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Mathematical modeling of sulfuric acid leaching of pyrite cinders after preliminary chemical activation

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ABSTRACT

Pyrite cinders, waste products of pyrite concentrate processing by firing to produce sulfuric acid, can serve as raw materials for the extraction of precious, ferrous, and non-ferrous metals. The paper considers the possibilities of obtaining non-ferrous metal concentrate from pyrite cinders by sulfuric acid leaching. This operation is one of the stages in the integrated technology. To increase the extraction of non-ferrous metals during leaching, the method of preliminary chemical activation was used. Chemical activation was carried out in a solution containing 40-120 g/dm^3 $NaHCO_3$ at temperatures of 90-230 ° C and a duration of 30-300 minutes. Sulfuric acid leaching of pyrite cinder after activation was carried out in H_2SO_4 solutions with a concentration of 5-20 % at a temperature of 60 ° C, duration of 30 minutes, and pulp density of 33 %. To determine the optimal conditions for the sulfuric acid leaching of pyrite cinders, a mathematical planning method was used, which allows to assess with a high degree of reliability the influence of the main factors (temperature, pulp density, the concentration of the solution $NaHCO_3$ and duration) and predict an increase in the efficiency of the process by analyzing the numerical values of the regression equations. As a result of sulfuric acid leaching of pyrite cinders after preliminary chemical activation under optimal conditions determined by a mathematical model, the extraction of iron and non-ferrous metals into a solution is 10-15% higher than without activation.

Keywords: pyrite cinders, non-ferrous metals, model, factor, extraction.

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Introduction

One of the methods of sulfuric acid production is the firing of pyrite concentrate to produce sulfur dioxide [[1], [2], [3], [4], [5]]. Production waste - pyrite cinders are stored, which creates a large amount of man-made waste and poses a serious environmental threat [[6], [7], [8]]. At the same time, pyrite cinders can serve as raw materials for complex processing with the extraction of precious, ferrous, and non-ferrous metals [[9], [10]]. The development of rational processing technology is relevant.

The paper considers the possibilities of obtaining non-ferrous metal concentrate from pyrite cinders by sulfuric acid leaching [[11], [12],

[13]]. This operation is one of the stages in the integrated technology.

The study of the parameters and indicators of the process of leaching pyrite cinders was carried out using the method of mathematical planning of the experiment and the selection of technologically significant factors.

The extensive use of mathematical models of technological processes is explained by the fact that the model makes it possible to establish in a phenomenon, subject, or process the main regularities that are characteristic of them, and to neglect the secondary, auxiliary features [[14], [15], [16], [17], [18]]. Development of a mathematical model of the process is directly related to the planning of the experiment.

A full factorial experiment [19] has been used to study the technology of pyrite cinders processing including preliminary chemical activation and sulphuric acid leaching. The method of the full factorial experiment includes consequent stages of mathematical modeling:

- selection of the optimization parameter and affecting factors (temperature, pulp density, $NaHCO_3$ solution concentration, and duration);
- selection of the basic level and interval of variation for each factor;
- checking the reproducibility of the experimental results;
- construction of a mathematical model with calculation of regression equation coefficients;
- testing the adequacy of the regression equation.

Chemical activation of pyrite cinders in a solution of sodium hydrogen carbonate was performed in order to increase the efficiency of sulphuric acid leaching. The use of the given method of preliminary chemical activation in the processing of mineral raw materials has a positive effect on the degree of extraction of useful components [[20], [21], [22]].

The experimental part

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

Chemical analysis was performed on an optical emission spectrometer with inductively coupled plasma (Optima 8300 DV, PerkinElmer, Waltham, MA, USA). The random error component is 2.0%.

X-ray phase analysis was performed using D8 Advance (Bruker, Billerica, Massachusetts, USA).

Discussion of results

The subject of the study was the magnetic fraction of pyrite cinders from the sulphuric acid production of the Tselinnyy Mining and Chemical Combine.

Chemical composition of the magnetic fraction of pyrite cinders wt.%: Na_2O 1.4; MgO 0.74; Al_2O_3 5.69; SiO_2 23.22; P_2O_5 1.1; $SO_3$6.24; Cl^-0.01; K_2O 0.44; CaO 2.52; $TiO_2$0.32; $Fe_2O_3$52.84; CuO 0.25; ZnO 0.53; As_2O_3 0.24; SeO_2 0.3; BaO 2.4; HgO 0.08; PbO 0.16; п.п 1.82; precious metal content, g/t: Au 2.69; Ag 19.3

The phase analysis of the magnetic fraction of the pyrite cinders is shown in Table 1 and Figure 1.

Table 1 – Phase content of the magnetic fraction of pyrite cinders

Name	Formula	%
Magemite	Fe_2O_3	25.1
Hematite	Fe_2O_3	19.1
Quartz	SiO_2	18.0
Albite	$Na(AlSi_3O_8)$	10.2
Trinatrium phosphate zinc oxide hydrate	$Na_3Zn_4O(PO_4)3(H_2O)_6$	9.5
Sodium aluminosilicate	$NaAl_3Si_3O_{11}$	6.7
Barium ferrite	$BaFe_2O_4$	4.7
Natrozharosite	$(Na_{0.67}(H_3O)_{0.33})Fe_3(SO_4)_2(OH)_6$	4.2
Dolomite	$CaMg(CO_3)_2$	2.5

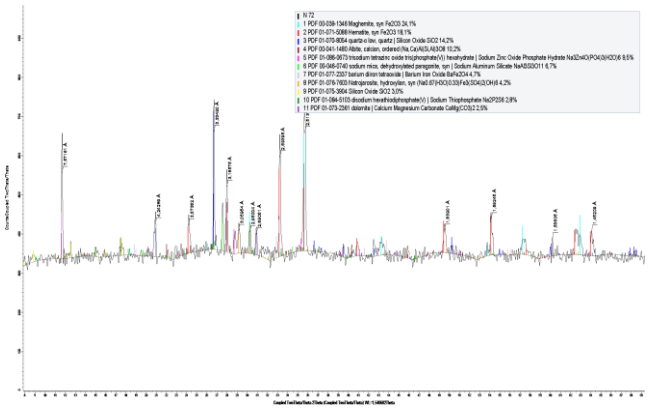

Figure 1 - X-ray diffraction of the magnetic fraction of pyrite cinders

Chemical activation of pyrite cinders was performed in a solution containing 40-120 g/dm^3 $NaHCO_3$ at pulp density from 20 to 80 % and a working temperature of 90-230 °C using a

thermostatically controlled unit containing 6 autoclaves rotating through the head, with a working volume of 250 cm^3. The activation time was 30-300 minutes.

Sulfuric acid leaching of pyrite cinders after preliminary chemical activation was performed in H_2SO_4 solutions with a concentration of 5-20% at a temperature of 60 °C, duration of 30 minutes, and L: S=3.

A matrix of full factor experiment with the calculation of the main level and interval of variation was made up (Table 2).

The experiment was performed using the planning matrix. Each experiment was duplicated three times during the practical realization of the planning matrix. The results of Fe_2O_3, CuO, and ZnO leaching experiments are given in Tables 3, 4, and 5.

Table 2 - Matrix of the complete factor experiment

Indicators	Factors			
	X_1- temperature , °C	X_2- conc. $NaHCO_3$, g/dm^3	X_3- duration, min	X_4- ratio S:L
Basic level	160	90	180	1:6
Variation interval	70	30	120	1:4
Upper level	230	120	300	1:10
Lower level	90	60	60	1:2

Table 3 - Experimental results for Fe_2O_3 leaching matrix

Batch	**Experiment No.**	**Factor X_1**	**Factor X_2**	**Factor X_3**	**Factor X_4**	**Extracted in solution Fe_2O_3, %**	**y_{exp}**	**$S_i^{2(Fe)}$**
1	1	1	1	1	1	6.26	6.17	0.0171
	2	-1	1	1	1	6.23	6.17	
	3	1	-1	1	1	6.02	6.17	
2	1	-1	-1	1	1	5.28468	5.06636	0.041493
	2	1	1	-1	1	5.033	5.06	
	3	-1	1	-1	1	4.8814	5.06	
3	1	1	-1	-1	1	10.695	10.36	0.453225
	2	-1	-1	-1	1	10.8	10.36	
	3	1	1	1	-1	9.585	10.36	
4	1	-1	1	1	-1	4.9	4.62	0.088433
	2	1	-1	1	-1	4.67	4.62	
	3	-1	-1	1	-1	4.31	4.62	
5	1	1	1	-1	-1	6.16	5.73	0.253433
	2	-1	1	-1	-1	5.87	5.73	
	3	1	-1	-1	-1	5.18	5.73	
6	1	-1	-1	-1	-1	13.05	12.4	0.390633
	2	1	1	1	1	12.43	12.42	
	3	-1	1	1	1	11.8	12.42	
7	1	1	-1	1	1	26.0	23.89	2.838933
	2	-1	-1	1	1	22.23	23.89	
	3	1	1	-1	1	22.07	23.89	
8	1	-1	1	-1	1	10.65	10.23	0.313433
	2	1	-1	-1	1	10.54	10.27	
	3	-1	-1	-1	1	9.63	10.27	

Table 4 - Test results for CuO leaching matrix

Batch	Experiment No.	Factor X_1	Factor X_2	Factor X_3	Factor X_4	Extracted in solution Fe_2O_3, %	y_{exp}	$S_i^{2(Fe)}$
1	1	1	1	1	1	22.72	22.64	0.0148
	2	-1	1	1	1	22.7	22.64	
	3	1	-1	1	1	22.5	22.64	
2	1	-1	-1	1	1	21.35508	21.27	0.00729
	2	1	1	-1	1	21.27	21.27	
	3	-1	1	-1	1	21.18492	21.27	
3	1	1	-1	-1	1	17.9192	17.23	0.47497
	2	-1	-1	-1	1	17.23	17.23	
	3	1	1	1	-1	16.5408	17.23	
4	1	-1	1	1	-1	8.92	8.74	0.07093
	2	1	-1	1	-1	8.88	8.74	
	3	-1	-1	1	-1	8.44	8.74	
5	1	1	1	-1	-1	18.89	18.51	0.32543
	2	-1	1	-1	-1	18.8	18.51	
	3	1	-1	-1	-1	17.86	18.51	
6	1	-1	-1	-1	-1	27.96	26.63	1.7689
	2	1	1	1	1	26.63	26.63	
	3	-1	1	1	1	25.3	26.63	
7	1	1	-1	1	1	43.05	41	4.2025
	2	-1	-1	1	1	41	41	
	3	1	1	-1	1	38.95	41	
8	1	-1	1	-1	1	17.73	16.89	0.7056
	2	1	-1	-1	1	16.89	16.89	
	3	-1	-1	-1	1	16.05	16.89	

We calculated the values of regression coefficients, having received experimental data by formula $b_i = \frac{\sum Y_i}{n}$, where, Y_i-value of optimization parameter in the i-th experiment, N - number of experiments. Regression equations describing metals extraction during sulfuric acid leaching of pyrite cinders were calculated according to obtained coefficients:

$$y_{Fe}=12.32 + 1.4\ x_1-1.65x_2+1.05x_3-7.82x \quad (1)$$

$$y_{Zn}=-21.62 +1.07x_1+0.21x_2+0,71x_3-11x_4 \quad (2)$$

$$y_{Cu}=-18.9 + 0.86x_1 - 0.43x_2+2.62x_3+ 11.53x_4 \quad (3)$$

Factor analysis of the results was conducted, to determine the intensity of the effect of the factors under study on the optimization criteria. The effects of factors $x_1 - x_4$, introduced into the plan at two levels were determined by formulas for linear orthogonal plans. Significant factors were determined for each criterion and ranks which have an effect on the extraction of certain metals were drawn up:

- for iron (y_1): $x_1 > x_3 > x_2 > x_4$;
- for zinc (y_2) : $x_1 > x_3 > x_2 > x_4$;
- for copper (y_3): $x_4 > x_3 > x_1 > x_2$.

The analysis of the obtained regression equations for the extraction process allowed us to conclude that for iron and zinc extraction the greatest contribution is made by factor X_1 - temperature. The coefficient value defines a quantitative measure of the effect of the factor. The sign of the coefficient determines the nature of the effect. The plus sign shows that the value of the factor X_1 increases with an increase in the value of the factor X_1, while the minus sign shows that the value of the optimization parameter decreases. The iron and zinc extraction is less affected by the ratio L:S. The ratio L:S and $NaHCO_3$ concentration, g/dm^3 have the greatest contribution to effective extraction of copper.

Table 5 - Test results for ZnO leaching matrix

Batch	Experiment No.	Factor X_1	Factor X_2	Factor X_3	Factor X_4	Extracted in solution Fe_2O_3, %	y_{exp}	$S_i^{2(Fe)}$
1	1	1	1	1	1	22.05	21.0	
	2	-1	1	1	1	21	21.0	1.1025
	3	1	-1	1	1	19.95	21.0	
2	1	-1	-1	1	1	23.38	22.2	
	2	1	1	-1	1	22.27	22.7	1.2321
	3	-1	1	-1	1	21.16	22.7	
3	1	1	-1	-1	1	12.47	11.8	
	2	-1	-1	-1	1	11.88	11.8	0.3481
	3	1	1	1	-1	11.29	11.8	
4	1	-1	1	1	-1	11.6	11.5	
	2	1	-1	1	-1	11.05	11.05	0.3025
	3	-1	-1	1	-1	10.5	11.05	
5	1	1	1	-1	-1	8.5	8.1	
	2	-1	1	-1	-1	8.1	8.1	0.16
	3	1	-1	-1	-1	7.7	8.1	
6	1	-1	-1	-1	-1	19.95	19	
	2	1	1	1	1	19	19	0.9025
	3	-1	1	1	1	18.05	19	
7	1	1	-1	1	1	47.25	45	
	2	-1	-1	1	1	45	45	5.0625
	3	1	1	-1	1	42.75	45	
8	1	-1	1	-1	1	13.5	12.9	
	2	1	-1	-1	1	12.9	12.9	0.36
	3	-1	-1	-1	1	12.3	12.9	

The results were analyzed using the following algorithm:

- for each series of parallel experiments, the arithmetic average of the response function was calculated;

- for each series of parallel experiments, we calculated the estimation of dispersion;

- we calculated regression equation coefficients;

- we performed the equation adequacy test using Fisher's criterion (Fp) and the table test (Fт)

- we estimated the reproducibility of experiments according to Cochran's criterion G_p;

- we estimated the variance of adequacy.

Calculations according to the above algorithm are shown in Table 6.

Based on the results of the planning matrix experiments, the optimum is the preliminary chemical activation of pyrite cinders in a solution containing 60 g/dm^3 $NaHCO_3$, at a ratio L: S=4 and temperature 120^{0}C. The best results were obtained at leaching in 15 % H2SO4 solution at temperature 60^{0}C after activation of cinders in these conditions. The extraction in sulphuric acid solution was, %: CuO 43.05; ZnO 47.25, and Fe_2O_3 26.0. Further increase in concentration does not lead to an increase of extracted non-ferrous metals in a solution. The degree of extraction of non-ferrous metals in a solution is lower on 10-15 % at leaching of pyrite cinders without chemical activation.

Table 6 - Results analysis

Regression analysis criterion	Fe_2O_3	CuO	ZnO
Equation adequacy dispersion	$S_{ad}^2 = \frac{1}{N-B}\sum Y_{exp} - Y_p$ S_{ad}^2=4.1515625	$S_{ad}^2 = \frac{1}{N-B}\sum Y_{exp} - Y_p$ S_{ad}^2=3.43	$S_{ad}^2 = \frac{1}{N-B}\sum Y_{exp} - Y_p$ S_{ad}^2=1.78
Number of degrees of freedom	f=3	f=3	f=3
Repeatability dispersion	$S_y^2 = \frac{\sum S_i^2}{N}$, where S_i^2 - dispersion of experience at the i-th point S_y^2 =0.54	$S_y^2 = \frac{\sum S_i^2}{N}$, where S_i^2 - dispersion of experience at the i-th point S_y^2 =0.94	$S_y^2 = \frac{\sum S_i^2}{N}$, where S_i^2 - dispersion of experience at the i-th point S_y^2 =1.18
Fischer's criterion	$F_p = \frac{\max(S_{ad}^2, S_{\bar{y}}^2)}{min(S_{ad}^2 S_{\bar{y}}^2)}$ F_p= 3.09≤F_{tab}=6.59– regression equation is adequate.	$F_p = \frac{\max(S_{ad}^2, S_{\bar{y}}^2)}{min(S_{ad}^2 S_{\bar{y}}^2)}$ F_p=1.81 ≤F_{tab}=6.59 – regression equation is adequate.	$F_p = \frac{\max(S_{ad}^2, S_{\bar{y}}^2)}{min(S_{ad}^2 S_{\bar{y}}^2)}$ F_p=1.32 ≤F_{tab}=6.59 – regression equation is adequate.
Cochran's criterion	$G_{calc} = \frac{S_{max}^2}{\sum S^2}$ G_{calc}=0,429<G_{crit}=0,438 – experiments are repeatable	$G_{calc} = \frac{S_{max}^2}{\sum S^2}$ G_{calc}=0,434<G_{crit}=0,438 – experiments are repeatable	$G_{calc} = \frac{S_{max}^2}{\sum S^2}$ G_{calc}=0,436<G_{crit}=0,438 – experiments are repeatable

Conclusions

To increase the degree of extraction of non-ferrous metals from pyrite cinders during sulfuric acid leaching, the method of preliminary chemical activation in $NaHCO_3$ solution was used.

To determine the optimal technological conditions of the process of sulfuric acid leaching of pyrite cinders, a mathematical model is constructed.

Based on the results of experiments conducted on the matrix, regression equations were compiled, which determined the adequacy of the compiled mathematical model.

The analysis of the regression equations showed that for the extraction of iron and zinc, the greatest contribution is made by the X_1 factor – temperature, and for copper, the X_2 factor – pulp density and X_4 - the concentration of $NaHCO_3$, g/dm^3.

As a result of preliminary chemical activation during sulfuric acid leaching of pyrite cinders, the degree of extraction of non-ferrous metals into the solution increased by 10-15%.

Conflict of interests

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Алдын ала химиялық белсендіруден кейінгі пирит күйіктерінің күкіртқышқылды шаймалау үдерісінің математикалық модельдеуі

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ТҮЙІНДЕМЕ

Пирит күйіктері – пирит концентратын күкірт қышқылын алу арқылы күйдіру әдісімен қайта өңдеудің қалдықтары. Олар асыл, қара және түсті металдарды алу үшін шикізат болып табылады. Жұмыста күкірт қышқылды ерітінділеу әдісімен пиритті күйіктен түсті металл концентратын алу мүмкіндігі қарастырылған. Бұл операция кешенді технологияның кезеңдерінің бірі болып табылады. Ерітінділеу кезінде түсті металдарды алуды арттыру үшін алдын-ала химиялық белсендіру әдісі қолданылады. Химиялық белсендіру 40-120 г/дм^3 $NaHCO_3$ бар ерітіндіде 90-230 ° С температурада және ұзақтығы 30-300 минут ішінде жүргізілді. Белсендірілгеннен кейін пирит күйіктерін күкіртқышқылды ерітінділеу концентрациясы 5-20% H_2SO_4 ерітінділерінде 60^{o}С температурада, ұзақтығы 30 минут және С:Ж қатынасы 3:1 кезінде жүргізілді. Пириттік күйіктерді күкіртқышқылды ерітінділеудің оңтайлы жағдайларын анықтау үшін негізгі факторлардың (температура, С:Ж қатынасы, $NaHCO_3$ ерітіндісінің концентрациясы) әсерін жоғары сенімділікпен бағалауға және регрессия теңдеулерінің сандық мәндерін талдай отырып, процесс тиімділігінің артуын болжауға мүмкіндік беретін математикалық модельдеу әдісі қолданылды. Математикалық модельмен анықталған оңтайлы жағдайларда алдын-ала химиялық белсендіруден кейін пирит күйіктерін күкірт қышқылымен ерітінділеу нәтижесінде темір мен түсті металдардың ерітіндіге шығарылуы белсендірілмегенге қарағанда 10-15% жоғары болды.

Түйін сөздер: пирит күйіктері, түсті металдар, модель, фактор, бөліп алу.

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Математическое моделирование сернокислотного выщелачивания пиритных огарков после предварительной химической активации

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АННОТАЦИЯ

Пиритные огарки, отходы переработки пиритного концентрата методом обжига с получением серной кислоты, могут служить сырьем для извлечения благородных, черных и цветных металлов. В работе рассмотрены возможности получения концентрата цветных металлов из пиритных огарков способом сернокислотного выщелачивания. Эта операция является одним из этапов в комплексной технологии. Для повышения извлечения цветных металлов при выщелачивании применен метод предварительной химической активации. Химическую активацию проводили в растворе, содержащем 40-120 г/дм3 NaHCO3 при температурах 90-230оС и продолжительности 30-300 минут. Сернокислотное выщелачивание пиритных огарков после активации проводили в растворах H_2SO_4 концентрацией 5-20 % при температуре 60оС, продолжительности 30 минут и Ж:Т=3. Для определения оптимальных условий проведения сернокислотного выщелачивания пиритных огарков использовали метод математического планирования позволяющий с высокой степенью достоверности оценить влияние основных факторов (температуры, отношения Ж:Т, концентрации раствора NaHCO3 продолжительности) и прогнозировать повышение эффективности процесса, анализируя численные значения уравнений регрессии. В результате проведения сернокислотного выщелачивания пиритных огарков после предварительной химической активации в оптимальных условиях, определенных математической моделью, получено извлечение в раствор железа и цветных металлов на 10-15 % выше, чем без активации.

Ключевые слова: пиритные огарки, цветные металлы, модель, фактор, извлечение.

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Engineering and Technology

SwissADME and pkCSM Webservers Predictors: an integrated Online Platform for Accurate and Comprehensive Predictions for In Silico ADME/T Properties of Artemisinin and its Derivatives

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ABSTRACT

In vivo ADME analysis is costly, laborious and puts animal lives at danger, whereas in silico ADME analysis is not dangerous, simpler, and quicker. This study will use *in silico* methodologies from SwissADME and pkCSM as an integrated online platform for precise and complete predictions to determine In Silico ADME/T Properties of Artemisinin and its Derivatives. The studied compounds' structures were converted to canonical SMILES files and then sent to the SwissADME and pkCSM webserver tools, which provide free access to different properties of compounds. A compound's ADME/T characteristics are critical for future study and the results obtained will be of beneficial use for researchers. Additionally, the results of this study give great guidance and show that chemical alterations to the reference molecule artemisinin can enhance its ADMET capabilities. The webservers used in this work are free, and several comparison trials show that pkCSM and SwissADME performed are better than a number of other frequently used methods. The designing or engineering of a novel drug molecule primarily requires knowledge of the features of ADME/T of the new drug compound.

Keywords: SwissADME, artemisinin derivatives, ChemDraw, silico prediction, pkCSM.

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Introduction

Artemisinin is a sesquiterpene based lactone along with a peroxide component [[1], [2]]. It is obtained from the leafy sections of artemisia annua, which is a herb and medicinal plant herb that has been used for ages to cure fever and chills [3]. Artemisinin, also known identified as Qinghaosu, was the first to be isolated. Dihydroartemisinin (DHA) was the main derivative to be created by converting the carbonyl groups to hydroxyl groups [2]. Others, for instance the more water-soluble artesunate and the further oil-soluble artemether and arteether, followed [4]. These compounds were ten times more effective than artemisinin [2], with artesunate getting a more beneficial pharmacokinetic-pharmacodynamic profile [5].

Artemisinins and their derivatives are preferentially taken up by parasite-infected erythrocytes and then localized in parasite membranes such as the mitochondrial, digesting vacuole, and parasite limiting membrane [[2], [4]]. All versions of medicine have an endoperoxide bridge (C-O-O-C) that is vital for its anti-malarial impact, where the molecule itself is stimulated by iron or heme to create free radicals. The latter free radicals subsequently alkylate malaria membrane-associated proteins, killing the parasite [4]. They have been discovered to be useful versus various strains of malaria, particularly those resistant to established gold standard medications. They are very effective, needing just nanomolar doses in vitro [4]. They are also fast-acting, with therapeutic ability as early as 20 hours following treatment. Furthermore, artemisinins have a comparatively low-profile toxicity, with the LD_{50} of 4223 mg/kg. Furthermore, despite the widespread use of the medicine, there was no indication of neurotoxicity in neuronal cells or animals at high-level doses [[2], [4]].

Artemisinin and its derivatives revealed further characteristics in illnesses other than malaria. Artesunate, for example, demonstrated anti-cancer effects as evidenced by its cytotoxic action versus 55

cancer cell lines via the control of numerous processes such as the damage of DNA and repair, apoptosis, as well as proliferation [[6], [7]]. Artesunate inhibited the creation of interleukin (IL)-1, IL-6, and IL-8 in TNF-stimulated rheumatoid arthritis fibroblast-like synoviocytes (RA FLS) via the NF-B and phosphoinositide 3 kinases (PI3K) pathways [8]. It also has antiviral characteristics, since artemisinin suppressed the duplication of human cytomegalovirus (HCMV) [9]. Several of these pathophysiological routes are also marked in respiratory illnesses. Hence, artemisinin and its derivatives might be used to treat respiratory illnesses as well. Because developing novel molecules for disease therapy is a difficult procedure, we provide in the current study a cheminformatic examination of a sequence of five artemisinin derivatives (Fig. 2).

The goal of this study is to use SwissADME [10] and pkCSM [11] webservers to forecast the physicochemical qualities, drug-likeness properties, ADME (absorption, distribution, metabolism, and excretion), and toxicity of five artemisinin derivatives to understand their pharmacokinetic behaviour. In addition to being free, the webservers utilized in this work have undergone several comparison trials that show that SwissADME and pkCSM present as well as or improved than numerous other frequently used techniques [[10], [11], [12], [13], [14], [15], [16]].

We did the same *in silico* investigation on the molecule for comparative reasons with artemisinin derivatives on which structural alterations were done. Information on a molecule's ADME/T characteristics is mostly required in the development of a novel medicinal compound [[12], [14], [15]].

Materials and Methods

1.1 Materials

ChemDraw software Professional 16.0 from Cambridge was used to drwa structures.. SwissADME from the Swiss Institute of Bioinformatics and pkCSM from the Biosig Lab University of Melbourne were utilized as ADMET prediction servers. SwissADME is a free of charge web tool for assessing compounds' physicochemical qualities, pharmacokinetics, drug-likeness, and medicinal chemistry easiness. It is extensively utilized due to its simplicity in determining the drug-likeness profile of compounds by including Lipinski's rule, which evaluated orally active substances to determine physicochemical parameters for the high chance of becoming an oral drug. The pkCSM technique predicts and optimizes pharmacokinetic and toxicity properties. The cut-off scanning idea was extended by pkCSM to create a prediction simulation of ADME/T characteristics for drug advance. The pkCSM program performed well in the outer validation dataset, with an accuracy of a value of 83.8% in the mutagenicity check. pkCSM has numerous endpoints, including LD_{50}, Ames test, highest daily dosage, and hepatotoxic.

1.2 Methods

Structures of artemisinin derivatives were generated with ChemDraw Professional 16.0. The derivatives were subsequently converted into canonical SMILES (simple molecular-input line-entry system) format [17] and run using SwissADME and pkCSM for ADMET Lipinski's so-termed Rule-of-Five established a link between pharmacokinetic and physicochemical characteristics [18]. Table 1 shows the code of each compound's SMILES.

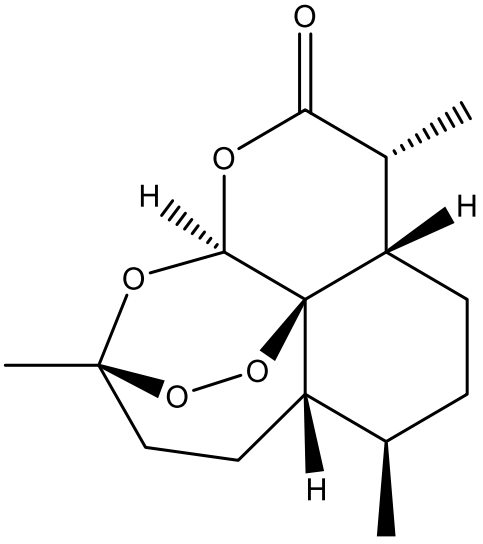

Figure 1 – The chemical structures of artemisinin.

