form of short glass fibers metallized by the CVD method (the initial reagent is nickel tetracarbonyl), a sample of which was obtained by injection molding using the developed device [1].

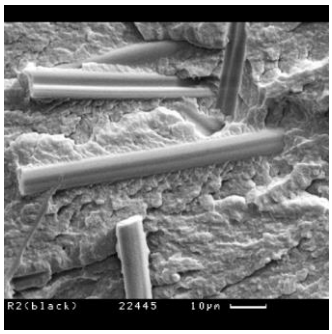


Figure 4 - Polyamide-6.6 armed with glass fibers in a nickel film

Comparative characteristics of composites based on polyamide-6.6 filled with metallized powders and fibers are presented in Table 2.

The developed composites were studied for the possibility of using for the production and restoration of machine parts (sliding bearings, seals for hydraulic system parts, etc.) operating in corrosive and abrasive environments with a limited supply of lubricants.

In particular, based on the analysis of a set of material properties, load-speed modes and operating conditions for the manufacture of guide bearings for the outreach mechanism of an MTA-160 crane installation with a maximum load of 10 kN, the optimal composite is polyamide-6.6 filled with metallized carbon fibers; filling - 20% (wt.).

Figure 5 shows a general view of the manufactured parts.

Figure 5 – Guide supports of the MTA-160 crane installation, made of polymer composite

In the course of operational tests of four crane installations in construction organizations of the Tver region of the Russian Federation, it was found that the wear of guide supports made from the developed polymer composite is 60 - 70% less than that of similar serial parts made from the VMT "Sipas"composite.

Table 2 - Comparative characteristics of composites based on polyamide-6.6 obtained by the developed technology

Properties	**Type and content of the filler**							
	Metal powders PG-US25		***Carbon fibers***		***Glass fibers***		***Particles of quartz sand***	
	OMC	***% (масс.)***	***OMC***	***% (wt.)***	***OMC***	***% (wt.)***	***OMC***	***% (wt.)***
	$Mo(CO)_6$	***10-50***	***$Ni(C_5H_5)_2$***	***10-20***	***$Ni(CO)_4$***	***10-20***	***$Fe(CO)_5$***	***10-50***
Hardness, MPa	111 - 140		110 - 138		110 - 150		115 - 151	
Shrinkage, %	0.60 - 1.30		0.85 - 1.50		0.90 - 1.60		0.62 - 1.40	
Heat resistance according to Martens, ℃	140 - 230		144 - 210		115 - 190		150 - 205	
Friction coefficient without lubricant	0.11 – 0.19		0.07 - 0.08		0.09 - 0.10		0.25 - 0.38	

Conclusions

Firstly, a fundamental approach to the development of an environmentally friendly technology for the production of polymer composites is proposed, which is based on the principles of low waste and resource saving, implemented through innovative solutions to optimize the properties of the filler through metallization by the CVD method of organometallic compounds.

Secondly, a device for molding composites based on thermoplastics under pressure has been developed, characterized by compactness, reliability, structural simplicity, controlled consumption of raw materials and a wide range of obtained samples of materials and parts, using which composites based on thermoplastics filled from 10 to 50% (wt.) powders and fibers metallized by the CVD method OMC, having shrinkage during injection molding 0.6 - 1.6%, friction coefficient when working without lubricants 0.07 - 0.38, heat resistance 115 – 230 ℃.

Thirdly, the results of comparative bench and operational tests of samples of materials and parts substantiate the feasibility of using the developed technology in the conditions of small innovative enterprises in the restoration and manufacture of machine parts.

Compliance with Ethical Statement

On behalf of all authors, the correspondent author declares that there are no potential conflicts of interest in this research.

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ТҮЙІНДЕМЕ

Ғылымды аса қажет ететін бәсекеге қабілетті өнімді инновацияларсыз жасау мүмкін емес. Бірақ оларды игеру барысында экологиялық қауіпсіздік талаптары сақтала бермейді, бұл табиғи орта мен адам денсаулығына жағымсыз жағдайларға әкеледі. Мақалада тозуға төзімді полимерлі композиттерді жасау және оларды майлау материалдарының жоқтығы немесе жеткізілімі шектеулі жағдайда абразивтік бөлшектердің әсерінен жұмыс істейтін машина бөлшектерін өндіруде ұтымды пайдалану бойынша авторлар тобының ғылыми-зерттеу жұмыстарының нәтижелері берілген. CVD әдісімен талшықтар мен ұнтақ бөлшектеріне металл жабындарын жағу әдісі әзірленді, онда металлорганикалық қосылыстардың буларының термиялық ыдырауы арқылы субстрат бетінде қалыңдығы 50 нм-ден көп металл жабын қабаты пайда болады және олардың негізіндегі термопластиктерді және композиттерді қысыммен қалыптауға арналған құрылғы жасалды. Металдандырылған талшықтармен және ұнтақтармен нығайтылған полиамид-6.6 негізіндегі инновациялық полимерлі композиттер жол құрылысына, авариялық құтқару және басқа да техника түрлеріне арналған бөлшектерді жасау үшін пайдаланылды. Кешенді зерттеуді жүзеге асыру нәтижесінде сериялық құрастыру қондырғыларына қатысты өндірілген бөлшектердің ресурсы ұлғайды. Шағын инновациялық кәсіпорындар жағдайында полимерлі композиттерді алу технологиясының экологиялық тазалығы реагенттерді қайта пайдалана отырып процесті тұйық циклде жүргізу арқылы қамтамасыз етіледі. Бұл қоршаған ортаға ластаушы заттардың түсуін болдырмайды және ресурс пен энергияны үнемдеу қағидаттарын іске асыруға мүмкіндік береді.

Түйін сөздер: CVD әдісі, металлорганикалық қосылыстар, полимерлі композиттер, ресурстарды үнемдеу, экологиялық қауіпсіздік, инновация.

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Исследование возможности разработки экологически безопасной технологии получения полимерных композитов в условиях малых инновационных предприятий

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АННОТАЦИЯ

Создание конкурентоспособной продукции с высокой степенью наукоемкости невозможно без применения инноваций. Однако в процессе их разработки не всегда соблюдаются требования экологической безопасности, что приводит к негативным последствиям для природной среды и здоровья человека. В статье приводятся результаты научно-исследовательской работы коллектива авторов по созданию износостойких полимерных композитов и их рациональному применению в процессах изготовления деталей машин, работающих в условиях воздействия абразивных частиц при отсутствии или ограниченном поступлении смазочных материалов. Разработан способ нанесения металлических покрытий на волокна и порошковые частицы CVD-методом, в котором на поверхности подложки формируется слой металлического покрытия толщиной от 50 нм посредством термического разложения паров металлоорганических соединений, и устройство для литья термопластов и композитов на их основе под давлением. Инновационные полимерные композиты на основе полиамида-6.6, армированного металлизированными волокнами и порошками, применялись для изготовления деталей дорожно-строительной, аварийно-спасательной и других видов техники. В результате реализации комплексного исследования зафиксировано увеличение ресурса изготовленных деталей относительно серийных сборочных единиц. Экологичность технологии получения полимерных композитов в условиях малых инновационных предприятий обеспечивается проведением процесса в замкнутом цикле с возможностью повторного использования реагентов. Это исключит поступление загрязняющих веществ в окружающую среду и позволит реализовать принципы ресурсо- и энергосбережения.

Ключевые слова: CVD-метод, металлоорганические соединения, полимерные композиты, ресурсосбережение, экологическая безопасность, инновации.

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Study of aluminosilicate microspheres using SEM – EPMA

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ABSTRACT

This work discusses the studies based on the microstructural properties of the improved ash and slag materials obtained after flotation enrichment with SEM-EPMA analysis (Scanning Electron Microscope and Electron Probe Microanalysis). According to the results of the analysis aluminosilicate microspheres was found in all four samples with a certain concentration and their similar morphology were identified. The microspheres are characterized by a spherical shape and a rough shell surface. Moreover, the shells are characterized by different morphology, which is typical after flotation enrichment. The size of the microspheres is less than 100 microns. The chemical composition of all four samples are inhomogeneous and was found by linear EDS (Energy-dispersive X-ray spectroscopy) analysis. However, the average values of the content of elements are quite close to each other. The special significance of the work is emphasized by the cross section of the shells of microspheres, which are similar to the crystallization structure of molten metal. They play an important role as materials in the construction industry. According to the results of SEM-EPMA studies, it is recommended to apply ash and slag materials, containing aluminosilicate microspheres, obtained after flotation enrichment, in construction industry.

Keywords: Ash and slag waste, aluminosilicate microspheres, scanning electron microscope, microstructure, microanalysis.

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Introduction

The current state of solid waste processing at thermal power plants is extremely low today, which leads to a significant accumulation of bottom-ash waste in ash-disposal areas. When burning coal in a boiler furnace at a state district power station, the composition of flue ash waste can consist of 95-98% of mineral compounds of aluminum oxides, silicon, calcium, titanium, iron, alkali oxides, sulfates, and sulfides. Processing of such ash products can be converted into valuable goods [[1], [2]], such materials as aluminosilicate hollow microspheres. several times lower than that produced by industrial methods.

For several decades, microspheres have been widely used all over the world in construction:

The aluminosilicate microspheres formed during the combustion of coal in power plant boilers as a result of granulation of the melt of the mineral part of the coal and the splashing of crushed small droplets with internal gases have a diameter from 10 to several hundred micrometers, on average about 100 microns. The wall thickness is from 2 to 10 microns, the melting point is 1400-1500°C, the density is 580-690 kg/m^3. The microspheres' properties are close to hollow microspheres which are obtained from melts by industrial methods. It is essential that the cost of hollow ash microspheres is

special cements, masonry mortars, plasters, liquid concrete; in the automotive industry: tires, brake friction pads, casting molds, body fillers; in the oil industry: plugging materials, drilling fluids, grinding

materials; in ceramics: refractories, tiles, aluminum cement, insulating coatings, etc.

Any technical problem where weight reduction is required with low thermal conductivity, high strength and volume savings, increased resistance to erosion, and aggressive media can be solved with the use of aluminosilicate microspheres.

In connection with the above, we have studied aluminosilicate microspheres using SEM-EPMA. This SEM-EPMA technique with a special electron probe microanalyzer will provide information on the chemical composition of the sample in an arbitrarily chosen area of microscopic dimensions with high accuracy.

Research method

The studies were conducted using JXA-8230 electron probe microanalyzer (JEOL) at an accelerating voltage of 25 kV and an electron beam current of up to 5 nA (Fig. 1). The technical capabilities of the device correspond to its passport data, according to which the detection of impurities or components of a substance (from boron to uranium) and the calculation of their concentrations are performed with standard methods based on JEOL own EPMA program. The dimensions and current of the electron beam were selected empirically to provide sufficient statistics for the collection of characteristic X-ray radiation (CXR) pulses, and the so-called “dead time” ranged from 10 to 30%.

The mounting corresponded to the perpendicular position of the sample concerning the electron beam, which makes it possible to obtain the results of automatic calculation of the detected pulses with high reliability.

The backscattered electron mode (COMPO), which gives better images of such objects compared to the observation and shooting mode in secondary electrons (SEI) was used for all areas selected for scanning electron microscope (SEM) studies. The main feature of the SEM contrast in the backscattered electron mode is the known fact of brighter emission of particles with a large atomic number in comparison with particles that make up the general background [3].

All automatic calculations in the EPMA program, which are used in the JXA-8230 electronic microanalyzer, are performed from the approximation of an absolutely flat surface located perpendicular to the electron beam. The most important consequence of not meeting flat

Figure 1 – JEOL JXA-8230

Table 1 – Chemical composition of samples of aluminosilicate microspheres

Elements compounds	Al_2O_3	SiO_2	SO_3	CaO	TiO_2	Fe_2O_3	Na_2O	P_2O_5
weight %	18.850–20.770	42.224–48.231	0.128 – 0.421	2,058 – 2.922	1.024 – 1.117	4.698 – 12.975	0.226 – 0.447	0.285 – 0.461

surface requirements are the loss of accuracy for sample analysis. The work used the techniques used in IMOB JSC.

Research results and their discussion

Samples of aluminosilicate microspheres produced after flotation concentration of ash from burning coal in TPP from various deposits in Kazakhstan were taken for the study.

The chemical composition of the samples (Table 1) is represented mainly by oxides of aluminum, silicon, iron, calcium, titanium, sulfur, sodium, and the content varies considerably depending on the composition of the original ash. As a result of the research, micrographs were produced in the mode of backscattered electrons and secondary electrons at magnifications from X100 to X3500.

Samples are free-flowing powder in the form of various particles of irregular shape, various structures and globules with a variety of morphological features: ideal spheres with an intact smooth or perforated surface, hollow spheres filled with small particles, in the form of fragments, and all kinds of porous grains of irregular shapes. The size range of the observable particles is from 1 to 150 microns.

The sample presented in Figure 2 demonstrates the most characteristic differences in the shape and morphological features of individual globules: ideal spheres with an intact smooth and rough surface, hollow spheres, and aggregates of small spheres on the surface or in cavities and dimples of large globules. According to COMPO data, the particles size is on average 1-150 microns. (Fig. 2). EDS analysis from the surface of the microspheres showed that the main elements of the shells consist of Al, Si, Ca, Fe, K, S, Ti, Mg, Mn, Cu, Zn. (Fig. 3).

It should be noted that the composition of the material is very heterogeneous for all samples, and this heterogeneity is also manifested for particles of the same sample with the same morphological characteristics. Figure 2 shows the EDS spectra of the particle morphology of microspheres of samples No. 1,2,3,4, which demonstrate a different set of elements.

The average elemental composition of the microsphere material according to the EDS analysis is shown in Table 2.