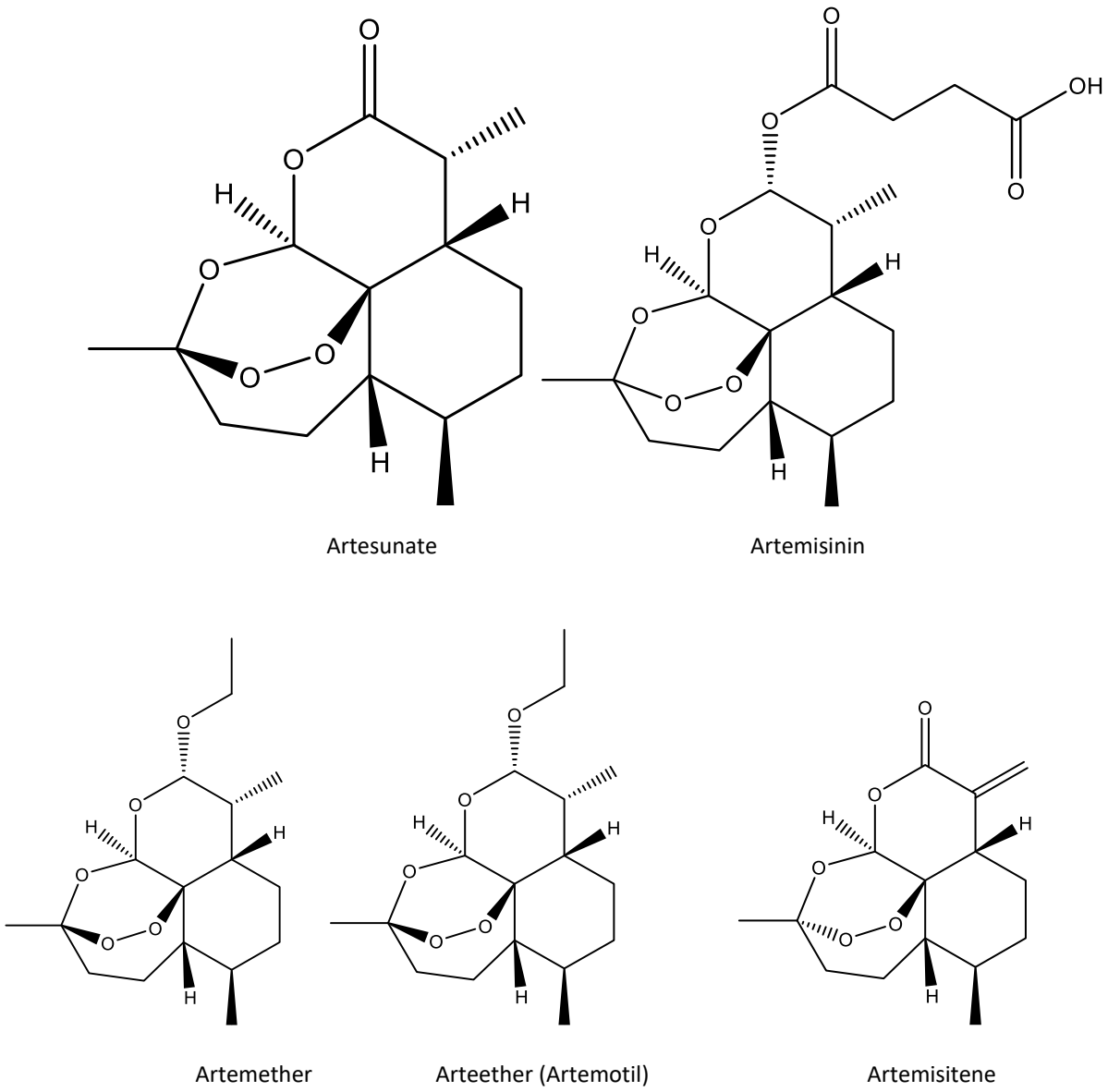

Figure 2 – The chemical structures of artemisinin and its derivatives

Table 1. The SMILES code of all artemisinin derivatives

No.	Derivatives	CANONICAL SMILES
1	Artemisinin	CC1CCC2C(C(=O)OC3C24C1CCC(O3)(OO4)C)C
2	Artesunate	CC1CCC2C(C(OC3C24C1CCC(O3)(OO4)C)OC(=O)CCC(=O)O)C
3	Artemether	CC1CCC2C(C(OC3C24C1CCC(O3)(OO4)C)OC)C
4	Arteether (Artemotil)	CCOC1C(C2CCC(C3C24C(O1)OC(CC3)(OO4)C)C)C
5	Artemisitene	CC1CCC2C(=C)C(=O)OC3C24C1CCC(O3)(OO4)C

Results and Discussion

Computational approaches in biology and chemistry are crucial in many fields impacting life, notably drug design (computer-aided drug design) [[16], [19], [20], [21], [22], [23]]. For the desired molecule to be established and used as a drug, the subsequent step in the computer-aided drug model pipeline to deal with is the pre-clinical optimization. A wide range of *in silico* techniques (e.g., pkCSM, preADMET [24], admetSAR [25]) contribute to the

Table 2. *In silico* calculated physicochemical properties of artemisinin and its derivatives

No.	Derivatives	Formula	MW	HBD	HBA	Log P	NRB	PSA	MR	Log S	Violations
1	Artemisinin	$C_{15}H_{22}O_5$	282.336	0	5	2.75	0	53.99	70.38	-3.42	0
2	Artesunate	$C_{19}H_{28}O_8$	384.425	1	8	2.62	0	100.52	92.46	-3.08	0
3	Artemether	$C_{16}H_{26}O_5$	298.379	0	5	3.19	1	46.15	76.07	-3.85	0
4	Arteether (Artemotil)	$C_{17}H_{28}O_5$	312.406	0	5	3.50	2	46.15	80.88	-4.10	0
5	Artemisitene	$C_{15}H_{20}O_5$	280.320	0	5	2.62	0	53.99	69.90	-3.27	0

goal of calculating ADMET parameters from the molecular structure but change in their computational methodology.

Physicochemical Parameters

The physicochemical property is a molecular attribute which affects efficacy, safety, or metabolism and can be anticipated utilizing Lipinski's rule of five, Veber's rule, or Muegge's rule. In this research, we employed Lipinski's rule to create an orally active medication, which proves the number of hydrogen bonds acceptor (HBA) of less or equal to 10, hydrogen bonds donor (HBD) of less or equal to 5, molecular weight (MW) of less than 500 Da, and Log P of less or equal to 5 [16]. Artemisinin, as a reference chemical, and its synthesized variants are uploaded to the SwissADME website one by one in the standard SMILES format..

Lipophilicity and solubility are the other two major determinants that are examined for optimal medication development. Table 2 summarizes the physicochemical properties of artemisinin and its derivatives predicted by SwissADME. Table 2 indicates that all compounds match each single condition of Lipinski's rule of five and hence totally conform the rule. As a result, all the examined compounds exhibit a favourable drug-likeness profile, as they are predicted to be rapidly absorbed and to have great permeability and bioavailability.

Furthermore, the molecular refractivity of a drug molecule must not exceed 130 $m^3.mol^{-1}$ and must not be less than 40 $m^3.mol^{-1}$ [16]. All derivatives have a $m^3.mol^{-1}$ range of 69.90 - 92.46 $m^3.mol^{-1}$. According to the work of Cerqueira and colleagues, for optimal medication distribution and absorption, PSA readings must be greater than 140 and less than 20 Å, implying that a molecule with PSA larger than 140 Å or less than 20 Å is not a (good) therapeutic candidate. The PSA values of the complete artemisinin derivatives range from 46.15 to 100.52 Å, indicating an excellent therapeutic profile of druggability. Artesunate has the maximum PSA value (100.52 Å) of the further derivatives, allowing for stronger interaction with the receptor.

The sum of rotatable bonds (NRB) in a molecule is a further indicator of its flexibility. When a medication candidate has more than 9 rotatable bonds (too flexible), it is projected that it would not be orally accessible [16]. As a result, artemisinin derivatives are versatile and are expected to be bioavailable. Solubility is another important factor regulating absorption. Many drug development tasks are substantially facilitated by having a soluble molecule, particularly the simplicity of handling and formulation. The compound's solubility is described as insoluble if it is more negative than -10. It varies from weakly soluble to very soluble, with a value ranging from -10 to higher than zero. The weakly soluble chemicals have values between -10 and -6. A value more than -6 and less than -4 is considered somewhat soluble.

The solubility of the compounds varies between -4 and -2. Values between -2 and 0 are extremely soluble, whereas values greater than zero are extremely soluble. Because their solubility values range between -4 and -2, all artemisinin derivatives are soluble.

Prediction of ADMET Properties

Because the design and advancement of new drugs is both laborious and expensive, particularly when it comes to through an experiment assessing the compound's pharmacokinetic outline. In fact, a good computational method can provide the same information as an experimental result rather than one that produces the same outcomes as experimentation. A compound's pharmacokinetic

Table 3. The pharmacokinetic profile and toxicity prediction of artemisinin and its derivatives

Parameter	Artemisinin	Artesunate	Artemether	Arteether (Artemotil)	Artemisitene
Absorption Water solubility (log mol/L)	-3.678	-3.097	-3.927	-3.908	-3.643
Caco-2 permeability (log Papp, cm/s)	1.295	0.863	1.311	1.332	1.291
HIA (%)	97.543	72.19	96.855	96.488	97.69
Skin permeability (log K_p) (cm/s)	-3.158	-2.735	-2.929	-3.345	-3.161
BioS (from SwissADME) (Bioavailability Score)	0.55	0.56	0.55	0.55	0.55
Distribution VDss (human) (log L/kg)	0.457	0.172	0.611	0.448	0.453
BBB permeability (log BB)	0.235	-0.954	0.861	0.253	0.235
BBB perm. (SwissADME)	Yes	No	Yes	Yes	Yes
Metabolism CYP2D6	No	No	No	No	No
CYP3A4	Yes	Yes	Yes	Yes	Yes
Excretion Total clearance	0.98	0.969	1.031	1.068	1.082
Renal OCT2 substrate	No	No	No	No	No
Toxicity AMES test	Yes	No	No	No	Yes
Hepatotoxicity	No	No	No	No	No
Oral rat acute toxicity (LD_{50}, in mol/kg)	2.459	3.112	2.429	2.32	2.449

profile describes its absorption, distribution, metabolism, and excretion (ADME) characteristics.

Through the early phases of drug study, the chemical chosen as a hit must be noncarcinogenic and non-hepatotoxic [[16], [26]]. Toxicity assessment (ADMET, T for Toxicity) predicts mutagenicity and carcinogenicity, among other things. The toxicity endpoints used include Ames toxicity, hepatotoxicity, and oral rat acute toxicity (LD_{50}). The lethal dosage (LD_{50}) was selected since its value and the Globally Harmonized System (GSH) categorization of chemical toxicity allow for the prediction of a substance's toxicity degree. Table 3 contains a list of these ADMET options. The ADMET characteristics of artemisinin and its derivatives demonstrate that they have strong solubility, which indicates their good absorption and enhanced elimination through the urinary system.

The values of human intestinal absorption (HIA) are extremely high-level, indicating that artemisinin and all derivatives except artesunate (72.19) have a more than 95% chance of being absorbed by the human intestine. The Caco-2 cell line is generally utilized as an *in vitro* example of the human intestinal mucosa to calculate drug absorption by assessing the log of the apparent permeability coefficient (log Papp; log cm/s). A chemical is considered to have high-level Caco-2 permeability for the pkCSM webserver if its log Papp value is more than 0.90 cm/s. Table 3 shows that all artemisinin and its derivatives have high Caco-2 permeability, except for artesunate (0.863 cm/s).

The recommended value of skin permeability (log Kp), which is a significant factor for enhancing drug effectiveness and is especially relevant in the creation of transdermal drug administration, is more than -2.5 cm/h [27]. The calculated log Kp values for all compounds differ from -2.735 to -3.345 cm/h. As a result, all artemisinin derivatives are expected to have high skin penetration. The bioavailability score of 0.55 shows that all examined compounds have excellent absorption because they may have greater than 10% bioavailability in rats [28].

The volume of supply at steady state (VDss) and the blood-brain barrier (BBB) are two significant factors to consider when evaluating a drug's capacity to be

dispersed in the body. The higher the VD, the more medication is delivered to tissue rather than plasma. This type is based on the estimate of the steady-state volume of distribution (VDss). Pires et al. observed that a chemical has good dispersion if its VDss value is greater than 0.45 [16]. Except for artesunate, practically all artemisinin derivatives have VDss values of 0.45 or greater (0.172).

In terms of the BBB, which determines a drug's capacity to enter the brain while boosting effectiveness (fewer adverse effects), a molecule is capable of moving across the blood-brain barrier quickly when log BB is greater than 0.3. As a result, because the log BB values of all examined derivatives are less than 0.3, they can only cross the blood - brain barrier marginally [[16], [29]]. Table 3 also includes BBB permeability findings from the SwissADME website, revealing significant differences between pkCSM and SwissADME results.

The parameters of excretion (also known as elimination) consisting of total clearance and OCT2 (organic cation transporter 2) substrate are supplied in the lower portion of table 3. The OCT2 protein transporter plays an important role in the renal uptake, disposition, and clearance of pharmacological molecules. This suggests that overall clearance is directly proportional to renal OCT2.

Assessing a suggested compound's transfer by OCT2 provides significant information about not just its clearance but also its possible contraindications [29]. Amazingly, pKCSM predicts that all artemisinin derivatives are not OCT2 substrates. The toxicity studies show that all artemisinin derivatives are not mutagenic, however, they are hepatotoxic.

Conclusions

The major goal of the current study was to determine the pharmacokinetic profile and toxicity of five artemisinin derivatives utilizing SwissADME and pkCSM *in silico* or computational approaches. A compound's ADME/T characteristics are critical for future study, particularly when assessing its pharmacological actions. The findings of this study offer outstanding guidelines and determine that chemical modifications to artemisinin as a reference compound can enhance its ADMET chracteristics, as all examined derivatives are expected to have a good therapeutic profile of druggability as well as being safe, regardless of some slight weaknesses.

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SwissADME және pkCSM болжау веб-серверлері: Артемизинин және оның туындыларының in Silico ADME/T қасиеттерін дәл және жан-жақты болжауға арналған интеграцияланған онлайн-платформа

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ТҮЙІНДЕМЕ

In vivo ADME сынағы қымбат, уақытты қажет етеді және жануарлардың өміріне қауіп төндіреді, ал silico ADME сынағы қауіпсіз, қарапайым және жылдамырақ. Бұл зерттеу SwissADME және pkCSM силико әдістемелерінде Artemisinin және оның туындыларының Silico ADME/T қасиеттерін анықтау үшін дәл және жан-жақты болжамдарға арналған біріктірілген онлайн платформа ретінде пайдаланылады. Зерттелген қосылыстардың құрылымдары канондық SMILES пішіміне аударылды, содан кейін қосылыстардың әртүрлі қасиеттеріне еркін қол жеткізуді қамтамасыз ететін SwissADME және pkCSM веб-сервер құралдарына жіберілді. Қосылыстың ADME/T сипаттамалары болашақ зерттеу үшін өте маңызды және алынған нәтижелер зерттеушілер үшін пайдалы болады. Сонымен қатар, бұл зерттеудің нәтижелері үлкен нұсқаулық береді және артемизинин сілтеме молекуласының

химиялық өзгерістері оның ADMET мүмкіндіктерін жақсарта алатынын көрсетеді. Бұл жұмыста пайдаланылатын веб-серверлер ақысыз және бірнеше салыстыру сынақтары орындалған pkCSM және SwissADME басқа жиі қолданылатын әдістер қатарынан жақсырақ екенін көрсетеді. Жаңа дәрілік молекуланы жобалау немесе жобалау, ең алдымен, жаңа дәрілік қосылыстың ADME/T ерекшеліктерін білуді талап етеді.

Түйін сөздер: SwissADME, artemisinin туындылары, ChemDraw, кремнийді болжау, pkcs.

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Веб-серверы SwissADME и pkCSM прогнозирования: интегрированная онлайн-платформа для точного и всестороннего прогнозирования свойств In Silico ADME/T артемизинина и его производных

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АННОТАЦИЯ

Тестирование ADME in vivo является дорогостоящим, трудоемким и подвергает риску жизнь животных, тогда как тестирование ADME in silico безопаснее, проще и быстрее. В этом исследовании будут использоваться методологии in silico от SwissADME и pkCSM в качестве интегрированной онлайн-платформы для точных и всесторонних прогнозов для определения свойств артемизинина и его производных In Silico ADME/T. Структуры исследуемых соединений были переведены в канонический формат SMILES, а затем переданы в инструменты веб-сервера SwissADME и pkCSM, которые обеспечивают свободный доступ к различным свойствам соединений. Характеристики ADME/T соединения имеют решающее значение для будущих исследований, и полученные результаты будут полезны исследователям. Кроме того, результаты этого исследования дают отличные рекомендации и показывают, что химические изменения в эталонной молекуле артемизинина могут улучшить его возможности ADMET. Веб-серверы, используемые в этой работе, бесплатны, и несколько сравнительных испытаний показывают, что pkCSM и SwissADME работают лучше, чем ряд других часто используемых методов. Проектирование или создание новой молекулы лекарственного средства в первую очередь требует знания особенностей ADME/T нового лекарственного соединения.

Ключевые слова: SwissADME, производные артемизинина, ChemDraw, силиконовое предсказание, pkcs.

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Engineering and technology

Study of refractory raw materials of the Republic of Kazakhstan

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ABSTRACT

Important aspects of increasing the competitiveness of domestic metallurgy and mechanical engineering are increasing the durability of thermal units and involving non-traditional, cheaper energy resources in production. One of these resources is carbon waste from the aluminum industry - electrode scrap and waste from the carbon lining of electrolyzers. The problem with their use as substitutes for solid fuels (coke coal) in the metallurgical, engineering, and energy industries is fluorine- and alkali-containing salts that impregnate them, destroying the traditional lining of thermal units. The development of effective refractories resistant to fluorine- and alkali-containing corrodents (melts and gases) makes it possible to increase the competitiveness and efficiency of thermal units both through the use of cheaper energy carriers and by increasing the duration of their campaign. An important aspect is the simultaneous disposal of hazardous industrial waste and the reduction of the environmental burden on the ecosphere of the Republic of Kazakhstan. The basis for the development of new refractory materials resistant to fluorine- and alkali-containing corrodents is the analysis of the existing raw material base of the Republic of Kazakhstan and the choice of materials that make it possible to obtain aluminosilicate refractories with increased chemical resistance. In the work, the phase and chemical composition of refractory clays and kaolins of the Republic of Kazakhstan were studied, and their rheological and thermophysical properties were investigated. Selected raw materials for the development of technology for the production of dense aluminosilicate refractory products.

Keywords: aluminosilicate refractories, refractory clays, kaolins, chamotte, plasticity, sintering, open porosity, water absorption.

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Introduction

The most important task of the metallurgical and energy complexes of the Republic of Kazakhstan is to increase the competitiveness of products and industries, with the maximum possible combination of interests of the Republic, its regions, and specific joint-stock companies.

Among the main manufacturing industries of the Republic of Kazakhstan, an important place is occupied by metallurgy (43.7% of GDP) and mechanical engineering (12.3% of GDP) [[1], [2]]., while the metallurgical and machine-building complex remains energy- and resource-intensive, where at least 15% of primary fuel, 35% of electricity, 40% of fossil raw materials are used. Reducing costs through the involvement of secondary resources in the production, and waste disposal is the most urgent task for the development of the industry of the Republic of Kazakhstan.

Currently, the cost of coke fluctuates around $550-600/t, and the cost of anthracite is at the level of $412-418/t at the shipping station [[3], [4]]. Replacing coke with cheaper fuel will improve the technical and economic performance of thermal units.

It should also be considered that the expansion of the use of secondary raw materials, including carbon-containing ones, is an important factor in the efficiency of the entire industry of the Republic of Kazakhstan [[4], [5]]. On the other hand, JSC "Kazakhstan Electrolysis Plant" (KEP), which is part of ENRC (Eurasian Natural Resources Corporation) (Pavlodar), annually generates up to 1,500 tons of waste carbon refractory lining and up to 25,000 tons of cinders of baked anodes [[6], [7]]. with a minimum carbon content of 85 wt. % contaminated with harmful substances from cryolite-alumina melt. The presence of alkaline cations (Na +, K +) and fluorine in the waste do not allow storing them in sludge fields to avoid a negative impact on the environment. The simplest and most efficient way to dispose of such wastes is to use them as fuel instead of expensive and scarce coke in the metallurgical, engineering, or energy industries, where fluorine and alkaline salts will also help to liquefy the slag, saving more on use fluorite slag modifiers [[8], [9]].

At the same time, the presence of alkali cations and fluorine anions in the composition of the melting charge significantly complicates the service conditions of the aluminosilicate lining of thermal units.

The solution to this problem can be the development of the densest (non-porous) aluminosilicate refractories, which requires researching the raw material base of aluminosilicate refractories of the Republic of Kazakhstan, choosing the most promising raw materials, and developing technology for dense refractory products with a maximum mullite content with high chemical resistance.

The production of aluminosilicate should include the production of a dense, durable mullite-containing aggregate (chamotte) with water absorption of no more than 1%, the preparation of a binder of plastic clay, and the production of actually dense products with an open porosity of no more than 5%.

Raw materials for the production of mullite-containing refractories can be [[10], [11]]: clays and kaolin, natural high-alumina raw materials (bauxites, aluminosilicates), and synthetic materials (commercial alumina, tabular alumina, fused corundum, reactive alumina).

At present, deposits of refractory clays, kaolin, and bauxites are known in the Republic of Kazakhstan, and it also has the production of technical alumina [[12], [13]].

The objects of study in this work are three types of refractory clay raw materials: clays of the Arkalyk (AG) and Berinsky (BG) deposits and kaolin of the Alekseevsky (AK) deposits, selected on the basis of an analysis of the physicochemical and technological properties of refractory raw materials the Republic of Kazakhstan.

The Akralyk deposit of refractory clays is located in the Arkalyk district of the Torgai region, in the suburbs of the city of Arkalyk. The characteristic features of the deposit are the unsustainable thickness of the layers, a sharp transition from one variety to another, as well as a predominantly dry type of clay products. Refers to highly basic raw materials with Al_2O_3 content up to 48 wt. % per calcined substance and an average content of coloring oxides (Fe_2O_3 + TiO_2) of 4.6 wt. %. According to the mineral composition, clay is a polymineral raw material with a predominant content of kaolinite and gibbsite. The coarsely dispersed part contains quartz and hematite. Part of the iron is associated with clayey rocks (mainly with gibbsite). The deposit is actively developed and used to produce lumpy refractory chamotte.

The Berlin deposit of refractory clays is located on the border of the Komsomolsky district of the Kostanay region and the Troitsky district of the Chelyabinsk region, 22 km west of the Buskol railway station. A characteristic feature of the deposit is a horizontal reservoir deposit of kaolinite-hydromicaceous clays of variable thickness from 0 to 9 m. It belongs to the main raw material with an Al2O3 content of up to 32 wt. % and an average content of coloring oxides (Fe_2O_3 + TiO_2) of 2.9 wt. %. According to the mineral composition, clay belongs to the monomineralic kaolinite-hydromicaceous raw material. Quartz is presented as an impurity. The birthplace is actively developed and used to produce both fired fireclay and plastic binder clays [[14], [15]].

The Alekseevskoye kaolin deposit is located in the Kokshetau district of the North Kazakhstan region, 33 km north of the city of Kokshetau, southeast of the village of Alekseyevka. A characteristic feature of the deposit is the variable power of the lenses lying in at various levels, a smooth transition of color from white to grayish-

yellowish, as well as a predominantly harsh type of rocks. Along with crackers, there are also loose varieties. Refers to a highly basic raw material with an Al_2O_3 content of up to 44 wt. % and an average content of coloring oxides (Fe_2O_3 + TiO_2) 1.1 wt. %. According to the mineral composition, the raw material is represented by kaolin, quartz, and feldspar impurities. The deposit is being developed and used to obtain enriched kaolin, quartz-kaolinite mixtures and quartz-feldspar concentrate [[16], [17]].

The experimental part

The results of assessing the granulometric composition of clay raw materials by the sedimentation method according to GOST 21216-2014 are given in Table 1 and in (figure 1), allow us to classify Berlin clay as a highly dispersed raw material with a particle content <0.001 mm of more than 99%, and Arkalyk clay and Alekseevsky kaolin as a medium-disperse raw material with a particle content <0.001 mm of less than 60%.

According to the Okhotin diagram, clay from the Berlin deposit belongs to the group of plastic raw materials, clay from the Arkalyk deposit and kaolin from the Alekseevsky deposit belong to the group of low-plastic clay raw materials.

Table 1 - Granulometric composition of the studied raw materials

Raw material	Content of particles, wt. %, size, mm					
	1.00-0.25	0.25-0.06	0.06-0.01	0.01-0.005	0.005-0.001	< 0.001
Arkalyk clay	7.0	1.8	23.2	9.6	17.7	31.6
Berlinsk clay	0	0	12.0	5.2	12.4	70.3
Alekseevskiy kaolin	5.5	14.5	31.6	7.5	24.4	16.5

The mineralogical composition of the clay raw material was evaluated by X-ray phase analysis performed on a Miniflrex 600 diffractometer (CuKα radiation, λ=1.541862 Å, survey interval – 3.00–60.00°, scanning step – 0.02°). The samples were taken without heating in an air atmosphere at a counter speed of 1 deg/min.

Analysis of the obtained data shows that the phase composition of the Arkalyk clay is represented mainly by kaolinite, with an admixture of gibbsite, and quartz and hematite are present as non-plastic impurities; Berlin clay - kaolinite; quartz, hydromica, and montmorillonite; Alekseevsky kaolin - kaolinite; quartz, hydromica and calcium feldspar.

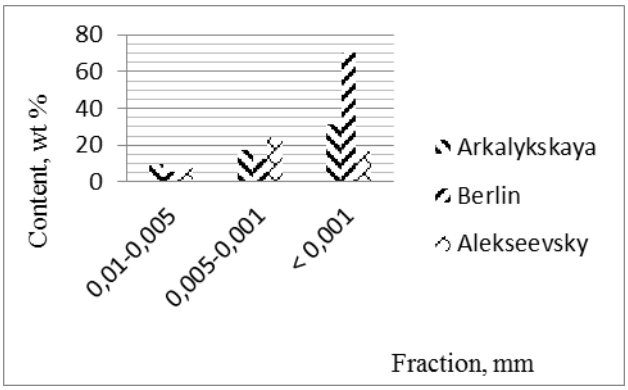

Figure 1 – Histogram of distribution of particles by fractions and raw materials under study

The main technological properties of aluminosilicate raw materials to produce refractories include plasticity, sintering, air and fire shrinkage, and fire resistance [[18], [19]].

The plastic properties of the studied raw materials were evaluated by the Atterberg plasticity number (GOST 21216-2014), which is the difference in the percentage of water at the upper and lower limits of plasticity, i.e., at the boundaries of the transition of clay paste from plastic to fluid and semi-solid condition. The plastic properties of the studied clays are given in Table. 2.

Table 2 - Plasticity of the investigated raw materials

Raw material	Limit fluidity, %	The border rolling, %	Number plasticity	Classification according to GOST 9169-2021
AC	33.33	20.00	13.33	moderately plastic
BC	33.41	15.35	18.06	medium plastic
AK	25.34	12.01	13.27	moderately plastic

AC – Arkalyk clay BC – Berlin clay; AK – Alekseevskiy kaolin

From the analysis of the data in Table 2, it can be seen that Berlin clay belongs to plastic raw materials, and Arkalyk clay and Alekseevsky kaolin belong to moderately plastic raw material.

In the production of products based on clay raw materials, drying is the most important technological factor. The choice of the drying mode is largely determined by the properties of the mass, the shapes, and the sizes of the products.

The determination of the sintering properties of the studied clays was carried out according to GOST 21216-2014. From an average test sample with a particle size of less than 1 mm, mixed with water to the state of a working dough, samples were made in the form of tiles 50 × 50 mm and cubes 25 × 25 mm in a plastic way, dried to an air-dry state, after which they were fired in a laboratory furnace with silicate heaters from 1000 to 1550 C with an interval of 50 C and holding at the final firing temperature for 2 hours.

Table 3 - Technological properties of the investigated aluminosilicate raw materials

Properties	AC	BC	AK
Number plasticity	14	24	5.0
Connectivity, MPa	5.0	5.6	3.5
Binding capacity (% standard sand)	45	65	-
Sensitivity to drying, Kch	1.95	3.4	0.55
Air shrinkage, %	1.4	2.5	0.3
Sintering start temperature, C	1350	1200	1350
Fire resistance,°C	> 1720	1630	>1720

In addition, one of the most important indicators of the quality of refractory clays is fire resistance, and technological properties - binding capacity, sensitivity to drying, and air shrinkage [[20], [21]].

Under certain test conditions, refractoriness depends only on the chemical composition and partly on the mineralogical composition, that is, it characterizes the purity of the raw material under study. The results of calculating the refractoriness and some technological properties of the studied clay raw materials are given in Table. 3.

Conclusions

Features of granulometric (high content of fine particles), chemical and mineralogical compositions, as well as the state of the structure (a disorder of kaolinite) will favorably affect the sintering of the studied aluminosilicate raw materials. At the same time, Arkalyk clay can be recognized as the most promising in the technology of superdense aluminosilicate refractories as a raw material to produce fireclay, the monomineral composition of which and the disorder of kaolinite will favorably affect both its rheological and ceramic properties. The high plasticity of Berlin clay allows it to be used as raw material, both to produce fireclay and for use as a binder clay.

Thus, according to the totality of the considered properties, Arkalyk and Berlin clays, as well as Alekseevsky kaolin, are of practical interest for the production technologies of aluminosilicate refractory materials. At the same time, Arkalyk clay and Alekseevsky kaolin are promising in the technology of aluminosilicate refractory products as a raw material to produce fireclay, and Berlin clay can be used in the technology of aluminosilicate refractories as a binder.

Conflict of interest

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

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Қазақстан Республикасының отқа төзімді шикізатын зерттеу

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ТҮЙІНДЕМЕ

Отандық металлургия мен машина жасаудың бәсекеге қабілеттілігін арттырудың маңызды аспектілері жылу қондырғыларының ұзақ мерзімділігін арттыру және өндіріске дәстүрлі емес, арзанырақ энергия ресурстарын тарту болып табылады. Осы ресурстардың бірі алюминий өнеркәсібінің көміртекті қалдықтары – электрод сынықтары мен электролизерлердің көміртекті қаптамасының қалдықтары. Оларды металлургия, машина жасау және энергетика салаларында қатты отынның (кокс көмірі) алмастырғыштары ретінде пайдалану мәселесі термиялық қондырғылардың дәстүрлі төсемдерін бұзатын, оларды сіңіретін фтор және сілті бар тұздар болып табылады. Құрамында фтор және сілті бар коррозияға (балқымалар мен газдар) төзімді, тиімді, отқа төзімді материалдарды әзірлеу арзанырақ энергия тасымалдаушыларды пайдалану арқылы да, олардың науқанының ұзақтығын ұлғайту арқылы да жылу қондырғыларының бәсекеге қабілеттілігі мен тиімділігін арттыруға мүмкіндік береді. Қауіпті өндірістік қалдықтарды бір мезгілде көму және Қазақстан Республикасының экосферасына экологиялық жүктемені азайту маңызды аспект болып табылады. Құрамында фтор және сілті бар коррозияға төзімді жаңа отқа төзімді материалдарды әзірлеудің негізі Қазақстан Республикасының қолданыстағы шикізат базасын талдау және химиялық тұрақтылығы жоғары алюмосиликатты отқа төзімді материалдарды алуға мүмкіндік беретін материалдарды таңдау болып табылады. Жұмыста Қазақстан Республикасының отқа төзімді саздары мен каолиндерінің фазасы мен химиялық құрамы зерттеліп, олардың реологиялық және термофизикалық қасиеттері зерттелді. Тығыз алюмосиликатты отқа төзімді бұйымдарды алу технологиясын жасау үшін іріктелген шикізат.

***Түйін сөздер*:** алюмосиликатты отқа төзімді заттар, отқа төзімді саздар мен каолиндер, шамот, пластикалық, агломерация, ашық кеуектілік, суды сіңіру,.

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АННОТАЦИЯ

Важными аспектами повышения конкурентоспособности отечественной металлургии и машиностроения является повышение стойкости тепловых агрегатов и вовлечение в производство нетрадиционных, более дешёвых энергоресурсов. Одним из таких ресурсов являются углеродистые отходы алюминиевой промышленности – электродный бой и отходы углеродистой футеровки электролизеров. Проблемой их применения в качестве заменителей твердого топлива (угля кокса) в металлургической, машиностроительной и энергетической промышленностях являются пропитывающие их фтор- и щелочесодержащие соли, разрушающие традиционную футеровку тепловых агрегатов. Разработка эффективных огнеупоров, стойких к воздействию фтор- и щелочесодержащих корродиентов (расплавов и газов) позволяет повысить конкурентоспособность и экономичность тепловых агрегатов как за счёт использования более дешевых энергоносителей, так и за счёт повышения длительности их кампании. Немаловажным аспектом является одновременная утилизация вредных промышленных отходов и снижение экологической нагрузки на экосферу Республики Казахстан. Основой разработки новых огнеупорных материалов стойких к воздействию фтор- и щелочесодержащих корродиентов, является анализ существующей сырьевой базы Республики Казахстан и выбор материалов, позволяющих получить алюмосиликатные огнеупоры с повышенной химической стойкостью. В работе исследованы фазовый и химический состав огнеупорных глин и каолинов РК, исследованы их реологические и теплофизические свойства. Выбраны сырьевые материалы для разработки технологии производства плотных алюмосиликатных огнеупорных изделий.

	Ключевые слова: алюмосиликатные огнеупоры, огнеупорные глины и каолины, шамот, пластичность, спекаемость, открытая пористость, водопоглощение.
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Effect of a complex modified additive on the setting time of the cement mixture

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ABSTRACT
The article presents studies of the effect of a complex modified additive on the setting time of cement paste. The work describes the method of determining the setting time of the cement paste of standard consistency, the selection of the optimal composition of the additive at different percentages of its components, allowing accelerating the setting time. In this work, the authors used a complex modified additive including alkali (caustic soda NaOH), post-alcohol bard (alcohol production waste), and hardening accelerator (gypsum) in different percentages. Performed a comparative study of the effect of additives on changes in setting time. The analysis suggests that the additive in the optimal amount leads to changes in the setting time compared with the reference sample, but within the standards. It is shown that the combined use in the composition of a complex modified additive, having well-compatible mechanisms of their influence on the processes of hydration, setting, and hardening of the cement paste, mutually complements and enhances the effect of each ingredient of the additive. Increasing the concentration of the complex modified additive in the cement paste not only affects the liquefaction process but also reduces the setting time and hardening of the cement paste.

Keywords: cement paste, hardening accelerator, post-alcohol bard, complex modified additive, setting time.

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Introduction

In modern conditions of development of construction in Kazakhstan on the background of rapidly developing technologies, the question is raised about the introduction of new quickly recouped technologies, which are based on the extensive use of local raw materials and new technical methods in order to obtain highly efficient materials.

The basis of modern concrete technology is the creation of high-quality artificial stone, characterized by high dispersion, a small imperfection, and structural stability. Improvement in the quality of concrete compositions can be achieved both by the use of chemical additives, and when using local components to create a new generation of concrete, which is a highly relevant objective of concrete technology. A new generation of concrete is high-tech, high-quality, multi-

concrete mixtures and compositions with additives that preserve the required properties at a service in all operating conditions. Growing multicomponent concretes are due to significant systemic effects, which enables to manage of the structure formation at all stages of the technology, ensuring receipt of composites of "directed" quality, composition, structure, and properties [[1], [2], [3], [4], [5], [6], [7]].

Modern cement concrete is a composite building material, which can be produced with the specified characteristics for certain service conditions by modifying its structure and properties with various admixtures [[8], [9], [10], [11]]. This provides the material with durability, performance reliability, ecological safety, and applicability in any service conditions [12].

The present economic constraints require acceleration in the speed of work in the construction industry. The need for concrete with sufficient strength at a very early age is in many situations very important. Such concrete is obtained through the use of some admixtures such as water-reducing superplasticizers, set accelerators, and hardening accelerators. Standards about admixtures for concrete and mortar differentiate between set and hardening accelerators namely:

– Set accelerator is defined as an admixture that decreases the initial setting for the transition of the mix from the plastic to the rigid state.

– Hardening accelerator is defined as an admixture that increases the rate of development of early strength in the concrete with or without affecting the setting time [13].

A wide range of domestic and imported chemical additives makes it difficult to make a choice. Concrete manufacturers seek to improve its properties by modification while reducing the consumption of cement, reducing energy costs in the production of reinforced concrete, and minimizing the cost of additives under stable terms of their quality. It is quite a challenging task that can be solved using a variety of waste and coproducts of many industries as mineral and chemical modifiers of concrete [[14], [15], [16], [17], [18]]. Most often, the properties of concrete are modified by chemical additives. At the same time, optimal characteristics, such as strength, workability, and so on are achieved at a certain critical dose of the chemical modifier, after which the effect falls off [[19], [20], [21], [22], [23]].

The setting of concrete is identified as the transition of fresh concrete from the liquid phase to the solid phase. It is important to identify this phase change to plan to transport and place concrete [24].

It is known that the main purpose of plasticizing additives is to increase workability, which provides a reduction in energy and labor costs for laying. On the other hand, the use of such additives allows, by reducing the water-cement ratio, while maintaining the given mobility of the mixture, to increase significantly the strength and durability of products. In addition, the introduction of plasticizers can affect the setting time and hardening kinetics of cement, increase strength, frost resistance, and water resistance of concrete due to water reduction, as well as reduce cement consumption and energy consumption for the production of concrete, mortars, etc. Therefore, the development of compositions of modified heavy concretes is relevant for general construction purposes with improved technological parameters by using effective modifying additives.

The composition of the complex modified additive includes gypsum (hardening accelerator), alcohol production waste (post-alcohol bard), and alkali (caustic soda, NaOH) to neutralize the acidity of post-alcohol bard, this is due to the fact that the purification is not done well and post-alcohol bard retains acidity. Thus, the combined use of gypsum, alkali (caustic soda NaOH), and plasticizer (post-alcohol bard) improve the physical and mechanical properties. The post-alcohol bard or sulfite-yeast bard is a waste product of alcohol production. After distillery bard is a valuable product, which can be used in solving the problems of environmental pollution and obtaining cheap raw materials.

The aim of the study is to develop a complex modifying additive (CMA) and study its effect on the physical and mechanical properties of cement systems.

As part of this study, a set of laboratory tests to assess the physical and mechanical properties of experimental samples, followed by a comparative analysis of changes in the qualitative characteristics of the cement and the effect of a complex modifier on it. However, within the framework of this article the results of the first stage of the study will be presented, exactly the effect of the variable composition of CMA on the setting time of the dough of standard consistency, as well as its effect on the flow of the mixture.

In order to achieve the goal, the following tasks were solved:

1. Selection of the optimal composition of the additive at different percentages of its components

2. Preparation of samples of variable composition of additive components in laboratory conditions

3. Laboratory research of physical and mechanical properties of experimental samples.

Experimental technique

To conduct research and fulfill the set goal and objectives we used materials that meet the requirements and standards.

Cement. Raw materials were taken according to the geographical location of the factories of manufacturers, as well as the qualitative indicators of the material. Portland cement of M400 grade was used as a binder, due to the availability of this binder.

Modifying additive. The main component of the modifying additive is post-alcohol bard - the residue after the distillation of alcohol from brewers, ethanol production waste, which meets the requirements of TU 1110 RK 00393896 OJSC -01-2003, in amounts of 2.5%, 5.0%, 7.5%, 10%, a multiple of 2.5%. It is supplied in liquid form by the manufacturer JSC “Aydabul distillery”.

Hardening accelerator - gypsum which accelerates the hardening process in amounts of 1%, 1.5%, 2.0%, 2.5% of cement mass, a multiple of 0.5%.

At the first stage, the joint effect of the optimal composition of CMA on the setting time of the paste of standard consistency (beginning and end of setting) was studied, and determined in accordance with the requirements of GOST 310.3-76 types of cement. Methods for determining the normal thickness, timing of setting and volume change uniformity". The consistency, initial and final setting of the cement paste were investigated using a Vica device, as shown in Figure 1. Setting time of cement paste is one of the most important parameters of the concrete mixture, as they determine the further performance properties of the material.

The setting time test was carried out using six mixing proportions (17 samples) consisting of Portland cement, additive, and water. The sample (Type 1) containing only cement and water was called the reference sample, while the proportion of additives was varied as shown in Table 1. The reference sample (100% Portland cement, which is equivalent to 350 g and water weight of about 105 g). Consumption of raw materials of mortar samples (required for measuring the setting time) is presented in Table 1.

Table 1 – Composition of compared samples

Type of sample	Cement, g	Gypsum, g	Post-alcohol bard, g	Caustic soda, g	Water, g
Type 1 Reference sample	350	-	-	-	105
Type 2-1	346.5	3.5	8.75	0.4375	95.8125
Type 2-2	346.5	3.5	17.5	0.875	86.625
Type 2-3	346.5	3.5	26.25	1.3125	77.4375
Type 2-4	346.5	3.5	35	1.75	68.25
Type 3-1	344.75	5.25	8.75	0.4375	95.8125
Type 3-2	344.75	5.25	17.5	0.875	86.625
Type 3-3	344.75	5.25	26.25	1.3125	77.4375
Type 3-4	344.75	5.25	35	1.75	68.25
Type 4-1	343	7	8.75	0.4375	95.8125
Type 4-2	343	7	17.5	0.875	86.625
Type 4-3	343	7	26.25	1.3125	77.4375
Type 4-4	343	7	35	1.75	68.25
Type 5-1	341.25	8.75	8.75	0.4375	95.8125
Type 5-2	341.25	8.75	17.5	0.875	86.625
Type 5-3	341.25	8.75	26.25	1.3125	77.4375
Type 5-4	341.25	8.75	35	1.75	68.25

Figure 1 – Determination of the setting time of the cement paste on the Vica device

Results and Discussion

On the diagram (figure 2) of the setting times, the first peak corresponds to the beginning of setting, the second to the end. The arrangement of the types of compositions compared in ascending order from bottom to top, where red corresponds to type 1 - the control sample (reference sample) without additives, with respect to which comparisons are made. Setting the time of cement paste is one of the indicators that characterize the manufacturability of the preparation of cement concrete mixtures. The introduction of additives can reduce the time between the beginning setting and the end of the setting. This is of practical interest, as the introduction of additives - in small quantities will accelerate the process of making products.

The choice of additive was determined based on the main mechanism of their action. Post-alcohol bard has hydrophilic and hydrophobic properties. Post-alcohol bard has a plasticizing effect, which leads to obvious consequences, i.e. reducing the w/c ratio and maintaining mobility of the concrete mixture, increasing workability, and giving strength and durability to structures. This additive wets the surface of cement particles, thus providing a decrease in the w/c ratio. The combined use of a complex additive, which has well-compatible mechanisms of their influence on the processes of hydration, setting, and hardening of the cement mass, mutually complements and enhances the effect of each ingredient of the additive.

It may be noted that in the case of the effect of CMA on the time of setting of cement paste to a greater extent associated with the dosage. The effect of the studied compositions may be due to the presence in their composition gypsum, which traditionally are hardening of cement setting and additives that form shells on the cement particles, preventing the penetration of water for hydration.

According to Table 1, it is the sodium compounds indicator that changes with changes in the quantitative indicator of the post-alcohol bard. Sodium compounds were used in small quantities (previous studies have revealed the optimal concentration), exactly in the amount to get a neutral medium, i.e. to stabilize the hydrogen index (pH) of the additive. Consequently, the sodium compound values do not become uneconomical for cement systems production. The hydrogen index needs neutral because increased acidity slows down the setting time of the concrete.

It can be seen from the test results in Figure 1 that not only the setting time is reduced, but also its end. The complex additive has a coarse effect on the system, that is, when increasing the dosage sharply reduces the process of cement setting compared with samples without additives (Type 1), and intensifies the hardening of cement in the early hydration time at the age of 3 and 7 days.

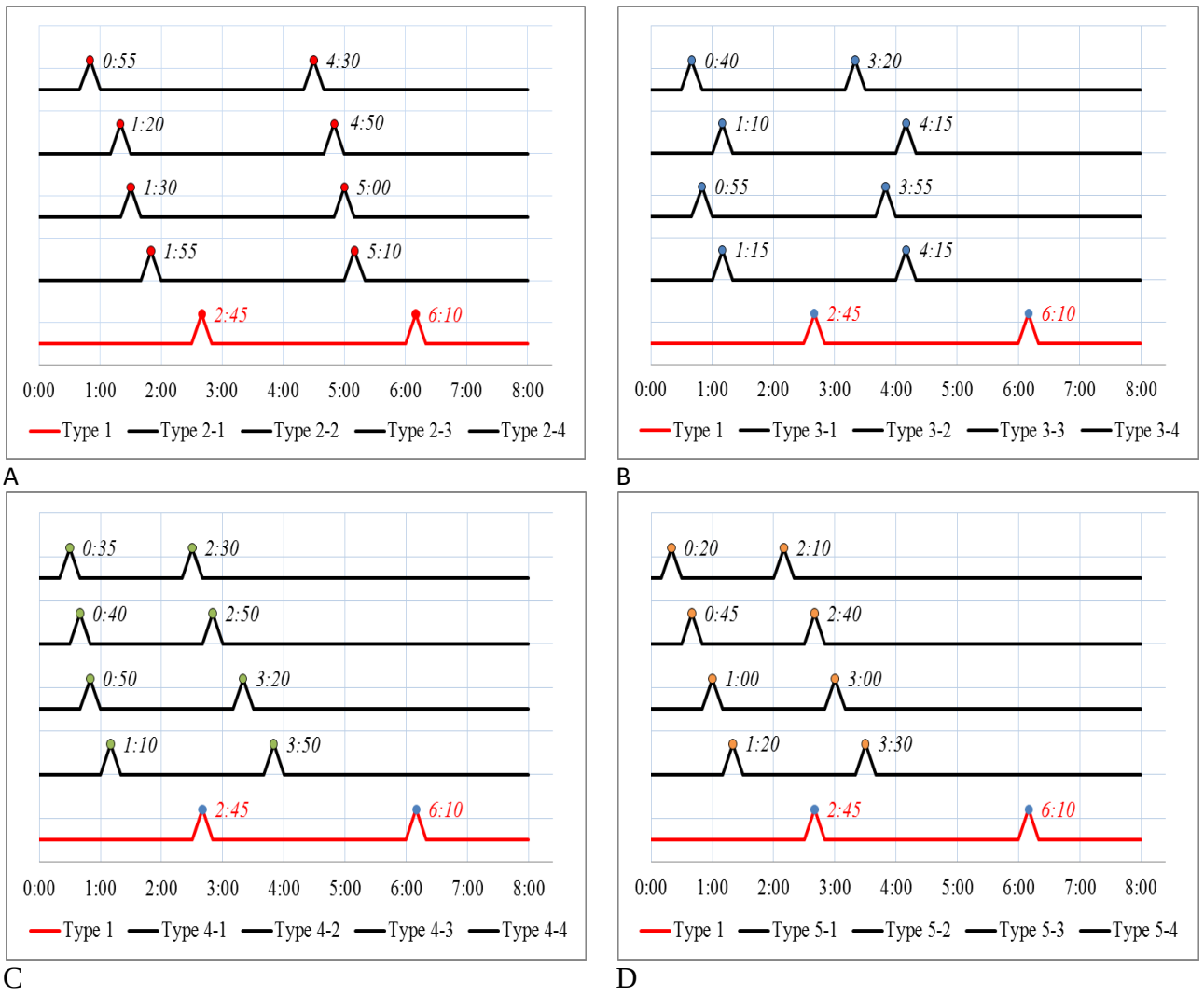

Figure 2 – Results of testing the setting time of the cement mixture

According to the results (figure 2) of the study determined the setting time of the compositions for:

Type 1. The beginning of setting of the cement mass without additives is 2 h 45 min, and the end of setting 6 h 10 min.

Type 2-1. When adding the composition with 1.0 % gypsum (by weight of cement of the standard) and 2.5% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 55 min, and the end of setting time is 5 h 10 min, respectively.

Type 2-2. When adding the composition with 1.0 % gypsum (by weight of cement of the standard) and 5.0% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 30 min and the end of setting time is 5 h 00 min, respectively.

Type 2-3. When adding the composition with 1.0 % gypsum (by weight of cement of the standard) and 7.5% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 20 min and the end of setting time is 4 h 50 min, respectively.

Type 2-4. When adding the composition with 1.0 % gypsum (by weight of cement of the standard) and 10 % additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting is 55 min and the end of setting time is 4 h 30 min, respectively.

Type 3-1. When adding the composition with 1.5 % gypsum (by weight of cement of the standard) and 2.5 % additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 15 min and the end of setting time 4 h 15 min, respectively.

Type 3-2. The addition of 1.5 % gypsum (by weight of standard cement) and 5.0% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 55 min and the end of setting time is 3 h 55 min, respectively.

Type 3-3. When adding the composition with 1.5 % gypsum (by weight of cement of the standard) and 7.5 % additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 10 min and the end of setting time is 4 h 15 min, respectively.

Type 3-4. When adding the composition with 1.5 % gypsum (by weight of cement of the standard) and 10 % additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 40 min and the end of setting time is 3 h 20 min, respectively.

Type 4-1. When adding the composition with 2.0 % gypsum (by weight of cement of the standard) and 2.5 % of additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 10 min and the end of setting time is 3 h 50 min, respectively.

Type 4-2. When adding the composition with 2.0% gypsum (by weight of cement of the standard) and 5.0% of additive (post-alcoholic bard) is introduced into the cement paste, the beginning setting time is 50 min and 3 h 20 min for the beginning and the end of setting time is 3 h 20 min, respectively.

Type 4-3. When adding the composition with 2.0% gypsum (by weight of cement of the standard) and 7.5% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 40 min and the end of setting time is 2 h 50 min, respectively.

Type 4-4. When adding the composition with 2.0% gypsum (by weight of cement of the standard) and 10% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 35 min and the end of setting time is 2 h and 30 min, respectively.

Type 5-1. When adding the composition with 2.5% gypsum (by weight of cement of the standard) and 2.5% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 20 min and the end of setting time is 3 h 30 min, respectively.

Type 5-2. When adding the composition with 2.5% gypsum (by weight of cement of the standard) and 5.0% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 1 h 00 min and the end of setting time is 3 h 00 min, respectively.

Type 5-3. When adding the composition with 2.5% gypsum (by weight of standard cement) and 7.5% masterbatch (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 45 min and the end of setting time is 2 h and 40 min, respectively.

Type 5-4. When adding the composition with 2.5% gypsum (by weight of cement of the standard) and 10% additive (post-alcohol bard) is introduced into the cement paste, the beginning of setting time is 20 min and the end of setting time is 2 h 10 min, respectively.

As can be seen from the results, the maximum plasticizing effect of the additive in mortar cement mixture is achieved at a concentration of 5-10% (post-alcohol bard) and 1.5-2.5% (gypsum) in relation to the mass of cement at w/c ratio = 0.3. The introduction of the additive into the mortar mixture has a plasticizing effect, which allows reducing the water-cement ratio by 10% as compared to the control composition. The effect of plasticizing cement paste is explained by the adsorption of hydrophobic molecules on the surface of dispersed cement particles. The setting time of mortar mixtures significantly depends on the concentration of the additive in them. Increasing the additive concentration in the cement mixture up to 10% (post-alcohol bard) and up to 2.5 % (gypsum) of the cement mass not only affects the process of liquefaction of the cement mortar, but reducing the time of setting and hardening of the cement paste, but also increases the compressive strength of the cement stone.

Analyzing the graph in Figure 2, the authors concluded that the additives have a different effect: with the addition of additives in cement, there is a beginning of setting at about 20 min - 1 h 55 min, while in the without additives (Type 1) cement begins to set after 2 h 45 min. Taking into account it can be argued that these additives have a higher efficiency than the without additives (Type 1) composition. Analyzing the graph in Figure 2, it can be noted that the additives have the same effect, but with different efficiencies. With the introduction of a complex additive setting time is reduced by up to 30% compared with pure cement. In this case, obviously, the duration of the cement paste remains unchanged, as the setting time is reduced by reducing the time of the end of the setting. At the same time, the interval between the beginning and the end of the setting is reduced by

40 %. This index is important for dry construction mixtures, as it enables cement-containing compositions after hardening with water to keep plasticized state during adjustable time intervals depending on additive content and to set quickly after application, which results in accelerated speed of construction works.

The question of fast setting is highly topical because the tendency of reduction of terms of construction goes at the expense of fast stripping. Influences of alcohol production waste consumption up to ≈ 10% showed the rationality of this range, i.e. with an increasing quantitative indicator of post-alcohol bard we do not get the specified effect. The maximum optimal range was determined by optimizing the composition. The additive range was determined by a complex of studies such as strength, water absorption, and other indicators that affect the workability of concrete, so within this article only the indicators of the setting time are shown.

The amount of the additive introduced was set from the condition of the greatest effect of accelerating hardening, as well as obtaining the maximum increase in the strength of the samples compared to their counterparts without additives. The results obtained show that CMA acts as a good hardening accelerator. Consequently, this additive can be used as a setting time regulator.

Conclusions

Based on the experimental studies, the following conclusions can be made that the complex modifying additive (CMA) has a better water - reducing effect than the without additive composition (Type 1). The addition of the additive (CMA) tended to accelerate both initial and final setting times. The addition of the additive (CMA) gave the best results because it delayed the initial setting time from (1 h 55 min) to (20 min) and the final setting time from (5 h 10 min) to (2 h 10 min). According to the results of studies, the authors concluded that the introduction of additives - plasticizers (post-alcohol bard) reduces the amount of water by 35%. Thus, the experiments showed that when mixing cement paste with CMA there is a plasticizing effect on cement paste and a significant reduction of the time at the beginning and end of the setting time of cement. This is of practical interest, as the introduction of additives will accelerate the process of making products.

Studies have shown that the use of gypsum in combination with sodium compounds and post-alcohol bard significantly increases the physical and mechanical properties, creating a synergistic effect.

The use of plasticizers in concrete technology allows to reduce porosity and increase the strength of samples. The use of plasticizers in the concrete mixture significantly increases the resistance and durability of heavy concrete. Consequently, the use of a complex modifying additive allows you to purposefully change the structure of concrete and thus significantly increase the complexity of physical and mechanical parameters and durability of modified concretes.

Conflict of interest

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

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ТҮЙІНДЕМЕ

Мақалада цемент қамырының ұстасу мерзіміне кешенді модификацияланған қоспа әсерінің нәтижелері көрсетілген. Жұмыста қарапайым консистенциядағы қамырдың ұстасу мерзімін анықтау әдістемесі, ұстасу уақытын үдетуге мүмкіндік беретін компоненттердің әртүрлі пайыздық қатынасуында оңтайлы қоспа құрамын таңдау сипатталған. Бұл жұмыста авторлар құрамында әртүрлі пайыздық қатынаста сілті (каустикалық сода NaOH), этил спирт өндірісінің қалдығы (спирттік кейінгі барда) және қатуды реттегіш (гипс) бар кешенді модифицирленген қоспаны қолданды. Ұстасу мерзімінің өзгеруіне қоспаның әсер ететіндігіне салыстырмалы зерттеу жасалды. Талдау негізінде оңтайлы мөлшердегі қоспа бақылаумен салыстырғанда белгілі бір шекте ұстасу мерзімінің өзгеруіне алып келеді деуге болады. Кешенді модификацияланған қоспа құрамында цемент қамырының қатаюы мен ұстасуы, гидратация үрдістеріне әсер ететін жақсы үйлесімді тетіктері бар, оларды толықтырады және ондағы әрбір ингредиенттің әрекетін күшейтеді. Цемент қамырында кешенді модифицикацияланған қоспа мөлшерін арттыру сұйылту үрдістеріне әсер етіп қана қоймай, сондай-ақ цемент массасының қатаюы мен ұстасу мерзімінің қысқаруына алып келеді.

Түйін сөздер: цемент қоспасы, қатуды үдеткіш, спирттік кейінгі барда, кешенді модификацияланған қоспа, ұстасу мерзімі.

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Влияние комплексной модифицированной добавки на сроки схватывания цементной смеси

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АННОТАЦИЯ

В статье приведены результаты влияния комплексной модифицированной добавки на сроки схватывания цементного теста. В работе описана методика определения сроков схватывания теста стандартной консистенции, подбор оптимального состава добавки при разном процентном соотношении его компонентов, позволяющие ускорить время схватывания. В данной работе авторы использовали комплексную модифицированную добавку, включающий в своем составе щелочь (каустическая сода NaOH), послеспиртовую барду (отходы спиртового производства) и регультор твердения (гипс) в разных процентных соотношениях. Выполнено сравнительное исследование влияния добавки на изменение времени схватывания. Анализ дает основание утверждать, что добавка в оптимальном количестве приводит к изменениям времени схватывания по сравнению с эталонным образцом, но в пределах норм. Показано, что совместное использование в составе комплексной модифицированной добавки, обладающей хорошо совместимыми механизмами их влияния на процессы гидратации, схватывания и твердения цементной массы, взаимно дополняет и усиливает действие каждого ингредиента добавки. Увеличение концентрации комплексной модифицированной добавки в цементную смесь не только воздействует на процессы разжижения, а также на сокращения времени схватывания и твердения цементной массы.

Ключевые слова: цементная смесь, ускоритель твердения, послеспиртовая барда, комплексная модифицирующая добавка, сроки схватывания.

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Metallurgy

Effect of micro-arc oxidation on the properties of aluminum alloy samples

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ABSTRACT
Currently, modern manufacturing industries impose special requirements on structural materials such as aluminum, titanium, and their alloys. Various methods are used to improve the physicomechanical and corrosion properties of these materials. One of the promising ways to modify the surface in order to give it multifunctional properties is the treatment of micro-arc oxidation. A distinctive feature of the process is the formation of the oxide coatings on valve metals because of exposure to micro-arc discharges. At the same time, coatings with unique properties are formed. However, the effect of the micro-arc oxidation process on the properties of the base material has been little studied. The purpose of this work is to study the effect of the micro-arc process, implemented in pulsed mode, on the properties of oxide layers, and the base material. Modification of the alloy surface was carried out in the anode mode, with small values of the duration of the anode current pulse. An alkaline electrolyte solution was used as the electrolyte. Studies of the microhardness of the oxide layer, as well as the metal layer from the interface – oxide layer /metal deep into the metal, have shown that micro-arc discharges affect not only the properties of the oxide layer but also structural changes in the thickness of the metal. It is shown that the formed oxide coating is characterized by high microhardness. The oxide coatings obtained at the duration of the anode current pulse of 100 μs – 200 μs are wear-resistant, the coatings do not collapse, and do not wear to the ground under the accepted test conditions.

***Keywords**:* valve metals, plasma electrolytic oxidation, microplasma discharges, oxide coating, microhardness, transition layer.

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Introduction

Structural materials are widely used in many industries. Improvement of the physical and mechanical properties of materials can be carried out in various ways. The method of plasma spraying (PS) is used to create multifunctional coatings in various industries [[1], [2]]. With PS, the coating is formed by the impact of molten particles on the surface of the material. As a result, there are changes in the structure of the surface layers of the metal, and its mechanical characteristics [[3], [4]]. *However, a low adhesive strength of the coating is observed while using this method. Currently, the micro-arc oxidation (MAO) method is increasingly used to modify the surface of various alloys.* A distinctive feature of this process is the formation of many microplasma discharges on the surface of the processed material, which have a significant effect on the properties of the coating [[5], [6], [7]]. The oxide-containing coatings formed during MDO are characterized by high wear resistance [[8], [9]], corrosion resistance [[10], [11], [12], [13]], heat resistance [14]. Biologically active coatings obtained by this method are also well known [[15], [16], [17]]. When applying this method, close attention is paid to the effect of microplasma discharges on the formed oxide coating. At the same time, it should be noted that microplasma discharges can affect the processed material from

the interface of the oxide layer-metal deep into this material. It is known that high temperatures of 6000 °C and higher can develop in the area of the base of the combustion of micro-discharges [[18], [19]].

The MAO method, which is carried out in pulse mode, is also energy-saving. At the same time, the properties of oxide layers in their physicomechanical and other characteristics are not inferior to the properties of coatings obtained under stationary conditions [[20], [21]]. This work aims to study the effect of the micro-arc process, implemented in pulsed mode, on the properties of oxide layers, the base material.

Experimental part

Flat samples made of aluminum alloy A0 were used for the research. The samples were processed in pulse mode. The duration of the anode current pulse was: 50 microseconds, 100 microseconds, 150 microseconds, and 200 microseconds. The frequency of the anode pulses was maintained at 50 Hz. The polarizing voltage was equal to 300 V; the current density was about 115 A/dm^2. Pretreatment of samples included the following operations: grinding, degreasing, and drying. Since the MAO process proceeds with the release of heat, it is necessary to ensure the cooling of the electrolyte solution. Various types of cooling are used for this purpose. In this work, during the research, the electrolyte in the bath was cooled by a water cooling jacket (Figure 1). Running cold tap water flowed through the cooling jacket.