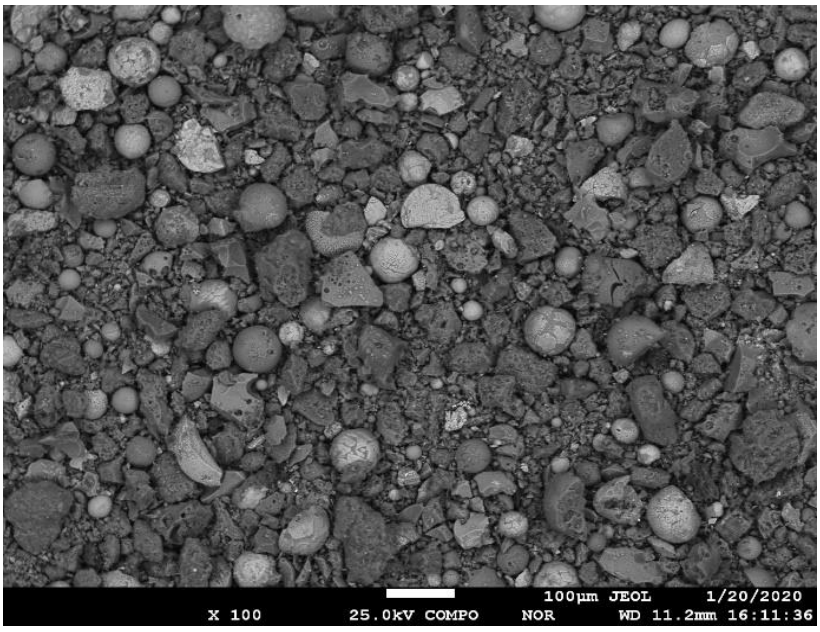

Figure 2 – General view of the accumulated aluminosilicate microspheres (X100)

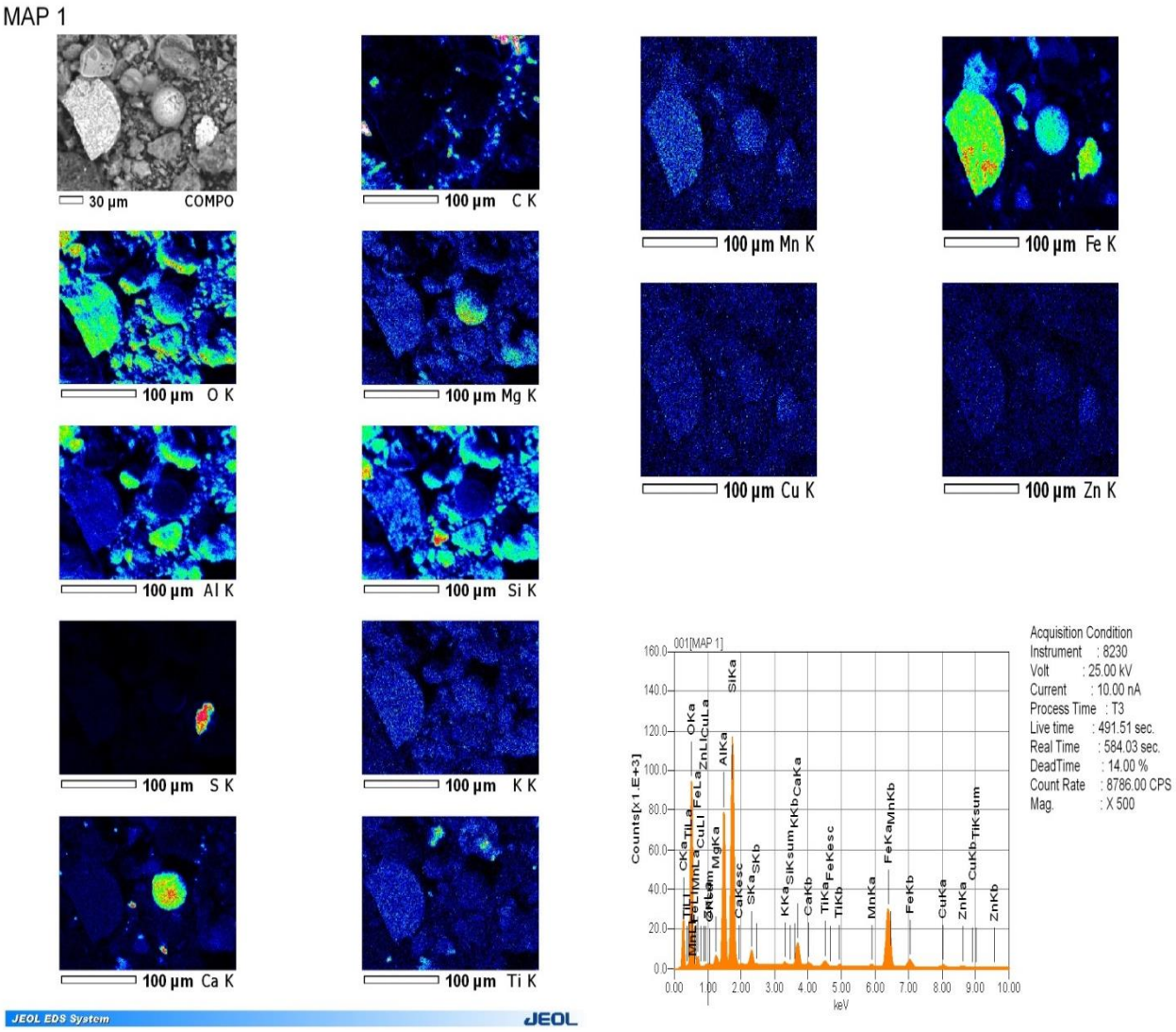

Figure 3 – EDS analysis from the surface of microspheres (X500)

Table 2 – Average elemental composition of the surface of microspheres

Element *(in % wt)*	**Sample No. 1**	**Sample No. 2**	**Sample No. 3**	**Sample No. 4**
O	50.15	51.42	49.54	47.34
Mg	0.65	0.34	0.48	0.69
Al	7.05	6.98	8.95	8.12
Si	9.85	12.11	13.98	13.76
S	0.81	0.07	0.05	0.03
K	0.12	0.32	0.29	0.27
Ca	1.41	0.11	1.29	2.45
Ti	0.44	0.27	0.65	0.32
Mn	0.28	0.18	0.04	0.87
Fe	8.85	3.44	2.45	28.78
Cu	0.62	0.57	0.69	0.51
Zn	0.41	0.39	0.55	0.42

These samples are characterized by an almost spherical shape and a rough surface of the shell, which have different morphologies. The microspheres are less than 100 µm in size (Fig. 4).

More detailed results of the analyzes are given in our work [4].

In previous works, the study of aluminosilicate microspheres from the ash and slag waste of the Aksu State District Power Plant is considered, which the chemical and elemental composition revealed using scanning electron microscopy with an X-ray spectral microanalyzer confirm the same composition. The paper [5] also states that the use of ash and slag waste (ASW) from thermal power plants brings the technology of thermal power plants closer to waste-free by 80%. When coal is burned from the Ekibastuz deposit, about 40-50% of silicon ash is formed. Alumina can be obtained from this ash, and cement can be obtained from alumina production waste.

However, despite the heterogeneity of the chemical composition of the samples, the averaged values for the content of elements are quite close (Table 2).

You can also see spheres with shells similar to the crystallization structure of the molten metal [[6], [7], [8]]. From Table 2 and Figure 4, the chemical composition of the areas marked with a yellow cross may indicate the content of phases resembling fayalites, magnetites, hortonolites, ferrites, spinels, ganites, or hypoeutectic silumins [[9], [10]].

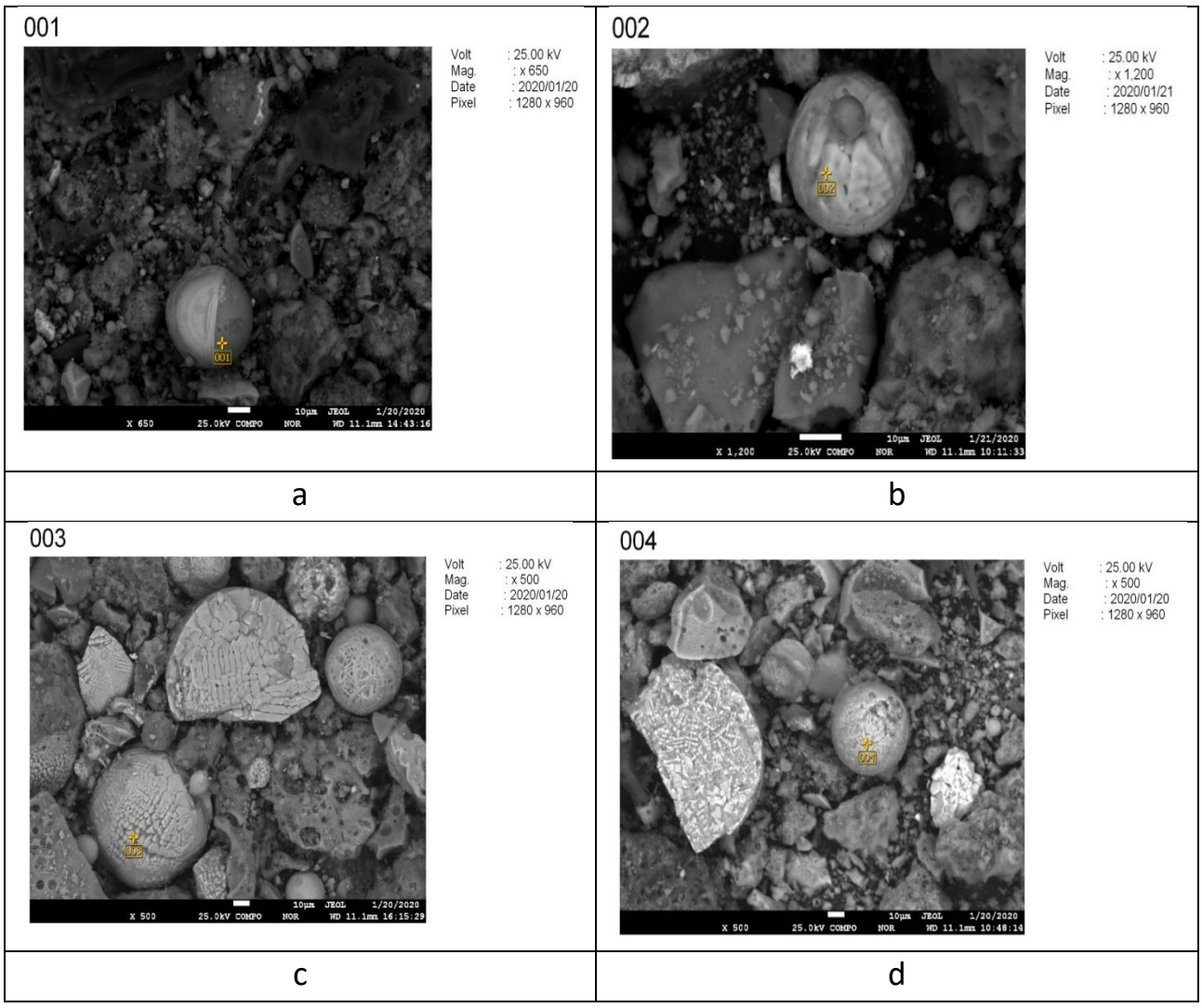

Figure 4 – Photographs of microspheres in enlarged form from X500 to X1200 (a - sample No. 1 (X650), b - sample No. 2 (X1200), c - sample No. 3 (X500), d - sample No. 4 (X500))

From the point of view of greater detail, it is recommended to perform X-ray diffractometric measurements with large statistics after the separation of the components in the ash.

Conclusions

The research results indicate that aluminosilicate microspheres from bottom-ash waste from state district power stations can be used as ready-made microspheres after flotation ash concentration. Its use in the industry and the construction industry is one of the strategic ways to solve environmental problems. Ash has good prospects for widespread use to save resources that are to solve economic problems associated with the preservation of natural resources, building materials, non-ferrous, rare metals, and other materials.

The paper presents new data on the concentration composition associated with the microstructure. The microstructure gives us the ability to visually predict the general state of the microspheres, which is applicable to the construction industry. In the construction industry, aluminosilicate microspheres are used as a filler in: inorganic building materials, lightweight structural materials and ultralight concretes, wall blocks, dry mortars, lime mortars, cement, plaster, high-strength wear-resistant floor coverings for industrial premises, paint, insulating roofing and soundproofing materials, finishing and plaster gypsum for insulation of external walls of buildings, sound and heat insulating coatings, decorative materials, as well as for mastics when sealing cracks and joints, fillers, sealants, etc.

Studies have shown that our microsphere is superior in quality to imported ones, and its acceptable cost leads to a reduction in the cost of finished products and a direct economic benefit to the manufacturer. So, expensive lime and cement can be replaced with aluminosilicate microsphere up to 50 wt.%, and the plasticizer up to 30 wt.%, while the properties of the materials are improved.

According to rough estimates, the cost of such microspheres is ten or more times lower than that of microspheres produced by industrial methods.

Conflicts of interest

On behalf of all authors, the author declares that there is no conflict of interest.

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РЭМ-РСМА көмегімен алюмосиликатты микросфераларды зерттеу

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ТҮЙІНДЕМЕ

Мақалада флотациялық байытудан кейін алынған күл-шлак материалдарын микроқұрылымдық зерттеу нәтижелері келтірілген. Растрлық электронды микроскопияны және рентгендік спектрлік микроанализді (РЭМ-РСМА) талдау нәтижелері бойынша белгілі бір концентрациясы және ұқсас морфологиясы бар алюмосиликатты микросфералар анықталды. Барлық төрт сынамада анықталған микросфералар сфералық пішінмен және қабықтың өрескел бетімен сипатталады. Сондай-ақ, қабықтар флотациялық байытудан кейін тән әр түрлі морфологиямен сипатталады. Микросфералардың мөлшері 100 мкм-ден аз. Сызықтық ЭДС (Энергодисперсиялық рентген спектроскопиясы) анализімен анықталған барлық төрт үлгінің химиялық құрамы біркелкі емес. Алайда, осыған қарамастан, элементтердің құрамы бойынша орташа мәндері өте жақын. Сынамалардың бетін сканерлеу элементтер мен олардың пішіндерінің орналасуын көрсетті. Жұмыстың ерекше маңыздылығын балқытылған металдың кристалдану құрылымына ұқсас микросфералардың қабықтарының көлденең қимасы баса көрсетеді. Олар құрылыс саласындағы маңызды материалдар болып табылады. Балқытылған металдың

	кристалдануы сияқты шығу тегі параллель жүретін екі қарапайым процестерден тұрады: кристалдану шоғыры және осы кристалдану шоғырының өсуі. РЭМ-РСМА зерттеулерінің нәтижелері бойынша өнеркәсіпте және құрылыс индустриясында алюмосиликатты микросфералары бар флотациялық байытудан кейін алынған күл-шлак материалдарын қолдану ұсынылады. ***Түйін сөздер:*** Күл-шлак қалдықтары, алюмосиликатты микросфералар, растрлық электрондық микроскоп, микроқұрылым, микроталдау.
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Исследование алюмосиликатных микросфер с помощью РЭМ-РСМА

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АННОТАЦИЯ

В статье приведены результаты микроструктурных исследовании золошлаковых материалов, полученных после флотационного обогащения. По результатам анализов растровой электронной микроскопий и рентгеноспектрального микроанализа (РЭМ-РСМА) выявлены алюмосиликатные микросферы с определенной концентрацией и схожей морфологией. Обнаруженные микросферы во всех четырех пробах характеризуются сферической формой и шероховатой поверхностью оболочки. Также оболочки характеризуются различной морфологией, которой свойственно после флотационного обогащения. Размер микросфер составляет менее 100 мкм. Обнаруженные линейным ЭДС анализом химический состав всех четырех проб неоднороден. Однако, несмотря на это, усредненные значения по содержанию элементов достаточно близки. Сканирование поверхности проб показал расположение элементов и их формы. Особую значимость работы подчеркивает поперечное сечение оболочек микросфер, похожие на структуру кристаллизации расплавленного металла. Они являются важными материалами в сфере строительства. Такие происхождения как кристаллизация расплавленного металла состоит из двух элементарных параллельно протекающих процессов: зарождения зародышей, или центров кристаллизации, и роста этих центров кристаллизации. По результатам РЭМ-РСМА исследований рекомендуется применение золошлаковых материалов полученных после флотационного обогащения, с содержанием алюмосиликатных микросфер в промышленности и строительной индустрии.

Ключевые слова: Золошлаковые отходы, алюмосиликатные микросферы, растровый электронный микроскоп, микроструктура, микроанализ.

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Accounting for creep of the rock mass around the sides of the quarry

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ABSTRACT

Since open-pit mining operations on the elements of development systems have areas with dynamically changing stresses and deformations of the rock mass, the stress-strain state of the array around the sides of the quarry is considered. The objective of the research is to determine the parameters of the stress-strain state of the array that affect the stability of the sides of the quarry. Studies are conducted to determine the parameters of the stress-strain rock mass around the sides of the quarry. A mathematical model has been developed for determining the factors affecting the stability of the sides of the quarry. A multifactorial mathematical model of the stability of the sides of the quarry from mining geological and mining technical factors was obtained, taking into account the creep of the rock mass of the sides of the quarry. According to the formula obtained for the multidimensional model, it is possible to find a set of factors affecting the stability of the sides of the quarry. The obtained dependence makes it possible to determine the desired value from the known values of the factors.

Keywords: massif, rocks, side, ledge, berm, slope, quarry, stress-strain state, deformation, stress, stability, creep, mathematical model, strength conditions.