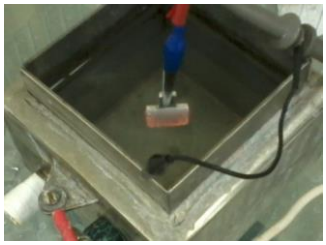


Figure 1 - Electrochemical bath with water cooling jacket

The bath body was used as the cathode, the anode served as the processed samples. Processing time 1200 sec. The electrolyte temperature was maintained within 20 °C – 25 °C. A solution of the composition was used as an electrolyte solution: sodium phosphoric acid 2- substituted, 12 aqueous (40 g/l), sodium tetraborate 10 aqueous (30 g/l), boric acid (22 g/l), ammonium fluoride (10 g/l). To prepare the electrolyte solution were used chemicals of the brand "chemically pure", and "pure for analysis". Electrolytes were prepared in distilled water.

The thickness of the oxide coatings was measured using a NOVOTEST TP-1 thickness gauge with an NF2 sensor. This work shows the arithmetic mean value of the coating thickness based on the results of seven measurements on both sides of the sample.

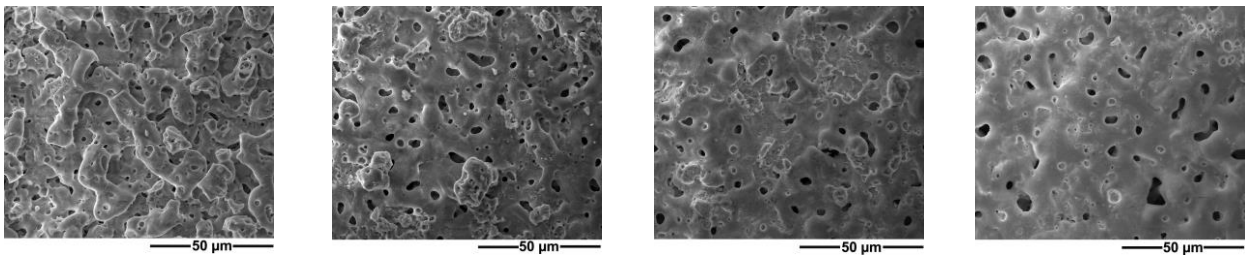
The microhardness of the oxide layers and the transition layer deep into the metal was studied on a NanoHardness Tester on pre-prepared grinds. When testing samples with an oxide coating, indentation of the indenter with a diamond tip occurred at a load of 20.0 mN. After the load reached the maximum value, the indenter began to unload. That is, the load acting on it was gradually reduced to zero, and it returned to its original position. The experimental data were processed based on the measurement results of at least 3 prints obtained under the same experimental conditions.

To evaluate the tribological characteristics were obtained the friction quotient curves on the THT-S-AX0000 tribometer. Conditions for tribological tests: load 1.0 N; number of revolutions 1000; linear velocity 2.5 cm/s; temperature 25°C; air humidity 50%.

Morphological studies were carried out on a Quanta 200 3D scanning electron microscope. The porosity of the coatings was determined by the number of pores per surface unit, and the planimetry method was used to evaluate their shapes by processing micrographs of the surface of oxide coatings [22].

Results and discussion

The structure of the oxide layers formed at different durations of the anode current pulse is porous (Figure 2). The pores are predominantly rounded and oval in shape. The thickness of the oxide layers is 8.0 microns, 11.0 microns, 20.0 microns, 27.0 microns, obtained respectively at the duration of the anode current pulse of 50.0 microseconds, 100.0 microseconds, 150.0 microseconds, 200.0 microseconds. The coatings are dense, evenly distributed in thickness over the entire surface of the sample.



50.0 microseconds 100.0 microseconds 150.0 microseconds 200.0 microseconds

Figure 2 – Microstructure of the surface layer of coatings at different values of the duration of the anode current pulse

Table 1 - Microhardness measurement data for samples processed at different durations of the anode current pulse

Depth along the transverse section, microns	Microhardness of the oxide layer, MPa	Depth along the transverse section, microns	Microhardness of metal, MPa
1. MAO at the duration of the anode current pulse of 50 microseconds (the thickness of the oxide layer is 8.0 microns)			
0	1523.0	15	1899.0
5	1622.0	20	1997.0
10	1032.0	25	1936.0
		30	1636.0
		40	1372.0
2. MAO at the duration of the anode current pulse of 100 microseconds (the thickness of the oxide layer is 11.0 microns)			
0	1894.0	15	1467.0
5	1889.0	20	1470.0
10	1887.0	25	1046.0
		30	964.0
		40	884.0
3. MAO at the duration of the anode current pulse of 150 microseconds (the thickness of the oxide layer is 20.0 microns)			
0	3776.0	25	1997.0
5	3808.0	30	1689.0
10	4891.0	40	1230.0
15	5330.0	55	978.0
20	2863.0		
4. MAO at the duration of the anode current pulse of 200 microseconds (the thickness of the oxide layer is 27.0 microns)			
0	33344.0	30	1914.0
5	30579.0	40	1493.0
10	29661.0	55	1167.0
15	33744.0	60	1004.0

The coatings are characterized by a surface porosity of 6% to 14%. Pores are known to form because of exposure to microarc discharges [23]. Figure 2 shows that as the result of the thickness of the coating increases with an increase in the duration of the anode pulse, some pores become overgrown, and the coating becomes more uniform. This trend is in good agreement with the earlier research conducted by the references [[24], [25]]. When studying the microhardness of the transverse section of the treated samples along the thickness of the coating and from the coating/metal interface deep into the metal, the effect of micro-arc discharges was found not only on the properties of the oxide layers formed but also on structural changes in the thickness of the metal from the oxide/metal interface. Table 1 shows the results of measuring the microhardness of the transverse section of samples from the zero surface (the oxide layer) deep into the metal during the processing of MAO, depending on the duration of the anode current pulse. For comparison, the microhardness of an uncoated aluminum sample was experimentally established, which was 261 MPa.

According to the available model concepts [26], during the microplasma process, both the coating and the metal are exposed to temperature. Structural changes occur in the oxide layer and in the thickness of the metal. High current densities in the micro-arc channel lead to phase structural changes in the surface layers of the metal, to metal melting. At the same time, a part of the metal can be ejected through the channel (pore) to the outside. Then the ejected metal is converted into oxide and embedded in the coating. With the termination of the combustion of the micro-discharge, the oxides formed because of the process fill the breakdown channel. The pores become overgrown, their diameter decreases, and in some cases, they are completely closed by the products of plasma chemical reactions. The molten metal at the bottom of the pores undergoes a crystallization process.

Structural changes also depend on the thickness of the coating in the oxide layer. The thin oxide layers are formed at short durations of the anode pulse. In thin coatings, the cooling rate is higher, so the structural changes under the influence of temperature are less. In thicker coatings, temperature influences act for a longer time. Significant structural changes occur both in the oxide layer and in the metal. Comparative microhardness data (Table 1) confirm this. Thus, at the duration of the anode current pulse of 200 microseconds, the thickness of the oxide layer is 27.0 microns, and the microhardness is significantly higher than that of the oxide layer obtained at the duration of the anode current pulse of 50 microseconds, in which the coating thickness is 8.0 microns.

Part of the heat released because of micro-discharge penetrates deep into the metal. As a result, the tension in the metal is removed and the metal is released. As a result of structural changes in the aluminum alloy, under the influence of MAO, its microhardness from the oxide layer/metal interface deep into the metal is higher than the microhardness of aluminum not treated with MAO. As the distance deep into the metal from the oxide layer/metal interface increases, the microhardness decreases and eventually will be equal to the microhardness of the aluminum alloy (Figure 3).

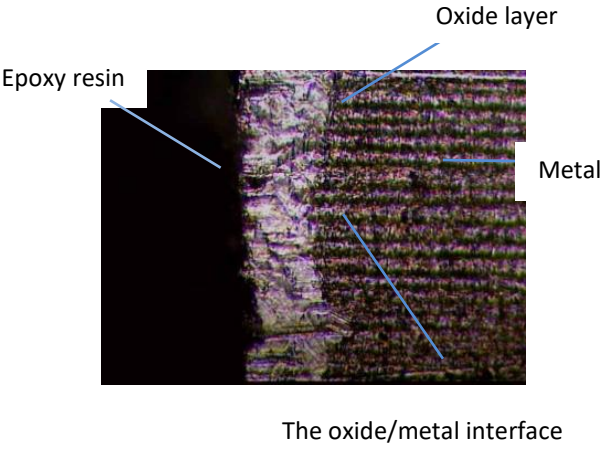


Figure 3 – Microplate of the sample processed by MAO

In previous studies, the effect of the micro-arc process on the crystal structure of the metal from the coating into the depth of the base material was observed [27]. According to the authors, a bath of molten metal is formed in the zone of thermal impact of microarc discharges at the interface of the metal oxide layer. With the termination of the micro-discharge, the process of metal crystallization begins. The metal bath cools down, while the bulk of the heat is withdrawn deep into the metal, affecting its structural changes [27].

Studies in the field of mechanics of contact interactions in the surface layers of rubbing materials show that the material in these layers changes its physical state during friction, the process of wear occurs. Three stages of wear are known (Figure 4). The first section of the curve

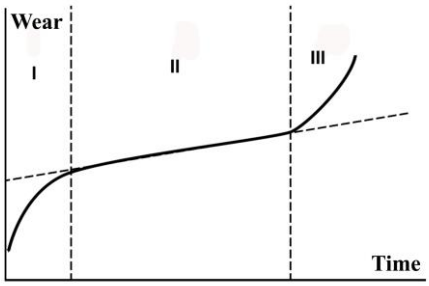
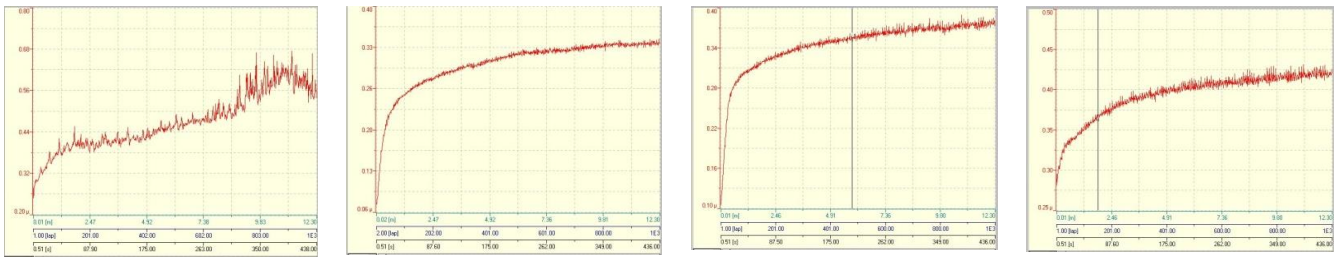


Figure 4 - Stages of the wear process



a b c d

Figure 5 – Curves of the quotient of friction of coatings obtained at different durations of the anode current pulse: a - 50 microseconds, b – 100 microseconds, c – 150 microseconds, d – 200 microseconds

(stage I) represents the initial wear period during which the rubbing surfaces adapt to each other, and this stage is called the burn-in stage. At this stage, there is a high intensity of wear. After the run-in stage, there comes a stage of steady wear (stage II), which has the longest duration. This stage is characterized by stable friction conditions and almost constant and relatively low wear intensity. During its development, wear gradually increases, which is accompanied by damage to the surface. Eventually, there is a significant change in the friction conditions, the intensity of wear increases sharply and catastrophic wear occurs (stage III).

Analysis of the curves of the friction quotient of oxide layers on aluminum obtained by the MDO method at different values of the duration of the anode current pulse shows that there are zones of run-in of the tribosystem, as well as a period with a stable friction condition (Figure 5). The oxide layer obtained at the duration of the anode current pulse of 50 microseconds is characterized by all stages of wear up to the wear of the coating (Figure 5 a). For other coatings, there is no sharp change in the quotient of friction characteristic of the destruction of the coating (Figure 5 b, c, d). The coatings don’t break down and don’t wear to the ground under the accepted test conditions.

Conclusions

The oxide coatings on aluminum alloy A0 were obtained in the pulse mode of the MAO. It is shown that structural changes under the influence of microplasma processes in the oxide layer make it possible to obtain wear-resistant coatings. When analyzing the friction quotient curves, it was found that the oxide coatings obtained at the duration of the anode current pulse of 100 μs – 200 μs are wear-resistant, the coatings don't collapse, don't wear to the ground under the accepted test conditions. The study of microhardness has shown that the microplasma process affects structural changes not only in the oxide layer, but also in the metal thickness. As a result of the thermal effect during the combustion of the microarc, an aluminum layer is formed with excellent physical and mechanical properties from aluminum that wasn’t subjected to MAO treatment.

Conflict of interest

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

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Алюминий қорытпасы үлгілерінің қасиеттеріне микро доғалық тотығудың әсері

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ТҮЙІНДЕМЕ

Қазіргі уақытта заманауи өндіріс салалары алюминий, титан және олардың қорытпалары сияқты құрылымдық материалдарға ерекше талаптар қояды. Бұл материалдардың физика-механикалық, коррозиялық қасиеттерін жақсарту үшін әртүрлі әдістер қолданылады. Оларға көп функциялы қасиеттер беру үшін бетті түрлендірудің перспективті әдістерінің бірі – микро доғалық тотықтыру арқылы өңдеу. Процестің айрықша ерекшелігі – микро доға разрядтарының әсерінен клапан металдарында оксид жабындарының пайда болуы. Бұл жағдайда ерекше қасиеттері бар жабындар пайда болады. Алайда, микро доғалық тотығу процесінің негізгі материалдың қасиеттеріне әсері аз зерттелген. Бұл жұмыстың мақсаты импульстік режимде жүзеге асырылатын микро доғалық процесінің оксид қабаттарының қасиеттеріне және негізгі материалға әсерін зерттеу болып табылады. Қорытпаның бетін модификациялау анод режимінде, токтың анодтық импульсі ұзақтығының аз мәндерінде жүргізілді. Электролит ретінде электролиттің сілтілі ерітіндісі қолданылды. Оксид қабатының микро қаттылығын, сондай – ақ металл қабатының – оксид қабаты/металлдың ішкі бөлігіндегі металл қабатын зерттеу микро доға разрядтары тек оксид қабатының қасиеттеріне ғана емес, сонымен қатар металл қалыңдығындағы құрылымдық өзгерістерге де әсер ететіндігін көрсетті. Түзілетін оксид жабыны жоғары микро қаттылықпен сипатталады. 100 мкс – 200 мкс токтың анодты импульсінің ұзақтығы кезінде алынған оксидті жабындар тозуға төзімді болып табылады, жабындар бұзылмайды, сынақтың қабылданған жағдайында соңына дейін тозбайды.

Түйін сөздер: вентильді металдар, плазмалық электролиттік оксидтеу, микроплазмалық разрядтар, оксидтік жабын, микроқаттылық, ауыспалы қабат

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Влияние микродугового оксидирования на свойства образцов из сплава алюминия

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АННОТАЦИЯ

В настоящее время современные производства предъявляют особые требования к конструкционным материалам, таким как алюминий, титан и их сплавы. Для улучшения физико-механических, коррозионных свойств этих материалов применяют различные методы. Одним из перспективных способов модификации поверхности с целью придания ей многофункциональных свойств является обработка методом микродугового оксидирования. Отличительной особенностью процесса является образование оксидных покрытий на вентильных металлах в результате воздействия микродуговых разрядов. При этом образуются покрытия с уникальными свойствами. Однако влияние процесса микродугового оксидирования на свойства основного материала изучено мало. Целью данной работы является исследование влияния микродугового процесса, реализуемого в импульсном режиме, на свойства оксидных слоев, основного материала. Модификацию поверхности сплава проводили в анодном режиме, при малых значениях длительности импульса анодного тока. В качестве электролита использовали щелочной раствор электролита. Исследования микротвердости оксидного слоя, а также слоя металла от границы раздела – оксидный слой/металл вглубь металла показали, что микродуговые разряды влияют не только на свойства оксидного слоя, но и на структурные изменения толщины металл. Показано, что сформированное оксидное покрытие характеризуется высокой микротвердостью. Оксидные покрытия, полученные при длительности импульса анодного тока 100 мкс – 200 мкс, износостойкие, покрытия не разрушаются, не изнашиваются до основания при принятых условиях испытаний.

Ключевые слова: вентильные металлы, плазменное электролитическое оксидирование, микроплазменные разряды, оксидное покрытие, микротвердость, переходный слой.

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Металлургия

Investigation of optical and physico-chemical properties of titanium-doped V_2O_5 nanofilms

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ABSTRACT
In this paper, undoped and Ti-doped V_2O_5 thin films were fabricated and deposited onto glass substrates using a «doctor blading» method. Then, the effects of Ti-doping on the optical properties of the thin films were investigated. Titanium doping concentration of 0.25-0.75 at.% has been investigated. After treatment in air at different temperatures, the obtained films was characterised by various techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL). It was found that the as-obtained doped films possessed thermochromic properties and optical switching characters. According to optical tests, thin linings of vanadium dioxide alloyed with Ti have optical properties that are effective for application. Because of their capacity to automatically control interior solar irradiation, lower air-conditioning energy consumption, and maintain a comfortable internal thermal climate, smart windows have drawn increased interest in recent years. The doping strategy and integrating with functional coatings can regulate the properties of obtained V_2O_5 films.
***Keywords*:** vanadium pentoxide, nanofilms, doping, smart windows, optical properties.

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Introduction

Vanadium dioxide is a material that experiences a metal–conductor phase transition at a temperature of 67 °C. This phase transition is a transition of the first kind with a latent transition heat of 4190 kJ/mol or 1000 kcal/mol. During such a transition, both the optical and electrical constants of the material experience a change. Above a temperature of 67 °C, the material has metallic conductivity, at a temperature below 67 °C, the material has semiconductor properties [[1], [2], [3]]. The conductivity of the material of sunlight, infrared rays decreases 3-5 times. In connection with the above-mentioned properties, scientific and technical interest in the optical and thermo-optical properties of vanadium oxides films used in the production of smart windows is growing [[4], [5]]. After applying vanadium gels to the substrate (by pulverization or centrifugation) and carrying out some additional technological operations, it is possible to obtain thin films of appropriate compositions on the surface of the substrate. Among the modern methods of thin film synthesis (magnetron sputtering and electron beam evaporation, laser ablation, decomposition and gas-phase chemical deposition of organometallic compounds, anodic, including plasma, oxidation, etc.), a special place is occupied by liquid-phase deposition (LPD) methods [[6], [7], [8]]. The advantages of LPD methods for producing thin films are as follows. Liquid phase deposition allows films

to be applied directly to substrates in such simple ways as immersion, pulverization or centrifugation. Unlike vacuum methods, in this case, the use of complex expensive equipment is not required. In addition, the films can be applied to large surfaces and substrates of complex shape [[9], [10]]. The main reason for this increase in interest is the specifics of the optical properties of vanadium coating, which is often alloyed with variable valence metals. That is, these alloy coatings, which are made on the surfaces of glass windows, have the property of "regulating" the sun's rays when used to construct buildings. The mechanism of the "regulatory" property of such sunlight can be explained by the following phenomenon [[11], [12], [13]]. During alloying with some metals, vanadium oxide is partially filled with d-orbitals and form a complex chemical structure. Under the influence of this, the nanoparticle coating applied to the surface of a glass window forms the properties of metal bonds and the variability of optical conductors. Under the influence of a small increase in the temperature that occurs in the packaging materials when the sun goes down, the electrons move from the lower d-Orbital to the higher-energy free orbital, resulting in the formation of conductive electrons and space in the packaging structure [[14], [15]].

There is another theory describing this phenomenon, which is interpreted as follows. When an electron moves in narrow zones, its kinetic energy is comparable to the energies of electron-phonon and interelectronic interactions, which can lead to the disappearance of the initial metallic state with the appearance of a dielectric gap in the electronic spectrum. Thus, it is the specific features of d and f unfilled electron shells that are the cause of the unique properties of transition and rare earth metal compounds, and f-electrons are relatively highly localized, and the behavior of d-electrons combines both band and atomic (localized) properties at the same time [[16], [17], [18]].

The resulting materials - Smart windows - are gaining popularity due to a wide range of advantages, such as multifunctionality, matte covering, light scattering at different angles. Thanks to the use of unique glazing, heat loss and energy costs are significantly reduced, glass can be used simultaneously as curtains or blinds, creating shade or letting light in sunny and clear weather [19]. By using of Smart glass for decorative purposes, the color range and practicality, ease and speed of modernization with adhesives increase. In general, the global smart glass market is currently developing very rapidly and in the next few years the Smart glass market will only grow, discovering new features and introducing unique technologies [20].

In the present work, vanadium oxide co-sputtered with titanium on quartz substrates. Resulted coatings are the characterstic by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The optical properties of the film are evaluated by photoluminescence (PL).

Experimental Details

To apply thin films of vanadium and titanium alloy (V-Ti) to the surface of the matrix layer, the "doctor blading" method was chosen. Alloying of vanadium oxide with titanium was carried out from 0.25 % to 0.75 %. The geometric parameters of the applied films were controlled by the number of cycles. Each cycle consists of applying a well-mixed suspension of V-Ti nanoparticles, polyethylene glycol and distilled water. The alloy (V-Ti) is prepared using nanoparticle powders, 25 nm in size. The proportion of V-Ti to polyethylene glycol is 0.96 g. per 2 ml, respectively. For magnetron sputtering of thin films, the MAGNA TM-200-1 magnetron sputtering unit was used. The formation of thin films on the glass surface by magnetron deposition proceeded in the mode of operation of the energy source at direct current. The deposition process was accompanied by feeding into a chamber with a high vacuum ($2.95 \cdot 10^{-5}$ millibars) mixtures of working gases argon (99.95%) and oxygen (99.92%). The elimination of oxides from the surface of the metal target was achieved by pre-spraying the vanadium target material in argon plasma for 15-25 minutes. The physical atomization of the V-Ti alloy proceeded by bombarding the surface of a vanadium target with accelerated ions of sputtering argon gas, the purity of which was 99.98%, followed by the reaction of vanadium atoms torn from the target surface with reactive oxygen gas. The supply of argon and oxygen gases was carried out through channels of independent gas intakes with controllers of a mass gas flow meter. The magnetron's power was 500 watts. The subsequent treatment consists in drying in an atmosphere of air (bringing to the state of a gel layer) and heat treatment. Heat treatment consists of two stages: calcination and annealing. Annealing of the formed coating at a temperature of 130 °C for 15 minutes reduces the level of cracking of the film. Annealing of the coating makes it possible to remove residual and by-product polymer molecules from the surface, and also improves crystallinity. The annealing temperature is 500 °C, the duration is 2

hours. X-ray studies were carried out using a Panalytical Epsilon 4. Energy-dispersive spectroscopy (EDS) analysis was performed on the basis of a MIRA 3 TESCAN scanning probe microscope with energy dispersive prefixes for microprobe analysis.

Results And Discussion

The XRD structural analysis spectrum shown in Figure 1 demonstrates the main peaks related to the anatase phase, with small inclusions of the rutile phase. Also, the XRD structural analysis revealed the orientation of orthorhombic V_2O_5 crystallites according to the file (JCPDS:00-041-1426) in the growth directions (101), (301), (011) and (020) corresponding to 2 theta 26.1°, 32.4°, 34.3°.

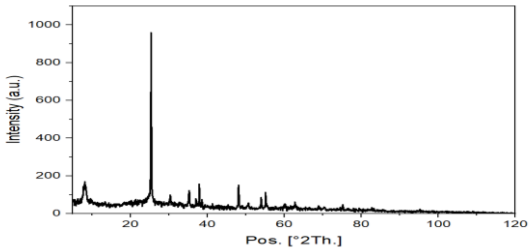


Figure 1- XRD patterns of V_2O_5/TiO_2 films

The morphology of the sample obtained by hydrothermal synthesis of TiO_2 was studied by Tessap scanning electron microscopy (Figure 2). A uniform array of TiO_2 structures consists of rods with a diameter of 170-200 nm, directed mainly perpendicular to the substrate. The remaining peaks belong according to the card file (JCPDS: 01-078-1510) to the faces of anatase/rutile TiO_2 crystals (110), (101), and (211).

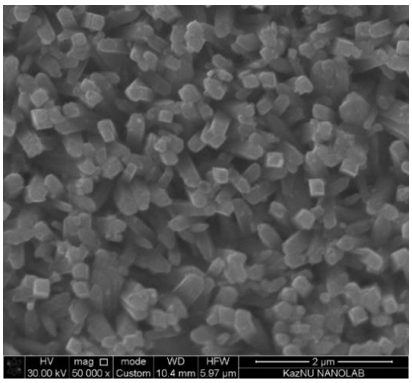
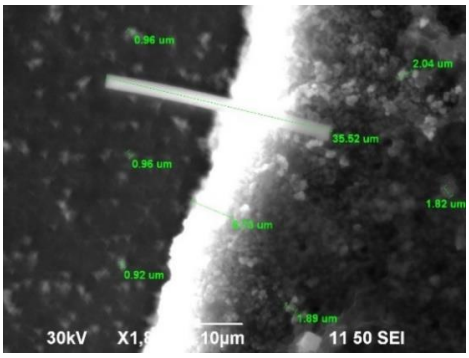
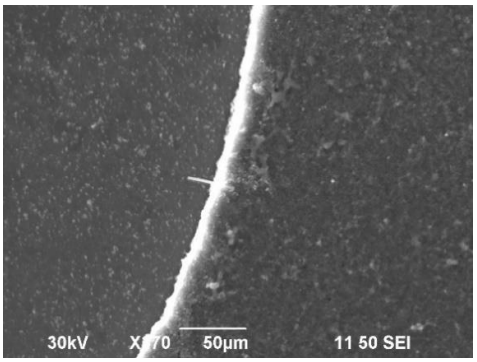


Figure 2 - SEM image of the morphology of the TiO_2/V_xO_y coating surface.

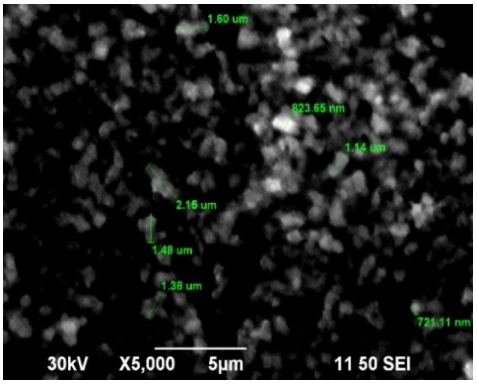
The study of the morphology of the obtained samples shows the formation of uniform V_2O_5/TiO_2 coatings with rare inclusions of objects with large dimensions (relative to the surface) related to coatings (Figure 3 (a-b)). In Figure 3 (c-d), the film growth boundary is clearly visible, created to understand the nature of the coating.



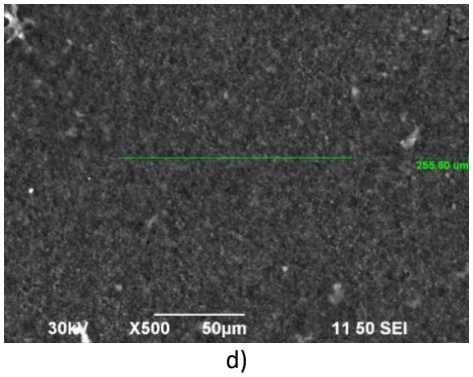
а)



б)



с)



d)

Figure 3 - SEM images of the surface morphology of V_2O_5/TiO_2 nanocomposites

The figure shows that the section appears with a sharp protrusion on the surface of the sample. After applying layers of TiO_2 nanoparticles to create a V_2O_5/TiO_2 nanocomposite, the surface consisted of microspheres, the average size of which varies from 0.9 to 2 microns (Figure 3 (a, b)).

When applying TiO_2 thin films in the amount of 5 "doctor blading" cycles, the average particle size evenly distributed on the sample surface does not increase (Figure 3 (c, d)).

The study of the morphology of the obtained samples shows the formation of uniform V_2O_5/TiO_2 coatings with rare inclusions of objects with large dimensions (relative to the surface) related to coatings (Figure 3 (a-b)). In Figure 3 (c-d), the film growth boundary is clearly visible, created to understand the nature of the coating.

Table 1 - Optical properties of the obtained coatings.

№	Components of the coating	W Doping level, %	IR reflectance / %	Solar reflectance / %
1	V_2O_5	-	27	18
2	V_2O_5 +Ti	0.25	31	29
3	V_2O_5 + Ti	0.50	33	34
4	V_2O_5 + Ti	0.75	34	39

Table 1 shows some optical properties (IR and Solar reflectance) of the samples in order to determine the possible of practical application of the obtained coatings. As Table 1 indicates, the coating that consists of only vanadium pentoxide reflects only 18.0 % of the sun's rays; when doped with 0.75 % titanium, the percentage of reflection increased to 39.0 %. The properties of reflectance of infrared rays were also studied. According to the research results, when alloying titanium pentoxide with 0.25 % to 0.75 %, the degree of reflection of infrared rays increased from 27.0 % to 34.0 %.

Conclusion

Titanium–vanadium oxide films with various compositional ratios were prepared by magnetron sputtering deposition and then the optical and physico-chemical properties were examined. The XRD analysis shows the amorphous nature of Ti-doped nanofilms. SEM images reveal columnar nanorod, that confirms the nano structure of the fabricated film. Furthermore, the optical switching property of obtained TiO_2/V_xO_y was studied and it was found that it possessed good thermochromic properties and optical switching characters.