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Introduction

The rapid development of computer technology and its implementation in almost all spheres of life has led to the fact that today a competent specialist in any field of knowledge should be well-versed in the world of computers and possess the necessary software tools. A modern engineer is not successful without knowledge of computer-aided design and analysis systems. The introduction, in this regard, of automated calculations based on mathematical modeling allows for a comprehensive analysis and optimization of object parameters.

The experience of implementing such systems shows the need to use effective numerical methods and flexible software that implements the solution of various tasks. The most commonly used numerical method is the finite element method (FEM). The use of such programs helps project organizations to shorten the development cycle. The finite element method is used in solving a wide variety of problems of mathematical physics and engineering, in particular, in the presented work, the FEM is used to study the stress-strain state (SSS) of the rock mass around the sides of the quarry in order to predict the stability of the instrument arrays [[1], [2], [5], [6], [7], [8], [9], [10]].

Research analysis

The design scheme of the modeling object is constructed, a mathematical model and regression dependences of the studied parameters are obtained.

An array of rocks is a complex physical environment with a number of specific features that

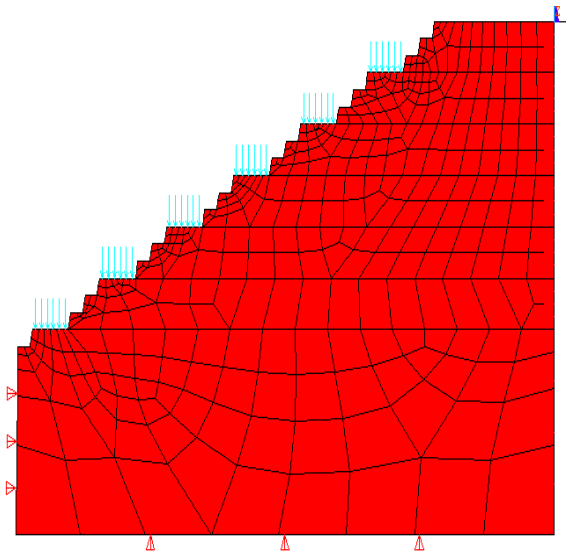

Figure 1. Calculation scheme of the problem

largely determine its mechanical state. Therefore, for a mathematical description of the processes occurring in the array, when developing methods for calculating the stability of slopes, they are forced to resort to schematization of the phenomena and properties of the rock mass under consideration. The side of the quarry, as a man-made structure, is the main supporting technological element in the open-pit development of deposits. The objective of the research is to determine the parameters of the stress-strain (SSS) array that affect the stability of the sides of the quarry. The vertical section of the array around the ledges is considered. A rectangular plane in a plane-deformed state, which is divided by a grid of triangular elements with appropriate boundary conditions, is chosen as the design scheme (Fig. 1).

In the design scheme, q is the load acting on the transport berm;

An unconventional method of constructing multidimensional mathematical models is used to process studies on determining the VAT of a rock mass, in particular, to determine the stable sizes of ledges and berms during field development [9].

In order to obtain a mathematical model of the type $y = f(x_1, x_2, x_3, x_4, x_5, x_6)$, where y is the maximum main tensile stress; $x_1 = h_1$, $x_2 = h_2$, $x_3 = h_3$, $x_4 = \gamma_1$, $x_5 = \gamma_2$, $x_6 = E$. 25 variants of the VAT array have been investigated. In each variant, the problem of determining the SSS of the FEM array was solved.

When solving the planar FEM problem, the parameters (geotechnical factors) changed within the following limits:

$h_1 = 10 \div 30$ (m) – the height of the ledge with an interval of 5 m;

$h_2 = 10 \div 18$ (m) - is the width of the berm with an interval of 2 m;

$h_3 = 2 \div 10$ (m) is the width of the slope projection with an interval of 2 m;

$\gamma_1 = 1200 \div 2000$ (кг/м^3) - density with an interval of 200;

$\gamma_2 = 2000 \div 3600$ (кг/м^3) - density with an interval of 400;

$E = 10^4 \div 6 \bullet 10^4$ (МПа) - is the modulus of elasticity of rocks with an interval of $1{,}5 \bullet 10^4$

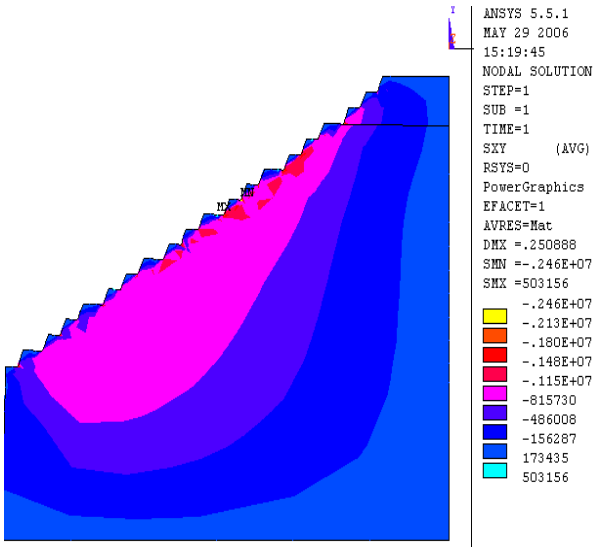

Figure 2. Tangential stress isolines

Figure 2 shows the tangential stress isolines for one of the options.

According to the above program, a mathematical model has been obtained that takes into account a complex of factors:

$$\sigma_1^{max} = f(x_1, x_2, x_3, x_4, x_5, x_6).$$

The maximum main voltage is selected as the function.

With a correlation coefficient R = 0.965, a generalized equation of the following form is obtained:

$$Y(\sigma_1^{max}) = Y(h_1)*Y(h_3)*Y(\gamma_2)*Y(h_2) + Y(E) + Y(\gamma_1) \quad (1)$$

where h_1 - is the height of the ledge, E – is the modulus of elasticity, γ_1 – is the volume weight of the upper layer, h_2 is the berm width, γ_2 – is the volume weight of the lower layer, h_3 – is the projection of the slope.

According to the formula (1) obtained for the multidimensional model, it is possible to find a set of factors affecting the stability of the sides of the quarry.

According to this dependence, the desired value is determined from the known values of the factors from the following rock strength condition:

$$\sigma_1^{max} \le \sigma^p_{adm},$$

where σ^p_{adm} – is the allowable tensile stress

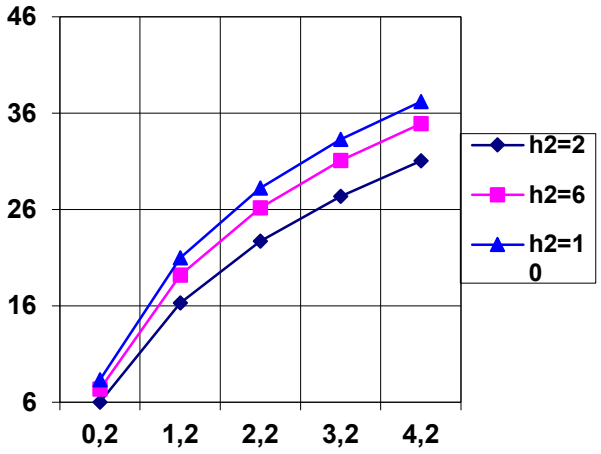

Figure 3. The dependence of the height of the ledge on σ^p_{adm}

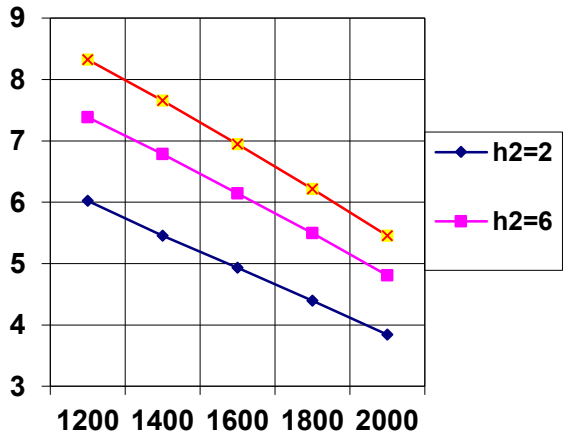

Figure 4. The dependence of the height of the ledge on γ_1

Figures 3-5 show graphs of the distribution of the dependence of the height of the ledge on various factors. When one of these values was changed, the values of the others were fixed. The quarry side, as a man-made structure, is "in operation" for a long time (more than 1 year), therefore, the conditions for the development of the array can be attributed to a viscoelastic environment with small deformations in time of the elements of the development systems.

To solve viscoelastic problems with small deformations, an effective calculation method using variable modules has been developed. It is known [10] that the solution of linear hereditary creep is reduced to the replacement of elastic constants by integral operators. In mining geomechanics, the Abel kernel $\delta(t-\tau)^{-\alpha}$. Is most often used as the creep core (operator). When using the method of variable modules, the solution of the linear-hereditary creep problem under constant boundary conditions is reduced to the formulation of the elasticity theory problem in the corresponding solution, no longer an operator, but a function of time.

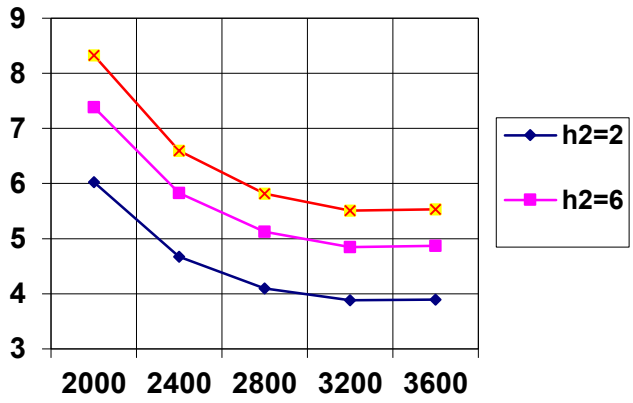

Figure 5. The dependence of the height of the ledge on γ_2

To solve viscoelastic problems with small deformations, an effective calculation method using variable modules has been developed. It is known [10] that the solution of linear hereditary creep is reduced to the replacement of elastic constants by integral operators. In mining geomechanics, the Abel kernel $\delta(t-\tau)^{-\alpha}$. Is most often used as the creep core (operator). When using the method of variable modules, the solution of the linear-hereditary creep problem under constant boundary conditions is reduced to the formulation of the elasticity theory problem in the corresponding solution, no longer an operator, but a function of time.

The work uses a time operator of the following form:

$$E_t = E / (1+F_t), \qquad (2)$$

where $F_t = \delta t^{1-\alpha} / (1-\alpha)$, α, δ – are creep parameters, t is time.

The objective of the research is to determine the parameters of the stress-strain state (SSS) of the array, which affect the stability taking into account creep.

Formula (1) using the method of variable modules has the following form:

$$Y(\sigma_1^{max}) = Y(h_1) * Y(h_3) * Y(\gamma_2) * Y(h_2) + Y(E / (1+ \delta t^{1-\alpha} / (1-\alpha)) + Y(\gamma_1) \quad (3)$$

According to the formula (3) obtained for the multidimensional model, it is possible to find a set of factors affecting the stability of the sides of the quarry.

According to this dependence, the desired value is determined by known values from the following rock strength condition:

$$\sigma_1^{max} \leq \sigma^p_{adm}, \quad (4)$$

where σ^p_{adm} – is the allowable tensile stress.

Thus, the mutual influence of the size of the quarry ledge varies over time.

When one of the factors changes, the values of the others are fixed.

Thus, the research methodology makes it possible to establish technologically necessary ratios of elements of development systems depending on specific conditions

Conclusions

According to the formula obtained for the multidimensional model, it is possible to find a set of factors affecting the stability of the sides of the quarry. The resulting dependence makes it possible to determine the desired value from known values.

As we can see from the results, the methodology gives adequate answers to the tasks set.

The research methodology makes it possible to establish technologically necessary ratios of elements of development systems depending on specific conditions

Optimization of parameters will affect the level of regulatory losses and ensure stability during the extraction of reserves.

Conflicts of interest

On behalf of all authors, the author declares that there is no conflict of interest.

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Карьер ернеулерінің айналасындағы тау жыныстары массивінің жылжуын есепке алу

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ТҮЙІНДЕМЕ

Игеру жүйелерінің элементтері бойынша ашық тау-кен жұмыстары тау жыныстары массивінің динамикалық өзгеретін кернеулері мен деформациялары бар учаскелерге ие болғандықтан, карьердің ернеулері айналасындағы массивтің кернеулі-деформацияланған күйі қарастырылады. Зерттеудің міндеті карьердің борттарының тұрақтылығына әсер ететін массивтің кернеулі-деформацияланған күйінің параметрлерін анықтау болып табылады. Карьердің ернеулері айналасындағы тау жыныстарының кернеулі-деформацияланған массивінің параметрлерін анықтау бойынша зерттеулер келтірілген. Карьер ернеулерінің тұрақтылығына әсер ететін факторларды анықтаудың математикалық моделі әзірленді. Тау-кен және геологиялық және тау-кен техникалық факторлардан карьер қабырғаларының тұрақтылығының көпфакторлы математикалық моделі карьер қабырғаларының айналасындағы тау жыныстарының массасының сусылуын ескере отырып алынған. Көп өлшемді модель үшін алынған формула бойынша карьердің бүйірлерінің тұрақтылығына әсер ететін факторлар жиынтығын табуға болады. Алынған тәуелділік факторлардың белгілі мәндерімен қажетті мәнді анықтауға мүмкіндік береді.

Түйін сөздер: массив, тау жыныстары, борт, Кемер, берма, көлбеу, карьер, кернеулі-деформацияланған күй, деформация, кернеу, орнықтылық, жылжу, математикалық модель, беріктік шарттары.

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Учет ползучести массива горных пород вокруг бортов карьера

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АННОТАЦИЯ

Так как открытые горные работы по элементам систем разработки имеют участки с динамически изменяющимися напряжениями и деформациями массива горных пород, рассматривается напряженно-деформированное состояние массива вокруг бортов карьера. Задачей исследований является определение параметров напряженно-деформированного состояние массива, влияющие на устойчивость бортов карьера. Приводятся исследования по определению параметров напряженно-деформированного массива горных пород вокруг бортов карьера. Разработана математическая модель определения факторов, влияющих на устойчивость бортов карьера. Получена многофакторная математическая модель устойчивости бортов карьера от горногеологических и горнотехнических факторов с учетом ползучести массива горных пород вокруг бортов карьера. По формуле, полученной для многомерной модели, можно найти комплекс факторов, влияющих на устойчивость бортов карьера. Полученная зависимость дает возможность определить по известным значениям факторов искомую величину.

Ключевые слова. массив, горные породы, борт, уступ, берма, откос, карьер, напряженно-деформированное состояние, деформация, напряжение, устойчивость, ползучесть, математическая модель, условия прочности.

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Methods of silica removal from pyrometallurgical processing wastes of ilmenite concentrate

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ABSTRACT

This article presents a study on the processing of waste dust from electrical smelting of ilmenite concentrates with the removal of silica from them by alkaline and fluoride methods. The study of the smelting dust leaching by caustic soda solutions included investigation of the effect of sodium hydroxide concentration, process time, temperature, S:L ratio. The optimum conditions of concentrate electric smelting dust leaching - temperature 80-90 °C, duration 90-120 minutes, S:L ratio = 1:5, sodium hydroxide solution concentration 110-115 g/dm^3 were determined. The optimum conditions for fluorination of electric melting dust were determined, at which the sublimation degree of silicon fluoride was 84.2 %. Studies have been performed to decomposite obtained silicon-containing sublime in the presence of ammonia agent. The optimum pyrolysis modes that provide the separation of fluoride and silicon oxide - temperature 530-560 °C and duration of 60-80 min have been determined based on the results of thermal analysis and studies on the process duration effect. The silicon oxide content in the obtained product was 96.3%.