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Титанмен легирленген V_2O_5 наноқаптамасының оптикалық және физика-химиялық қасиеттерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыста легірленбеген V_2O_5 және V_2O_5 - тің титанмен легірленген қоспалары жасалып «доктор блейдинг» әдісімен шыны субстраттар бетін қаптауға қолданды. Алынған қаптамалардың физико-химиялық және оптикалық қасиеттері зерттелді. Ванадий пентаоксидін легірлеуде титан концентрациясы 0,25-0,75 %-ды құрады. Алынған қаптамаларды сканерлейтін электронды микроскопия (SEM), рентгендік дифракция (XRD) және фотолюминесценция (PL) сияқты әртүрлі әдістермен зерттелді. Легірленген қаптамалар термохромды және оптикалық қасиеттерге ие екендігі анықталды. Оптикалық сынақтарға сәйкес, Ті-мен легирленген ванадий диоксидінің жұқа қаптамалары тұрмыста қолдануға тиімді оптикалық қасиеттерге ие екендігі анықталды. Өзінің тұрғын үйлер мен кеңселер ішіндегі күн сәулесін автоматты түрде реттеу, қолданылатын кондиционерлердің

	энергия тұтынуын төмендету және ішкі жылу жағдайларын тиімді деңгейде ұстау қабілетінің арқасында "смарт терезелерге" соңғы жылдары қызығушылықты арттыруда. Легирлеу дәрежесі және функционалды жабындармен біріктіру, алынатын V_2O_5 пленкаларының әртүрлі қасиеттерін алуға мүмкіншілік беретіні анықталды.
	Түйін сөздер: ванадий пентоксиді, наноқаптамалар, легірлеу, смарт терезелер, оптикалық қасиеттер
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Исследование оптических и физико-химических свойств нанопокрытия V_2O_5 легированного титаном

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АННОТАЦИЯ

В работе были изготовлены тонкие нанопокрытия, состоящие из нелегированного V_2O_5 и легированного с титаном V_2O_5 которые были нанесены на стеклянные подложки методом «doctor blading». Изучены физико-химические и оптические свойства полученных покрытии. При легировании пентаоксида ванадия концентрация титана составляла 0,25-0,75%. Полученные покрытия были исследованы различными методами, такими как сканирующая электронная микроскопия (SEM), рентгеновская дифракция (XRD) и фотолюминесценция (PL). Установлено, что легированные покрытия обладают термохромными и оптическими свойствами. Согласно оптическим испытаниям, было установлено, что тонкие пленки оксида ванадия, легированные с Ti, обладают оптическими свойствами, эффективными для использования в быту. Благодаря своей способности автоматически регулировать солнечное излучение внутри помещений, снижать энергопотребление кондиционеров и поддерживать комфортный внутренний тепловой климат, "умные окна" в последние годы вызывают повышенный интерес. Определено, что стратегия легирования и интеграция с функциональными покрытиями могут регулировать свойства получаемых пленок V_2O_5.

Ключевые слова: пентоксид ванадия, нанопокрытия, легирование, смарт-окна, оптические свойства

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Metallurgy

Research on hydrometallurgical processing of titanium-magnesium production sludge with niobium extraction in solution

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ABSTRACT

The material composition of sludge deposits from titanium-magnesium production was studied by chemical, X-ray, and microprobe analysis methods. Studies of the phase composition of the collector sludge showed that niobium is mainly bound with aluminum and titanium in oxide compounds. The particles of these compounds are very small and surrounded by the clay and carbonate component of the sludge collector. The chemical and mechanical activation processes of the sludge from the titanium-magnesium production sludge collector were executed based on the data obtained on the material composition. Alkaline leaching of sludge from sludge collector after preliminary activation was executed. The optimum conditions for the niobium extraction from the sludge of the sludge dump from the titanium-magnesium production were determined: sodium hydroxide concentration of 200 g/dm^3, glycerol 5 g/dm^3, S:L = 1:10, temperature 95 °C, leaching process duration - 4 hours. The addition of glycerol during alkaline leaching of sludge inhibits the transition of hexaniobate into insoluble sodium metaniobate enabling to increase the niobium extraction by 1.3 times with transfer into the solution of up to 80% of the extracted metal.

Keywords: sludge from the sludge collector, niobium, activation, leaching, sodium hydroxide.

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Introduction

Niobium (Nb) is a rare metal used in high-quality steel production [1]. It is used in the production of ferroniobium which accounts for more than 90% of niobium production. The largest consumers of niobium are China, North America, and Europe. The substantial economic growth in emerging markets, especially the BRIC's economies, and increased use of niobium in steel production boosted prices for the metal up to US$32.63/kg in 2007 and further up to the US $60.00 per kg in 2012. Niobium is expected by analysts to be in demand in the near term, and prices for the metal will remain high.

What sets niobium apart is that it combines a high level of corrosion resistance with a low weight.

The material is used in coin inserts of all colors, corrosion-resistant evaporation bowls for use in coating methods, and mold-resistant crucibles for growing diamonds. Due to its high biocompatibility level, niobium is also used as an implant material. The high transition temperature also makes niobium an ideal material for superconducting cables and magnets [2].

Niobium belongs to the group of refractory metals. Refractory metals are metals whose melting point exceeds the melting point of platinum (1772 °C). The energy that binds individual atoms is extremely high in refractory metals. Refractory

metals are characterized by high melting points combined with low vapor pressure, high elasticity modulus, and high thermal stability. Besides, refractory metals have a low thermal expansion coefficient. Compared to other refractory metals, niobium has a relatively low density of only 8.57 g/cm^3 [3].

High-tech production of tantalum and niobium implants is planned in East Kazakhstan. Implants made of tantalum and niobium are considered an advanced technology in modern dentistry and orthopedics because of their high biocompatibility. One of the first enterprises in Kazakhstan that produced tantalum and niobium is Irtysh Chemical and Metallurgical Plant. The production is located in Pervomaisky settlement, Shemonaikha district of East Kazakhstan region. Irtysh Chemical and Metallurgical Plant was built in 1956 and it was the main enterprise in Kazakhstan for the production of niobium, tantalum, and rare-earth metals [4].

In Ust-Kamenogorsk, East Kazakhstan, Ulba Metallurgical Plant JSC produces ingots, rolled products, powders, and niobium pentoxide, as well as NbTi, and NbZr ingots. However, on export sales of rare metals, the volume of sales of niobium products has been decreasing in recent years for 2016 was 52.1 tons, for 2017. - 23.7 tons, for 2018 - 22.9 tons, for 6 months of 2019 - 0.1 tons [5]. It is most likely due to the shortage of niobium concentrates, both foreign and domestically produced.

Chlorination methods for niobium-containing mineral raw materials are known [[6], [7], [8], [9]]. Ore concentrate is chlorinated with chlorine gas in the presence of a reducing agent - charcoal or petcoke. Either briquette charge or ore concentrate is chlorinated in a salt melt. Besides, ore raw materials are chlorinated in autoclaves with liquid carbon tetrachloride or silicon tetrachloride. However, all of them have a number of disadvantages inherent to traditional chlorination; carbon monoxide, phosgene, hydrogen chloride, and chlorohydrocarbons are still produced.

In the modern hydrometallurgical industry extraction and sorption are widely used to improve the quality of raw materials and products and deep purification of technological solutions [[10],[11]].

Niobium is often a companion of titanium along with vanadium, zirconium, and hafnium; therefore, it is present in titanium concentrates obtained from ilmenite placer and ores [12].

Titanium and magnesium production generates thousands of tons of solid waste annually. Reserves of wastes in sludge collectors at Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UK TMP JSC) alone amount to 1270 thousand tons. These wastes contain 0.4 to 2 % of niobium, which is almost comparable with the content of niobium in industrial ores of pyrochlore carbonatites [13].

The accumulation of niobium occurs in the waste of titanium production during titanium-containing slag chlorination to produce titanium tetrachloride. It is established that 40-45 % of niobium from its content in the initial slag goes to the technical titanium tetrachloride, 50-55 % - into solid chloride sublimations, and 4-5 % into the drained melt of the chlorination unit [14].

The niobium content analysis in solid waste of titanium slag chlorination process for 2005-2007 at UK TMP JSC showed that the niobium content in the pulverized slag of the titanium chlorination unit was from 0.26 to 0.6 %. The subsoil is diluted with water, the resulting chloride sludge is discharged into the acid drain and then neutralized with lime milk under the existing technology.

Analysis of the available scientific and technical and patent literature shows that most of the studies have been performed for conditioned niobium-containing raw materials, while very few studies on niobium extraction from titanium production waste have been performed [[15], [16], [17], and there is no rational technology intended to produce intermediate products containing and concentrating niobium compounds in the amounts suitable for further use for titanium-magnesium production. Niobium extraction from the collector sludge into marketable concentrate will enable to extract the valuable component and dispose multitonnage waste.

Materials and methods

Materials and equipment are sodium hydrogen carbonate, purity grade "chemically pure (C.P.)"; sodium hydroxide, purity grade "chemically pure (C.P.)"; glycerol, laboratory grade; sludge from the sludge collector of titanium-magnesium production provided by UK TMP JSC. Contents of the main sludge components of the titanium production sludge collector, mass in %: 12.70 TiO_2; 0.73 Nb_2O_5; 32.90 CaO; 2.00 MgO; 3.40 Al_2O_3; 4.10 SiO_2; 2.70 Fe_2O_3; 0.26 MnO; 0.29 V_2O_5.

IV-6 Vibro distiller (Russia), reactor equipped with a reflux condenser, ES VELP stirrer (Velp Scientifica), IKA RW16 stirrer (Germany), Shimadzu

scales (Japan), SNOL drying cabinet (Lithuania), distiller (Russia).

Experimental method. The necessary amount of leaching solution was put in the reactor, heated up to 95 °C, the specified quantity of sludge was brought in, and stirring was started up. Duration of pulp activation was 4 hours. The sludge was filtered at the end of the experiment. The sludge was washed with hot water to remove sodium hydroxide, glycerol, and soluble salts. The products were analyzed for the content of niobium, vanadium, aluminum, and silicon, the solubility of which in alkaline solutions is high enough.

Analysis methods: X-ray experimental data were obtained with the BRUKER D8 ADVANCE device with copper radiation at an accelerating voltage of 36 kV, and a current of 25 mA. X-ray fluorescence analysis was performed with a Venus 200 PANalytical B.V. (PANalytycal B.V., Holland) spectrometer with wave dispersion. Chemical analysis of the samples was performed with an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer). Mapping of elemental and phase composition of the samples was executed on a JXA-8230 electron-probe microanalyzer by JEOL (Japan). Thermal analysis of the provided sample was executed using the device of synchronous thermal analysis - STA 449 F3 Jupiter (Germany).

Results and discussion

The titanium production sludge was crushed, averaged, and dried before the physical and chemical studies. The result of the X-ray phase analysis is presented in Table 1 and Figure 1, where it is seen that the basis of the sludge is calcium carbonate, niobium is bound to calcium and embedded along with titanium in the lattice of aluminum oxide.

The main feature of thermal analysis is the possibility to determine small impurities on the background of the thermal inertness of the main components. It is seen on the derivatogram of the sludge sample from the sludge collector (Fig. 2) that endothermic effects of varying intensity are manifested on a rather long temperature segment of 100 - 900 °C on the DTA curve. They developed against the background of reducing the mass of the sample. Most likely, the manifestation of decomposition of various carbonates takes place here. Pyroaurite ($Mg_6Fe_2(OH)_{16}CO_3{\times}4H_2O$), chantite $CaMg_3(CO_3)_4$, and calcite. For example, the combination of endothermic effects with extremes at 203.3 °C, 427 °C, and 820 °C is characteristic of the manifestation of lamellar pyroaurite with calcite. $Mg_6Fe_2[CO_3](OH)_{16}{\times}4H_2O$ is pyroaurite.

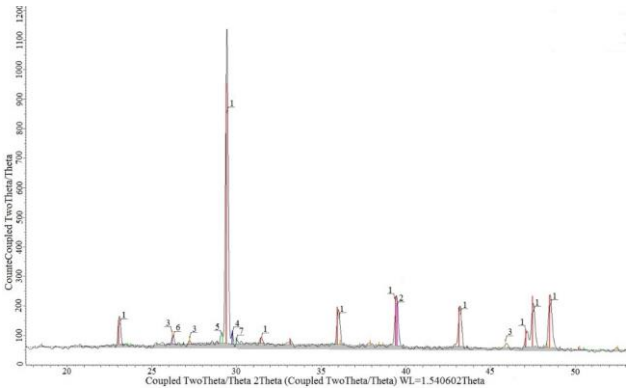


Figure 1 - Sludge diffractogram

Table 1 - Results of X-ray phase analysis of sludge

Phase number in Figure 1	Compound name	Formula	Content, %, relative.
1	Calcite	$Ca(CO_3)$	79.7
2	Aluminum Niobium Titanium	$Al_{0.12}Nb_{0.38}Ti_{0.5}0$	6.5
3	Aragonite	$Ca(CO_3)$	3.9
4	Calcite, magnesian	$(Mg_{0.129}Ca_{0.871})(CO_3)$	3.1
5	Fersmite	$CaNb_2O_6$	2.4
6	Iron(III) aluminium titanium oxide Iron Aluminum Titanium Oxide	$FeAlTiO_5$	2.3
7	Wollastonite-2M	$CaSiO_3$	2.1

The weak endothermic effect with the extremum at 307 °C on the DDTA curve shows melting of the $FeCl_3$impurity or sublimation of the $HfCl_4$ impurity. The endothermic effect with extremum at 674.3 °C on the DTA curve shows the enantiotropic polymorphic transformation of $2CaOSiO_2$. It is mentioned in [18] that "peritectic equilibrium" is observed in the Al - Nb system at 661.4 °C. The endothermic effect with extremum at 765.8 °C characterizes the melting of $CaCl_2$, KCl, $NdCl_3$ impurities.

Endothermic effect with extremum at 918.7 °C shows polymorphic transformation of strontium carbonate. The weak endothermic effect with extremum at 1219.4 °C shows the phase transition of $Nb_2O_5Al_2O_3$ impurity. The kink at 1270.4 °C may show the melting of the sample.

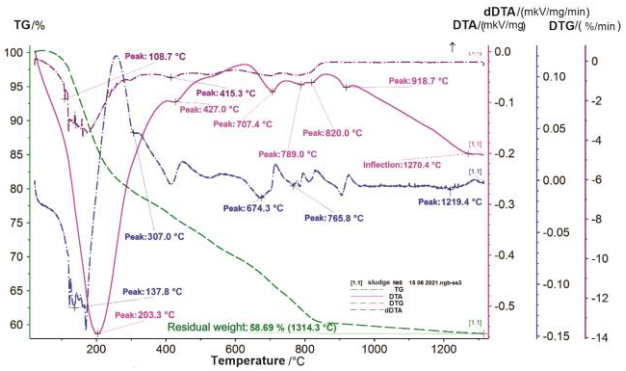


Figure 2 - Derivatogram of the sludge sample from the sludge collector (sample size of 0.2 g)

Endothermic effect with extremum at 918.7 °C manifests the polymorphic transformation of strontium carbonate. The weak endothermic effect with extremum at 1219.4 °C shows the phase transition of $Nb_2O_5Al_2O_3$ impurity. The kink at 1270.4 °C may show the melting of the sample. Thus, the thermal analysis data confirm the presence of a niobium-aluminum bond.

Next, the sludge deposit was studied on an electron-probe microanalyzer. The electron-probe study was executed in COMPO mode - backscattered electron imaging of minerals. A peculiarity of the COMPO image is an increased resolution enabling to register images of particles with small sizes. Thus, bright small particles including niobium compounds became visible at image magnification of 1000 times (Fig. 3).

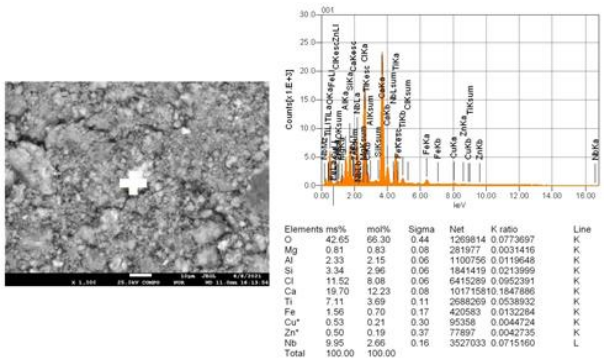


Figure 3 - COMPO image of the sludge from the sludge collector and its particle spectrum

Thus, the physicochemical studies of the phase composition of the sludge collector have shown that niobium is mainly bound to aluminum and titanium in oxide compounds. The particles of these compounds are very small and surrounded by clay and carbonate component of the sludge collector.

Activation of the sludge from sludge collector before leaching. The main task of sludge activation is to release the surface of niobium-containing particles. It will ensure effective access of the leaching agent and increase the niobium extraction degree into the solution.

Aragonite turns into calcite as a result of sludge activation with sodium hydrogen carbonate solution at elevated temperature. Chloride ion passes into the solution and calcite with magnesium forms a solid solution of $(Mg_{0.03}Ca_{0.97})CO_3$ (Figure 4, Table 2). The duration of the experiments was 0.5 h, 2 h, 4 h, and 6 h at 120 °C. The disadvantages of this method shall be referred to the accumulation of chlorine ion in the sodium bicarbonate solution during solution turnover.

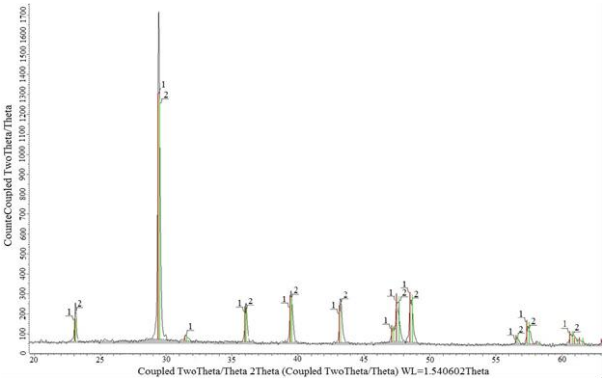


Figure 4 - Diffractogram of activated sludge from the sludge collector
(6 h, 120 °C, 60 g/dm^3 $NaHCO_3$)

Table 2 - Results of X-ray phase analysis of activated sludge from sludge collector

Phase number in the figure 4	Compound name	Formula	Contents content, %, t.r.f.
1	Calcite, magnesian, syn	$(Mg_{0.03}Ca_{0.97})(CO_3)$	50.3
2	Calcite, syn	$Ca(CO_3)$	49.7

After activation of sludge from the sludge collector with sodium bicarbonate solution, the test object was mechanically activated on a vibrating scrubber. The effect of the mechanical activation

duration on the disperse composition of the sludge from the sludge collector is shown in Table 3. Studies were executed during 0,5 - 5 min [19].

The crystal lattice deformation of the main components of the sludge from the sludge collector was estimated by means of X-ray diffraction analysis. Diffractograms of the initial and 5 min activated sludge from the sludge collector in the superposition are shown in Figure 5. A comparison of diffractograms showed distortion of the crystal lattice of calcite and aragonite in the activated sludge sample from the sludge collector.

Table 3 - Effect of mechanical activation duration on the disperse composition of sludge

Activation time, min	Fraction, mm				Loses, %
	+0.315	-0.315 +0.1	-0.1 +0.064	-0.064 +0.056	
0	26.7	50.5	18.2	3.6	1.0
0.5	17.7	69.1	11.5	0.8	0.9
1.0	17.7	72.1	8.8	0.9	0.5
2.0	16.0	76.2	6.0	0.9	0.9
3.0	13.5	80.1	49.0	0.5	1.0
5.0	7.0	89.3	2.2	0.5	1.0

As follows from the data in Table 3, the share of large +0.315 and small - 0.1+0.056 mm particles significantly decrease with an increase in mechanical activation duration. Probably, the fine particles are mutually attracted to the formation of agglomerates during the abrasion of sludge from the sludge collector. From Fig. 6, it can be seen that there are also larger particles in the image of the sludge activated for 5 min besides the fine particles. Note that the presence of small particles in the image of activated sludge is a reflection of particles containing niobium absent in the image of the original product. Thus, mechanoactivation of sludge from the sludge collector provides a contact of the reagent with the surface of niobium-containing particles which will increase the leaching process efficiency.

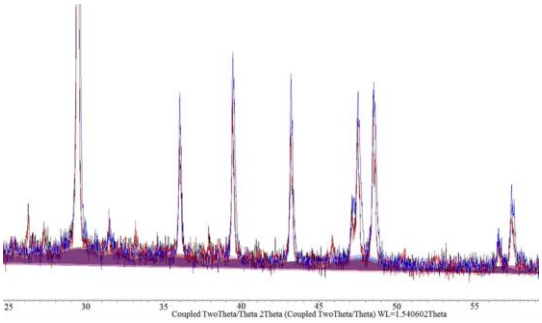


Figure 5 - Diffractograms of the initial and activated sludge from the sludge collector in overlay (red - original, blue - activated)

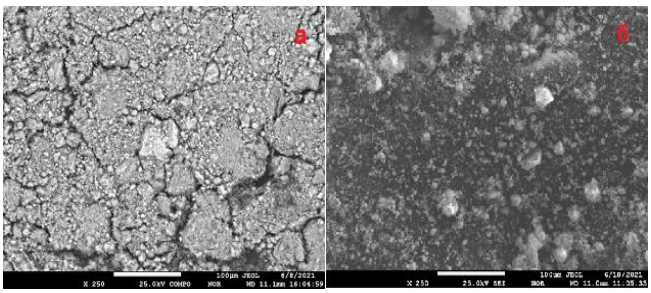


Figure 6 - Images of the initial (a) and activated (b) sludge from the sludge collector

Study of the sludge leaching process with an alkali solution. It is known [20] that niobium compounds are soluble not only in strong acids but also in strong alkali solutions indicating the presence of marked signs of amphotericity. The niobium extraction in solution occurs in solutions of caustic alkalis, due to the formation of water-soluble niobates with a Na_2O/Nb_2O_5 ratio greater than one [21].

It was found in [22] that the solubility of niobium oxide increases tens of times in alkaline solutions containing the five-atom alcohol xylite. It was noted that the solubility was 3.9 mg/dm^3 Nb_2O_5 in a pure alkaline solution with a sodium hydroxide concentration of 160 g/dm^3.

It should be noted that preliminary experiments showed that the use of alkaline solution with sodium hydroxide content of more than 200 g/dm^3 in the presence of glycerol results in the formation of poorly filterable pulp and requires a large amount of water to wash the sludge. In this regard, studies on the niobium extraction in solution were executed with solutions of 100 and 200 g/dm^3 NaOH.

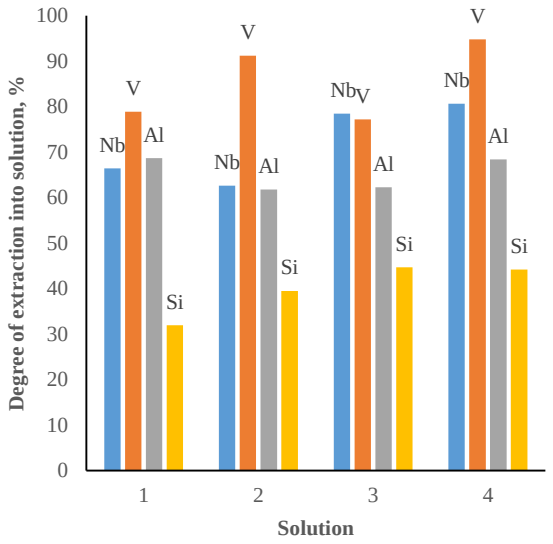
From the data in Table 4, it can be seen that increase in the concentration of alkali in the solution containing 2 g/dm^3 of glycerol from 100 to 200 g/dm^3 has practically no effect on the concentration of soluble aluminum compounds. At the same time, the aluminum extraction degree into the solution is 68.7 and 62.4 rel. %, respectively. An increase in the glycerol content up to 5 g/dm^3 has little effect on the extraction degree of aluminum compounds in the solution (Figure 7).

The concentration of sodium hydroxide and glycerol has no noticeable effect on the content of sodium metasilicate in the solution under the studied conditions of sludge leaching (Table 4).

Table 4 - Effect of glycerol on the transition of niobium, vanadium, aluminum, and silicon in alkaline solution under hydrothermal conditions (S: L = 1:10, 95 °C, 240 min)

Concentration in solution, g/dm3		Cake output, %	Content in the cake, wt. %				Concentration in solution, mg/dm^3			
NaOH	glycerin		Nb_2O_5	V_2O_5	Al_2O_3	SiO_2	Nb_2O_5	V_2O_5	Al_2O_3	SiO_2
100	2	64.6	0.375	0.126	1.626	2.880	282	179	1.353	1.094
100	5	71.0	0.380	0.048	2.275	2.230	301	235	1.157	1.039
200	2	61.2	0.254	0.144	2.065	3.567	378	199	1.391	1.177
200	5	63.0	0.222	0.032	2.069	3.180	386	244	1.187	1.164

It is known [23] that the solubility of iron oxide (Ⅲ) in sodium hydroxide solution (200-240 g/dm^3) even at 120-220 °C is ~ 0.1 g/dm^3. Therefore, the behavior of iron was not controlled.



1 - NaOH 100, glycerin 2; 2 - NaOH 100, glycerin 5; 3 - NaOH 200, glycerin 2; 4 - NaOH 200, glycerin 5 (95 °C, 4 h, S: L = 1:10)

Figure 7 - Dependence of niobium, vanadium, aluminum, and silicon extraction rates on leaching solution composition, g/dm^3

The degree of niobium extraction in the solution is greatly influenced by the concentration of alkali - by increasing the concentration of caustic soda from 100 to 200 g/dm^3 the degree of extraction increases by 1.2-1.3 times. The maximum concentration of niobium in the solution is 380 mg/dm^3. Glycerol in this case restrains the transition of hexaniobate formed during the interaction of alkali with sludge into insoluble sodium metaniobate.

It is of interest to study the behavior of another valuable component of sludge - vanadium. Since the acid properties of vanadium are higher than those of niobium, the extraction degree into the solution under the studied conditions reaches 91-95%. The effect of the solid-to-liquid ratio was studied in the range 1:(4÷12).

Figure 8 shows that an increase in the S: L ratio and, accordingly, the alkali consumption rate results in an increase in the degree of niobium transfer into the solution up to S: L = 1: 10, and with a further increase in the ratio that becomes practically constant. Vanadium extraction into the alkaline solution also increases with the increase of the S: L ratio. At the same time the vanadium transfer degree into the solution is higher than niobium.

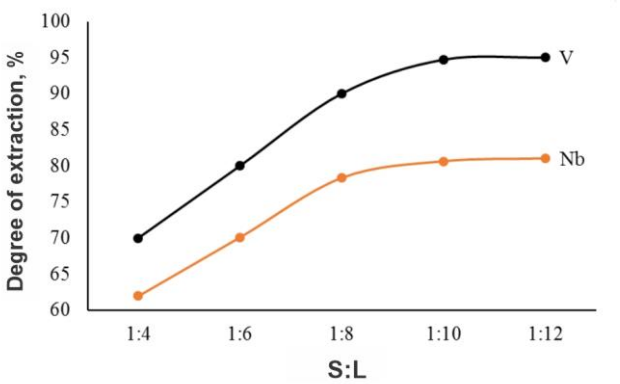


Figure 8 - The dependence of the niobium and vanadium extraction degree on the ratio S: L (NaOH 100 g/dm^3, glycerol 2 g/dm^3, 95 °C, 4 h)

Thus, experimentally it was found that the optimum conditions for niobium extraction in the solution of sludge from the sludge collector of titanium-magnesium production - sodium hydroxide concentration of 200 g/dm^3, glycerol 5 g/dm^3, S: L = 1:10, temperature 95 °C, the duration of the leaching process 4 h.

Conclusions

Physical and chemical properties of sludge collector wastes were studied. Chemical and X-ray fluorescence analyses determined the content of the main components, wt. %: 12.7 TiO_2; 0.73 Nb_2O_5; 32.9 CaO; 2.0 MgO; 3.4 Al_2O_3; 4.1 SiO_2; 2.7 Fe_2O_3; 0.26 MnO; 0.29 V_2O_5. X-ray phase analysis showed the following phase composition: calcite 79.7 %, aluminum-niobium-biotite-titanium oxide 6.5 %, aragonite 3.9 %, magnesian calcite 3.1 %, fersmite 2.4 %, iron-aluminum-titanium oxide 2.3 %, wollastonite 2.1 %. The base of the sludge deposit is calcium carbonate, with niobium bound to calcium and embedded along with titanium in the aluminum oxide lattice.

Thermal analysis confirmed the presence of calcite, pyroaurite, calcium, potassium chlorides, and niobium bond with aluminum.

It was found that aragonite transforms into calcite when the sludge is activated with sodium hydrocarbonate solution at elevated temperatures. Chloride ion passes into the solution, and calcite with magnesium forms a solid solution of $(Mg0.03Ca0.97)CO_3$. It was determined that with an increase in mechanical activation duration the proportion of large +0.315 and small -0.1+0.056 mm particles significantly decreases. Probably, the fine particles are mutually attracted to the formation of agglomerates during sludge abrasion.The process of sludge leaching by alkali solution was studied. If the caustic soda concentration is increased from 100 to 200 g/dm^3, the extraction degree of niobium increases 1.2-1.3 times, and the maximum concentration of niobium in the solution reaches 380 mg/dm^3. Glycerol in this case restrains the transition of hexaniobate formed during the interaction of alkali with sludge into insoluble sodium metaniobate. The extraction of vanadium in the alkaline solution also increases with the increase in the S: L ratio. At the same time, the degree of vanadium transition into solution is higher than that of niobium.

The optimum conditions for the niobium extraction from the titanium-magnesium production sludge - sodium hydroxide concentration 200 g/dm^3, glycerol 5 g/dm^3, S: L = 1:10, temperature 95 °C, leaching process duration 4 h.