Keywords: fine dusts, leaching, sodium hydroxide, silicon dioxide, fluorination

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Introduction

The largest producers of titanium sponge are China, Japan, Russia, Kazakhstan, the USA, and Ukraine [[1], [2], [3]]; and one of the leading suppliers is Kazakhstan enterprise - Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMP JSC) that produces about 18 % of the world sponge titanium production. The raw material used to produce titanium is ilmenite concentrate that is reductively smelted to produce titanium slag and substandard pig iron. UKTMP JSC uses a one-stage electric smelting of ilmenite concentrates to produce titanium slag and pig iron, the charge for smelting is supplied in a loose state accompanied by a high dust content. During the smelting of ilmenite concentrates at 1600-1700 °C, silica contained in the charge is sublimed, and together with gases is entrained into the gas duct system, it condenses as amorphous silica SiO_2 in scrubbers and falls into fine bag filters. Due to the high silica content, the dust cannot be recycled to the smelting process or fed to the chlorinators. In the first case, high silica content causes boiling of the melt and in the second case, the presence of silica will affect the quality of titanium tetrachloride produced during slag chlorination, because subsequently the silica will transfer to titanium tetrachloride and deteriorate the grade of titanium sponge. Because of the inability to recycle the captured dust back into the process, it is

deposited together with other solid waste in designated areas, landfills. Annually at maximum capacity utilization UKTMP produces up to 76,000 t of chloride wastes, including about 600 t of fine sleeve filter dust. Under the influence of natural precipitation and wind, the waste is eroded and dispersed, polluting water and soil basins [4]. The enterprise has to pay huge fines for the maintenance of the accumulated waste.

The main sources of industrial production of precipitated silica are silicate blocks prepared by the fusion of sand with sodium hydroxide [5]. The essence of obtaining precipitated silica from silicate blocks is as follows: the block is obtained by fusion of sand with sodium hydroxide at 1700 ^{0}C, then it is boiled in an autoclave at high temperature and pressure. Amorphous silica is extracted from the obtained solution of sodium silicate after its clarification and dilution by carbonation with carbon dioxide, then neutralization of the solution with sulphuric acid. The process used in industry to produce precipitated silica ("white carbon black") is is energy and labor-intensive.

Waste gases absorbed in the production of wet-process phosphoric acid and superphosphate containing a mixture of gaseous silicon tetrafluoride and hydrogen fluoride produce silica-silica solution [6]. In the studies [[7], [8], [9]], silicon dioxide is obtained by mixing silicicofluoric acid solution or a mixture of hexafluorosilicate and ammonium fluoride solutions with ammonia water. The specific surface area of the resulting white carbon black is 100-220 m^2/g. In the way [10] silica gel is used to produce silica that is a waste product of aluminum fluoride production, in this way the silica gel is treated in suspension by a mixture of ammonia and water steam at a ratio of ammonia to water steam 1:30-100 at 500-700 °C. In another process [11], to obtain silicon dioxide and aluminum fluoride used in aluminum metallurgy, a solution of silicon hexafluoric acid is mixed with an aluminum hydroxide suspension, as a result of their interaction to obtain a solution of aluminum fluoride and silica gel precipitate. In the method [12] inactive silica gel is treated with a mixture of ammonium fluoride and sulphuric acid, with subsequent neutralization of silica gel with ammonia, separation, washing, and drying of silica precipitate. Strong mineral acid H_2SO_4 is used to dissolve silica gel, so an acidic silica solution is formed, and during neutralization with ammonia silica precipitation occurs in the presence of sulphation that significantly deteriorates the quality of the main product. The disadvantage is also the formation of a by-product - ammonium sulfate, the use of which is very limited.

As mentioned above, due to the high silica content, dust from the electric smelting of ilmenite concentrates cannot be recycled back into the smelting process. In this research work, two methods have been shown to remove silica from electrosmelting dusts. The first method is by leaching dust with sodium hydroxide solutions, the second method is by hydrofluorination of dust and sublimation of silicon fluorides. Both methods make it possible to remove silicon from the dust, after which the dust can be returned to electric smelting.

Methods of analysis

X-ray experimental data were obtained on BRUKER D8 ADVANCE apparatus on copper radiation at accelerating voltage 36 kV, current 25 mA.

X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V. wave dispersion spectrometer. (PANalytycal B.V., Holland).

Chemical analysis of samples was performed on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, PerkinElmer).

Mapping of elemental and phase composition of samples was performed on electron-probe microanalyzer JXA-8230 by JEOL (Japan).

Thermal analysis was performed on a TG-DTA/DSC synchronous thermal analyzer with a Jupiter STA 449 F3 quadrupole mass spectrometer (Germany).

Materials: sodium hydroxide grade "high" ("Kaustik" JSC, Russian Federation). The fine dust of electric smelting of ilmenite concentrate, provided by UKTMP JSC, Republic of Kazakhstan, the content of the main components is given in Table 1.

Table 1 - Contents of the main components of the electric smelting dust of ilmenite concentrate, wt.%

Content, wt. %						
TiO_2	Fe_2O_3	SiO_2	ZnO	MgO	Cr_2O_3	MnO_2
46.37	26.90	10.04	3.18	1.55	0.45	2.90

Methods of experiments

Experiments on leaching with sodium hydroxide were performed in thermostatic reactors of 0.5 dm^3 volume. The slurry was stirred with a glass stirrer. A certain amount of sodium hydroxide solution was poured into the reactor and heated to a given

temperature. When the temperature reached the desired value a sample of dust was added and leaching was started. At the end of the process, the pulp was filtered and the cake was washed with distilled water. The content of uncontrolled components in the washed cake was determined.

During the experiments, the following components were used: pure sour ammonium fluoride GOST 9546-72, 10 and 25% ammonia, the dust of bag filters for electrofusion of ilmenite concentrates of UKTMP JSC.

The methodology of the experiment was as follows. A sample with thoroughly mixed ammonium bifluoride and dust in a certain ratio was transferred into an alundumina boat that was placed in a steel tube located in a horizontal tubular furnace. Argon was fed through the steel tube and the furnace was heated to a predetermined temperature within a certain time interval. At the end of the experiment the outgassed ammonium hexafluorosilicate was collected at the end of the steel tube and the gas-air mixture was captured in a flask with ammonia water. The ammonium hexafluorosilicate and the remaining char in the flask were subjected to ammonia alkaline hydrolysis. After alkaline hydrolysis amorphous silica was subjected to pyrolysis to distill the remaining fluorine. The content of the components was determined by chemical and X-ray fluorescence methods.

Results and discussion

Destruction of silicate bases of electro-smelting dusts of ilmenite concentrates can be performed by the so-called alkaline desiliconization method that consists of leaching dust in solutions of sodium hydroxide. In this approach the silicates have to be dissolved, with silicon passing into the alkaline solution as a soluble sodium silicate - Na_2SiO_3 and titanium must remain in an insoluble residue.

Physico-chemical properties of the dust of electro smelting of ilmenite concentrate: the results of XRD analysis of the dust are shown in Figure 1.

The data of X-ray diffraction analysis shows that the substance of the dust sample is in the X-ray amorphous state and the background of the diffractogram is high.

It should be noted that iron in the dust is in trivalent state and the harmful impurity silicon is connected with magnesium.

The content of trace impurities and forms of entrails in the dust of electro-smelting of ilmenite concentrate was determined by electron microscopy (Figures 2, 3). The presence of particles of solid solution $nFe_2O_3 \cdot mTiO_2$ was established (Figure 3).

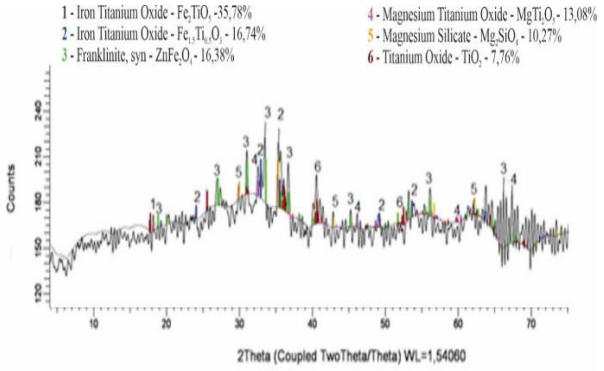

Figure 1 - Diffractogram of electric smelting dust of ilmenite concentrate

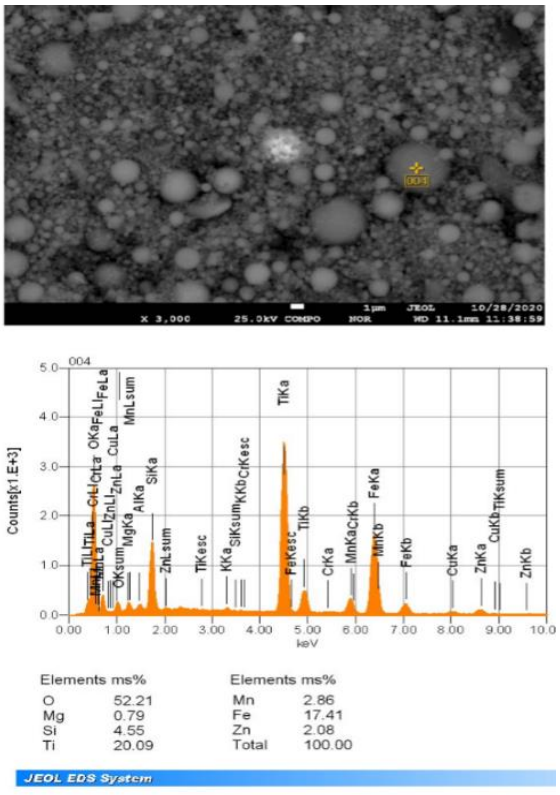

Figure 2 - Image and spectrum of [MnO $2TiO_2$]·[$Fe_2O_3 \cdot TiO_2$] anosovite particles in SiO_2 and ZnO cover

The phase which radiographically characterized as Fe = Mn – TiO [13] system may be referred to anosovite (Figure 2). It is noted that a part of anosovite particles is in the cover from oxides of silicon and zinc (Figure 3) and a part is in the cover from oxides of silicon, zinc, and lead. In addition, rare earth metal phosphates and particles of lead

and zinc oxides are present in the electric smelting dust of the ilmenite concentrate. The image obtained in the secondary electrons showed the fine dispersion of the object. The results of physicochemical investigations of the dust of electro-smelting of ilmenite concentrate showed that part of titanium is bound in hard-to-recover anosovite that can be enclosed in a shell of amorphous silicon oxide.

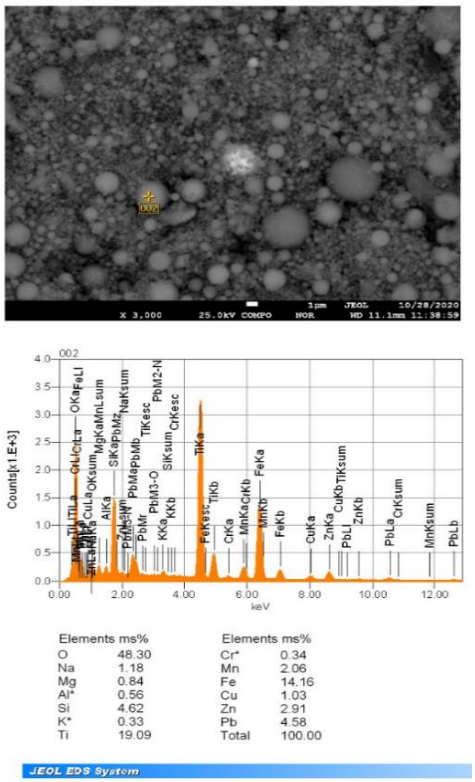

Figure 3 - Image and spectrum of anosovite particles in SiO_2, ZnO, PbO cover

The fine dust condition should contribute to the efficiency of the leaching of the injurious impurity, silicon.

Effect of concentration of sodium hydroxide solution. Study of the influence of concentration of sodium hydroxide solution on the extraction of silicon, chromium, manganese, zinc, and iron in the solution was performed in the concentration range of 50-130 g/dm^3. The duration of the experiments was 2 h, S:L = 1:5. The stirrer speed was 600 rpm.

Figure 4 shows curves of the degree of leaching of controlled elements into the solution. It is seen from the course of the curves that silicon leaches into the solution most completely - 77.7 %. It is explained by the good solubility of sodium silicate in alkaline solutions.

Increasing the concentration of sodium hydroxide in the leaching of electro-smelting dust of ilmenite concentrate led to a decrease in the cake yield (Figure 5).

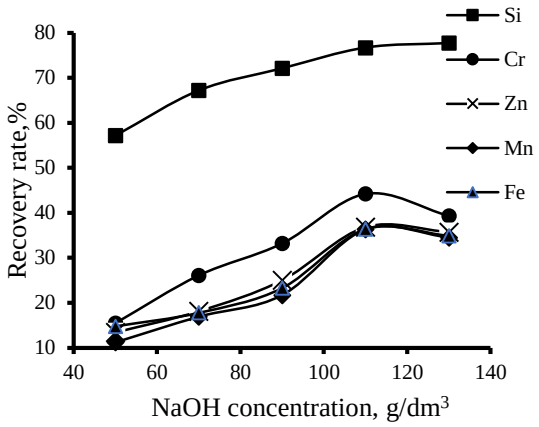

Figure 4 - Dependencies of the degree of leaching of controlled elements into solution on the concentration of sodium hydroxide

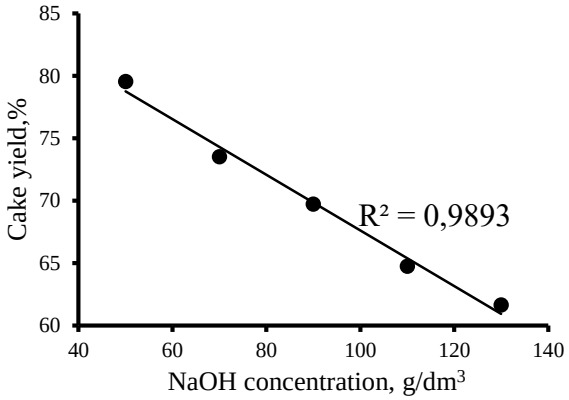

Figure 5 - Dependence of cake yield on sodium hydroxide concentration

The chromium leaching degree is considerably lower – 44.4 %. Franklinite decomposes to form hydroxo complex $Zn(OH)^-_3$ [14]. Silicon and iron in combined presence in the alkaline solution can form different iron-silicon complexes. This fact increases the solubility of iron in alkaline solution [[15], [16]].

The curves of solubility of metal oxides on alkali concentration have ascending and descending branches with a distinct maximum. Under the conditions of current studies, the maximum is reached at sodium hydroxide concentration of 110-115 g/dm^3.

Thus, it was experimentally determined that the optimum concentration of sodium hydroxide for leaching of electro-smelting dust of ilmenite concentrate is 110-115 g/dm^3.

Effect of the leaching process duration. Effect of duration of leaching of silicon, chromium, zinc, manganese, and iron from electrical smelting dust of

ilmenite concentrate was studied in the range of 15-120 minutes, temperature 80 °C, S:L = 1:5, sodium hydroxide concentration 130 g/dm^3. The stirrer speed was 600 rpm.

Figure 6 shows that even in the first 15 minutes of leaching the degree of transition of silicon in an alkaline solution reaches a significant value of 57.7 %. At the same time, the recovery of other controlled impurities does not exceed 13-18 %.

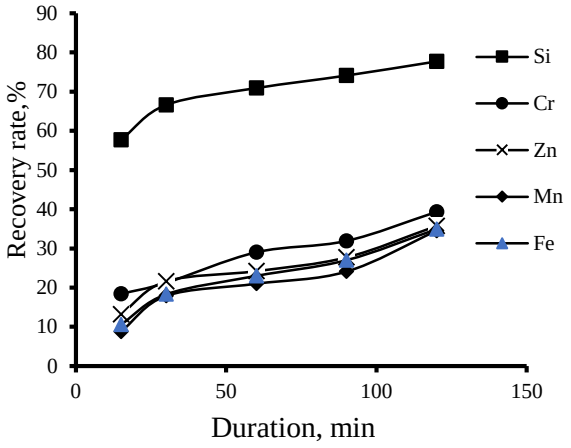

Figure 6 - Effect of leaching duration on the extraction of silicon, chromium, zinc, manganese, and iron in the alkaline solution from the electric smelting dust of the ilmenite concentrate

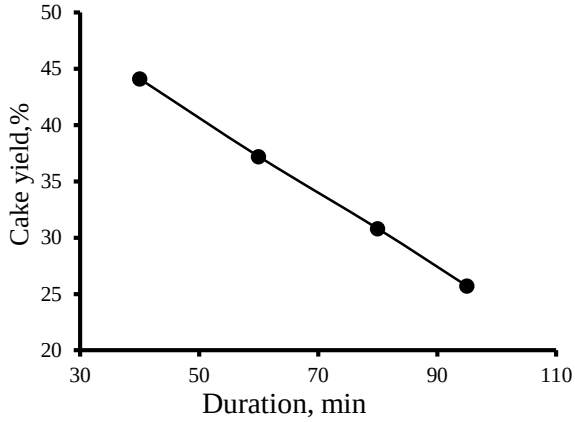

Figure 7 - Dependence of cake yield on the duration of leaching of electrowinning dust of ilmenite concentrate (80 °C, S:L = 1:5, NaOH concentration 130 g/dm^3)

Increasing the duration of the dust processing with an alkaline solution beyond 90 minutes does not cause a significant effect.

With increasing duration of the process of interaction of smelting dust of ilmenite concentrate with alkali-soluble formations pass into solution and cake yield decreases (Figure 7).

Thus, the optimum duration of leaching of electro-smelting dust of ilmenite concentrate with sodium hydroxide solution is 1.5-2 hours.

Effect of temperature on leaching process. The influence of leaching temperature on the extraction of chromium, silicon, zinc, manganese, and iron in solution was studied in the range of 40-95 °C. The duration of the experiment was 2 h, S:L = 1:5, sodium hydroxide solution concentration was 130 g/dm^3. The stirrer speed was 600 rpm.

It follows from the data in Table 2 that with increasing temperature from 40 to 60 °C the silicon extraction degree increases by 23 %, further increasing of leaching temperature from 60 to 80 °C leads to less considerable silicon extraction degree increase - by 13 %. Dust leaching at 95 °C allowed 82.8 % of silicon to be transferred into a solution that is only 5 % more than at 80 °C.

Table 2 - Effect of the temperature of the electric smelting dust leaching process of the ilmenite concentrate on the degree of extraction of the controlled components in the solution, %

Temperature, °C	Cake yield, %	SiO_2	Cr_2O_3	ZnO	MnO	Fe_2O_3
40	88.2	41.8	3.8	6.5	1.0	3.4
60	74.4	64.7	32.8	19.4	16.5	17.8
80	61.6	77.7	39.3	36.8	36.3	36.4
95	51.4	82.8	42.0	43.8	43.5	41.1

The behavior of other controlled impurities is similar to that of silicon when the temperature regime of the leaching process is changed.

Therefore, the optimum temperature for leaching of electro-smelting dust of ilmenite concentrate is 80-90 °C.

Effect of S:L ratio on leaching process. The research of influence of the ratio of smelting dust of ilmenite concentrate to sodium hydroxide solution was performed in the range 1:4÷10 at 80 °C, time - 120 min, stirring speed 600 rpm, sodium hydroxide solution concentration 130 g/dm^3.

Analysis of the data presented in Table 3 showed that changing the ratio of solid to liquid 1:5 or more has little effect on the extraction of chromium, zinc, manganese, and iron in the solution.

An increase in the volume of alkaline solution per unit mass of dust from 1:3 to 1:8 leads to an increase in the degree of silicon extraction into the solution. A further increase in the sodium hydroxide flow rate has practically no effect on the transition of silicon into solution.

Studies of the effect of solid to liquid ratio on the efficiency of the leaching process of electrowinning ilmenite concentrate dust have shown that the ratio of 1:5 is optimum.

Table 3 - Effect of S:L ratio on the recovery of silicon, chromium, zinc, manganese, and iron in solution, %.

S:L	Cake yield, %	SiO_2	Cr_2O_3	ZnO	MnO	Fe_2O_3
1:3	80.0	65.4	22.8	16.7	13.0	13.5
1:5	61.66	77.7	31.3	35.7	34.5	34.9
1:8	56.3	81.1	41.0	37.0	35.3	35.7
1:10	54.7	82.1	42.4	37.7	35.1	35.4

Therefore, optimal conditions of leaching of electro-smelting dust of ilmenite concentrate were determined experimentally: temperature 80-90 °C, duration 90-120 min, ratio S:L = 1:5, sodium hydroxide solution concentration 110-115 g/dm^3. The residue from dust leaching with the content of 46 % TiO_2, 26.4% Fe_2O_3, 3.6 %SiO_2 is returned to the technological process.

The experiments on fluorination of dust from electric smelting of ilmenite concentrate were performed with the help of specially made installation that included argon cylinder or air, manometer, flowmeter, horizontal tubular furnace, refrigerator-condenser, a gas-sink system consisting of two flasks filled with 10 % ammonia-water solution.

As a result of the works the optimum conditions for fluorination of electric melting dust of ilmenite concentrate were determined: the temperature 260 °C, the duration 6 hours, the mass ratio of dust to ammonium hydrodifluoride was 1:1. Under these conditions, the sublimation degree of silicon fluoride was 84.2 %.

According to X-ray phase analysis, the silicon-containing sublime is represented by oxonium hexafluorosilicate and to a small extent by ammonium hexafluorosilicate (Table 4).

Table 4 - Phase analysis of silica-containing substrate (260 °C, 6 h, dust: NH_4HF_2 = 1:0.9)

The component	Formula	Content in the sample, %
Ammonium hexafluorosilicate	$(NH_4)_2SiF_6$	1.9
Oxonium hexafluorosilicate	$(H_3O)_2SiF_6$	98.1

Ammonium and oxonium hexafluorosilicates are highly soluble in water at room temperature. To precipitate silicon oxide it is necessary to act with an alkali, e.g. ammonia by reactions:

$$(NH_4)SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O \quad (1)$$

$$(H_3O)_2SiF_6 + 6NH_4OH = SiO_2 + 6NH_4F + 6H_2O \quad (2)$$

Precipitation of amorphous silicon oxide according to thermodynamic calculations should be performed in the temperature range of 25 - 100 °C [16]. In a solution containing hexafluorosilicate ion heated to 40 °C 10 % and in the second case 25 % ammonia solution up to pH 7.5 - 8 were injected under active stirring in portions in the first case.

During the investigation of influence of ammonia solution concentration on amorphous silicon oxide precipitation efficiency, it was noticed that the preset pH value is reached in 20-30 minutes. However, the formation and precipitation of silicon oxide flakes require suspension soaking.

With 25 % ammonia solution- about 80 min; and with 10 % ammonia solution -90 min (Figure 8). The composition of the precipitated amorphous product is shown in Table 5.

Table 5 - Contents of main components and impurities in the precipitated amorphous product, wt %

SiO_2	NH_4F	Fe	Cu	Zn	As	Sr	Pb	other
81.6	12.9	0.045	0.005	0.025	0.014	0.003	0.017	5.4

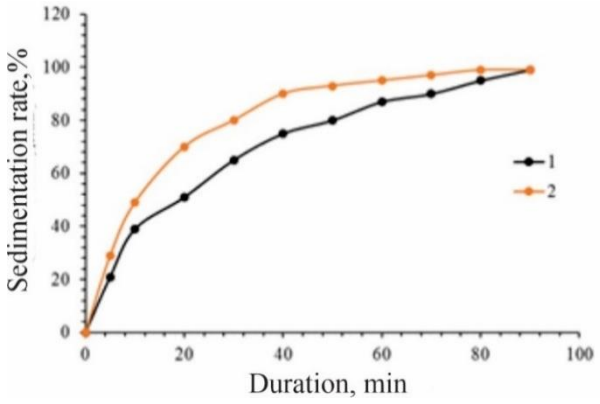

Figure 8 - Dependence of amorphous silicon oxide precipitation

Table 5 shows that the product does not contain any heavy metals or arsenic. The presence of ammonium fluoride is due to its absorption by amorphous particles and cannot be removed by washing the sludge with water. Ammonium fluoride is known to decompose on heating. In this connection, a thermal analysis of the obtained amorphous silicon oxide was performed. The result is presented in Figure 9. The combination of

exothermic effects with peaks at 310.9 °C and 1060.7 °C on the dDTA curve is an indication of amorphous silica. The combination of endothermic effect with extremum at 126.2 °C and exothermic effect with a peak at 1233.1 °C on the dDTA curve characterizes the melting of FeF_2 impurity. The endothermic effect with the extremum at 1144 °C on the DTA curve shows the release of previously adsorbed gases. The weak endothermic effect with the extremum at 1292.3 °C on the DTA curve reflects the sublimation of aluminum fluoride impurity.

The analysis of the DTG curve showed that at 526.4 °C the weight loss of the sample increased due to hydrogen fluoride removal. Therefore, the temperature of 530-560 °C is adopted for the pyrolysis of the product, the composition of which is shown in Table 3. The effect of duration was studied in the range of 20-80 min. The results are shown in Figure 10.

The curve of Figure 10 shows that the pyrolysis process duration of 60-80 min provides the purification of silicon oxide from fluorine at 95-99 %.

The composition of the amorphous silica obtained is shown in Table 6.

on process duration (1 – 10 % NH_4OH; 2 – 25 % NH_4OH).

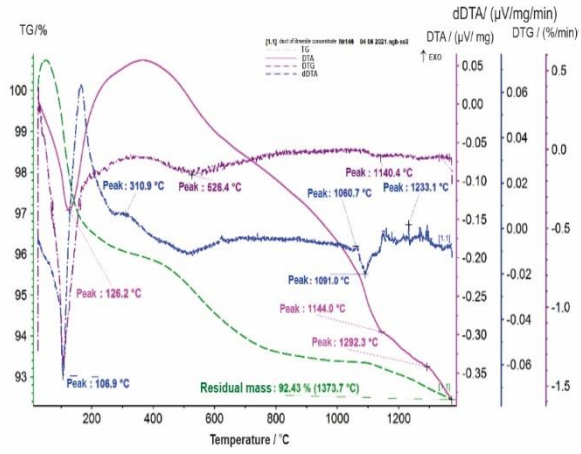

Figure 9 - Derivatogram of amorphous silicon oxide (sample weight 0.088 g)

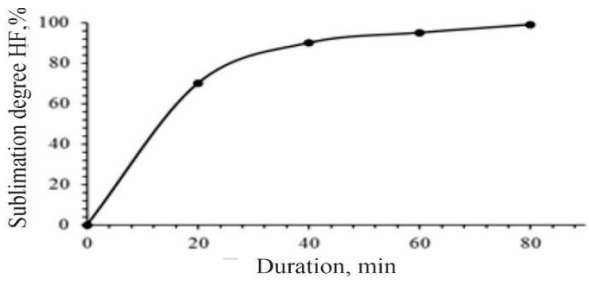

Figure 10 - Effect of pyrolysis duration on the degree of hydrogen fluoride sublimation

Table 6 - Contents of main components and impurities in amorphous silica, wt.% (converted to oxides)

SiO_2	F	Fe_2O_3	Al_2O_3	ZnO	CaO	TiO_2
96.3	ND	0.14	0.16	0.02	0.03	0.15

X-ray phase analysis of the obtained product showed amorphous silicon dioxide monophase.

Therefore, the optimum pyrolysis regime for the separation of fluoride and silicon oxide should be considered as 530-560 °C and a duration of 60-80 min. The conducted studies have shown the possibility of obtaining commodity amorphous silica from waste dust of electric smelting of ilmenite concentrate.

After alkaline hydrolysis of the residue in the boat was obtained titanium-containing product composition, wt. %: 42.5 TiO_2, 26.0 Fe_2O_3, 2.4 MnO_2, 1.3 SiO_2, 0.9 Al_2O_3, 0.2 K_2O, 1.2 ZnO, 0.014 ZrO_2, 0.9 PbO. The product can be returned to electromelting together with ilmenite concentrate.

Conclusions

Physical and chemical study of electric smelting dust of ilmenite concentrate has shown that a part of titanium is bound in hard-to-recover anasovite that can be enclosed in the shell of amorphous silicon oxide. The finely dispersed state of the dust should contribute to the efficiency of the leaching of the harmful impurity - silicon.

Optimal parameters of sodium alkali leaching of electric melting dust of ilmenite concentrate have been determined: NaOH concentration - 110-115 g/dm^3; S:L- 1:5; temperature - 80-90 °C; duration - 90-120 min. The degree of extraction of silicon in the solution was 77,7 %. The titanium-containing product obtained after alkaline leaching of dust contained 48 % TiO_2, 26 % Fe_2O_3 that can be returned into the technological process.

The process of silicon sublimation from fine dusts of electro-smelting of ilmenite concentrates was investigated. The optimum conditions of fluorination of smelting dust of ilmenite concentrate were determined: temperature 260 °C, duration 6 hours, the mass ratio of dust to ammonium bifluoride = 1:1. Under these conditions, the degree of silicon fluoride sublimation was 84.2 %.

The conditions of amorphous silica precipitation from the process duration at 25 % ammonia concentration were studied. Amorphous product with 81.6 % SiO_2, 12.9 % NH_4F was obtained. Optimum pyrolysis conditions that provide the

separation of fluoride and silicon oxide: temperature 530-560 °C and duration 60-80 min have been determined. The content of silicon oxide in the product obtained was 96.3 %.

After alkaline hydrolysis of the cinder, a titanium-containing product containing 48 % TiO_2, 26,0 Fe_2O_3 was obtained that is returned to the technological process.

Conflict of interests. On behalf of all authors, the correspondent author declares that there is no conflict of interests.

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Ильменит концентратын пирометаллургиялық өндеуде түзілген қалдықтардан кремний диоксидін алу әдістері

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ТҮЙІНДЕМЕ

Мақалада ильменит концентраттарын электрлік балқыту кезінде түзілген қалдық шаңды өңдеп, одан кремнийді сілтілі және фторидті әдістермен алу бойынша зерттеулер көрсетілген. Электробалқыту шаңын натрий гидроксиді ерітінділерімен шаймалау, натрий гидроксиді концентрациясының әсерін, процестің ұзақтығын, температураны және Қ:С қатынасын зерттеуді қамтиды. Ильменит концентратын электробалқыту кезіндегі түзілген шаңды шаймалаудың оңтайлы шарттары белгіленді: температура 80–90 °С, ұзақтығы 90–120 мин, қатынасы Қ:С = 1:5, натрий гидроксиді ерітіндісінің концентрациясы 110–115 г/дм^3. Электробалқыту шаңын фторлаудың оңтайлы шарттары анықталды, бұл жағдайда кремний фторидінің сублимациялану дәрежесі 84,2% құрады. Алынған кремнийі бар возгонды аммиак агентінің қатысуымен ыдырату бойынша зерттеулер жүргізілді. Термиялық талдау және процестің ұзақтығының әсерін зерттеу нәтижелері бойынша фторид пен кремний оксидінің бөлінуін қамтамасыз ететін пиролиздің оңтайлы режимдері белгіленді: температура 530–560 °С және ұзақтық 60–80 мин. Алынған өнімдегі кремний оксидінің мөлшері 96,3% құрады.