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Титан-магний өндірісінің шламжинағыш шөгіндісінен ниобийді ерітіндіге шығара отырып, гидрометаллургиялық өңдеу бойынша зерттеулер

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ТҮЙІНДЕМЕ

Химиялық, рентгендік және микрозондты талдау әдістерімен титан-магний өндірісінің шламжинағыш шөгінділерінің заттық құрамы зерттелді. Шламжинағыш шөгіндісінің фазалық құрамын зерттеу ниобий негізінен алюминий және титанның оксидті қосылыстарына қосылатындығын көрсетті. Бұл қосылыстардың бөлшектері өте кішкентай және шламжинағыш шөгіндісінің сазды және карбонатты компонентімен қоршалған. Заттық құрамы бойынша алынған деректер негізінде титаномагний өндірісінің шламжинағыш шөгінділерінің химиялық және механикалық белсендіру процестері жүзеге асырылды. Алдын ала белсендіруден кейін шламжинағыш шөгіндісін сілтілі шаймалау жүргізілді. Титаномагний өндірісінің шламжинағыш шламынан ниобийді алудың оңтайлы шарттары белгіленді: натрий гидроксидінің концентрациясы 200 г/дм^3, глицерин 5 г / дм^3, Т:Ж = 1:10, температура 95 °с, шаймалау процесінің ұзақтығы 4 сағат. Шламды сілтімен шаймалау кезінде глицерин қосу гексаниобаттың ерімейтін натрий метаниобатына ауысуын тежейді, бұл ниобийді алу дәрежесін 1,3 есеге арттырып, алынатын металды 80% - ға дейін ерітіндіге ауыстыруға мүмкіндік береді.

Түйін сөздер: шламжинағыш шөгіндісі, ниобий, белсендіру, шаймалау, натрий гидроксиді.

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Исследования по гидрометаллургической переработке осадка шламонакопителя титаномагниевого производства с извлечением ниобия в раствор

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АННОТАЦИЯ

Изучен вещественный состав осадков шламонакопителей титаномагниевого производства методами химического, рентгеновского и микрозондового анализа. Исследования фазового состава осадка шламонакопителя показало, что ниобий связан в основном с алюминием и титаном в оксидные соединения. Частицы этих соединений очень мелкие и окружены глинистой и карбонатной составляющей осадка шламонакопителя. На основании полученных данных по вещественному составу, осуществленены процессы химической и механической активации осадка шламонакопителя титаномагниевого производства. Проведен щелочное выщелачивание осадка шламонакопителя после предварительной активации. Установлены оптимальные условия извлечения ниобия из шлама шламоотвала титаномагниевого производства: концентрация гидроксида натрия 200 г/дм^3, глицерина 5 г/дм^3, Т:Ж = 1:10, температура 95 °С, продолжительность процесса выщелачивания 4 ч. Добавление глицерина при щелочном выщелачивании шлама ингибирует переход гексаниобата в нерастворимый метаниобат натрия, что позволяет увеличить степень извлечения ниобия в 1,3 раза с переводом в раствор до 80 % извлекаемого металла.

Ключевые слова: осадок шламонакопителя, ниобий, активация, выщелачивания, гидроксида натрия.

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Metallurgy

Extraction of gold from low-sulfide gold-bearing ores by beneficiating method using a pressure generator for pulp microaeration

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ABSTRACT

Research results on the study of the material composition of low-sulfide gold-bearing ore from the East Kazakhstan deposit are presented. The main non-metallic minerals of the original sample and beneficiation products include quartz, chlorite (clinochlore), carbonates (calcite and dolomite). Pyrite is present predominantly in the form of cubic crystals, sometimes in the form of clusters. The grain size is from 0.03 to 0.40.5 mm, the size of the clusters reaches several mm. Iron oxides (goethite, hydrogoethite) were formed on pyrite, possibly magnetite and ilmenite. The assay test found that the test sample contains 6.04 g/t Au and 7.9 g/t Ag. The content of sulfide minerals is 11.81%. A significant part of gold (85.51%) is in a finely disseminated state in sulfides, as well as in rock-forming minerals 1.22%. The paper presents the results of laboratory studies of the gold- ore beneficiation ability using gravity concentration processes. Gravity enrichment tests were performed on laboratory equipment: Knelson KS-MD 3 centrifugal concentrator, SKO-05 concentration table, and a two-chamber diaphragm jig (OML TsNIGRI type (jig of Central Geological Research Institute for Nonferrous and Precious Metals)). The obtained results of ore beneficiation on the concentration table show the possibility of obtaining a gravity concentrate with a gold grade of 48.9 g/t with a gold recovery of 40.08%. When separating the gravity concentrate on a jig, the gold extraction was 31.6% at a content of 51.4 g/t. It was found that that according to a single-stage beneficiation scheme in a centrifugal concentrator, a gold-bearing concentrate with a gold content of 58.3 g/t was obtained with a recovery of 80.6%. The dependence of the gold extraction and its content in the gravity concentrate on the output at the Knelson centrifugal concentrator is shown. The results of ore flotation beneficiation show the possibility of obtaining waste grade flotation tailings with a gold grade of 0.8 g/t. The extraction of gold into the combined concentrate, with a gold content of 49.7 g/t, is 88.88%.

Key words: gold-bearing low-sulfide ore, mineral composition, phase composition, gravitational beneficiation, gold extraction, concentrate, tailings, oxidizing agent.

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Introduction

At present, gold-bearing ores classified as "refractory" are involved in processing. The "refractoriness" of ores is explained by the fine dissemination of gold in sulfides and rock - forming minerals. Gold-pyrite and gold-arsenic ores and their concentrates take pride of place among sulfide gold-bearing raw materials. The reserves of such ores are continuously replenished with new promising objects. One of these objects is the additionally explored sulfide gold-bearing ores of the East Kazakhstan deposit.

In order to avoid losses of coarse gold (more than 200 μm) during the processing of gold-bearing ore, the scheme includes gravity concentrate production processing using such equipment as classifying screens, jigs, concentration tables, centrifugal concentrators before flotation [[1], [2], [3]]. The existing process flow schemes for the processing of gold-bearing ores include the production of gravity concentrates and tailings. Centrifugal concentrators (Knelson, Itomak) are used to extract fine and thin gold.

Data shows [[4], [5], [6]] that due to poor, refractory and technogenic raw materials, it is possible to increase the mineral resource base of gold, which can be achieved as a result of increasing the efficiency of processing technology and the completeness of extraction of a valuable component. A significant part of noble metals in sulfide ores is concentrated in a finely dispersed phase. Free and sulfide-bound gold is efficiently recovered by gravity methods.

The combination of jigging and centrifugal gravitational enrichment technologies allows for separating minerals with a small difference in density. The authors proposed an ore processing scheme using a Knelson concentrator at a lower pulp feed rate and lower pressure to ensure higher accuracy (instead of 1000 g/min at 25 kPa, the feed was 400 g/min at 12 kPa). The total extraction of gravitational gold was 61.85 % with content in the concentrate of 1037.04 g/t [[7], [8], [9]]. In the course of investigations, it was also decided to work out a variant of the experiment on gravitational enrichment using alternative parameters taking into account the results of the above mentioned experiment.

The paper [10] presents the results of benefecation of various types of raw materials: sulfide ores of the Balakhchino deposit. The content of sulfides in ores exceeds 10%, gold is mostly finely disseminated in sulfides. It is known [[11], [12], [13], [14]] that gold is extracted from weathered ores by leaching, therefore, the use of gravity concentration at the head of the process flow scheme will make it possible to extract coarse gold and thereby reduce its losses and increase the productivity of the cyanidation process.

In order to achieve the best results in the processing of refractory sulfide gold-bearing ores, it is necessary to study their material composition and, based on the results obtained, develop a technology for obtaining gold-bearing concentrate, taking into account modern technological solutions [[15], [16], [17], [18]].

During gravitational enrichment, coarse, film-coated gold gets into the concentrate; however, its further extraction from the concentrate requires the use of special methods [19]. Based on previously published data [20], the authors selected the optimal conditions for extracting gold from low-sulfide gold-bearing ore by combining the processes of gravity and flotation beneficiation.

One of the promising technologies for processing gold-bearing raw materials is the choice of an efficient leaching system using oxidizing agents, which does not require large material costs [[19], [21], [22]]. It is most difficult to extract dispersed gold from sulfide minerals, especially with a finely disseminated structure of ores. In order to intensify the process of refractory ores oxidation and increase the extraction of gold, the laboratory staff proposed to perform combined oxidation. In this case, it is possible to ensure high rates of gold recovery during subsequent cyanidation using a chlorine-containing oxidizing agent for the oxidation of sulfide fragments. Previous studies have shown the use of various chemical additives, oxidizers, and an activator reagent [[2], [22]] including biooxidation [23] to intensify the cyanidation process by dissolving films of compounds that passivate the metal surface.

Employees of the “Institute of Metallurgy and Ore Beneficiation” JSC special hydrometallurgy methods laboratory named after Beisembaev B.B. performed work, which resulted in the selection of technological equipment for extracting gold from gold ore into gravity concentrate. Development of a highly efficient technology for extracting gold from finely dispersed gold-bearing raw materials using a pressure generator for pulp microaeration on a column flotation machine of the apparatus and an algorithm for calculating its design parameters in order to implement the technology for efficient flotation of fine particles and emulsion impurities of gold-bearing raw materials. One of the new and effective methods created on the basis of the physical action on the flotation process, which makes it possible to achieve simultaneously high recovery and selectivity in the separation of finely dispersed components with increased specific productivity of the apparatus. The structure and principle of operation of this column flotation machine are characterized by the possibility of simultaneously obtaining finely dispersed bubbles and using them at an increased speed of the downward pulp flow, which provides a higher specific productivity of the pulsating layer of the

column compared to pneumatic flotation machines currently used.

Dispersion elements in the column body, fixed on the aeration fittings provide the formation of microbubbles while air supplies under pressure. A vortex pulp flow aeration fitting is mounted in the bottom cone of the installation column with the inclusion of a reagent tank for the injection of basic and additional reagents [[24], [25], [26], [27], [28]].

The purpose of the work is to study the material composition of the gold-bearing ore of the East Kazakhstan deposit, and conduct research on the gravity and flotation enrichment of low-sulfide ore and the choice of technological equipment for obtaining gravity and flotation concentrate, to study the extraction of gold from ore, gravity and flotation concentrate and beneficiation tailings using pressure pulp microaeration generator.

Experimental part

The fundamental possibility of the investigated initial size material beneficiation was studied on Knelson KS-MD 3 centrifugal separators [[4], [7]], as well as on the SKO-05 concentration table and a two-chamber diaphragm laboratory OML type (TsNIGRI) jig.

The extraction of gold into the combined concentrate was 40.08% at 60% fineness of the 0.074 + 0 mm class on the concentration table. When separating the gravity concentrate on a jigging machine, the extraction of gold amounted to 31.6%. While testing the ore sample on the Knelson concentrator, standard production technological parameters were initially worked out: centrifugal acceleration of 60 G; flow rate of fluidizing water 3.5 l/min.; solid productivity 0.5-0.6 kg/min; excess pressure of fluidizing water 15 kPa; the solids content in the pulp fed to gravity separation is 25-30%.

When enriching ore with an 85% size of -1.7 + 0 mm class on a 3-inch Knelson centrifugal concentrator, the recovery was 66.0%. 90% size ore of -0.071 mm class was beneficiated also using Knelson centrifugal concentrate according to a one-stage scheme. In addition to increasing the grinding fineness of the supplied raw materials, the following technological parameters were also worked out: centrifugal acceleration 60 G; flow rate of fluidizing water is 1.75 l/min., productivity of solid is 0.3 kg/min.; excess pressure of fluidizing water is 15 kPa; the solids content in the pulp fed to gravity separation is 25-30%.

The results obtained showed that after grinding the ore in a ball mill to 90% fineness of the -0.071 mm class and with a centrifugal acceleration of 60 G (Table 1), the extraction of gold into the gravity concentrate increased to 80.6% with 8.3 product yield.

Table 1. Results of laboratory experiments of gravitational benefication of an ore sample at a 90% fineness of -0.071 mm class

Product name	Yield		Content	Extraction
	g	%	Au, g/ton	Au, %
Concentrate	166	8.3	58.3	80.6
Tailings	1834	91.7	1.27	19.4
Total:	2000	100	6.03	100.0

The gold content averaged 58.3 g/ton in concentrate and 1.27 g/ton in tailings. The estimated content (according to the balance) of gold in the ore is 6.03 g/toBeneficiationion at standard parameters made it possible to achieve almost the same recovery (80.1%) but at the expense of a higher concentrate yield of 12.5%. The gold content in the concentrate was only 40 g/t.

Thus, from the considered processes, the best performance when grinding ore to a fineness of 90.0% of the class -0.071 + 0 mm was obtained on the Knelson concentrator with the preservation of such parameters as centrifugal acceleration 60 G, fluidizing water pressure 15 kPa, but with a simultaneous decrease in the pulp feed rate (capacity for solids 0.3 kg/min, the flow rate of fluidizing water 1.75 l/min).

The results of chemical and X-ray phase analysis of the ore indicate the presence of a small amount of pyrite in the ore.

An experiment on the original ore was set up to develop a flotation concentrate for hydrometallurgical research. Staged flotation (Table 2) was performed in a closed cycle: I main flotation — at the 80–85% grinding size of the -0.074+0 mm class, II main flotation – at 90–95% of the -0.044+0 mm class. Total flotation time is 40 min, consumption of reagents amounts to 75 g/ton copper sulphate, 290 g/ton butyl xanthate, T-92 - 130.

Table 2 - Results of flotation beneficiation of ore from the East Kazakhstan deposit

Product	Yield, %	Gold content, g/ton	Extraction, %
Concentrate 1+2	8.33	57.5	75.17
Concentrate 3	3.07	28.5	13.71
United concentrate	11.4	49.7	88.88
Flotation tailings	88.6	0.8	11.12
TOTAL	100.0	6.37	100.0

The results of staged flotation ore enrichment show the possibility of obtaining dump gold flotation tailings with a gold grade of 0.8 g/ton. The extraction of gold into the combined concentrate, with a gold content of 49.7 g/ton, is 88.88%. The beneficiation products were sent for hydrometallurgical research.

The experiment in the flotation column required the process of at least 90 kg of initial ore, crushed to minus 0.071 mm 80% - taking into account the working volume of the column 360 l and the solids content of 25% in the pulp. The ore raw materials pulp obtained was loaded using slurry pumps in the open upper part of the column.

As a result of the experiment at a pressure in the pressure generator of 2.0 atm., the concentrate yield was 7.0% with a gold content of 8.0 g/ton, which gives 66.7% recovery. Increasing the pressure to 4.0 atm. contributed to an increase in the concentrate yield up to 8.6%, while the gold content was 7.22 g/ton, and already 73.9% was extracted into the concentrate. The mass yield of the concentrate reached 9.0% at a pressure of 6.0 atm. in the pressure generator dispersion system and with a gold content of 8.12 g/ton, the extraction increased to 87.0%.

Subsequent options with pressure increase up to 8.0 and 10.0 atm. led to the increase in the mass yield of concentrates to 12.1-14.65%, while the gold content decreased to 5.42 and 4.28 g/t, respectively. This also led to a decrease in recovery to 78.1% at 8.0 atm. and 74.6% at 10.0 atm. The diagram in Figure 9 shows the dependence of the recovery and quality indicators of gold concentrates, on the parameters of the pressure generator, and the pressure in the disperser system. As a result of the experiment at a pressure in the pressure generator of 2.0 atm., the concentrate yield was 7.0% with a gold content of 8.0 g/t, which gives a recovery of 66.7%. Increasing the pressure to 4.0 atm. contributed to an increase in the concentrate yield up to 8.6%, while the gold content was 7.22 g/t, and already 73.9% was extracted into the concentrate.

Table 3 – Results of experiments on flotation beneficiation in a column unit under different pressure conditions.

Pressure generator parameters, pressure, atm	Name of products	Yield, %	Au Content, g/ton	Au Extraction, %
2.0	Concentrate	7.0	8.0	66.7
	Tailings	93.0	0.3	33.2
	Total	100.0	0.84	100.0
4.0	Concentrate	8.6	7.22	73.9
	Tailings	91.4	0.24	26.1
	Total	100.0	0.84	100.0
6.0	Concentrate	9.0	8.12	87.0
	Tailings	91.0	0.12	13.0
	Total	100.0	0.84	100.0
8.0	Concentrate	12.1	5.42	78.1
	Tailings	87.9	0.21	22.0
	Total	100.0	0.84	100.0
10.0	Concentrate	14.65	4.28	74.6
	Tailings	85.35	0.25	25.4
	Total	100.0	0.84	100.0

At a pressure of 6.0 atm. in the dispersion system of the pressure generator, the mass yield of the concentrate reached 9.0%, and with a gold content of 8.12 g/t, the extraction increased to 87.0%. Subsequent options with an increase in pressure to 8.0 and 10.0 atm., led to an increase in the mass yield of concentrates to 12.1-14.65%, while the gold content decreased to 5.42 and 4.28 g/t, respectively. (Figure 1).

This also led to a decrease in extraction to 78.1% at 8.0 atm. and 74.6% at 10.0 atm. The diagram in Figure 1 shows the dependence of the extraction and quality indicators of gold concentrates, on the parameters of the pressure generator - the pressure in the disperser system.

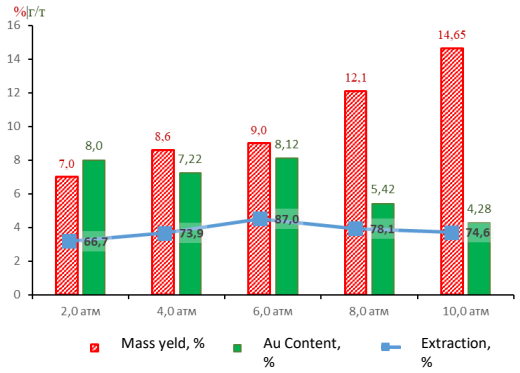

Figure 1 - The dependence of the extraction and quality of concentrates on the air pressure in the dispersion system.

Results and discussion

A sample of sulfide ore from the East Kazakhstan deposit was used as a feedstock during the research. In preparation for the research, the entire sample was crushed in stages to a particle size of -25+0 mm, cut, mixed, and reduced in accordance with the standard method of sampling (sampling) for technological research and study of the material composition.

Samples are mainly represented by quartz (54.7%), calcite, and dolomite.

The chemical composition of the studied ore sample is represented by the following components, %: 4.27 Fe; 0.952 total; 0.010As; 0.072 Zn; 0.016 Cu; 6.4 g/t Au; 7.9 g/t Ag. The other components were determined by X-ray fluorescence and X-ray phase analysis: the ore is represented by oxides that are part of the rock-forming components, the main of which is silica (54.7%) and alumina (10.8). Calcite (12%) and clinochlore (11.2%) are also present, dolomite (6.3%), and albite (5.0%) are present in small amounts.

The products of the gravitational beneficiation of the ore — concentrate, and tailings — were analyzed by atomic adsorption and assay methods.

Mineralogical analysis of an ore sample with an initial fineness of 89% class 10 microns (-0.01 mm) was performed to find the looks of gold. The polished section (∅ = 25 mm, sub-sample weight = 10-15 grams) formed from this material was studied with Axio Scope.A1 optical microscope.

As a result, 36 gold particles were found, of which: 30 particles in free form - 83.33%, Au size from 0.5 to 18.8 mkm, gold; 4 particles in intergrown with waste rock - 11.11%, with parameters - Au from 0.7 to 7.4 mkm (Figure 1);

2 facts of the gold particles occurrence in waste rock with thin phenocrysts of arsenopyrite particles in it - 5.56%, the size range of gold particles is within: Au from 0.5 to 6.8 mkm. The particle size is within: Au (0.5-18.8mkm), i.e. ultrafine (0.1-1.0 mkm) finely dispersed gold (1.0-10.0 mkm) and visible pulverized gold (10.0-50.0 mkm), ("nuggets" according to Petrovskaya's classification).

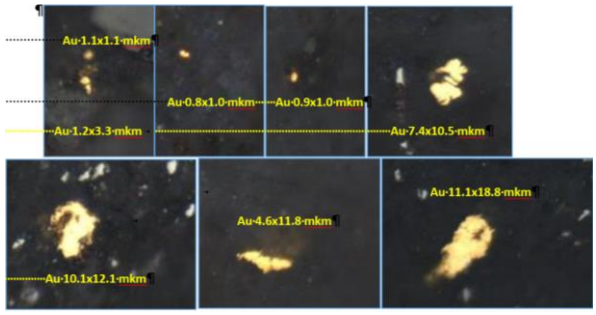

Figure 2 - Free gold particles in polystyrene

Figure 3 below shows the occurrence of gold particle "inclusions" in grains of waste rock with thin arsenopyrite phenocrysts in it.

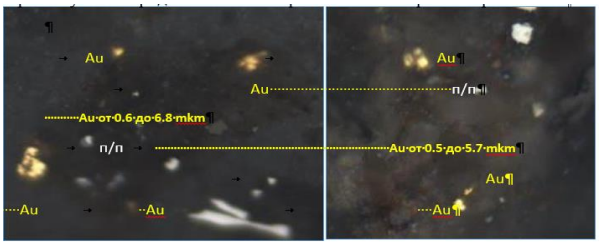

Figure 3 - The fact of the occurrence of gold particles in grains of waste rock with thin arsenopyrite phenocrysts in it

The gold deportment, the nature of gold's relationship with ore and non-metallic components, and assessment of its disclosure during grinding were determined through a phase (rational) analysis of a head ore sample, crushed to 95% fineness of the -0.071 mm class (Table 3).

The phase analysis technique included a number of operations. The 1st operation is the determination of free gold and gold in open aggregates – cyanidated gold. The 2nd operation is treatment of the first cyanidation tailings with a solution of hydrochloric acid in the presence of tin chloride to dissolve iron oxide films on gold particles. The 3rd operation is the determination of gold covered with films. The 4th operation is welding of the tails of the second cyanidation in aqua regia. The content of finely dispersed gold in waste rock was determined in the residue after parting. The amount of gold associated with sulfides was determined

from the difference in the contents in the tails of the second cyanidation and the parting tails.

Table 3 - Results of phase analysis for gold of a crushed head ore sample with a size of 95% of the class -0.071 mm

Gold deportment	Gold distribution	
	g / ton	%
Free and in the form of intergrown	5.02	85.51
Associated with acid soluble minerals (carbonates, hydroxides, chlorites, etc.)	0.12	1.46
Associated with sulfides	0.97	11.81
Finely disseminated in rock-forming minerals	0.10	1.22
Total in the sample (according to balance)	6.21	100.0

It is shown that the content of free gold and gold in open intergrown (cyanidated gold) is 85.51% in total. Gold grains are dendritic, octahedral, and needle-shaped. The sizes of gold grains range from 0.025 mm to 0.05 mm, dominated by 0.025-0.075 mm. The presence of finely disseminated gold in sulfides is one of the main reasons why gold is extracted from minerals with difficulties. 11.81% of gold is associated with sulfides, 1.46% is associated with acid-soluble compounds, and 1.22% is with rock-forming minerals.

Based on the results of rational analysis, it can be stated that rather high rates of gold dissolution up to 90% of the extracted gold should be expected during the cyanidation of ore.

The data of X-ray phase analysis of the sample showed that the total content of pyrite is 1.8%. The main rock-forming mineral is quartz, 54.7%. The content of albite, a mineral of the plagioclase group, is about 5%.

Conclusions

The study of the material composition found that the calculated gold content in the test sample is 6.04 g/t, silver 7.9 g/t. Gold is found in the form of very small grains in sulfides (pyrite, arsenopyrite), as well as in a finely disseminated state in silicate minerals. The ore is characterized by a multicomponent mineral composition with a predominance of pyrite.

The mineralogical and X-ray phase analysis of the sample showed that the main ore part is represented by pyrite, and quartz as rock-forming minerals. The rational analysis found that gold is distributed in the studied ore, crushed to a fineness of 95.0% of the class 0.071 + 0 mm, as follows: 85.51% free and in intergrown, 11.81% gold associated with sulfides, 1.46%associated with acid-soluble compounds, 1.22% in rock-forming minerals.

When enriched in a centrifugal concentrator, a gold-bearing concentrate was obtained with a gold content of 58.3 g/t with the extraction of 80.6%, and the loss of gold with the tailings of the centrifugal separator is 19.4% with a content of 1.27 g/t.

Centrifugal gravity separators, and in particular the Knelson concentrator, have proven to be a very effective circuit element in the technological chains of modern enterprises processing precious metal ores and sands. In this regard, the most preferable is the use of gravity technologies for extracting gold using gravity equipment that can provide a high degree of concentration of valuable components, the safety of the process, and a favorable state of the environment.

The obtained results of ore beneficiation on the concentration table show the possibility of obtaining a gravity concentrate with a gold grade of 48.9 g/t with a recovery of 40.08%. The tailings of the concentration table with a gold content of 3.8 g/t can be directed to additional extraction of gold by the flotation method.

When separating the gravity concentrate on a jig, the extraction of gold was 31.6%, with a content of 51.4 g/t. Based on the results of gravity beneficiation of ore in a centrifugal separator, it was found that the optimal size of grinding is 90% of -0.071 + 0 mm class.

Thus, based on the results obtained, it can be concluded that the Knelson centrifugal concentrator using of optimized operating mode is the best equipment for obtaining gravity concentrates from the ore of the East Kazakhstan deposit.

The head ore of the East Kazakhstan deposit is enriched by flotation quite effectively. The experiment on the head ore benefication with a particle size of 80% 0.074 mm is resulted with a flotation concentrate with a gold grade of 49.7 g/t

with a yield of 11.4% and a recovery of 88.88%. The gold content in the flotation tailings was 0.8 g/t.

The results of the experiments showed that the most optimal parameter of the pressure generator in terms of pressure supplied to the dispersion system is 6.0 atm. A further increase in pressure promotes intensive transfer of waste rock into concentrates, which significantly increases the mass yield, but at the same time reduces the gold content in them. The 6.0 atm. indicator allows for achieving the optimal balance in terms of mass yield and content of the noble metal in the concentrate.

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Conflict of Interest Statement

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

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Аз сульфидті кендерден қысымды микроаэрация генераторын қолдану арқылы байыту жолымен алтын алу

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ТҮЙІНДЕМЕ

Шығыс Қазақстан кен орнының құрамында күкірті аз алтын бар кеннің заттық құрамын зерттеу бойынша зерттеу нәтижелері келтірілген. Бастапқы сынама мен байыту өнімдерінің негізгі кенсіз минералдары кварц, хлорит (клинохлор), карбонаттар (кальцит және доломит) болып табылады. Пирит негізінен текше тәрізді кристалдар түрінде, кейде кластерлер түрінде болады. Дәндердің мөлшері 0,03-тен 0,40,5 мм-ге дейін, кластерлердің мөлшері бірнеше мм-ге жетеді. темір оксидтері (гетит, гидрогетит) пирит, мүмкін магнетит және ильменит арқылы түзілген. Сынамалық талдаумен зерттелетін сынамада 6,04 г/т Au және 7,9 г/т Ag бар екендігі анықталды. Сульфидті минералдардың мөлшері 11,81% құрайды. Алтынның едәуір бөлігі (85,51%) сульфидтерде, сондай-ақ 1,22% тау жыныстарын құрайтын минералдарда жұқа қапталған күйде. Жұмыста гравитациялық байыту процестерін қолдана отырып, құрамында алтыны бар кенді байытуды зертханалық зерттеу нәтижелері ұсынылған. Гравитациялық байыту бойынша сынақтар зертханалық жабдықта: knelson КС-МД 3 орталықтан тепкіш концентраторында, СҚО-05 концентрациялық үстелінде және екі камералы диафрагмалық шөгу машинасында (ЗНИГРИ АМЛ типі) өткізілді. Концентрациялық үстелде кенді байытудың алынған нәтижелері 40,08 % алтын алу кезінде құрамында 48,9 г/т алтын бар гравитациялық концентрат алу мүмкіндігін көрсетеді. Шөгу машинасында гравитациялық концентрат бөлінгенде, құрамында 51,4 г/т болған кезде алтын алу 31,6% құрады. Бір сатылы байыту схемасы бойынша ортадан тепкіш концентраторда 80,6% алу кезінде құрамында 58,3 г/т алтын бар концентрат алынғаны анықталды. Алтын алу мен оның гравитациялық концентраттағы құрамының Knelson орталықтан тепкіш концентраторының шығуынан тәуелділігі көрсетілген. Кенді флотациялық байыту нәтижелері құрамында 0,8 г/т алтын бар флотацияның алтын бойынша үйінді қалдықтарын алу мүмкіндігі туралы көрсетеді, құрамында 49,7 г/т алтын болған кезде Алтынды біріктірілген концентратқа алу 88,88% - ды құрайды.

Түйінді сөздер: құрамында алтыны бар аз сульфидті кен, минералды құрамы, фазалық құрамы, гравитациялық байыту, алтын алу, концентрат, қалдықтар, тотықтырғыш

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Извлечение золота из малосульфидных золотосодержащих руд методом обогащения с использованием напорного генератора микроаэрации пульпы

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АННОТАЦИЯ

Приведены результаты исследований по изучению вещественного состава малосульфидной золотосодержащей руды месторождения Восточного Казахстана. Основными нерудными минералами исходной пробы и продуктов обогащения являются кварц, хлорит (клинохлор), карбонаты (кальцит и доломит). Пирит присутствует преимущественно в виде кристаллов кубической формы, иногда в виде скоплений. Размер зерен от 0,03 до 0,40,5 мм, размер скоплений достигает нескольких мм. Оксиды железа (гетит, гидрогетит) образовались по пириту, возможно магнетиту и ильмениту. Пробирным анализом установлено, что в исследуемой пробе содержится 6,04 г/т Au и 7,9 г/т Ag. Содержание сульфидных минералов составляет 11,81 %. Значительная часть золота (85,51 %) находится в тонковкрапленном состоянии в сульфидах, а также в породообразующих минералах 1,22 %. В работе представлены результаты лабораторных исследований обогатимости золотосодержащей руды с использованием процессов гравитационного обогащения. Тесты по гравитационному обогащению проведены на лабораторном оборудовании: центробежном концентраторе Knelson КС-МД 3, концентрационном столе СКО-05 и двухкамерной диафрагмовой отсадочной машины (типа ОМЛ ЦНИГРИ). Полученные результаты обогащения руды на концентрационном столе показывают возможность получения гравитационного концентрата с содержанием золота 48,9 г/т при извлечении золота 40,08 %. При выделении гравитационного концентрата на отсадочной машине извлечение золота составило 31,6 % при содержании 51,4 г/т. Установлено, что по одностадиальной схеме обогащения на центробежном концентраторе получен золотосодержащий концентрат с содержанием золота 58,3 г/т при извлечении 80,6 %. Показана зависимость извлечения золота и его содержания в гравитационном концентрате от выхода на центробежном концентраторе Knelson. Результаты флотационного обогащения руды показывают о возможности получения отвальных по золоту хвостов флотации с содержанием золота 0,8 г/т. Извлечение золота в объединенный концентрат, при содержании золота 49,7 г/т составляет 88,88 %.