Түйін сөздер: ұсақдисперсті шаңдар, шаймалау, натрий гидроксиді, кремний диоксиді, фторлау.

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Способы удаления кремнезема из отходов пирометаллургического передела ильменитового концентрата

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АННОТАЦИЯ

В статье представлены исследования по переработке отвальных пылей электроплавки ильменитовых концентратов с удалением из них кремния щелочным и фторидным методами. В исследование выщелачивания пыли электроплавки растворами едкого натра входило изучение влияния концентрации гидроксида натрия, продолжительности процесса, температуры, соотношения Т:Ж. Установлены оптимальные условия выщелачивания пыли электроплавки ильменитового концентрата: температура 80-90 °С, продолжительность 90-120 мин, соотношение Т:Ж = 1:5, концентрация раствора гидроксида натрия 110-115 г/дм^3. Определены оптимальные условия фторирования пыли электроплавки, при которых степень возгонки фторида кремния составила 84,2 %. Проведены исследования по разложению полученного кремнийсодержащего возгона в присутствии аммиачного агента. На основе результатов термического анализа и исследований по влиянию продолжительности процесса, установлены оптимальные режимы пиролиза, обеспечивающего разделение фторида и оксида кремния: температура 530-560 °С и продолжительность 60-80 мин. Содержание оксида кремния в полученном продукте составило 96,3 %.

Ключевые слова: тонкодисперсные пыли, выщелачивание, гидроксид натрия, диоксид кремния, фторирование.

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Investigation of dielectric and strength properties of organoplastics. Review

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ABSTRACT

Currently, the production and use of military UAVs in the direction of robotic complexes is actively developing. The purpose and use of military UAVs differ from civilian ones, based on two functions: reconnaissance purpose and a carrier of a warhead. The specifics of military UAVs are their invisibility to enemy radars and ensuring stable transmission of information from the command post. For these purposes, first of all, the UAV material must have the properties of radio transparency. For the production of UAV hulls, power elements, high-strength PCM are needed, which include organoplastics, carbon fiber, fiber glass. The choice of materials for parts of components and assemblies of aviation equipment depends on their operating conditions: operating loads, material properties. Organoplastics (OP) fully meets these requirements among polymer composite materials (PCM). OP have high strength properties along with low dielectric losses (radio transparency) compared to other fiber composites. This paper presents an overview of studies of dielectric and strength properties, as well as ways to improve the mechanical properties of organoplastics. The analysis of the work has shown that for radiotransparent organoplasty, the optimal frequency range of permittivity is 1kHz-12 GHz. The ultimate strength of organoplastics varies in the range from 320 MPa to 1 GPa. The possibilities of increasing the strength of aramid fibers and ways of modifying organoplastics epoxy resins are considered.

Keywords: unmanned aerial vehicles, fairing, organoplastics, permittivity, tensile strength.

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Introduction

One of the most important structural elements of an unmanned aerial vehicle (UAV), which determines the aerodynamic characteristics, the quality of radio signal transceiver with a command post, and the accuracy of targeting, is the nose antenna fairing [1].

A set of requirements is imposed on the materials of UAV antenna fairing: high radio performance, resistance to thermal shock, low thermal conductivity, high strength, high impact strength, low density – as a factor in weight reduction. For these purposes, more advanced radio-transparent and high-strength materials with low dielectric permittivity, low dielectric losses, and high mechanical strength are required.

Organoplastic (OP) is the most promising radiotransparent material that meets these requirements. The use of organoplastic materials to protect transceiver antenna devices placed on board the UAV from external influences will ensure maximum radio transparency, which will not interfere with the transmission and reception of an electromagnetic wave of a certain frequency. The combination of high strength, fracture toughness with low density puts organoplastics into the category of materials that effectively work as protective shock-resistant PCM.

The relative permittivity of OP is much lower than that of metal alloys and carbon fiber, which are widely used in aircraft [[2], [3]].

Radio transparency is the ability of materials to transmit radio waves in a wide frequency range with low losses [4]. Radiotransparent materials (RM) include organic and inorganic dielectrics that provide transmission of electromagnetic radiation in the radio frequency range of $10^5 – 10^{12}$ Hz. [5]. RM is used mainly for the manufacture of antenna fairing for high-speed aircraft. The transparency of these materials for radio waves is ensured by the choice of dielectrics with low dielectric characteristics (dielectric loss tangent $tg\delta \leq 0,02$, dielectric constant $\varepsilon = 1,1 – 9,0$) and the corresponding electrodynamic calculation of the layer thickness [[2], [3], [6]]. In other words, the lower the dielectric constant, the more radio transparent the material. Such RM provides minimal distortion of the electromagnetic field in a given spectrum of operating frequencies. For this reason, for epoxy composite structures used in the construction of military UAV, the dielectric properties of the materials are very important.

The study of the properties of radio transparency and strength properties of epoxy composites, as well as ways to improve the mechanical properties of organoplastics, is relevant for the scientific and military industries. This paper presents the results of scientific work on the study of the dielectric (radiotransparent) and strength properties of OP, as well as ways to improve the strength characteristics of the composite.

Dielectric (Radiotransparent) properties of organoplastics

In the aerospace industry, especially in UAV, lightweight materials are needed to increase flight time, namely composites of glass, aramid, carbon fibers. In particular, carbon fiber is the most suitable material for UAV due to its high strength to weight ratio. However, the use of carbon fiber composites can interfere with the transmission of radar signals during flight. This is due to its high dielectric constant, therefore, to achieve the radio transparency of the UAV body, the use of composites of aramid and glass fibers are more effective [[7], [11]].

In aviation and rocket and space technology, radiotransparent fairings are used as protection against external influences of transceiver antenna devices. Their shape when placed on aircraft is determined by the configuration of the antenna devices and their location [12]. The operating range of the UAV antenna systems depends on the requirements for the communication channel between the UAV and the ground control complex. For communication systems of small UAV, the decisive factors in choosing the frequency range are the weight and dimensions of the airborne transceiver and antenna-feeder device. It is expedient to choose a range of microwave frequencies. One suitable frequency band is the 2,4 GHz band. Also, a promising direction in the development of communication systems with UAVs is the use of frequency bands above 5 GHz [13]. Therefore, the UAV antenna fairing must be radiotransparent at high frequencies and provide minimal distortion of the electromagnetic field in a given operating frequency spectrum, which can be approached with low parameters of dielectric properties. Therefore, for composite structures used in electrical and aerospace applications, the dielectric properties of materials can be important as they directly affect the speed and energy loss during signal transmission [14].

Over the past few decades, the dielectric properties of composites have been widely studied for layered composites [[8], [9], [15], [16], [17], [18], [19], [20], [21], [22]]. For example, in the work [15] the authors investigated the dielectric properties of aramid, glass, carbon plates in the range of 8 – 12 GHz with vertical and horizontal polarizations. A UHF sweep generator is used to generate the signal. Vertical polarization is when the direction of the electric field vector of the microwave signal is parallel to the direction of the fibers, and horizontal polarization is when the electric field vector is orthogonal to the direction of the fiber. The test results are shown in tables 1 and 2. As the test results showed, the dielectric constant (DC) of carbon composites is several times higher than that of aramid and glass plastic.

As can be seen from tables 1 and 2, the dielectric constant values of aramid plastic for vertical polarization are slightly higher than for horizontal polarization. The authors attribute this to the electric field. In the vertical case, it is parallel to the directions of the fiber, which results in more of the signal entering the sample and gives a higher permittivity. From a comparison of all composites, the aramid composite has the smallest DC, and carbon fiber has the largest DC. Organoplastic and glass plastic showed good results in terms of radio transparency.

Table 1 – DC results for composite materials (vertical polarization) [15]

Frequency (GHz)	Dielectric constant of aramid plastic	Dielectric constant of glass plastic	Dielectric constant of carbon plastic
8.0	4.63	4.71	26.6
8.5	4.30	4.83	18.2
9.0	4.27	4.85	20.9
9.5	4.59	5.12	13.4
10.0	4.63	4.98	14.2
10.5	4.57	5.04	10.5
11.0	4.72	5.24	7.3

Table 2 – DC results for composite materials (horizontal polarization)

Frequency (GHz)	Dielectric constant of aramid plastic	Dielectric constant of glass plastic	Dielectric constant of carbon plastic
8.0	3.40	5.19	29.4
8.5	3.42	4.58	22.8
9.0	3.61	4.50	21.6
9.5	3.53	4.52	17.6
10.0	3.42	4.32	15.1
10.5	3.62	4.57	11.5
11.0	3.50	4.54	10.5

Table 3 – Results of testing the strength properties of composite materials

Composite laying type	Reinforcement content, %	Matrix content, %	Tensile strength, MPa	Impact strength, J	Dielectric constant at 1000 MHz
17C	61.5	38.5	504.2	1.76	4.9
3A11C3A	57.5	42.3	540.4	1.67	4.4
5A7C5A	56.1	43.9	472.8	1.63	3.9
7A3C7A	51.4	48.6	673.3	1.19	3.95
17A	49.6	50.4	676.5	1.35	3.97

In the next work [16] were investigated for the dielectric properties of organoplastics, glass plastic and a hybrid of these composites (aramid/glass). For the manufacture of plates, aramid fabric (Twaron 1000) manufactured by Akzo and E-glass EDR14 300-778 manufactured by JushiGroup (Zhejiang, China) were used. The resin system was ER 618 and hardener Iminazole 5510 manufactured by Shanghai Resin Company (China). In the manufacture of composites, five types of three-dimensional reinforcement geometries with 8 base layers and 9 fabric layers were adopted – 17C, 3A11C3A, 5A7C5A, 7A3C7A and 17A. (A – AF and C – fiberglass). The research results are shown in table 3. The dielectric constant and dielectric losses of the composites were obtained in the frequency range from 1 MHz to 1000 MHz.

It can be seen from table 3 that the DC of the composites decreases as the AF content increases, when the volume fraction of AF was lower than that of 5A7C5A, then the opposite happened. This indicates the low dielectric parameters of the AF, which increases the radio transparency of the material. A good DC result was shown by the 5A7C5A composite, but with the lowest tensile strength of 472.8 MPa.

At present, there are various methods developed in practice for determining the dielectric properties of composites, including the waveguide method, the free space method, the resonator method and the coaxial method, etc. The waveguide method is based on measuring the parameters of the scattering matrix (S-matrix) of the waveguide in which the sample is placed of the material under study in the form of a plate filling the cross section of the waveguide [17]. The DC of basalt/ER and AF (Kevlar 129)/ER composites were studied in [18], as well as fabricated intralayer three-dimensional orthogonal fabric hybrid composites basalt/AF/ER and measured their dielectric properties by the waveguide method in the frequency range of 8-12 GHz. In the manufacture of composites, 4 geometries of reinforcement with six layers of base and seven layers of filler were adopted, namely, composites with intermediate hybrid, intralayer hybrid, with basalt and with aramid type. In the intermediate hybrids, AF or basalt yarn was placed in different layers, while in the intralayer hybrids, the two types of yarn were placed alternately in each layer of the warp or filler. Measurements of the dielectric properties were performed on an Agilent 8722ES vector network analyzer. The test results are shown in figure 1.

From the results, it was determined that the DC of the basalt composite increases with increasing frequency. The authors explain this as the phenomenon of achieving electronic resonance. The other three types of composites tend to slowly decrease as frequency increases, which may be in the range of dipole relaxation and electronic resonances. It has been observed that the DC of the AF composite exhibits a relatively faster downward trend than that of the hybrid types, showing unstable AF dielectric properties as previously reported [16].

The free space method makes it possible to measure the dielectric properties of a material under various external influences. For example, the authors of the study [[8], [19]] used this method to characterize the effect of a damaged AF/ER composite surface on the wave transmission characteristics of radomes. In work [20], the authors studied the dielectric parameters of a unidirectional and quasi-isotropic AF/ER composite at various strains. The tensile values of the composite are given as, initial stage (IS), 0,001 D, 0,002 D, 0,003 D. The resulting DC results are shown in figure 2. Figure 2a shows the DC of a unidirectional AF/ER composite that looks like a wavy line with different frequencies.

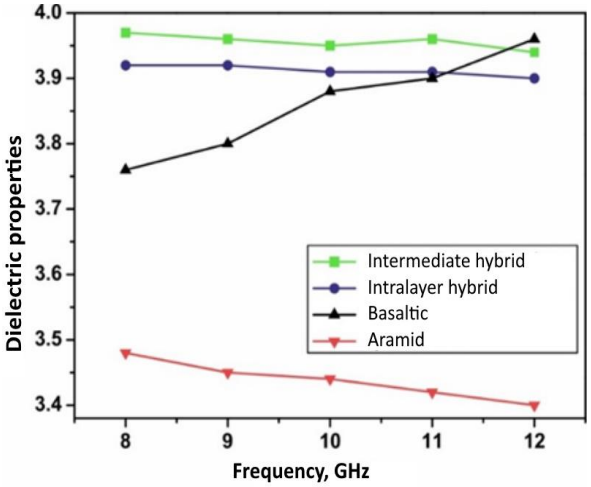

Figure 1– Dielectric constants of four types of composites [18]

in X-range up to the application of tensile loads, and the maximum change in DC with different frequencies is within 0,061. When tensile loads are applied, the shape of the DC curves practically does not change. However, it has been shown that the DC of the composite increases with increasing tensile strain. The electromagnetic parameters of the quasi-isotropic AF/ER composite were also measured under various strains, which are shown in figure 2b. It is seen, that the dielectric constants increase when the sample is stretched. According to the results of the authors, the DC increases by 0,045 per 0,001 strain. In addition, the DC of quasi-isotropic composites is lower than that of a unidirectional composite due to the different orientation of the fibers within the composite.

The DC of epoxy composites increases with increasing filler content (Kevlar 49) and temperature. This conclusion was reached by the authors of [21]. In their opinion, the permittivity and losses of composites are mainly affected by interfacial polarization, which occurs due to inhomogeneities at the interfaces introduced by the filler. In [22] compared the mechanical and dielectric properties of OP based on AF Kevlar 49, Kevlar 49, Kevlar 149 and ER with lamination geometry [0,90]. The best results were shown by an OP based on Kevlar 149 with a DC of 3,9 at a frequency of 10^6 Hz.

Tables 4 and 5 present the dielectric properties of the composites. Thus, according to the literature data, OP reinforced with AF have low dielectric constants in comparison with other fibrous composites. According to the analysis, the optimal frequency range for measuring dielectric properties (radio transparency) is 1 kHz – 12 GHz. Because, according to extensive studies in this range, they show the best results of DC.

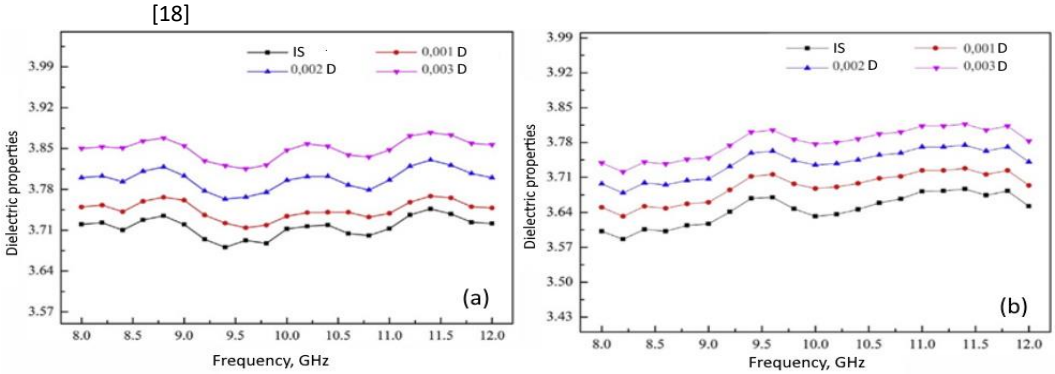

Figure 2 – Dielectric properties of the aramid-epoxy composite under various deformation conditions: (a) unidirectional and (b) quasi-isotropic AF/ER composite [20]

Table 4 – Dielectric properties of aramid fabric reinforced epoxy matrix composites at a frequency of 10^3 Hz [22]

Textile	The dielectric constant	Dissipation factor
Kevlar®29	4.51	0.0135
Kevlar®49	4.44	0.0131
Kevlar®149	4.14	0.0103

Table 5 – Dielectric properties of aramid fabric reinforced epoxy matrix composites at a frequency of 10^6 Hz [22]

Textile	The dielectric constant	Dissipation factor
Kevlar®29	4.19	0.0171
Kevlar®49	4.14	0.0170
Kevlar®149	3.90	0.0142

Table 6 – Tensile strength of the obtained composites [29]

Composite	Trial 1	Trial 2	Trial 3	Average value, MPa
30% AF + 70% ER	510	520	517	515
35% AF +65% ER	545	547	548	546
45% AF + 55% ER	534	531	526	530

To achieve high dielectric parameters in the composite, the aramid fabric layer should be one layer larger than the base layer. In the above works, the smallest DC, which is equal to 3,4, has an ER/AF composite with six base layers and seven filler layers [18]. In addition, the DC of quasi-isotropic composites is lower than that of a unidirectional composite due to the different orientation of the fibers within the composite.

Strength properties of organoplastic

When designing UAV, the strength of epoxy composites plays an important role [[23], [24], [25], [26], [27]]. For ER reinforced AF is characterized by high strength, it is insufficient compared to metals. In a number of scientific papers [[28], [29], [30], [31], [32], [33], [34]], the results of work related to the change and increase in strength properties depending on the composition of AF and ER, the type of AF, the type of reinforcement, the number of layers and the order of fabrics, as well as the direction of the fibers are presented.

BenniF. et al. [28] conducted a comparative study on the mechanical properties of the UAV skin for AF, glass fiber E and glass fiber S, as well as their hybrid arrangement, made using ER and a vacuum infusion process. The authors used Renlam LY 5138-2 and RenHy 5138 hardener (Huntsman, Indonesia) as ER. EW 130 E-glass fiber and SW220B-90A, AF S-glass fiber were used to reinforce the ER. In a typical experiment, eighteen layers of fibers were arranged and covered with a bag film that was connected to the inlet and outlet streams of the tube. The ER in the container was pumped through the tube to wet the entire laminate. The sample was placed at room temperature (25 ± 2 °C) for 3 hours to cure. As a result of complex analyzes, it was determined that the specific tensile strength and specific modulus of elasticity mainly depended on AF. However, AF had

little effect on the specific compressive strength, while the E-glass excellently withstood the compressive stress. The best tensile strength result was shown by a sample with 9 layers of AF and 9 layers of S-glass fibers (321 MPa).

In [29], the mechanical properties of an AF reinforced ER composite are studied by varying the percentage composition. The three different compositions of AF are 30 %, 35 % and 45 % by weight. The aramid-epoxy composite was produced by the vacuum method. The resulting composites are then cured in a hot air oven for 180 minutes. The results of the work are shown in table 6. The composite with the composition of 35 % AF + 65 % ER demonstrated the maximum tensile strength and hardness due to the uniform distribution of ER and the best interface between AF and ER.

The authors of [30] studied polymer composites based on AF with increased shear strength for aircraft products. The main task of the work was to study the interlayer strength of aramid OP after transverse reinforcement. The volume fraction of reinforcing fibers in the cured OP was 52 – 55 %. OP was obtained by layer-by-layer deposition of prepregs, followed by compression of the package at elevated temperature and pressure. The results showed that the use of a unidirectional reinforcing filler or a three-dimensional six-layer fabric

Table 7 – Physical and mechanical properties of organotextolites [33]

Strength characteristics	Organotextolite based on fabric Rusar NT	Organotextolite based on fabric Ruslan
Density, kg/m^3	1380-1390	1340-1380
Tensile strength, MPa	930 / 900÷950	880 / 840÷900
Tensile modulus, GPa	42 / 41÷43	35 / 33÷37
Compressive strength, MPa	210 / 200÷230	210 / 190÷220
Bending strength, MPa	570 / 560÷590	470 / 450÷500
Modulus of elasticity in bending, MPa	34 / 32÷35	25 / 22÷27

increases the interlayer strength of PCM by 22 %. And the use of voluminous two-component fabrics doubles them compared to conventional single-layer fabrics. J. Wu and XH Cheng [31] prepared aramid-epoxy unidirectional composites, in which the content of AF F-12 was 65 % vol. for all composite samples. The ratio between ERE-51 and hardener 593 was 100: 25 by weight. The results of interlaminar shear strength showed 54-60 GPa, shear strength 3,8-4,0 GPa depending on the surface treatment AF. M. Goodarz et al. [32] studied the low-speed impact response of aramid-epoxy plastics containing nano-layers of various thicknesses (17,5, 35, and 70 μm) and various stacking configurations (reverse, central, and two-sided alternation). The best results were obtained on composites containing a 35 μm spacer. The results show that the inclusion of nanofibers at the interface allows the composite to absorb significantly higher impact energy compared to plates without any nanofibers.

The aim of the work [33] was the development and manufacture of experimental reinforcing fillers from Rusar NT aramid fiber, a textile thread with a linear density of 14.3 tex, fabrics of a typical satin weave, as well as evaluating the effectiveness of new Rusar NT AF for reinforcing aviation organotextolite. Table 7 presents the physical and mechanical properties of samples of organotextolite based on fabric from the Rusar NT thread.

The article presents the results of a study of the physical and mechanical properties and moisture resistance of experimental organotextolites reinforced with AF fabric. Organotextolites for research were made from prepregs by autoclave molding. For the manufacture of prepregs from a solution of the binder EDT-69N(M), an impregnation unit UPST-1000 was used.

In [34], the mechanical behavior of an epoxy composite reinforced with unidirectional and fabric fibers was experimentally studied. Fabric glasses, aramid and carbon fibers, as well as unidirectional glasses and carbon fibers were used in the preparation of composite samples. Tensile, compression and shear tests were carried out to determine the mechanical properties of the composites (table 8). From the test results, it turned out that the mechanical properties of the reinforced AF composite are higher than those of glass and carbon fiber when we consider textile fiber types.

Thus, from the presented results it follows that the strength range of the OP starts from 320 MPa to 1 GPa. It is worth noting that the mechanical properties of the reinforced AF composite are higher than those of glass and carbon fiber, if we consider textile fiber types. High strength shows a composite with aramid fiber Rusar NT with a monolayer thickness in plastic of 0.11 – 0.12 mm, which is closer to 1 Gpa [33]. AF have a promising reinforcing effect on many resins, but the reinforcement mechanism needs further study. Therefore, the question of how to further enhance the interaction between the fillers and the matrix is of great importance for the application of this material in a wide industry, including military UAV.

The study of ways to improve the strength characteristics of organoplastic

Methods for modifying the surface of materials can be divided into four categories: mechanical,

Table 8 – Tensile strength of aramid epoxy composite [34]

Reinforcement type	Fiber volume V	Density [g/cm³]	Modulus of elasticity [MPa]	Shear modulus [MPa]	Poisson's ratio [-]	Tensile strength [MPa]	Tensile strength / density	Shear strength MPa]	Compression force [MPa]	Elongation at break
Glass fabric	30	1.55	14 352	4728	0.24	220	141.9	119	96	0.016
Aramid fabric	30	1.2	19 087	2585	0.38	357	297.5	53	64	0.019
Carbon fabric	30	1.31	42 000	12350	0.32	340	259.5	180	118	0.009
Unidirectional glass (0◦)	30	1.55	18 300	3895	0.25	432	278.7	30	71	0.028
Unidirectional glass (90°)	30	1.55	7940	3895	0.17	52	33.5	30	16	0.0096
Unidirectional carbon (0◦)	30	1.31	78 715	2195	0.4	826	630.5	20	118	0.0100
Unidirectional carbon (90°)	30	1.31	4 930	2195	0.25	37	28.2	20	27	0.0130

chemical, combustible and plasma. Since the diameter of conventional fiber is several micrometers, the use of mechanical methods and methods of burning on fibers becomes almost impossible to modify the surface of the fiber. Chemical surface treatment of fibers has long been widely used in industry. Another method that is mainly used is the surface oxidation of the fibers. However, chemical modification may have some disadvantages. When the fibers are oxidized in concentrated nitric acid, the equipment used must have good corrosion resistance, and the acid adsorbed on the surface of the fiber must be properly removed. This takes a long time and in most cases is accompanied by a decrease in fiber strength [11].

In the modern literature, many works are reported on the study of ways to improve the strength characteristics of the OP, and at present, the search for optimal technologies is underway. As is known from practical work, the main task in the manufacture of OP is to increase the strength characteristics. Strength characteristics directly depend on interfacial adhesion between fillers and matrices [36]. To improve interfacial adhesion between AF and ER matrices, various methods of fiber surface modification are used, such as chemical treatment (using binding agents and chemical grafting methods), plasma treatment, and others. The purpose of these surface modification methods is to increase the concentration of reactive functional groups or to roughen the fiber surface to increase physical contact with the resin matrix [35], [36], [37].

The formation of the fiber-resin interface is largely influenced by the polarity and total surface energy of the fiber surface. Thus, the addition of polar groups has been proposed to increase adhesion [38]. Various types of oxidative treatment constitute the basic fiber surface modification methodology, and these procedures cover: (1) gas oxidative treatment; (2) treating the solution with oxidation; and (3) electrochemical or electrolytic oxidation treatment. These treatments simply change the surface morphology of the fiber and may also change the surface energy and chemical composition. Naturally, changing the surface roughness also affects the chemical composition of the surface of the fibers. Lin J.S. [39] studied the use of bromination and metalation to change surface roughness and chemical composition. Very often, an effective and severe surface treatment leads to a deterioration in quality and a decrease in the strength and stiffness of the fibers, although the macroscopic properties of the composite may remain at an acceptable level or even at a high level. A typical surface treatment with solutions, namely AF sizing, is the use of emulsified solutions. Dimension based aqueous solutions of epoxypiperazine were studied by deLange et al. [40] and they reported improved adhesion.

In ways to improve the strength characteristics of OP, the most common method is chemical grafting. For example, Wu et al. applied the method

of graft modification of AF in [31], [41]. In the works, two types of fiber surface treatment were used to improve the strength characteristics: solutions of the modifier of rare earth elements (REE) and epoxychloropropane (ECP). For the modified ECP grafting treatment, F-12 aramid fibers were immersed in a KOH (0,7 %)/alcohol solution at 30 °C for 2 hours, then washed and dried. After that, these fibers were grafted into ECP at 90 °C for 6 h, then washed with distilled water and dried. For treatment in REE solutions, F-12 aramid fibers were immersed in a REE/alcohol solution at room temperature for 1 hour and dried in a vacuum oven at 110 °C for 4 hours. The results of [41] show that that both of these methods can improve interfacial adhesion. The REE surface treatment is superior to the ECP grafting treatment in providing interfacial adhesion between AF. The interfacial shear strength for the REE treated sample is 30.2 MPa, while the ECP grafted sample has 28.9 MPa. Meanwhile, the treatment of REE had almost no effect on the tensile strength of individual fibers.

The strength of the OP is increased by chemical grafting of AF with amino-functionalized graphene oxide [42] and supercritical carbon dioxide [[43], [44]]. In the first case [42], in order to functionalize the surface, AF 2 mm long was immersed in a buffer solution (pH = 8.5), and then dopamine was added. The above mixture was sonicated for 10 minutes and kept under constant stirring for 24 hours at room temperature. The coating was formed on the surface of the AF by dopamine self-oxidative polymerization. To obtain AF modified with amino-GO/dopamine, fibers from self-polymerized polydopamine-aramid were added to the amino-GO solution at 15 – 50 °C for 12 – 24 h. Next, a mixture of ER E-51 and m-xylylenediamine in a mass ratio of 100: 18.32 was applied to one AF with the formation of a resin microdroplet. The resin microdroplets were then cured at 60 °C for 1 hour and at 100 °C for 2 hours. The above process is shown in figure 3. The prepared resin microdroplets were used to test the interfacial properties of the modified fibers. As a result, at a higher reaction temperature of 60 °C, composites based on modified AF and ER showed an interfacial strength of 35.21 MPa, which is 34 % higher than that of composites based on pure AF/ER (26.31 MPa).

In [43] the mechanical and surface properties of AF were simultaneously improved by grafting with 1,4-dichlorobutane in supercritical carbon dioxide ($scCO_2$). For this purpose, the AF was placed in a stainless steel pressure vessel (1 l) where the treatment was carried out. An appropriate volume of 1.4-dichlorobutane was added to the vessel and the ratio of mass to volume of fiber and reagent was 1:60. When the vessel reached the desired temperature, CO_2 gas was injected through a high pressure syringe pump. Thus, seven samples were prepared in accordance with three conditions; the details are presented in table 9.

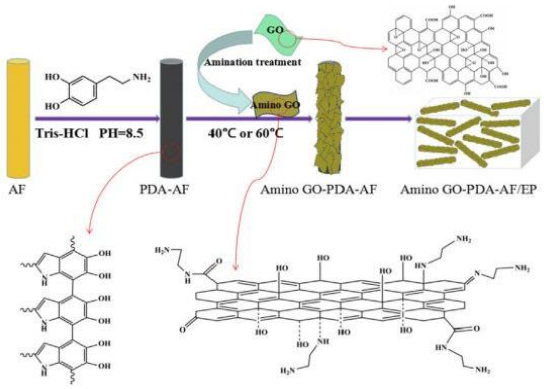

Figure 3. Illustration of the production process of modifying AF [42]

Thus, the authors developed a new strategy for improving the mechanical and surface properties of AF by treatment with 1.4-dichlorobutane in $scCO_2$. After the modification, the interfacial strength of the OP increased by 24.3 % from 51.29 to 63.91 MPa due to improved surface roughness and surface energy (figure 4b). In addition, the tensile strength of AF increased by 15.3 % from 3.14 to 3.62 GPa (figure 4a), which was attributed to improved crystallization of AF under tensile forces. In a similar work [44], the results show that the surface modification of AF in $scCO_2$ was an effective method for improving the adhesion characteristics between fibers and vinyl epoxy resin. The flexural strength of AF treated with $scCO_2$ vinyl epoxy composites was 18.1 % higher than that of untreated AF. Also, after treatment in $scCO_2$ with liquid isocyanate-terminated nitrile rubber, the interlayer shear strength increased from 42.5 MPa to 54.8 MPa.