Ключевые слова: золотосодержащая малосульфидная руда, минеральный состав, фазовый состав, гравитационное обогащение, извлечение золота, концентрат, хвосты, окислитель.

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Earth sciences

Assessment of the stability of the underworked sides and ledges of the quarry to determine the area of possible location of the shaft

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ABSTRACT

As known, the main methods of developing solid minerals are open and underground methods. However, an analysis of the world's practice of developing deposits of solid minerals also indicates the widespread use of the combined method of development in the last 50-60 years. Combined development of deposits at domestic and foreign mining enterprises is used due to the variable depth of deposits, which is typical mainly for deposits of steep and inclined fall. The essence of the combined development is that the upper horizons are developed in an open way, and the lower ones are developed underground. In such deposits, the following scheme has become widespread: the initial development of the upper section of the deposit by a shallow quarry (up to a depth of 80-100 m, sometimes more), then the construction of an underground mine, carried out in parallel with the completion of the quarry reserves. When opening sub-quarry reserves subject to underground mining, the resulting quarry space can be used. The penetration of vertical and inclined opening workings, tunnels, and exits from the berm sides or directly from the bottom of the quarry has become widespread. In parallel mining of reserves by open and underground methods, the joint use of transport workings is widely used for the delivery of ore mass from the quarry and underground mine, the placement of an underground crushing complex, auxiliary, and repair facilities in the quarry itself. In addition, the method of refining sub-quarry reserves with the opening of the underground part outside the quarry space has been widely used. After the end of open-pit mining, underground horizons are opened by capital mining workings (vertical, inclined shafts, tunnels).

Keywords: combined development, vertical mine roadways, shafts, underground reserves, open pit, side, slope.

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Introduction

Depending on the depth of the deposit, reserves lying below the quarry are most often opened by Vertical and inclined barrels that pass outside the quarry and are used for mining, unloading and lifting people, and ventilation. The advantage of these opening schemes is to significantly reduce the construction time of the underground mine and reduce capital costs by reducing the length of the main and auxiliary underground workings.

A fairly large practical experience of mining enterprises in Kazakhstan, Russia, and far abroad shows the widespread use of a combined method of mining solid mineral deposits using vertical mine trunks to open the underground part of the field [[1], [2]].

In addition, M. Khudey, M. Radosavlevich, and S. Vuynich studied the selection of the location of the vertical trunk using multimodel analysis in the Velenye region of Slovenia [[3], [4]].

Attention was paid to the work of researchers Qing Yu, Jinrong Ma, Hideki Shimada, and Takashi Sasaki, which provides a quantitative analysis of the

model of the impact of mining operations on the stability of the mine shaft [[3], [5]].

Experimental part

There are many specific engineering and geomechanical tasks that affect the efficiency of using combined excavation. Let's try to highlight the tasks that interest us, which are directly related to the choice of location and location of the main opening workings – in our case, vertical trunks.

The tasks that form the scientific and methodological basis for solving the scientific and technical problem of choosing a safe place for laying vertical trunks during combined digging include [6]:

1. *Selection of the method of field discovery, taking into account the specifics of mixed development*. In contrast to the traditional underground method of development of deposits, the peculiarity of choosing a safe scheme of opening during mixed development is the presence of open pit space and a displacement zone of rocks in contact with the quarry, that is, the fact of the emergence of a new factor of Man-Made influence. It is known that zones of sliding and falling rocks are formed around the quarry space, within which it is not allowed to place the main opening workings and carry out other works without applying the measures provided for in the safety rules.

2. *Determination of the size of the rock displacement zone around the contour of the quarry, extending from the surface of the earth to the final depth of the quarry*. This is one of the most important tasks, the solution of which directly depends on the choice of the location of vertical trunks.

3. *Determination of the maximum depth of the quarry*, where the contour coefficient of the trench is equal to the boundary coefficient of the trench. This parameter, first of all, serves to assess the possibility of an underground transition from an open method of development and determines the boundaries of this transition. On the other hand, this task is directly related to the discovery of the field, the order of depth and location of vertical trunks, as well as the process of formation, the geomechanical state and the dimensions of the area adjacent to the contour of the quarry, within which the construction of trunks is not allowed [7].

4. *Assessment of the stability of the slope of the quarry side, study of the features of the development of deformations on the slope and slope of the quarry, the influence of the slope on the distribution and value of stresses along the contour of the quarry in the conditions of transition to underground mining*. In the context of the transition to underground development, this process becomes more complex and develops according to an unknown pattern, depending on the conditions of rock formation and the technology of underground development. Any changes in the stress-deformable state of rocks lead to a change in the geomechanical state of the zone of the quarry near the contour, which depends on the choice of the location of vertical trunks. The Basic Laws of these deformations can be predicted with sufficient accuracy on the basis of well-known methods and recommendations before choosing the location of the trunk.

5. *A complex of engineering and geological surveys on the basis of Visual Studies and instrumental measurements on the study of the terrain, the structure of the Earth's surface, the presence of methods of transport routes (railways, highways), geological irregularities, reservoirs, and aquifers, etc. in order to assess and establish the possibility of constructing the mouth of vertical trunks*. It is possible to determine possible areas of surface deformation by means of movement zones. This makes it possible to make a decision on the placement of surface and underground hydraulic structures. The actual angles of movement may be smaller than those designed, so for safety reasons, ground structures are located at a certain distance from the traffic zone. This distance is called a security berm, which is regulated by safety regulations.

Taking into account the displacement of rocks, it is important to establish the boundaries of rock sliding along the entire depth of the quarry in order to determine the area of possible location of pits on the surface. To do this, it is important to know the mechanisms and patterns of its formation, methods for calculating and evaluating the stability of slopes and slopes, and its impact on the process of falling (sliding) rocks along the contour of the quarry, etc. [8].

To determine the location of vertical trunks on the surface of the Earth, it is important to establish the boundaries of rock slides along the contour of the quarry in the combined method. Knowledge of the mechanisms and patterns of their formation, methods of determining and evaluating the stability of slopes, bevels, their influence on the process of falling (sliding) rocks along the contour of the quarry, etc. is of great importance [9].

In connection with the need to switch to mixed geotechnologies in the conditions of one of the fields in the Republic of Kazakhstan "Ushkatyn-3", researchers of Karaganda State Technical University (KarSTU) conducted scientific and experimental studies to justify the size of the trunk (vertical position of the trunk during the transition to underground development). The purpose of this study was to identify a safe zone. For this purpose, in the southern and northern parts of the Ushkatyn-3 quarry, work was carried out to calculate the stability of the slopes and sides of the quarry, the result of which was to determine the value of the location of the vertical mine shaft at the edge of the quarry [10].

Discussion of results

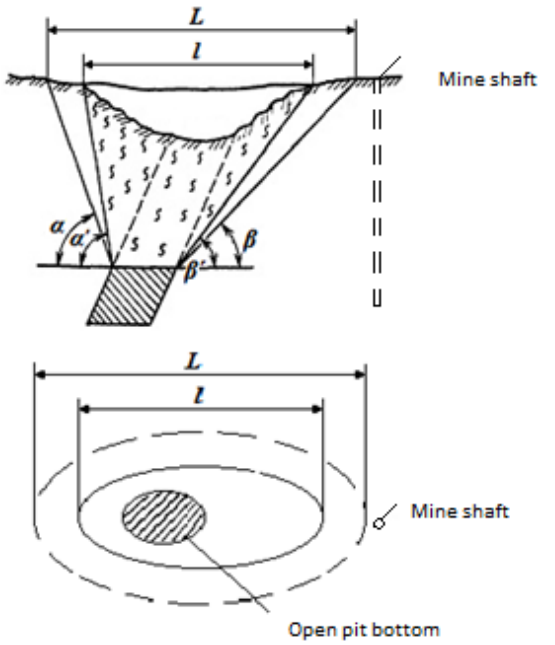
Scientific works of many outstanding scientists such as V.V. Rzhevsky, N.V. Melnikov, K.N. Trubetsky, G.L. Fisenko, E. . Shemyakin, S.G. Avershin, S.I. Popov, M.N. Mashanov, I.I. Popov, R.P. Okatov, P.S. Shpakov, F.K. Nizametdinova, G.G. Poklada, V.N. Dolgonosova, and others are devoted to the study of the stability of the sides of quarries and slopes.

In the course of this work, P.S. Shpakov's calculation classification of the geomechanical line model was used to determine the position of the vertical trunk during the transition to the quarry. It allows us to assess the stability of the quarry side when using the quantitative and analytical methods [[11], [12], [13]].

Figure 1 shows the scheme of displacement and collapse of rocks along the contour of the quarry after open-pit processing.

The essence of the research on the stability of slopes and slopes in the quarry to justify mixed development is that the designation of the sliding surface and boundaries of rocks along slopes and bevels opens up opportunities for determining the safe location of vertical trunks, taking into account the sliding factor of rocks. The figure shows the location of the mine shaft outside the rock displacement zone.

An approach based on the assumption that a collapse prism or sliding prism is formed in the massifs of beeches and beeches is widely used to assess the stability of the sides of quarries and beeches. As an example, we will consider the essence of a number of methods presented in the works [[14], [15]].



L – rock displacement zone; *l* – rock fall zone; *α, β* – rock displacement angle; *α´, β´* - the angle of fall

Figure 1 – Mountain range movement scheme

So, in the work [[15], [16]], the conditions for the stability of slopes with this approach are presented as follows:

$$\Sigma Si > \Sigma Ti \quad (1)$$

where ΣSi is the sum of the holding forces on the weakest surface of the prism;

ΣTi is the sum of the shear forces on the same surface.

The slope stability fund coefficient is as follows:

$$n = \Sigma Si / \Sigma Ti \quad (2)$$

n = 1 the surface is called the threshold or sliding surface. Rock shear resistance is determined as follows:

$$\tau = \tau_0 \sigma n \, tg\varphi \quad (3)$$

where τ_0 is the adhesion of rocks;

σn-normal voltage to the shear site;

τ is the tangential voltage acting in the shear zone;

ϕ is the internal friction angle.

In the case of a flat task, taking into account the dependence (1) is obtained:

$$\Sigma Ti = fcp \, \Sigma Ni \, L \, \tau cp \quad (4)$$

where ΣNi is the sum of normal (retaining) forces on the sliding surface;

τsr-the average value of the coefficient of friction and adhesion on the entire sliding surface;

L-the length of the sliding Surface (line in a flat task).

$$fcp = tg\varphi cp \quad (5)$$

To calculate the stability of the slope, use the calculation scheme shown in Figure 2, which shows the slope scheme with a round cylindrical sliding surface. An array of rocks bounded by the surface of the ABC and the circular cylindrical sliding surface of the AS1 and the constant vertical bare height of the rocks of the SS1 is divided into vertical strips A of the same width. As points of application of the mass of Qi strips, their average height is conditionally selected. By decomposing the mass of the Qi bands into tangents and normal components on the sliding surfaces, you get Ti and Ni.

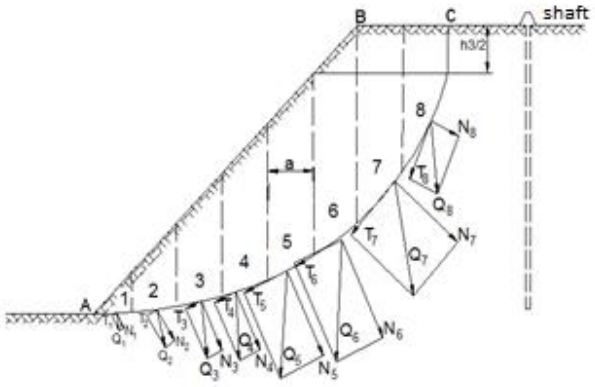


Figure 2 - Calculation of stability slope schemes using a circular cylindrical sliding surface

After the transformations, the slope stability fund formula (6) is obtained:

$$n = \frac{f_{\text{cp}} \Sigma N_i L \tau_{\text{cp}}}{\Sigma T_i} \quad (6)$$

In the upper part of the slope, there is a vertical segment of the slide line SS 1. This surface (tear line) is formed under the influence of tensile stresses hπ/2. It is recommended to determine this value by the dependence proposed by G.L. Fisenko [16]:

$$h_{\pi/2} = \frac{2\tau_0}{\gamma} ctg\left(\pi/4 - \frac{\varphi}{2}\right) \quad (7)$$

In the conditions of the ushkatyn-3 field, scientific and experimental work was carried out to determine the rational location of vertical mine shafts using these methods. For this field, the weighted average value of the rock strength coefficient on the M.M. Protodiakonov scale was 10. Taking into account the strata of rocks, the following angles of Motion are assumed: δ = 65; β = 50; β1 = 50. For the southern and northern parts of this quarry, stability calculations were performed for the geomechanical model of the uneven slope of the quarry side, as a result of which the location of the barrel was determined [[17], [18]].

Calculations were made for 5 sections that characterize the southern and northern parts of the ushkatyn-III quarry. The calculation of the stability of rocks in the quarry was made according to known methods. All methods take into account the physical and mechanical properties of rocks and the depth of development. Studies were conducted to determine the location of the vertical trunk under the condition of sliding of the Rock line. Below are the sliding zones laid out on the cross-section 1-1 of one of the five slices [19] (Figure 3).

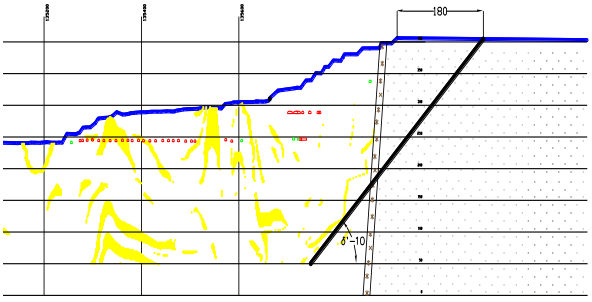


Figure 3 - 1-1 sliding zone by cross-section

5 lines of rock displacement zones were obtained by conducting profile lines in sections.

The following safe distances were determined by the calculations: 180 m; 165 m; 115 m; 0 m; -100 m.

By connecting the points of origin of the lines from movement to the surface of the Earth [20], a zone was finally obtained, within which it was not recommended to place a vertical trunk (Figure 4). The entire area located outside this zone is characterized by the integrity of an array of rocks that have not been affected by mining operations in the quarry. Inside this zone, located outside the contact zone of the quarry, the array is unstable, and the location of the trunk in it can lead to severe deformation and destruction of the trunk.

The mine shaft must be located outside the area shown in the figure. This method allows us to determine the safest place for the construction of

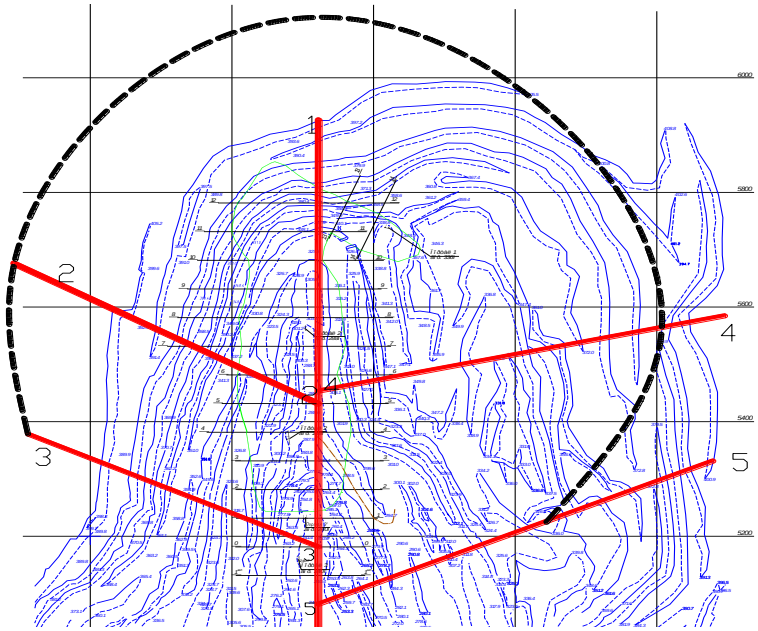


Figure 4 – Rock displacement zone in the northern part of the ushkatyn-3 quarry

vertical trunks in the combined technology of mineral deposit development under the conditions of displacement of massif rocks in the contact zone of the quarry.

Conclusions

When choosing the place of placement of trunks, it is necessary to provide for the possibility of surface treatment during underground work. Leaving protective centers near the trunk, if such a decision is made, will allow maintaining the stability and integrity of the array directly near the trunk, but no more. But the condition of the slopes and pits of the quarry may change. Carrying out underground mining operations in the impact zone of the quarry causes a redistribution of stresses in the treated massif and significantly changes the stability of the slopes and the surrounding area of rock displacement.

Conflict of interest

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

Gratitude

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Оқпандардың ықтимал орналасу орнын анықтау үшін карьердің өңделген ернеулері мен кемерлерінің тұрақтылығын бағалау

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ТҮЙІНДЕМЕ

Белгілі болғандай, қатты пайдалы қазбаларды игерудің негізгі тәсілдері ашық және жер асты тәсілдері болып табылады. Алайда, қатты пайдалы қазбалар кен орындарын игерудің әлемдік тәжірибесін талдау соңғы 50-60 жылда аралас игеру әдісінің кеңінен қолданылуын көрсетеді. Отандық және шетелдік тау-кен кәсіпорындарында кен орындарын аралас игеру кен орындарының өзгермелі тереңдігіне байланысты қолданылады, бұл негізінен тік және көлбеу құлау кен орындарына тән. Аралас қазудың мәні-жоғарғы деңгейжиектер ашық түрде, ал төменгі деңгейжиектер жер астында қазып алынады. Мұндай кен орындарында негізінен келесі схема таралды: кен орнының жоғарғы бөлігін терең емес карьермен бастапқы игеру (кейде 80-100 м тереңдікке дейін), содан кейін карьердің қорларын өндірумен қатар жер асты кенішінің құрылысы. Жер асты игеруге жататын карьер астындағы қорларды ашу кезінде пайда болған карьерлік кеңістік пайдаланылуы мүмкін. Берм борттарынан немесе тікелей карьердің түбінен тік және көлбеу ашылатын қазбалардан, штольнялардан, құламалардан үңгілеу кең таралған. Қорларды ашық және жер асты тәсілдерімен қатар өңдеу кезінде карьерден және жер асты кенішінен кен массасын шығару, жер асты ұсақтау кешенін, карьердің өзінде қосалқы және жөндеу шаруашылықтарын орналастыру үшін көлік қазбаларын бірлесіп пайдалану кеңінен қолданылады. Сонымен қатар, карьер астындағы қорларды карьерлік кеңістіктің шегінен тыс жер асты бөлігін ашумен аяқтау әдісі кеңінен қолданылды. Ашық тау-кен жұмыстары аяқталғаннан кейін жерасты горизонттары күрделі тау-кен қазбаларымен (тік, көлбеу оқпандармен, штольнялармен, гезенкалармен) ашылады.

Түйін сөздер: аралас игеру, тік қазбалар, оқпан, карьер астындағы қорлар, карьер, ернеу, қиябет.

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Оценка устойчивости подработанных бортов и уступов карьера для определения области возможного расположения стволов

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АННОТАЦИЯ

Как известно основными способами разработки твердых полезных ископаемых являются открытый и подземный способы. Однако, анализ мировой практики разработки месторождений твердых полезных ископаемых указывает также на широкое применение в последние 50-60 лет комбинированного способа разработки. Комбинированная разработка месторождений на отечественных и зарубежных горнодобывающих предприятиях применяется в связи с переменчивой глубиной залегания месторождений, что характерно в основном для залежей крутого и наклонного падения. Сущность комбинированной разработки заключается в том, что верхние горизонты разрабатываются открытым способом, а нижние подземным. На таких месторождениях распространение получило в основном следующая схема: первоначальная отработка верхнего участка залежи неглубоким карьером (до глубины 80-100 м иногда более), затем строительство подземного рудника, осуществляемое параллельно с доработкой запасов карьера. При вскрытии подкарьерных запасов, подлежащих подземной разработке, может использоваться образовавшееся карьерное пространство. Большое распространение получила проходка с берм бортов или непосредственно со дна карьера вертикальных и наклонных вскрывающих выработок, штолен, съездов. При параллельной отработке запасов открытым и подземным способами широко применяется совместное использование транспортных выработок для выдачи рудной массы из карьера и подземного рудника, размещения подземного дробильного комплекса, вспомогательного и ремонтного хозяйств в самом карьере. Кроме того, широкое применение получил способ доработки подкарьерных запасов со вскрытием

	подземной части вне пределов карьерного пространства. После окончания открытых горных работ подземные горизонты вскрываются капитальными горными выработками (вертикальными, наклонными стволами, штольнями, гезенками).
	Ключевые слова: комбинированная разработка, вертикальные выработки, ствол, подкарьерные запасы, карьер, борт, откос.
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Anchor bolt of rock massif in coal mines to decrease soil rock heaving of the workings

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ABSTRACT

During the maintenance of workings, the effects of soil rock heaving, caused by plastic deformation and extrusion into the excavation cavity under the action of the rock pressure, are usually eliminated. The identified patterns of change in the stress-strain state of coal-rock massifs (displacements, stresses, cracking zones), depending on the main mining-geological and mining-technical factors will allow to establish the optimal parameters of soil anchoring, technological schemes for decreasing soil rock heaving of mine workings to increase the stability of preparatory mine workings have been developed. The development and improvement of existing technologies of effective and safe stiffening of near-soil rocks at conducting mine workings on flat and inclined coal seams were substantiated. The modelling of the SSS shows that both side-rock and ground deformations are predominantly influenced by side anchorage which results in reduction of the effective deformations in the rocks surrounding the working and in a decrease of gas release from the coal massif. It is established that the deformations and stresses both side and in-soil rocks in the excavation are influenced by side anchors rather than near-soil ones.

Keywords: mine workings, study of deformation processes, anchor parameters, geomechanical processes, anchor bolt, manifestations of rock pressure.

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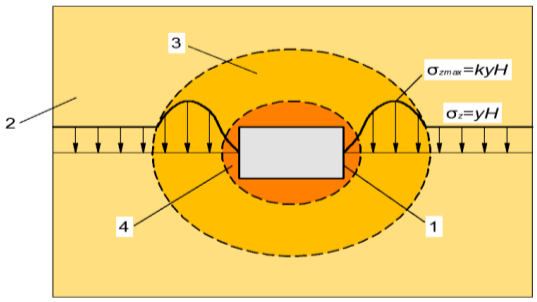
Introduction

In coal mines, the rocks in the immediate vicinity of the workings are weakened by cracking and plastic deformation, which leads to the formation of inelastic deformations around the workings, in which one can observe the restribution of the stresses, and the stress zone is moved into the rock mass [[1], [2], [3]]. Zones of increased and decreased stresses (support pressure zone) are formed in the rock mass surrounding the preparatory working (Figure 1).

For different mining conditions, mining development schemes and stages of working existence, rock heaving processes are different and this determines ways to control this phenomenon. The most often used is periodic undermining of soil rocks, which leads to disturbance of the equilibrium state of the system "bolt - zone of destroyed rocks", growth of rocks deformation intensity on the contours of workings and increase of soil rocks displacement.

The extraction of swelled rock reduces the passive back pressure on the ground by only 50-60 kN/m of the working. It is necessary to compensate



1 - preparatory working; 2 - natural stress zone; 3 - support pressure zone; 4 - decreased stress zone

Figure 1 - Stress distribution around the preparatory working

the back pressure of the excavated rock after undermining in order to ensure a stable condition of the working soil [3]. It is known that the higher the rock back pressure, the lower the rock displacement value, and the mechanical back pressure value is three orders of magnitude below the forces acting on the undermined zone perimeter. The mechanical support in mine workings at "Yuzhnodonbasskaya" mine No. 3, where the power train was located, was provided with the metal ropes with the help of which a distributed load of 0,03 MPa was set between the legs of the bolt and the soil of the mine working; this helped to reduce by 57 % the squeezing of the working ground [[3], [4]].

In order to compensate the back pressure of the extracted rocks, progressive technological solutions using dispersed purposeful load to increase the effect of counteracting the extrusion of soil rocks are required. One of them is conducting preparatory workings with strengthening of host rocks by the system of rod and cable (rope) anchoring bolts which are set for a particular working taking into account mining and geological conditions of development, character of interaction with rock massif at given loads and deformation rates.

In case of insignificant difference in strength parameters of the top, sides and soil, the deformation of rocks along the whole working perimeter occurs in conditions of full compression, while the tangential component of the stress tensor grows with its size increasing, and the shifts of contours increase. It is necessary to distinguish soil heaving, which is caused by the stress-strain state (SSS) of the whole rock mass around the working, from rock squeezing from under the pillars, which play the role of dies.

Heaving is most intense on the soil side of coal seams in preparatory workings. Soil layers covered by heavings are 2 - 5 m thick, and the thicker the weak rock layers, the more intense the heavings are [[5], [6], [7], [8], [9], [10]].

In preparatory workings, which are in the zone of cleaning operations influence (80 - 100 m), as the longwall face approaches the studied area, the growth of heaving intensity is noted up to a certain maximum. As the longwall face moves away (100 - 120 m), the intensity of heaving gradually decreases, asymptotically approaching to a certain constant value. In single workings, the heaving intensity tends to be monotonic and fades with time.

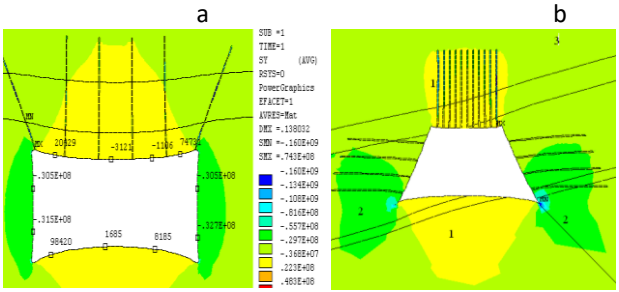
The sizes of coal pillars have a significant influence on the heaving: the smaller the pillar, the higher the heaving intensity. Increasing the width of pillars and protecting preparatory workings with rock strips reduces the heaving intensity, which lasts for 1 or 3 months. This regularity is widely used for wide workings with one-sided or two-sided rocking [5].

The classification criteria for heaving are rather subjective, due to the multifactorial nature of the phenomenon and are based on the intensity of its manifestation: "weak", "medium", "strong".

The experimental part

The decreasing of soil heaving in mine workings can be achieved by creating zones of decreased stress in the sides, by anchoring the top rocks with steel-polymer anchor bolts of increased load-carrying capacity. This increases the support area of the roof on the sides of the working and decreases the specific pressure on the soil. The area of maximum support pressure in this case is shifted from the edge of the massif by the length determined value, incline and density of the near-soil anchors.

The distribution of stresses along the working contour in a 5 m claystone layer is shown in Figure 2. An unstable rock zone is formed around the working, mainly in the roof and soil, but also on the sides in the lower part of the sides of the working contour. The maximum value of normal stresses occurs in the rightmost anchor of the working top at the place of its anchoring, and the maximum longitudinal stress occurs in the anchor located on the right-side surface of the working (first from the bottom) (Figure 2).



1 - highly unstable zone; 2 - unstable zone; 3 - unstable zone; 4 - medium stability zone; at the minimum point the zone is stable

Figure 2 - Distribution of normal (a) and longitudinal (b) stresses in a 5 m thick claystone layer

We have established the dependences of stress changes in zones 1, 2, 3 on anchor length for the claystone layer:

$$\begin{aligned}\sigma(l) &= -1{,}4 \cdot l - 8{,}8(1\ zone),\\ \sigma(l) &= -2{,}4 \cdot l - 20{,}9(2\ zone),\\ \sigma(l) &= -3{,}5 \cdot l - 32{,}9(3\ zone).\end{aligned} \quad (1)$$

The calculations of the SSS using Flac program [11] for different mining conditions of coal seams in Karaganda basin showed that the greatest effect of strengthening influence was obtained in rectangular cross-section of mine workings with side walls roof anchoring under combined scheme with their installation so that the upper side (usually, deep) anchor was located in the support pressure zone behind the workings contour in host rock. Such installation makes it possible to shift the peak of rock pressure deep into the massif beyond the zone of spreading deformation (destroyed rocks) in the zone of working influence. The lower deep anchor is placed in such a way as to create enclosing (isolating) zone preventing side soil rock spreading and extrusion into the working cavity (Figure 3). The results of SSS modeling show that the deformations and stresses in both side rocks and soil rocks are predominantly influenced by side anchors rather than near-soil ones, leading to reduction of the effective deformations in the rocks surrounding the working and decreasing of gas release from the coal-bearing massif.