Table 9 – Treatment conditions with supercritical carbon dioxide ($scCO_2$) for modification of AF [43]

Sample	Pressure (MPa)	Time (min)	Temperature (°C)
1	9.0	90	40
2	9.0	90	60
3	9.0	90	80
4	7.5	90	60
5	10.0	90	60
6	9.0	40	60
7	9.0	60	60

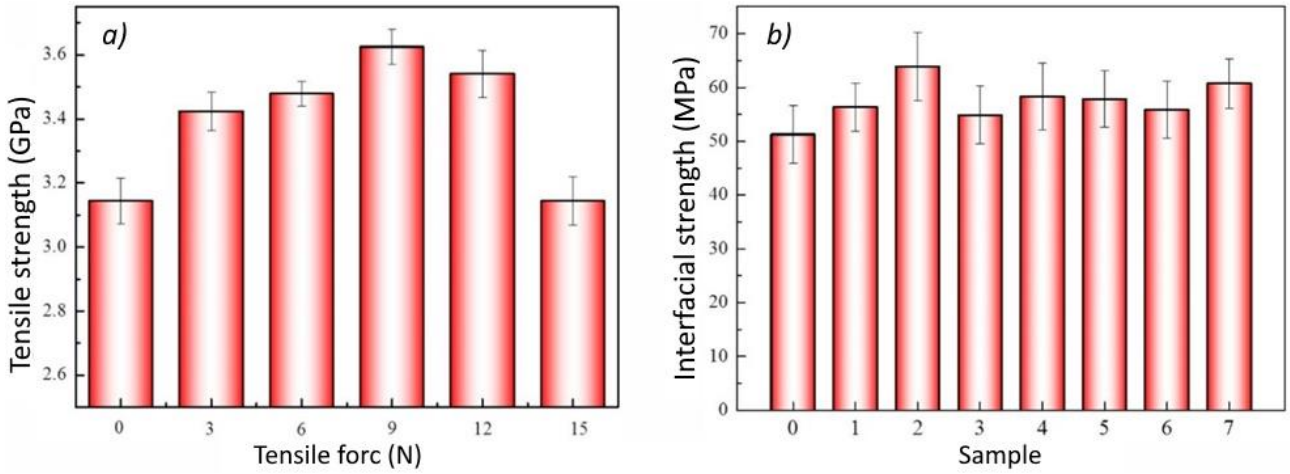

Figure 4 – Tensile strength of the fiber at tensile forces up to 15 N (sample 2 in table 2) (a) and interfacial strength of the OP before and after treatment with $scCO_2$ 1,4-dichlorobutane at a static tension of 9 N. (0): untreated fiber; (1-7): modified fibers of samples 1 – 7 in table 2 (b) [43]

Kevlar fiber was functionalized with phosphoric acid of various concentrations in [45]. The authors functionalized the fiber at room temperature with 10, 20, 30 and 40 wt.% phosphoric acid at 40 °C for 2 hours. It has been found that functionalization significantly increases the bond strength between Kevlar fiber and ER. The amount of surface oxygen and hydroxyl groups in Kevlar fiber can be significantly increased by functionalizing it with 40 wt.% phosphoric acid. As a result, the interfacial shear strength of composites reinforced with Kevlar fibers treated with phosphoric acid increases significantly up to ~35 MPa.

The authors of [46] studied the effect of modified aluminosilicates, including bentonite from armenia modified with quaternary ammonium salts (BAQAS) and phosphonium salts (BAQPS), on the mechanical properties and morphology of Kevlar/ER composites. Kevlar/ES composites containing 1.0 or 3.0 wt % modified bentonites were made using a hand layup technique. Mechanical properties were tested, including tensile strength, bending and in-plane shear. The results showed that the mechanical properties improved with increasing bentonite, as shown in table 10. The best results were obtained for composites containing 3 wt.% BAQAS, since most of the mechanical properties were significantly improved (tensile strength 302,9 MPa (+ 30 %), Young's modulus 16.3 GPa (+ 17 %), flexural modulus 23,4 GPa (+ 12.5 %), in-plane shear strength 22.8 MPa (+ 24.5 %) and in-plane shear modulus 677.2 MPa (+ 42 %)).

The next group of scientists use plasma treatments to improve the strength characteristics of OP. In particular, Brown and Mathys [47] applied ammonia and oxygen plasma treatment and reported improved performance of textolites in terms of interlaminar shear strength. Shaker et al. [48] used radio frequency (RF) plasma to modify aramid fibers and achieved improved textolite properties. The use of surface modifications to provide mechanical interlocking has been proposed by Palola et al. [49] and Wu et al. [50]. In [51], the authors increased the interfacial adhesion of epoxy composites reinforced with AF III due to low-temperature plasma treatment. Three technological regimes of low-temperature plasma treatment have been studied. Plasma treatment was carried out using a low-temperature DC glow-discharge plasma system (model HPD-280, Nanjing Suman Electronica Co. LTD, China) with an interelectrode gap of 30 mm, a reactor temperature of 20 °C, and a resonant frequency of 20 kHz. Sixteen treatment groups with various combinations of treatment power, treatment time, and treatment pressure were performed as shown in table 11.

Obviously, plasma treatment has an adverse effect on the tensile properties of AF III, and the detailed rates of reduction in tensile stress of AF III treated under different conditions. The results showed interfacial adhesion increased by 35.5 % to 30.44 MPa under optimal conditions, which were found to be a treatment power of 67.5 W, a treatment time of 11 minutes and a treatment pressure of 2500 Pa. After plasma treatment, the interfacial adhesion of the AF III/ER composites was improved, as shown by fragmentation testing of the monofilament composite material, but the tensile stress of a single strand of AF III was reduced. By surface morphology, chemical composition, AF III wettability, and fractured monofilament composite cross - sectional morphology, the interfacial

Table 10 – Tensile strength of composites reinforced with Kevlar [46]

Material	Tensile strength, MPa	Young's modulus, GPa	Elongation at break, %
ER/Kevlar	233.9 ± 12.5	13.9 ± 1.2	1.6 ± 0.2
ER+1% BAQAS/Kevlar	303.1 ± 11.8	13.1 ± 0.9	1.9 ± 0.4
ER+3% BAQAS/Kevlar	302.9 ± 17.7	16.3 ± 3.0	1.6 ± 0.5
ER+1% BAQPS /Kevlar	260.3 ± 9.0	12.8 ± 1.0	1.8 ± 0.3
ER+3% BAQPS /Kevlar	285.7 ± 19.6	15.5 ± 0.2	1.7 ± 0.3

Table 11 – Results of fiber tensile and fragmentation tests for various processing conditions [51]

No.	$\sigma 0$(MPa)	β	σ_f(MPa)	l_c(μm)	τ_{IFSS}(MPa)
0	4724.70	17.02	5466.06	2092.00	22.47
1	4673.06	15.70	5476.22	2072.67	22.72
2	4593.64	15.02	5433.28	2008.67	23.26
3	4465.58	13.18	5492.79	1632.53	28.94
4	4354.59	12.08	5468.55	1595.60	29.47
5	4638.23	16.41	5431.13	1876.00	24.90
6	4500.38	15.29	5364.76	1703.33	27.09
7	4330.79	14.43	5254.64	1535.20	29.44
8	4351.82	16.69	5136.90	1569.47	28.15
9	4573.80	13.14	5586.19	1803.07	26.65
10	4451.74	11.09	5700.61	1610.53	30.44
11	4435.38	13.68	5419.92	1610.40	28.94
12	4283.74	16.97	5061.05	1475.73	29.49
13	4523.26	14.28	5443.86	1774.40	26.38
14	4498.71	11.59	5684.69	1660.27	29.45
15	4113.07	15.63	4939.56	1428.93	29.73
16	4071.60	11.42	5217.84	1471.33	30.50

reinforcement mechanism of plasma-treated AF III reinforced epoxy composites can be summarized as four aspects:

1) van der Waals binding due to increased surface area of AF III;

2) mechanical adhesion of the rough surface AF III with the matrix;

3) good wettability of the AF III surface by the polymer;

4) chemical bond between oxygen-containing groups on the surface of AF III and the matrix.

In the literature, the work [52] is reported, where the authors developed a fast and economical surface treatment with a flame and treatment with a silane binder in order to improve the adhesive characteristics of light multilayer hidden fairing structures. The flame treatment was performed using propane gas, and the silane treatment was performed with c-methacryloxypropyltrimethoxysilane (c-MPS) and c-aminopropyltriethoxysilane (c-APS) under various processing conditions. The results of all treated composites are shown in figure 5. Flame treatment for 5 s and treatment with a silane coupling agent with a silane concentration of 0,5 wt.% on the surface of the OP had the highest bond strength of 10,9 MPa among all treatments.

Strength characteristics can be increased by incorporating multi-walled carbon nanotubes into aramid fabric-reinforced epoxy composites. The results obtained showed that the addition of 0,3 wt. % of multi-walled carbon nanotubes in aramid-epoxy composites is the optimal value, which significantly improves its mechanical properties [53].

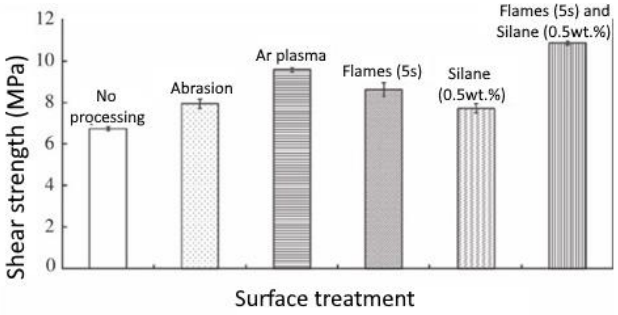

Figure 5 – Shear strength in relation to the surface treatment of the aramid-epoxy composite [52]

The authors in [54] studied the properties of epoxy compositions based on epoxy diano resin brand ED-20 and PEPA hardener with the addition of tricresyl phosphate (TCP) plasticizer. When using the composition of 70 % ED-20 + 30 % TCP + 15 % PEPA, the most optimal strength properties were obtained. The physical and mechanical properties are as follows: the impact strength increased from 9 to 14 kJ/m^2 compared to the composition without TCP modification, the bending stress increased to 98 MPa. The study [55] developed compositions based on ED-20 resin with TCP modifiers. PEPA hardener was used as the resin hardener. The samples were obtained in the form of compressed tablets with a thickness of 1 mm containing 70 % by weight of ED-20, 15 % PEPA, 30 % TCP. The tests were carried out for strength characteristics and for gelation time, epoxy curing time and temperature. The results of the study showed that the introduction of the TCP plasticizer into the resin composition improves impact strength by 3 times (10 kJ/m^2), bending by 3 times (57 MPa), and hardness by 59 % (197 MPa). It also increases the gelation time from 24 to 60 minutes, the curing time from 39 to 115 minutes and reduces the curing temperature from 125 to 44 °C.

Based on all of the above, we can conclude that it is expedient to process AF and ER. Among the above works, the AF/ER composite modified by treatment with 1,4-dichlorobutane in scCO^2 (63,91 MPa) has a high interlaminar shear strength [43].

The use of methods for increasing the strength characteristics of OP when creating PCM is an important and significant process for improving the interaction between the polymer matrix and the filler. This, in turn, increases the strength of the fairing material in UAV hulls, which brings it closer to the stringent requirements for the design of aerial vehicle.

Conclusions

According to the literature data, aramid fiber-reinforced organoplastics have low dielectric constants and high mechanical characteristics compared to other fiber composites. According to the analysis, the optimal frequency range for measuring dielectric properties (radio transparency) is 1 kHz – 12 GHz. To achieve high dielectric parameters in the composite, the aramid fabric layer should be one layer larger than the base layer. Based on the results of the work, it follows that the strength range of organoplastics starts from 320 MPa to 1 GPa. Mechanical properties of the composite, reinforced aramid fiber higher than glass and carbon fibers. Also, it can be concluded that it is reasonable to aramid fiber and epoxy resin. In many studies, surface treatment is achieved by increasing interfacial adhesion, which greatly increases the strength characteristics of the organoplastic. Using these methods, it is possible to improve the strength of epoxy composites by more than 30 %.

Thus, ways to improve the strength characteristics of OP is currently an area of active research and a topic for further study.

Conflict of interests. There is no conflict of interest.

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Органопластиктердің диэлектрлік және беріктік қасиеттерін зерттеу. Шолу

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ТҮЙІНДЕМЕ

Қазіргі уақытта роботты кешендер бағытында әскери ҰҰА өндіру және қолдану белсенді дамып келеді. Әскери ҰҰА мақсаты мен қолданылуы азаматтық функциялардан екі функцияға байланысты ерекшеленеді: барлау мақсаты және соғыс зарядының тасымалдаушысы. Әскери ҰҰА ерекшелігі олардың жау радарларына көрінбейтіндігінде және командалық пунктпен ақпараттың тұрақты берілуін қамтамасыз етеді. Осы мақсаттар үшін, ең алдымен, ҰҰА материалы радио мөлдірлігінің қасиеттеріне ие болуы керек. Корпустарды, ҰҰА қуат элементтерін өндіру үшін жоғары беріктігі бар ПКМ қажет, олардың қатарына органопластик, көмірпластик, шыныпластик кіреді. Авиациялық техниканың тораптары мен агрегаттарының бөлшектері үшін материалдарды таңдау олардың пайдалану шарттарына: қолданыстағы жүктемелерге, материалдың қасиеттеріне байланысты болады. Бұл талаптар композициялық Полимерлі композиялық материалдар (ПКМ), органопластик (ОП) арасында толық жауап береді. ОП басқа талшықты композиттермен салыстырғанда төмен диэлектрлік шығындармен (радио өткізгіштік) бірге жоғары беріктік қасиеттеріне ие. Бұл жұмыста диэлектрлік және беріктік қасиеттерін зерттеуге шолу, сондай-ақ органопластиктің механикалық қасиеттерін арттыру әдістері келтірілген. Жұмысты талдау көрсеткендей, радио өткізгіш органопластик үшін диэлектрлік тұрақтылықтың оңтайлы жиілік диапазоны 1кГц-12 ГГц құрайды. Органопластиктің беріктік шегі 320 МПа-дан 1 ГПа-ға дейін өзгереді. Органопластиктің эпосид шайырының модификациялаудың тәсілдері және арамидтік талшықтарының беріктігін арттыру мүмкіндіктері қарастырылады.

Түйін сөздер: ұшқышсыз ұшу аппараттары, ағын, органопластик, диэлектрлік тұрақты, беріктік шегі.

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Исследование диэлектрических и прочностных свойств органопластика. Обзор

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АННОТАЦИЯ

В настоящее время активно развивается производство и применение военных БПЛА в направлении роботизированных комплексов. Предназначение и применение военных БПЛА отличаются от гражданских, исходя из двух функций: разведывательное назначение и носитель боевого заряда. Специфика военных БПЛА заключается в их невидимости для радаров противника и обеспечения устойчивой приемопередачи информации с командным пунктом. Для этих целей, в первую очередь, материал БПЛА должен обладать свойствами радиопрозрачности. Для производства корпусов, силовых элементов БПЛА нужны высокопрочные ПКМ, к числу которых относятся органопластик, углепластик, стеклопластик. Выбор материалов для деталей узлов и агрегатов авиационной техники зависит от их условий эксплуатации: действующих нагрузок, свойств материала. Этим требованиям полно отвечает среди композиционных полимерных материалов (ПКМ) органопластик (ОП). ОП обладают высокими прочностными свойствами наряду с низкими диэлектрическими потерями (радиопрозрачность) по сравнению с другими волокнистыми композитами. В данной работе представлен обзор исследований диэлектрических и прочностных свойств, а также способы повышения механических свойств органопластиков. Анализ работ показал, что для радиопрозрачностого органопластика оптимальный диапазон частот диэлектрической проницаемости является 1кГц-12 ГГц. Предел прочности органопластиков варьируется в интервале от 320 МПа до 1 ГПа. Рассмотрены возможности увеличения прочности арамидных волокон и способы модификации эпоксидных смол органопластика.

Ключевые слова: беспилотные летательные аппараты, обтекатель, органопластик, диэлектрическая проницаемость, предел прочности.

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