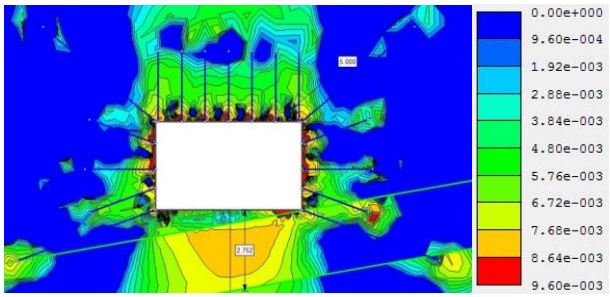


Figure 3 - Deformation pattern with displacement scales and strain distribution in the soil rock with 5 m upper side anchors and 5 m near-soil anchors

The evaluation of the required thickness of the strengthened rock layer in the soil, using the anchors installed in the soil to form supporting blocks to support the bearing vault of the working, is determined according to the method of Prof. P.M. Tsimbarevich. The depth of spreading of the heaving zone depending on the volume weight of soil and side rocks (σ t/m^3) and working height (h, m) are determined using a nomogram (Figure 4) [[6], [7], [8], [9], [10]].

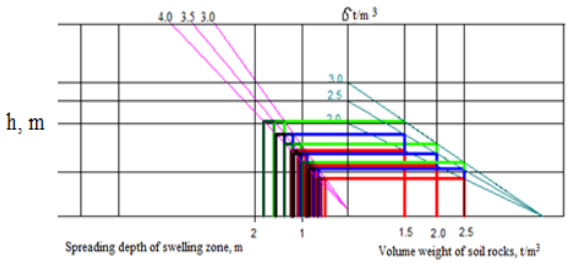
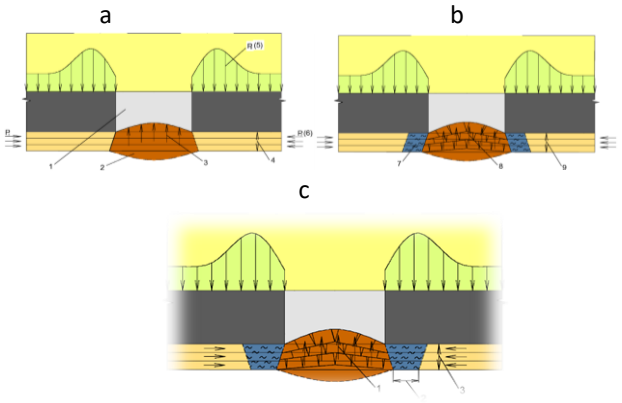


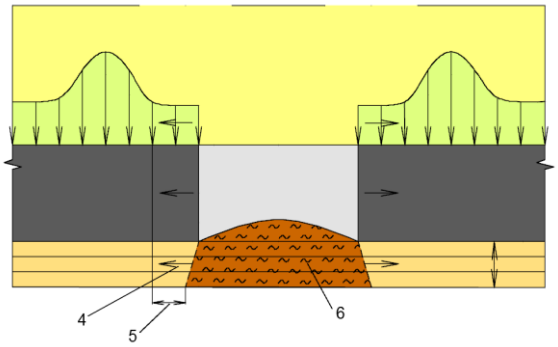
Figure 4 - Nomogram for determining spreading depth of heaving zones in the working soil depending on the influencing factors

In clay preparatory workings of the Karaganda coal basin when layered claystones and siltstones are deposited in the soil, three stages of deformation processes are distinguished: stratification along the layering surface without fracture of layered rocks (Figure 5, a); fracture of layered rocks under the workings into blocks in the form of multi-joint arches (Figure 5,b); destruction of soil under the workings sides with their squeezing into the workings (Figure 5,c). The character of stresses changes in the roof and decreasing of the soil friction intensity when strengthening the working contours with the steel-polymer anchorage (Figure 6) [[12], [13], [14], [15], [16], [17], [18]].



1 - cavity of the mine workings; 2 - soil deformations zone; 3 - deformations of heaving of mine workings; 4 - depth of delayering of mine workings; 5 – P_V =2kgH - vertical component of rock pressure; 6 – P_H - horizontal component of rock pressure; 7 - inelastic deformations zone; 8 - distraction deformations; 9 - distraction zone; a - rock extrusion deformations; b - zone subject to extrusion deformations; c - extrusion deformations

Figure 5 - Stages of deformation processes: a - delayering, b - fracture of stratified rocks, c - fracture of rocks in the sides of the working



4, 5 - direction and magnitude of maximum deformation zone movement deep into the rock mass; 6 – decreased deformation zone in the working soil

Figure 6 - Stress distribution pattern during strengthening of steel-polymer anchoring circuits

The general established regularity is that as the volume weight value of top roof grows, the spreading depth of the frost heave in the working soil decreases, while an increase in the side rock density and working height leads to an increase in the spreading depth of the heaving zone.

Discussion of results

The established patterns of stress-strain state change of coal-rock massifs (displacements, stresses, zones of delayering and cracking), depending on the main mining and geological-mining engineering factors allowed to determine the optimal parameters of soil rock anchoring. The technological schemes of heaving decreasing of soil rocks of mine workings are used in mines of Karaganda coal basin to increase the stability of preparatory mine workings. At the expense of effective and safe fastening of near-surface rocks when conducting mine workings on flat and inclined coal seams. The deformations and stresses both sides and in the soil rocks in the working are predominantly influenced by side anchors rather than near-soil ones. The schemes for anchoring the rock massif of the immediate soil are discussed below.

Near-soil anchors (Figure 7) are sunk into the soil along the faces of the mine in slanted boreholes at an angle of 20 to 40°. Their length is determined by the technical possibility of drilling (1.6; 2.4 and 2.9 m). The anchors are placed crosswise (at right angles) into the soil layers [[11], [19]].

The borehole has a larger diameter from the mouth to half of its depth and is not filled with a filler (Figure 7.b). This is necessary to unload the side rock in this area and then fill the 28 mm diameter borehole up to the face.

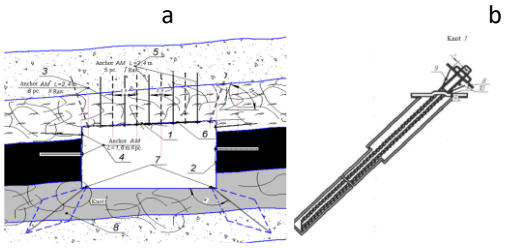


Figure 7 - Soil anchoring installation (a) and borehole design (b)

During the working for the next tunneling cycle, the boreholes are drilled in rows into the roof *1* and sides *2* of the excavation. The length, diameter and angles of the boreholes are determined by the work passport, as well as the size of the holes in the metal supports. The anchoring starts with the first row of six roof bolts *3* (2.4 m long) and four side glass fibre anchors *4* (1.8 m long). As the installation progresses, a second row of five roof steel-polymer anchors *5* (2.4 m long) is installed. Metal net *6* is pre-installed under the strips. Before excavation, before the start of cleaning works and after determining the thickness of the heaving layer, inclined steel-polymer anchors *7* (2,4 m long) are placed at a 30 - 45° angle to the rock stratum; as they are fastened in blast holes, cavities form rock blocks around the anchors, which are bound together by the cohesive forces of the rocks. As a result, a supporting dome (strengthening contour) *8* is created to reduce compressive forces from the sides of the excavation. To ensure the relief of soil from stresses, the boreholes *9* for anchor installation are drilled to the depth of 1.0-1.2 m with a diameter twice as big. This will disturb the integrity of the friable layer and slow down (exclude) the development of longitudinal and transverse bending of the layers. The rock layers cut through by the slot are relieved from horizontal stresses. In order to increase the carrying capacity and to ensure the suppleness of the anchor support elements, a cone spacer *10* is installed. Due to the support pressure ahead of the face, anchors are installed in the ground with irreducible advance of the working face by a value exceeding the length of the zone of advance support pressure by 1,5-2,0 times [[5], [6], [20]].

The length of the anchors to be installed in the working soil is determined according to an empirical formula:

$$L = \frac{К_э \cdot B \cdot П}{Р}, \text{ m} \quad (2)$$

where $K_э$ is an empirical coefficient (for the Karaganda coal basin it is 6.75);

B is the width of the excavation, m;

П - value of soil heaving, m;

P is the compressive strength of the soil, MPa.

It is recommended that the spacing of the on-soil anchors should be double the number of arches of metal arch anchor per 1 metre of working.

Conclusions

The identified patterns of change in the stress-strain state of coal massifs (displacements, stresses, cracking zones), depending on the main mining-geological and mining-technical factors will allow to establish the optimal parameters of ground mountings, technological scheme for reducing frost heaving of rocks of mine workings to increase the stability of preparatory mine workings. There are substantiated development and improvement of the existing technologies of the effective and safe ground support during mine workings on the flat and inclined coal seams. It is established that the deformations and stresses both lateral and in-soil rocks in the working are influenced by lateral anchors rather than near-surface ones.

Conflicts of interest

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

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Қазбалардағы топырақ жынысының қопсуын төмендету үшін көмір шахталарының тау-кен массивін анкерлік бекіту

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ТҮЙІНДЕМЕ

Пайдалану процесінде қазбаларды ұстау кезінде, әдетте, контурлық тау қысымының әсерінен оларды қазба қуысына сығып, пластикалық деформациялар кезінде пайда болатын топырақ жыныстарының шағылысуының салдарын жою бойынша жұмыстар жүргізіледі. Негізгі тау-кен-геологиялық және тау-кен техникалық факторларына байланысты көмір-жыныс массивтерінің (ығысулар, кернеулер, жарықшақ түзілу аймақтары) кернеулі-деформацияланған жай-күйінің өзгеруінің анықталған заңдылықтары топырақ жыныстарын бекітудің оңтайлы параметрлерін белгілеуге мүмкіндік береді. Тау-кен қазбаларын жұмсақ және көлбеу көмір қабаттарында жүргізу кезінде, контурға жақын жыныстарды тиімді және қауіпсіз бекітудің қолданыстағы технологияларын әзірлеу және жетілдіру негізделген. Қосымша құн салығын модельдеу, бүйір жыныстардағы, сондай-ақ топырақ жыныстарындағы деформациялар мен кернеулерде жер асты емес, жанама анкер басым болатындығын көрсетеді, бұл өндірісті қоршаған жыныстардағы қолданыстағы деформациялардың төмендеуіне және көмір жыныстарынан газ шығарудың төмендеуіне әкеледі. Бүйірлік және тау жыныстарындағы деформациялары мен кернеулерінде қазбада топырақ емес, бүйірлік анкер бар екендігі анықталды.

Түйін сөздер: тау-кен қазбалары, деформациялық процестерді зерттеу, бекіту параметрлері, геомеханикалық процестер, анкерлік бекітпе, тау-кен қысымының көріністері, технологиялық схемалар

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Анкерное крепление горного массива уголных шахт для снижения пучения пород почвы выработок

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АННОТАЦИЯ

При поддержании выработок в процессе эксплуатации, как правило, проводятся работы по устранению последствий пучения пород почвы, возникающего при пластических деформациях с выдавливанием их в полость выработки под действием контурного горного давления. Выявленные закономерности изменения напряженно-деформированного состояния угле-породных массивов (смещений, напряжений, зон трещинообразования), в зависимости от основных горно-геологических и горнотехнических факторов позволят устанавливать оптимальные параметры крепления пород почвы разработаны технологические схемы снижения пучения пород почвы горных выработок для повышения устойчивости подготовительных горных выработок. Обоснована разработка и совершенствование существующих технологий эффективного и безопасного крепления приконтурных пород при проведении горных выработок на пологих и наклонных угольных пластах. Моделирования НДС свидетельствует о том, что на деформации и напряжения в боковых породах, так и в породах почвы преимущественное оказывают не припочвенные, а боковые анкера, приводящих к уменьшению действующих деформаций в породах, окружающих выработку и снижению газовыделения из углепородного массива. Установлено, что на деформации и напряжения как боковых, так и в породах почвы в выработке оказывают не припочвенные, а боковые анкера.

***Ключевые слова*:** горные выработки, исследование деформационных процессов, параметры крепления, геомеханические процессы, анкерная крепь, проявления горного давления, технологические схемы.

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Earth sciences

Study of the mineral composition of promising copper ores of the Republic of Kazakhstan

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ABSTRACT
The article provides a brief overview of the problems of copper production in Kazakhstan. It is shown that the main current problem of copper-smelting production is the involvement of low-grade ores of complex mineral composition. Existing technologies are focused on the processing of ore with higher copper content, accordingly, it is necessary to adjust the existing enrichment and smelting technologies. To determine the mineral composition of some samples of promising copper-bearing ores of the Republic of Kazakhstan, an X-ray phase analysis was carried out. The identification and quantitative calculation of the mineral content were carried out using the DIFFRAC.EVA and DIFFRAC.TOPAS programs. It was shown that the main copper-bearing minerals in the samples are: chalcopyrite, bornite, chalcosiderite - group 1; malachite, lapis lazuli, atacamite, pseudomalachite, brochantite - group 2. The waste rock is represented by the following minerals: quartz, muscovite (mica), chlorite (layered silicate), albite (feldspar), pyrite, calcite, sodalite (feldspathoid), and gypsum. Based on the analysis, the mineral composition of the studied samples was established and a conclusion was made about the dominant nature of the ore. It is shown that in three samples the predominant nature of the ore is sulfide, in one sample it is oxide. The obtained results of the mineral composition and nature of the ore allow us to make practical recommendations on the most effective scheme for ore enrichment and further processing.

Keywords: Material science, composite, material engineering, design, biocomposite.

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Introduction

According to the data International Copper Study Group (ICSG) the deficit of copper in the world market amounted to 415 thousand tons in 2020 y, the deficit was already 439 thousand tons in 2021, and now this figure continues to grow [1]. Kazakhstan has huge reserves of copper ore and ranks seventh in the world in terms of copper production, 92% of which is exported abroad. The main industrial types of ores are cuprous sandstones (71%) and porphyry copper (24%) [2].

The Republic of Kazakhstan has extensive copper reserves of more than 35 million tons (70% of which are in the Zhezkazgan region), which is 4.7% of the world's reserves, and allows Kazakhstan to take 6th place in the world, after Chile, Australia, Peru, Mexico and the USA [2].

Copper in the composition of copper ore can be present in various minerals. Most often, copper is in the form of sulfur compounds: copper pyrite or chalcopyrite $CuFeS_2$, chalcocite Cu_2S, covelitte CuS; can occur in the form of oxides: cuprite Cu_20, tenorite CuO; or be part of hydrocarbonates:

malachite $CuCO_3 \bullet Cu(OH)_2$, azurite $2CuCO_3 \bullet Cu(OH)_2$.

The waste rock of the ores consists of pyrite FeS_2, quartz $Si0_2$, magnesium and calcium carbonates ($MgC0_3$ and $CaCO_3$), as well as various silicates containing Al_20_3, CaO, MgO, and iron oxides along with $Si0_2$.

The degree of opening of the mineral grain, and, consequently, the efficiency of subsequent enrichment will be determined by the mineral composition.

Copper is the most important resource for the development of the economy of Kazakhstan, with about 80% of refined copper being exported. Demand for refined copper is expected to increase in the near future, by about 2.2% annually. Copper is exported in the form of copper concentrate, copper ore, refined copper, and copper alloys [3].

According to the official website of KazMinerals PLC [3], the company produced 144 thousand tons of copper in 2016, 259 thousand tons in 2017, and 295 thousand tons in 2018. The company intends to continue to increase copper production by attracting new resources, optimizing technology, and recycling waste [4].

The increase in production is expected due to the expansion of existing mines, the development of new sections of existing deposits, and the construction of additional processing facilities. So, for example, the quarry at the Konyrat mine has already covered the entire ore body, so it can develop through the development of the sides (now - the eastern one, the ore from which with a copper content of 0.3% should be enough for 13 years, then the question will be raised about the development of the western sides) [5].

It should be noted that these numbers refer only to explored ores that are theoretically suitable for processing, i.e. balance sheet. According to official calculations, copper ores on the balance sheet will be enough for about another 30 years of development. There are more than 100 copper deposits on the state balance sheet, the ores of which can theoretically be processed using the technologies currently used, but the total number of copper deposits is about 8 thousand.

The main problem of copper production is that poorer ores are involved in processing, and this is a global trend. In 2007 the average copper content in the ore was 1.22% according to the Kazakhmys Corporation LLP, in 2017 this number decreased to 0.93% [2]. For example, the promising Bozshakol copper mine has an average copper grade of just 0.35% and the development of this deposit is a priority.

Given these circumstances, the process of enrichment of copper ore is a key factor that determines both the technology and the cost of cathode copper in general.

Another problem is the fact that the raw materials that are currently mined at the deposits are of worse quality or differ significantly in mineral and elemental composition from the raw materials for which processing technologies have been developed. At some factories of Kazakhmys Corporation LLP, they worked with ore, the copper content of which was at least 1.08%, and in the second decade of the 21st century, the copper content in active deposits decreased to 0.7-0.8%.

Thus, despite the fact that Kazakhstan has large reserves of copper, most of it is found in low-grade ores (less than 0.5% copper content), which were previously considered “waste” rock.

Taking into account the above problems, it can be unequivocally stated that in order to select the optimal beneficiation technology, it is necessary to have accurate knowledge of the mineral composition of the ore. In addition, the mineral composition of copper ore determines the composition of slags during smelting into matte and conversion, affects the durability of the lining, and determines the technical and economic parameters of the process. In other words, knowledge of the mineral composition of copper ore is the starting point for the selection and optimization of copper production technology in general.

Recently, the study of the mineral composition of ore by the multimodal microscopy methods has gained popularity, i.e. combination of optical and electron microscopy [[6], [7], [8], [9]]. Using the optical characteristics of minerals (color, reflectance, and refraction coefficients) in combination with the intensity of electronic peaks obtained from various phases, it is possible to obtain a complex picture that allows one to identify the mineral composition of the ore in sufficient detail.

However, this method requires a sufficiently large amount of time for analysis, depending on the professional level of the expert and the quality of the sample surface. Therefore, the method of powder X-ray diffraction remains the most

common, objective, and accurate method for identifying the mineral and phase composition of the ore.

Experimental part

The purpose of this study was to study the mineral composition of the presented copper-bearing samples to determine the nature of the ore. As objects of analysis, copper ores of various deposits and copper concentrates were used:

- ore copper sample No. 868
- ore copper sample No. 745
- copper concentrate, sample No. 688
- copper concentrate, sample No. 681

X-ray phase analysis was carried out on a D2 PHASER X-ray diffractometer with the following technical characteristics:

- Anode material: standard sealed X-ray tube: CuKα
- Reflected X-ray Detector: LYNXEYE Solid State Position Sensitive Detector.
- Focus size - 0.4 x 12 mm;
- Nominal operating mode of the X-ray source: 30 kV/10 mA;
- Vertical Theta/Theta goniometer, radius 140 mm;
- Scan method θs/θd related
- Range of scanning angles 2θ: from 3 to 80°;
- scan step 0.010
- scan step time 5 seconds

The following conditions were chosen for taking the diffractogram:

- voltage 30 kW;
- current 10 mA;
- sample rotation - 15 revolutions per minute (allows to obtain more complete data on the composition of the sample);
- shooting range 40.4° - 80.6°;
- shooting step - 0.02°;
- shooting delay time - 1 second.

Taking into account the selected shooting parameters, obtaining one diffraction pattern takes 67 minutes.

Discussion of results.

After the analysis, the following diffraction patterns (Fig. 1-4) [[10], [11]] of the samples were obtained.

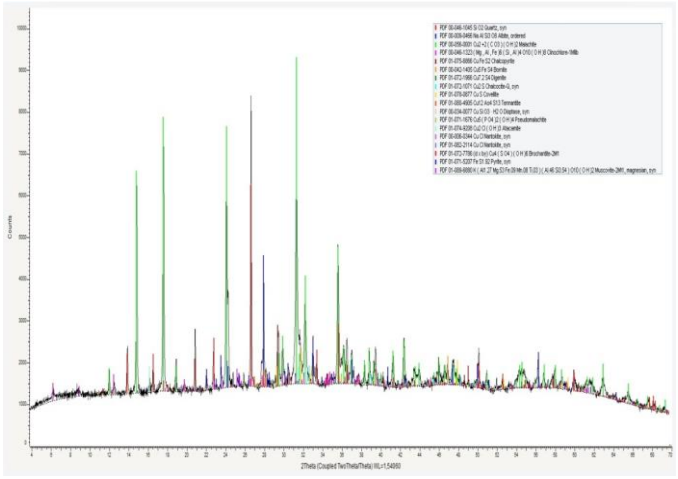

Figure 1 - Diffraction pattern of sample 681

Identification and quantitative calculation of the content of minerals were carried out in DIFFRAC.EVA and DIFFRAC.TOPAS software applications.

The results of the phase composition of the samples obtained by X-ray phase diffractometry are presented in Table 1 [12].

During the X-ray phase analysis, the following minerals were found:

- sulfide copper minerals - chalcopyrite, bornite, chalcosiderite;
- oxidized copper minerals - malachite, azurite, atacamite, pseudomalachite, brochantite;
- other minerals - quartz, muscovite (mica), chlorite (layered silicate), albite (feldspar), pyrite, calcite, sodalite (feldspathoid), gypsum [13].

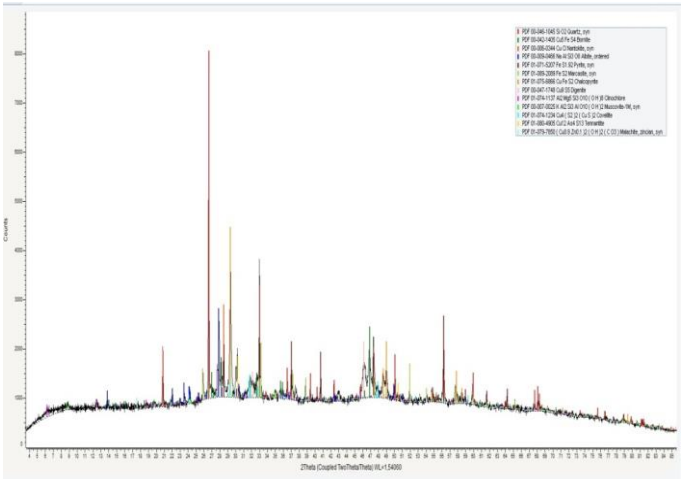

Figure 2 - Diffraction pattern of sample 688

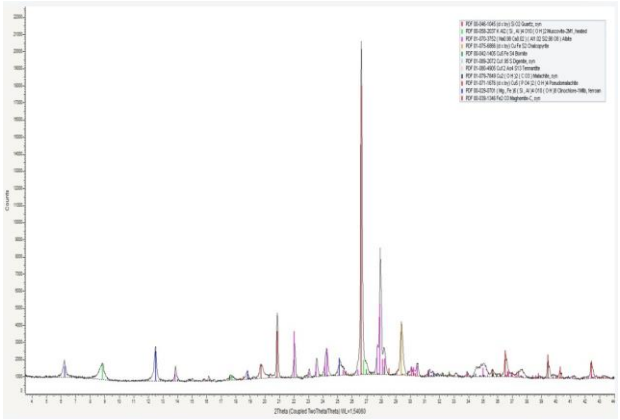

Figure 3 - Diffraction pattern of sample 745

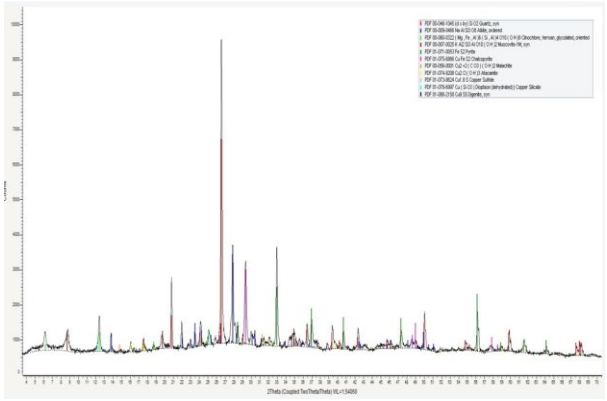

Figure 4 - Diffraction pattern of sample 868

Table 1 - Mineral composition of the studied samples

Mineral phase	Phase content in the sample, %					
	868	745	688	681		
Albite	34.9	21.5	11.6	10.1		
Atakamite	-	1.7	2.2	-		
Bornite	4.6	1.1	1.4	16.8		
Brochantite	-	-	9.1	-		
Digenite	2.2	1.1	2.0	5.2		
Dioptase	-	0.8	0.6	-		
Quartz	28.1	28.4	16.6	24.4		
Clinochlore	13.8	12.5	5.3	3.2		
Covellite	-	-	2.0	1.6		
Maghemite	1.6	-	-	-		
Malachite	1.2	3.0	-	2.7		
Marcasite	-	-	-	5.5		
Muscovite		8.1		15.4	6.3	3.0
Nantokite		-		-	1.1	11.0
Pyrite		-		9.9	3.0	9.6
Pseudomalachite		2.9		-	0.6	-
Tennantite		0.4		-	0.2	1.6
Chalcanthite		-		-	1.1	-
Chalcopyrite		2.2		4.7	1.5	5.4

To determine the nature of the ore, it is necessary to summarize the X-ray phase analysis data in accordance with Table 2 [14].

Table 2 - Constituent minerals of oxidized and sulfide ore

Group copper minerals	Constituent minerals
Oxidized	Cuprite, tenorite, malachite, pseudomalachite, azurite, atacamite, chrysocolla, dioptase, chalcanthite, etc.
Sulfide	Chalcopyrite, cubanite, bornite, chalcocite, covellite, digenite, tennantite, etc.

Comparison of the data of the PDF method and the Table 2 data allow us to conclude on the dominant character (oxidized or sulfide) of each of the presented samples (Table 3) [15].

Table 3 - Data on the nature of the mineral components of the presented samples.

Sample number	Group of copper minerals	X-ray phase analysis, %
868	Oxidized	2.08
	Sulfide	5.63
745	Oxidized	2.99
	Sulfide	5.17
688	Oxidized	28.50
	Sulfide	6.29
681	Oxidized	1.89
	Sulfide	29.9

The obtained results of X-ray phase analysis are new because the copper-containing ores and concentrates presented for analysis have not been studied before. Summarizing the data obtained, we can say that the mineral base is represented by characteristic copper-containing minerals that were previously studied and well described [[9], [11], [14], [16]]. The originality of the data obtained consists of obtaining the quantitative mineral composition of the studied samples, which, taking into account the latest literature data [[17], [18],

[19] [20]], allows us to determine the most optimal method of enrichment.

Conclusion

It can be concluded that the copper mineral components are dominant and, based on this, subsequently recommend a scheme for ore dressing and subsequent redistribution. Based on the analysis, it was found that the studied promising ores have the most effective scheme of research and further processing and require the development of research in order to create an effective environmentally safe technology for deep processing. Thus, it can be assumed that a thorough study of the structure of ore minerals and a number of physico-chemical properties is necessary.

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

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Қазақстан Республикасының перспективалы мыс кендерінің минералдық құрамын зерттеу

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ТҮЙІНДЕМЕ

Мақалада Қазақстандағы мыс өндірісінің мәселелеріне қысқаша шолу жасалды. Мыс балқыту өндірісіндегі негізгі мәселе күрделі минералды құрамдағы кедей кендерді тарту болып табылады. Қолданыстағы технологиялар мыс құрамы анағұрлым жоғары кенді қайта өңдеуге бағытталған, ал қолданыстағы байыту және балқыту технологияларын түзету қажет. Құрамында мыс бар перспективалы кендердің кейбір сынамаларының минералды құрамын анықтау үшін рентген-фазалық талдау жүргізілді. Минералдардың құрамын анықтау және сандық есептеу DIFFRAC.EVA және DIFFRAC.TOPAS бағдарламаларында жүргізілді. Сынамалардағы құрамында мыс бар негізгі минералдар: халькопирит, борнит, халькосидерит – 1 топ; малахит, лапис лазули, атакамит, псевдомалахит, брошантит – 2 топ. Бос жыныстарда келесі минералдар бар – кварц, мусковит (слюда), хлорит (қабатты силикат), альбит (дала шпаты), пирит, кальцит, содалит (фельдшпатоид), гипс. Жүргізілген талдау негізінде зерттелген сынамалардың минералды құрамы анықталды және кеннің доминантты сипаты туралы қорытынды жасалды. Үш сынамада кеннің басым сипаты сульфидті, бір сынамада – оксидті екендігі көрсетілген. Кеннің минералды құрамы мен сипатынан алынған нәтижелер кенді байытудың және одан әрі өңдеудің тиімді схемасы туралы практикалық ұсыныстар жасауға мүмкіндік береді.

Түйін сөздер: Материалтану, композит, материалтану, дизайн, биокомпозит.

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Исследование минерального состава перспективных медных руд Республики Казахстан

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АННОТАЦИЯ

В статье проведен краткий обзор проблем производства меди в Казахстане. Показано, что основной текущей проблемой медеплавильного производства является вовлечение бедных руд сложного минерального состава. Существующие технологии ориентированы на переработку руды с более высоким содержание меди, соответственно, необходима корректировка существующих технологий обогащения и выплавки. Для определения минерального состава некоторых проб перспективных медьсодержащих руд РК был проведен рентгено-фазовый анализ. Идентификация и количественный расчет содержания минералов проводилось в программах DIFFRAC.EVA и DIFFRAC.TOPAS. Было показано, что основными медьсодержащими минералами в пробах являются: халькопирит, борнит, халькосидерит – 1 группа; малахит, лазурит, атакамит, псевдомалахит, брошантит – 2 группа. Пустая порода представлена следующими минералами – кварц, мусковит (слюда), хлорит (слоистый силикат), альбит (полевой шпат), пирит, кальцит, содалит (фельдшпатоид), гипс. На основании проведенного анализа был установлен минеральный состав изученных проб и сделан вывод о доминантном характере руды. Показано, что в трех пробах преобладающий характер руды – сульфидный, в одной пробе - оксидный. Полученные результаты минерального состава и характера руды позволяют сделать практические рекомендации о наиболее эффективной схеме обогащения руды и дальнейшей переработке.

Ключевые слова: Материаловедение, композит, материаловедение, дизайн, биокомпозит

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